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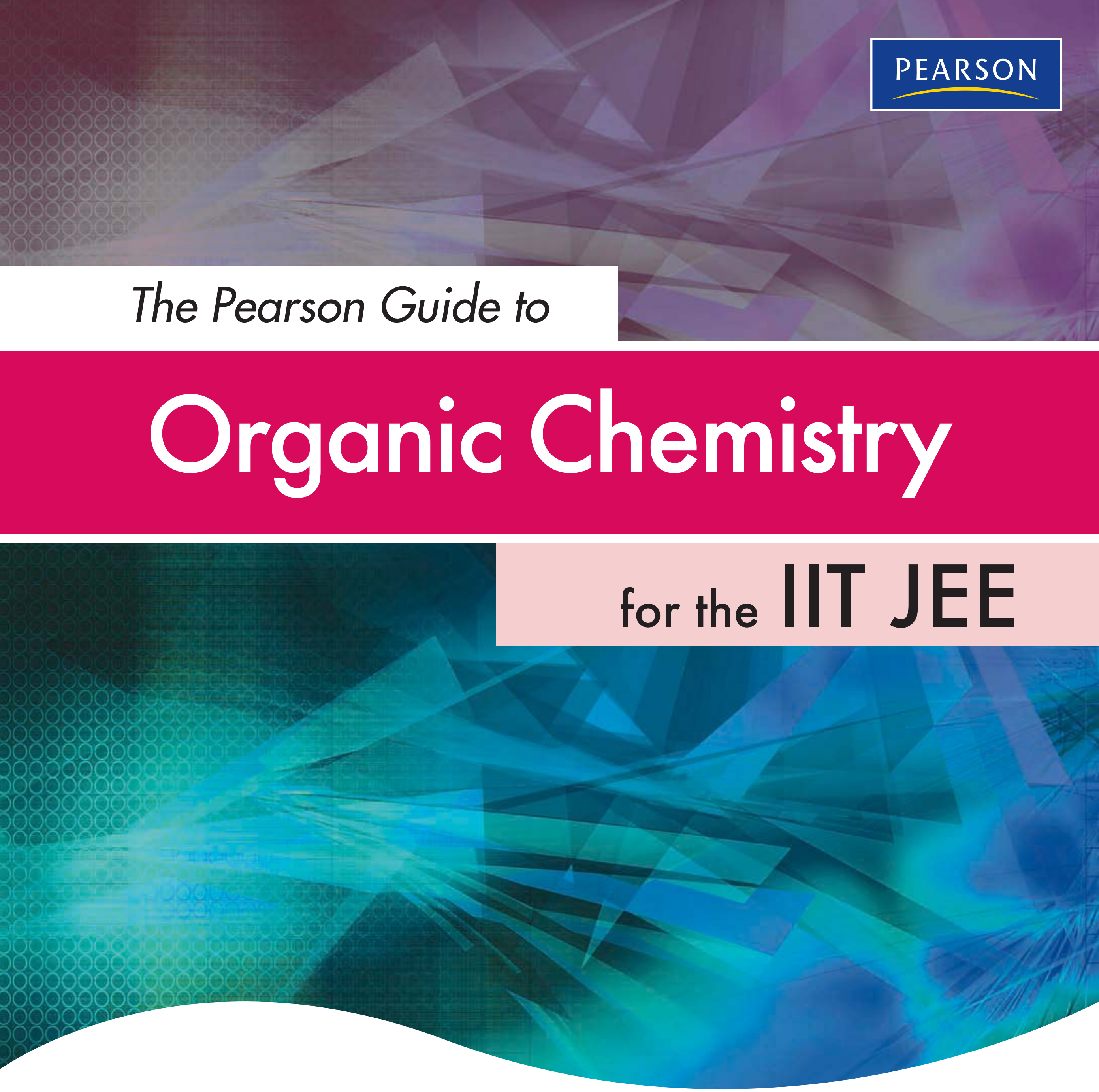

The Pearson Guide to
Organic Chemistry
for the IIT JEE

- Short-cut methods and problem-solving tricks
- As per the latest IIT JEE format
- Original questions from competitive exams
- Numerous examples and fully solved problems

Atul Singhal

THORPES

Organic Chemistry
for the
IIT-JEE

Atul Singhal

PEARSON

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To my grandparents,
parents and teachers

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CONTENTS

PREFACE

Organic Chemistry for the IIT-JEE is an invaluable book for all the students preparing for the prestigious engineering entrance examination. It provides class-tested course material and problems that will supplement any kind of coaching or resource the students might be using. Because of its comprehensive and in-depth approach, it will be especially helpful for those students who do not have enough time or money to take classroom course.

- A careful scrutiny of previous years' IIT papers and various other competitive examinations during the last 10 to 12 years was made before writing this book. It is strictly based on the latest IIT syllabus (2009–10) recommended by the executive board. It covers the subject in a structured way and familiarizes students with the trends in these examinations. Not many books in the market can stand up to this material when it comes to the strict alignment with the prescribed syllabus.
- It is written in a lucid manner to assist students to understand the concepts without the help of any guide.
- The objective of this book is to provide this vast subject in a structured and useful manner so as to familiarize the candidates taking the current examinations with the current trends and types of multiple-choice questions asked.
- The multiple-choice questions have been arranged in following categories:

Straight Objective Type Questions (Single Choice), Brainteasers Objective Type Questions (Single Choice), Multiple Correct Answer Type Questions (More than one choice), Linked-Comprehension Type Questions, Assertion and Reasoning Questions, Matrix-Match Type Questions and the IIT-JEE Corner.

This book is written to pass on to another generation, my fascination with descriptive inorganic chemistry. Thus, the comments of the readers, both students and instructors, will be sincerely appreciated. Any suggestions for added or updated additional readings would also be welcome.

Atul Singhal
singhal.atul@yahoo.com

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ACKNOWLEDGEMENTS

The contentment and ecstasy that accompany the successful completion of any work would remain essentially incomplete if I fail to mention the people whose constant guidance and support has encouraged me.

I am grateful to all my reverend teachers, especially, the late J. K. Mishra, Dr D. K. Rastogi, the late A. K. Rastogi and my honourable guide, Dr S. K. Agarwala. Their knowledge and wisdom has continued to assist me to present in this work.

I am thankful to my colleagues and friends, Deepak Bhatia, Er Vikas Kaushik, Er A. R. Khan, Vipul Agarwal, Er Ankit Arora, Er Wasim, Manoj Singhal, Vijay Arora, (Director, Dronacharya), Mr. Anupam Shrivastav (Career Point, Kota), Mr Rajiv Jain (MVN, Faridabad), Mr Ashok Kumar, Mr Y.R. Mittra and Mr N.C. Joshi (Brillant Tutorials).

I am indebted to my father, B. K. Singhal, mother Usha Singhal, brothers, Amit Singhal and Katar Singh, and sisters, Ambika and Poonam, who have been my motivation at every step. Their never-ending affection has provided me with moral support and encouragement while writing this book.

Last but not the least, I wish to express my deepest gratitude to my wife Urmila and my little,—but witty beyond years, daughters Khushi and Shanvi who always supported me during my work.

Atul Singhal
singhal.atul@yahoo.com

GENERAL ORGANIC CHEMISTRY-1

(NOMENCLATURE AND ISOMERISM)

CHAPTER 1

CHAPTER CONTENTS

Classification of organic compounds; IUPAC nomenclature of simple organic compounds (only hydrocarbons, mono-functional and bi- functional compounds); Conformations of ethane and butane (Newmann projections). Structural and geometrical isomerism; Optical isomerism of compounds containing upto two asymmetric centres, (R, S and E, Z nomenclature excluded); Determination of empirical and molecular formula of simple compounds (only combustion method) and various levels of multiple-choice questions.

INTRODUCTION

The word 'organic' means 'pertaining of life'. The compounds like sugars, fats, oils, dyes, proteins, vitamins etc., which were isolated directly or indirectly from the living organisms like animals and plants were called organic compounds and their study is called Organic Chemistry. The compounds like common salt, alum, nitre, blue and green vitriol etc., which were isolated from the non-living sources such as rocks and minerals were called inorganic compounds. CO , CO_2, CO_3^{-2}, HCO_3^-, HCN etc., not organic compounds.

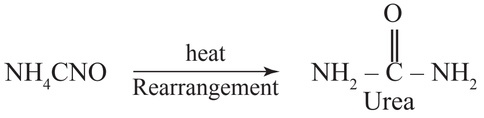
VITAL FORCE THEORY OR BERZELIUS HYPOTHESIS

According to it the organic compounds cannot be synthesized in the laboratory because they require the presence of a mysterious force that is, vital force which exists only in the living organisms.

FALL OF VITAL FORCE THEORY OR WOHLER'S SYNTHESIS

According to Wohler when ammonium cyanate (obtained by double decomposition of ammonium chloride and potassium cyanate) is heated, urea is formed. Urea was the first organic compound to be prepared in lab.

$$NH_4Cl + KCNO \longrightarrow \underset{\text{Amm. cyanate}}{NH_4CNO + KCl}$$



$$NH_4CNO \xrightarrow[\text{Rearrangement}]{\text{heat}} \underset{\text{Urea}}{NH_2 - \overset{\overset{\displaystyle O}{\|}}{C} - NH_2}$$

Modern Definition of Organic Chemistry

Organic compounds may be defined as hydrocarbons and their derivatives and the study of hydrocarbons and their derivatives is called organic chemistry.

For example, CH_3OH, CH_3CN etc.

Large Number of Organic Compounds

The main reasons for the large number of organic compounds are:

(i) Catenation The property of self-linking of carbon atoms through covalent bonds to form long straight or branched chains and rings of different sizes is called catenation. Carbon shows maximum catenation in the periodic table and this property is primarily due to its small size, electronic configuration and maximum bond energy or strength of carbon-carbon bonds for catenation.

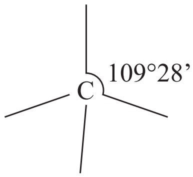
C > Si > S > P > …..

(ii) Electronegativity and Strength of Bonds The electronegativity of carbon (2.5) is close to a number of other elements like Hydrogen (2.1), Nitrogen (3.0), Phosphorous (2.1), Chlorine (3.0), Oxygen (3.5) so it can form strong covalent bonds with these elements.

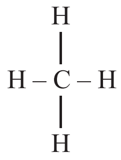
(iii) Tendency to Form Multiple Bonds Due to its small size, carbon atom has a strong tendency to form multiple bonds with Carbon, Oxygen and Nitrogen atoms.

(iv) Isomerism Many organic compounds show the phenomenon of isomerism by virtue of which a single molecular formula may represent two or more structures.

Tetravalency of Carbon

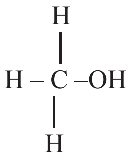


The tetravalent nature and tetrahedral structure of carbon was introduced by Liebel and Van't Hoff. The carbon atom is tetravalent, that is, one carbon atom can combine with four monovalent atoms or groups or with an equivalent number of atoms or groups having other valencies, thus,



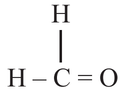
$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ H & - & C & - & H \\ & & | & & \\ & & H & & \end{array}$$

Methane



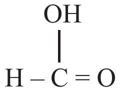
$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ H & - & C & - & OH \\ & & | & & \\ & & H & & \end{array}$$

Methyl alcohol



$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ H & - & C & = & O \end{array}$$

Formaldehyde



$$\begin{array}{ccccc} & & OH & & \\ & & | & & \\ H & - & C & = & O \end{array}$$

Formic acid

Equivalence of Four Carbon Valencies

All the four valencies of carbon are alike and symmetrical with respect to the atom that is, equal and equivalent to each other. It is obvious from the fact that methane forms only one mono-substituted isomer, that is, monochloromethane on chlorination.

Catenation Property of Carbon

- Carbon atoms possesses a great tendency to link with one another. The linking is possible through a single, double or triple bond as follows:

$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}$ $\overset{|}{\underset{|}{C}}=\overset{|}{\underset{|}{C}}$ $-C\equiv C-$

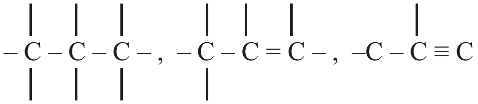
Triple bond

Single bond double bond

Carbon atoms may link to from
(a) an open chain which may be straight or branched
(b) a closed chain

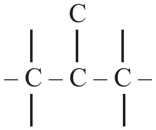
Both are as follows:

(a) Open Chain



$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-$, $-\overset{|}{\underset{|}{C}}-\overset{|}{C}=\overset{|}{C}-$, $-\overset{|}{C}-C\equiv C$

Straight chain



$-\overset{|}{\underset{|}{C}}-\overset{\overset{C}{|}}{C}-\overset{|}{\underset{|}{C}}-$

Branched chain

(a) Closed Chain

CLASSIFICATION OF ORGANIC COMPOUNDS

All the known organic compounds have been divided into following two classes:

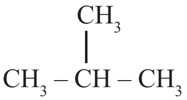
- Acyclic compounds (Aliphatic compounds)
- Cyclic compounds (Aromatic compounds)

Acyclic or Open Chain or Aliphatic Compounds

The organic compounds in which all the carbon atoms are linked to one another to form open chains either straight or branched are called acyclic or open chain or aliphatic compounds.

For example,

$CH_3CH_2CH_2CH_3$
Butane



$CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_3$
Isobutane

$CH_3CH_2CH_2OH$ Propanol

Cyclic Compounds The compounds which have at least one ring or closed chain of atoms are called cyclic compounds.

Types of Cyclic Compounds These are of two types:

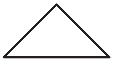
(a) Homocyclic Compounds Such compounds contain rings which are made up of only one kind of atoms.

- ***Carbocyclic Compounds*** If all the atoms in the ring are carbon atoms, they are called carbocyclic compounds.

  These are of following two types:

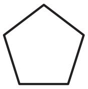
  (i) Alicyclic Compounds These are carbocyclic compounds which resemble aliphatic compounds in their properties.

  For example,

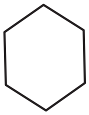


Cyclopropane

cyclobutane



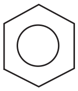
cyclopentane



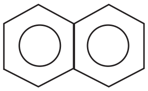
Cyclohexane

  (ii) Aromatic Compounds The compounds containing one or more fused or isolated benzene rings are called Aromatic or Benzoid compounds.

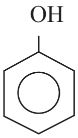
  For example,



Benzene



Naphthalene



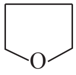
Phenol

(b) Heterocyclic Compounds The cyclic compounds having one or more heteroatoms (other than C-atom) (For example, O, N, S etc.) in the ring are called heterocyclic compounds.

These are of following two types:

(i) Alicyclic Heterocyclic Compounds Such compounds resemble with aliphatic compounds in their properties.

For example,

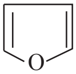


Tetrahydrofuran (THF)

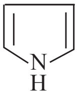
Piperidine

(ii) Aromatic Heterocyclic Compounds Those compounds which resemble benzene and other aromatic compounds in most of their properties are called aromatic heterocyclic compounds.

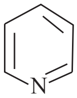
For example,



Furan



Pyrrole



Pyridine

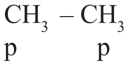
Functional Group: It is an atom or a group of atoms present in a molecule which determines its chemical properties, that is, site of chemical activity.

For example, –OH (hydroxy), –CHO (aldehydic)
–COOH (carboxylic) etc.

CLASSES OF CARBON ATOMS

- **Primary Carbon Atoms**: A carbon atom either alone or attached to not more than one other carbon atom is called a primary carbon atom and it is represented by 1° or p.

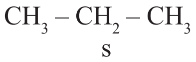
  For example,

  $$\underset{p}{CH_3}-\underset{p}{CH_3}$$

- **Secondary Carbon Atom**: A carbon atom which is attached to two other carbon atoms (2° or s).

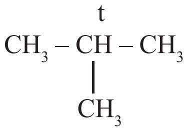
  For example,

  $$CH_3-\underset{s}{CH_2}-CH_3$$

- **Tertiary Carbon Atom**: A carbon atom which is attached to three other carbon atoms (3° to t).

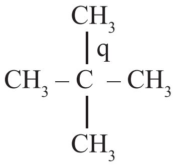
  For example,

  $$CH_3-\overset{t}{\underset{CH_3}{\underset{|}{CH}}}-CH_3$$

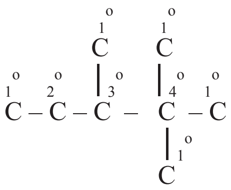
- **Quaternary Carbon Atom:** A carbon atom which is attached to four other carbon atoms (4° or q).

  For example,

  $$CH_3-\overset{\overset{CH_3}{|\,q}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$$

  For example,

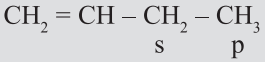
  

  $$\overset{1^o}{C}-\overset{2^o}{C}-\overset{\overset{1^o}{C}}{\overset{|\,3^o}{C}}-\overset{\overset{1^o}{C}}{\overset{|\,4^o}{\underset{\underset{C}{|\,1^o}}{C}}}-\overset{1^o}{C}$$

REMEMBER

- Hydrogen atoms attached to primary, secondary or tertiary carbon atoms are called primary, secondary or tertiary hydrogen atoms respectively.
- The hydrogen atoms attached to primary, secondary, tertiary and quaternary carbon atoms in alkanes are respectively three, two, one and zero.
- If a carbon atom is unsaturated it is not indicated as p, s, t carbon atom however it is counted for other atoms.

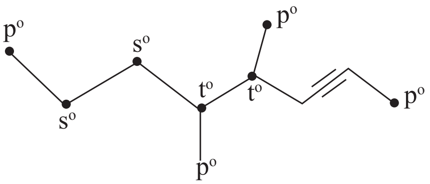
  For example,



$$CH_2 = CH - \underset{s}{CH_2} - \underset{p}{CH_3}$$

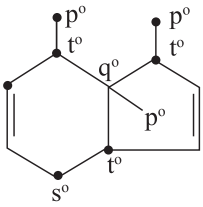
For example,

(1)



C-atom	H-atoms	
p^o	4	12
s^o	2	4
t^o	2	2

(2)



C-atom	H-atoms	
p^o	3	9
s^o	1	2
t^o	3	3
q^o	1	0

HOMOLOGOUS SERIES

It is a series of structurally similar compounds having same functional group in the increasing number of carbon atoms.

CHARACTERISTICS OF HOMOLOGOUS SERIES

- Any two successive members of a homologous series differ in their molecular formula by CH_2 group and their molecular weights differ by 14.
- All the members can be prepared by a number of general methods.
- The members have many similar chemical properties.
- The physical properties of the members show a regular gradation with increase molecular weight.
- The IUPAC names of all homologues have the same ending, as -ane in alkanes, -ene in alkenes, -ol in alkanols etc.

For example,

CH_4 (Methane)
C_2H_6 (Ethane)
C_3H_8 (Propane)
C_4H_{10} (Butane)

Hydrocarbon Radicals

Parent hydrocarbon (R–H) $\xrightarrow{-H}$ Hydrocarbon group (R –)
Alkane   Alkyl

For example, $CH_4 \xrightarrow{-H} -CH_3$
Methane   Methyl

$C_2H_6 \xrightarrow{-H} -C_2H_5$
Ethane   Ethyl

IUPAC SYSTEM "International Union of Pure and Applied Chemists".

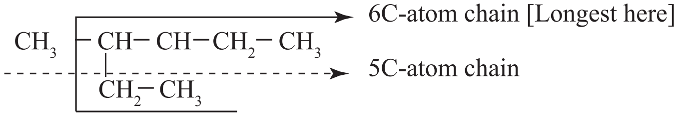
Basic Rules of nomenclature

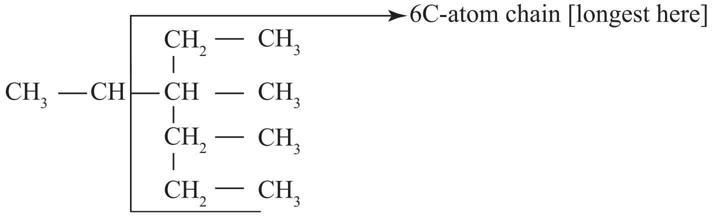
Carbon chain length	*Root word (Alk.)*	*Carbon chain*	*Root word*
C_1	Meth-	C_9	Non-
C_2	Eth-	C_{10}	Dec-
C_3	Prop-	C_{11}	Un dec-
C_4	But-	C_{12}	Do dec-
C_5	Pent-		
C_6	Hex-		
C_7	Hept-		
C_8	Oct-		

Selection of the longest chain of C-atoms

To write the IUPAC name, the first step is to select the longest chain, that is parent or main chain.

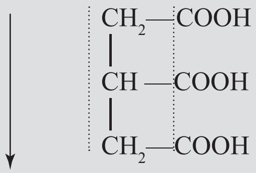
For example,





REMEMBER

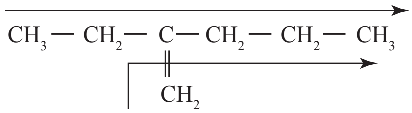
Prefer the chain having maximum or all possible functional groups, or (=) or (≡) bonds and for it longest chain rule can be neglected. For example (1)



$$\begin{array}{l} CH_2-COOH \\ | \\ CH-COOH \\ | \\ CH_2-COOH \end{array}$$

3 C-atom chain [since, it includes all the three functional groups so it is prefered here]

For example, (2)

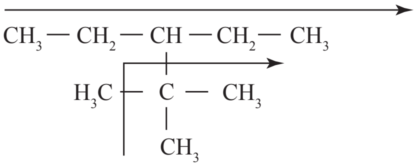


$$\begin{array}{l} CH_3-CH_2-\underset{\underset{CH_2}{\|}}{C}-CH_2-CH_2-CH_3 \end{array}$$

6C-atom[longest possible chain]
5C-atom chain including (=) bond so it is preferred

- If in a given compound there are two or more chains having similar number of C-atoms than a chain with maximum side chains is preferred.

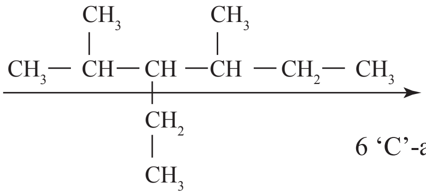
  For example,



$$CH_3-CH_2-\underset{\underset{\displaystyle H_3C-\underset{\underset{CH_3}{|}}{C}-CH_3}{|}}{CH}-CH_2-CH_3$$

5C-atom chain with one-side chain

5C-atom chain with 3-side chains so it is preferred



$$CH_3-\overset{\overset{CH_3}{|}}{CH}-\underset{\underset{\underset{\underset{CH_3}{|}}{CH_2}}{|}}{CH}-\overset{\overset{CH_3}{|}}{CH}-CH_2-CH_3$$

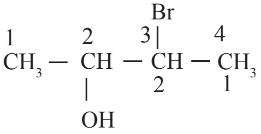
6 ‘C’-atom chain only two-side chains

6 ‘C’-atom chain with 3-side so it is preferred here.

RULES FOR NUMBERING OF C-ATOMS OF THE CHAIN

- For numbering of C-atoms of the chain priority order is given as follows:
  functional group > (=) or (≡) > substituent or alkyl group

For example,



$$\underset{}{\overset{1}{CH_3}}-\underset{\underset{OH}{|}}{\overset{2}{CH}}-\underset{2}{\overset{\overset{Br}{3|}}{CH}}-\underset{1}{\overset{4}{CH_3}}$$

Prefer it (as functional group is at more corner)

Neglect it

- In case of (=) or (≡) bond preference for numbering is given to the one which is at corner or has lower value of locant number.

For example,

1 2 3 4 5 6

$CH_2{=}CH-C\equiv C-CH_2-CH_3$ Prefer it

6 5 4 3 2 1 Neglect it

For example,

1 2 3 4 5 6 7 Prefer it

$CH\equiv C-CH_2-CH{=}CH-CH_2-CH_3$

7 6 5 4 3 2 1 Neglect it

- When both (=) and (≡) bond have same locant numbers prefer (=) bond.

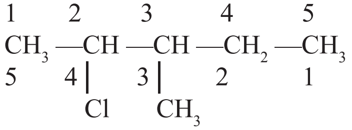
For example,

$CH_2=CH-C\equiv CH$

1 2 3 4

- Similarly, in case of substituent and alkyl groups prefer which has lower locant number value.

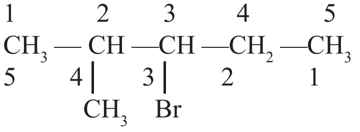
For example,



$$\underset{5}{\overset{1}{CH_3}}-\underset{\underset{Cl}{4|}}{\overset{2}{CH}}-\underset{\underset{CH_3}{3|}}{\overset{3}{CH}}-\underset{2}{\overset{4}{CH_2}}-\underset{1}{\overset{5}{CH_3}}$$

Prefer it as Cl is on 2nd C-atom that is, locant number is two

For example,

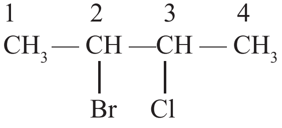


$$\underset{5}{\overset{1}{CH_3}}-\underset{\underset{CH_3}{4|}}{\overset{2}{CH}}-\underset{\underset{Br}{3|}}{\overset{3}{CH}}-\underset{2}{\overset{4}{CH_2}}-\underset{1}{\overset{5}{CH_3}}$$

Prefer it as CH_3 has lower locant number (2) while in case of Br-atom locant number is 3

- In case any two substituent or alkyl groups have same locant numbers prefer alphabetically.

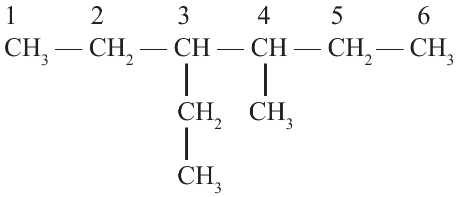
For example,



$$\overset{1}{CH_3}-\underset{\underset{Br}{|}}{\overset{2}{CH}}-\underset{\underset{Cl}{|}}{\overset{3}{CH}}-\overset{4}{CH_3}$$

2- bromo 3- chloro butane [correct]
3- bromo 2- chloro butane [incorrect]

For example,



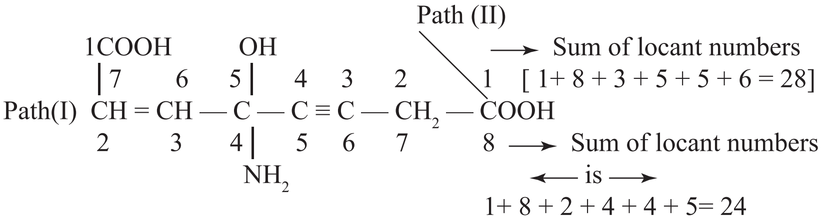
$$\overset{1}{C}H_3-\overset{2}{C}H_2-\overset{3}{C}H(CH_2CH_3)-\overset{4}{C}H(CH_3)-\overset{5}{C}H_2-\overset{6}{C}H_3$$

3-ethyl 4-methyl hexane [correct]
4-ethyl 3-methyl hexane [incorrect]

Lowest Sum Rule

When numbering of a chain is possible from more than one side, prefer numbering of the chain from the side having lowest sum of all the locant numbers.

For example,



$$HOOC-CH=CH-C(OH)(NH_2)-C\equiv C-CH_2-COOH$$

Path (II)

Sum of locant numbers [1+ 8 + 3 + 5 + 5 + 6 = 28]

Path(I)

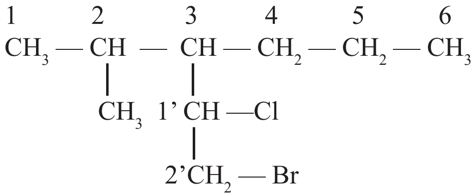
Sum of locant numbers is 1+ 8 + 2 + 4 + 4 + 5= 24

Since, in path (I) the sum is 24 whereas in path (II) it is 28 hence path (I) is preferred here for numbering.

Naming Of Complex Alkyl Substituents

- When a side chain further include another side chain it is numbered and named as,

  For example,

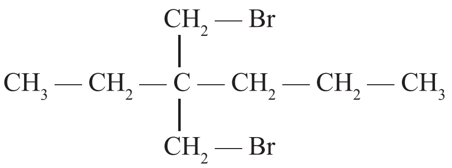


$$\overset{1}{C}H_3-\overset{2}{C}H(CH_3)-\overset{3}{C}H(\overset{1'}{C}H(Cl)-\overset{2'}{C}H_2-Br)-\overset{4}{C}H_2-\overset{5}{C}H_2-\overset{6}{C}H_3$$

3[2’-bromo 1’-chloro] ethyl 2-methyl hexane

- Prefixes like bis, tris, tetrakis etc., can also be used to indicates the multiplicity of substituted substituent.

  For example,

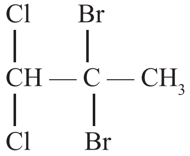


$$CH_3-CH_2-C(CH_2-Br)_2-CH_2-CH_2-CH_3$$

3, 3-bis [Bromomethyl] hexane

- Use prefixes like di, tri, tetra etc., in case of simple substituents with same times locant numbers.

For example,

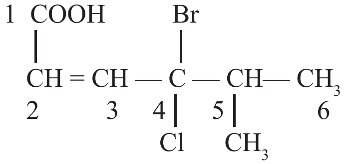


$$\underset{Cl}{\overset{Cl}{CH}}-\underset{Br}{\overset{Br}{C}}-CH_3$$

2, 2-dobromo 1, 1 dichloro propane

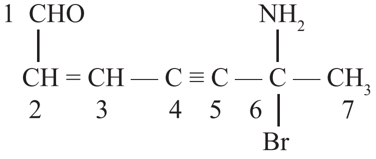
- All prefixes are written before alk (root word) as in above cases however, -ene, -yne or main functional group names, that is, suffix names are written after root word with their locant numbers are followed.
  ---------- Pref x names(Alphabetically) + Alk. + ---------- + ene or yne or main functional group name
  (------- means locant number and di, tri etc.)

For example,



$$\underset{2}{\overset{1\ COOH}{CH}}=\underset{3}{CH}-\underset{4\ Cl}{\overset{Br}{C}}-\underset{5\ CH_3}{CH}-\underset{6}{CH_3}$$

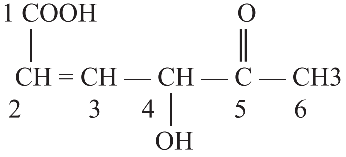
4-bromo 4-chloro 5-methyl-hex-2- en 1-oic acid



$$\underset{2}{\overset{1\ CHO}{CH}}=\underset{3}{CH}-\underset{4}{C}\equiv\underset{5}{C}-\underset{6\ Br}{\overset{NH_2}{C}}-\underset{7}{CH_3}$$

6-amino 6-bromo hept 2-ene 4-yn 1-al

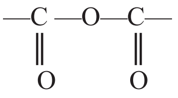
- If a compound has many functional groups the main functional group is named as suffix name while rest are given prefix names.



$$\underset{2}{\overset{1\ COOH}{CH}}=\underset{3}{CH}-\underset{4\ OH}{CH}-\underset{5}{\overset{O}{\overset{\|}{C}}}-\underset{6}{CH3}$$

4-hydroxyl 5-keto hex-2-en 1-oic acid

FUNCTIONAL GROUP PREFERENCE TABLE

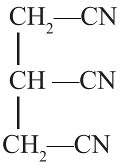
Prefix name	***Functional Group***	***Suffix name***
Sulpho-	$–SO_3H$	-Sulphonic acid
Carboxy-	–COOH	-oic acid
—	 $-\underset{O}{\underset{\|}{C}}-O-\underset{O}{\underset{\|}{C}}-$	-Alkanoic acid-Anhydride
Carbalkoxy-or alkoxy carbonyl-	–COOR	-oate

Continued

Prefix name	*Functional Group*	*Suffix name*
Chloroformyl-	$-COCl$	-oyl chloride
Carbamoyl-	$-CONH_2$	-amide
Cyano-	$-CN$	-nitrile
Isocyano-	$-NC$	-Isonitrile or -carbylamine
Aldo-or formyl-	$-CHO$	-al
Keto or oxo-	$>C=O$	-one
Hydroxy-	$-OH$	-ol
Mercapto-	$-SH$	-thiol
Amino-	$-NH_2$	-amine

* In case carbon atom of the functional group is not countable name them as follows:

-COOH (Carboxylic acid), -COOR (carbanoate), -COCl (carbanoyl chloride), $-CONH_2$ (carbanamide or carboxamide), -CN (carbo nitrile), -CHO (carboxaldehyde).



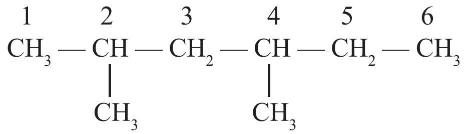
$$\begin{array}{l} CH_2-CN \\ | \\ CH-CN \\ | \\ CH_2-CN \end{array}$$

Propan, 1, 2, 3 -tri carbo nitrile

Examples of Nomenclature

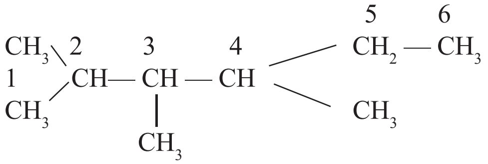
Hydrocarbons These are named as follows:

For example,

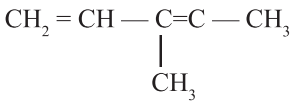


$$\overset{1}{CH_3}-\underset{\underset{CH_3}{|}}{\overset{2}{CH}}-\overset{3}{CH_2}-\underset{\underset{CH_3}{|}}{\overset{4}{CH}}-\overset{5}{CH_2}-\overset{6}{CH_3}$$

2, 4 di-methyl hexane

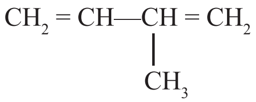


2, 3 , 4 - tri -methyl hexane



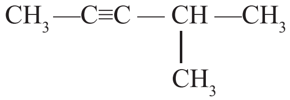
$$CH_2=CH-\underset{\underset{CH_3}{|}}{C}=C-CH_3$$

3-methyl penta 1, 3 di-ene



$$CH_2=CH-\underset{\underset{CH_3}{|}}{CH}=CH_2$$

3- methyl penta 1, 4 di-ene

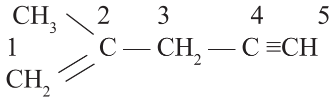


$$CH_3-C\equiv C-\underset{\underset{CH_3}{|}}{CH}-CH_3$$

4-methyl pent 2-yne

$$\underset{5}{CH_3}-\underset{2}{C}\equiv\underset{3}{C}-\underset{2}{CH}=\underset{1}{CH_2}$$

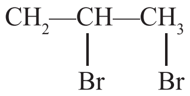
Pent-1-ene-3-yne



2-methyl pent-1-ene 4-yne

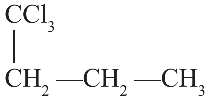
Halo alkanes These are named as follows

For example,



$$CH_2-\underset{\underset{Br}{|}}{CH}-CH_3 \quad (\text{Br on } CH_2)$$

1, 2-di-bromo propane



$$\begin{array}{l} CCl_3 \\ | \\ CH_2-CH_2-CH_3 \end{array}$$

Trichloro butane

or

1, 1, 1 tri-chloro butane

$$\overset{\overset{\mathrm{CHCl_2}}{|}}{\mathrm{CH_2}}-\mathrm{CH=CH_2}$$

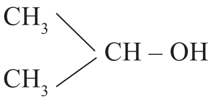
4, 4 di-chloro butene -1

Alcohols (R-OH)

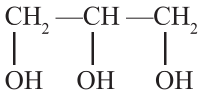
These are named as alkanols

Alkan + ol → Alkanol

For example,

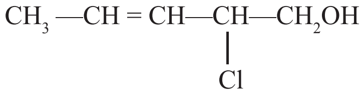


Propan 2-ol



$$\underset{\underset{\mathrm{OH}}{|}}{\mathrm{CH_2}}-\underset{\underset{\mathrm{OH}}{|}}{\mathrm{CH}}-\underset{\underset{\mathrm{OH}}{|}}{\mathrm{CH_2}}$$

Propan -1, 2, 3 tri-ol



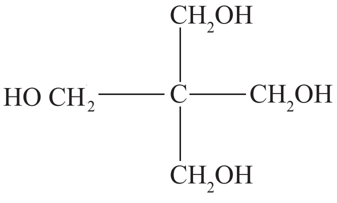
$$\mathrm{CH_3-CH=CH-}\underset{\underset{\mathrm{Cl}}{|}}{\mathrm{CH}}\mathrm{-CH_2OH}$$

2-Chloro-pent-3-en-1-ol

$\mathrm{CH_3-C\equiv C-CH_2OH}$

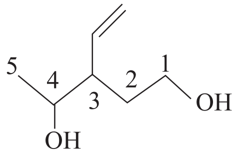
4 3 2 1

But-2-yn-1-ol

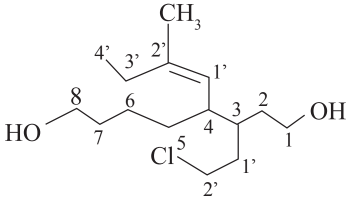


$$\mathrm{HO\,CH_2}-\overset{\overset{\mathrm{CH_2OH}}{|}}{\underset{\underset{\mathrm{CH_2OH}}{|}}{\mathrm{C}}}-\mathrm{CH_2OH}$$

Tetrakis (hydroxymethyl) methane



3-Vinyl pentan-1,4-diol



3-(2-Chloroethyl)-4-(2-methyl)-1-butenyl) octane-1, 8-diol

Ethers: [R —O —R]

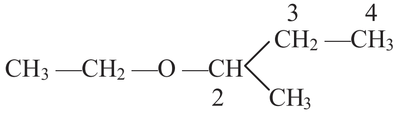
Ethers are named as alkoxy alkanes.

For example,

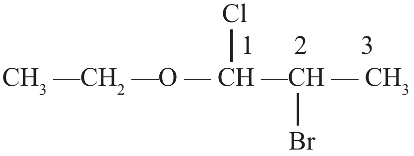
Alkoxy	Alkane
C-atom alkyl group	More C -atom alkyl group

$\mathrm{CH_3—O—CH_2—CH_2—CH_3}$

Methoxy propane



2-Ethoxy butane 1



$$\mathrm{CH_3-CH_2-O-}\overset{\overset{\mathrm{Cl}}{|}}{\underset{1}{\mathrm{CH}}}-\underset{\underset{\mathrm{Br}}{|}}{\overset{2}{\mathrm{CH}}}-\overset{3}{\mathrm{CH_3}}$$

Ethoxy 2-bromo 1-chloro propane

Aldehydes [R—CHO]

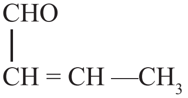
These are named as Alkanals.

Alkan + al → Alkanal

For example,

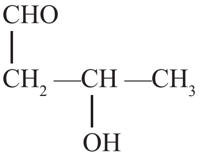
$\mathrm{CH_3—CH_2—CH_2—CHO}$

Butanal



$$\overset{\overset{\mathrm{CHO}}{|}}{\mathrm{CH}}\mathrm{=CH-CH_3}$$

But-2-en-1-al

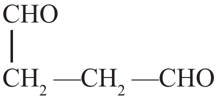


$$\overset{\overset{\mathrm{CHO}}{|}}{\mathrm{CH_2}}-\underset{\underset{\mathrm{OH}}{|}}{\mathrm{CH}}-\mathrm{CH_3}$$

3- hydroxy butanal

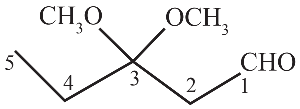
$\mathrm{C_6H_5—CH=CH—CHO}$

3- phenyl-prop -2-en -1-al

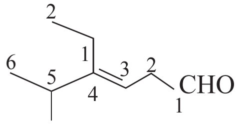


$$\overset{\overset{\mathrm{CHO}}{|}}{\mathrm{CH_2}}-\mathrm{CH_2-CHO}$$

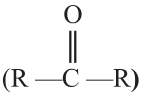
Butan 1, 4-di-al



3,3 -di-methoxy - pentanal



4-(1-Methylethyl)-5-methyl-3-hexenal

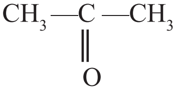


3. **Ketones** $(R-\overset{\overset{O}{\|}}{C}-R)$

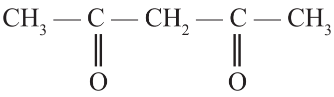
These are named as alkanones.

Alkane + one → Alkanone

For example,

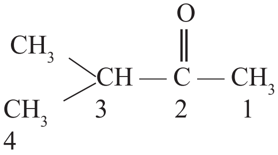


$CH_3-\underset{\underset{O}{\|}}{C}-CH_3$ Propan-2-one



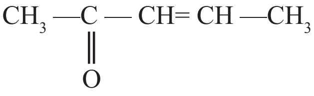
$$CH_3-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-CH_3$$

Pent 2, 4-di-one



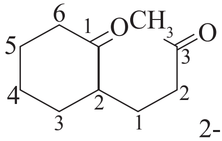
$$\begin{matrix}CH_3\\ CH_3\\ 4\end{matrix}\!\!>\underset{3}{CH}-\underset{2}{\overset{\overset{O}{\|}}{C}}-\underset{1}{CH_3}$$

3-methyl butan-2-one



$$CH_3-\underset{\underset{O}{\|}}{C}-CH=CH-CH_3$$

Pent-3-en-2-one

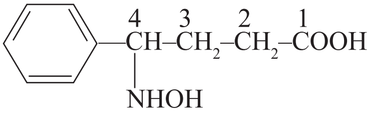


2-(-3-oxobutyl) cyclohexanone

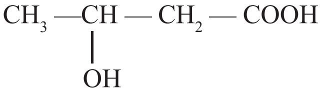
Carboxylic Acids (R—COOH)

These are named as alkanoic acids.

Alkan + oic acid → Alanoic acid

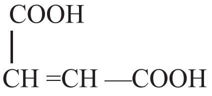


4-(Hyroxylamino)-4-phenylbutanoic acid



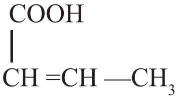
$$CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-COOH$$

3- hydroxyl butanoic acid



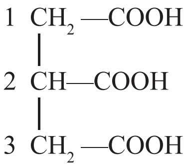
$$\overset{\overset{COOH}{|}}{CH}=CH-COOH$$

But-2-ene1, 4 di-oic acid



$$\overset{\overset{COOH}{|}}{CH}=CH-CH_3$$

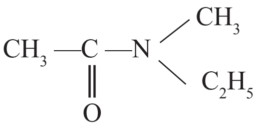
But 2-en-1-oic acid



$$\begin{array}{ll}1 & CH_2-COOH\\ & |\\ 2 & CH-COOH\\ & |\\ 3 & CH_2-COOH\end{array}$$

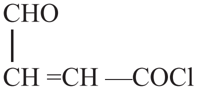
Propane 1, 2, 3-tri-carboxylic acid

Acid derivatives



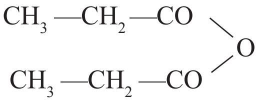
$$CH_3-\underset{\underset{O}{\|}}{C}-N\begin{matrix}\diagup CH_3\\ \diagdown C_2H_5\end{matrix}$$

N-ethyl N-methyl ethanamide



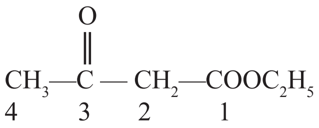
$$\overset{\overset{CHO}{|}}{CH}=CH-COCl$$

4-oxo-but 2-en 1-oyl chloride



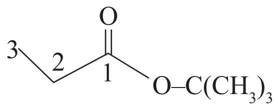
$$\begin{matrix}CH_3-CH_2-CO\\ CH_3-CH_2-CO\end{matrix}\!\!>O$$

Propanoic anhydride

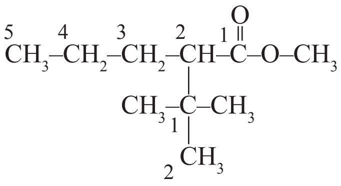


$$\underset{4}{CH_3}-\underset{3}{\overset{\overset{O}{\|}}{C}}-\underset{2}{CH_2}-\underset{1}{COOC_2H_5}$$

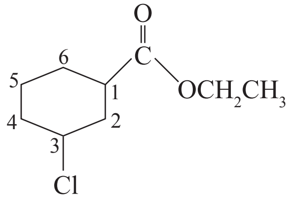
Ethyl 3-keto butanoate



tert-butyl propanoate



Methyl 2-(1, 1)-dimethylethy) pantanoate

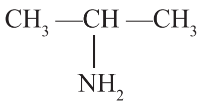


ethyl 3-chloro cyclohexane carboxylate

Amines Amines are named as follows:

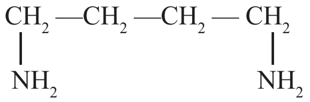
(A) **Primary Amines** [$R-NH_2$]: These are called amino alkanes or alkanamines.

$CH_3-CH_2-NH_2$
Amino ethane
or
Ethanamine



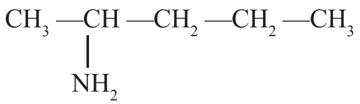
$$CH_3-\underset{\underset{NH_2}{|}}{CH}-CH_3$$

2-amino propane



$$\underset{\underset{NH_2}{|}}{CH_2}-CH_2-CH_2-\underset{\underset{NH_2}{|}}{CH_2}$$

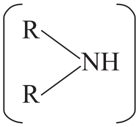
1, 4 -di- amino butane



$$CH_3-\underset{\underset{NH_2}{|}}{CH}-CH_2-CH_2-CH_3$$

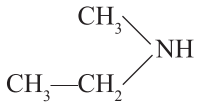
2-amino penptane

(B) **Secondary amines**

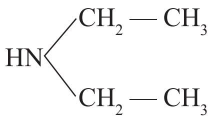


These are named as N-alkyl alkanamines.

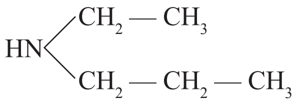
N-alkyl	alkanamine
for smaller	for longer
alkyl group	alkyl group



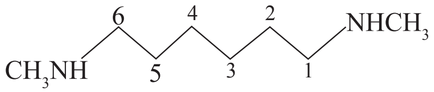
N-methyl ethanamine



N-ethyl ethanamine

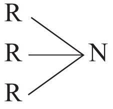


N-ethyl propanamine



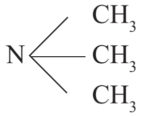
N, N'-di-methyl-hexane
–1, 6-di-amine

(C) **Tertiary amines (R_3N):**

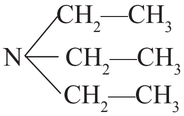


N-N di alkyl alkanamine
or
N alkyl N'-alkyl-alkan amine

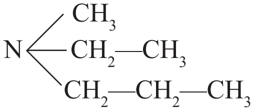
For example,



N, N-di-methyl methanamine



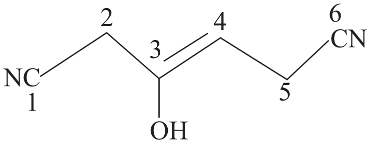
N-N di-ethyl ethanamine



N-ethyl N'-methyl propanamine

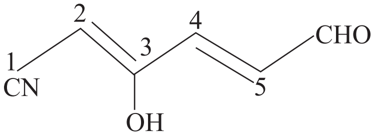
Cynides And Isocynides

(1)



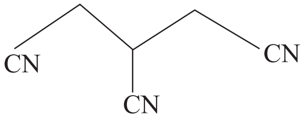
3- Hydroxy hex 3-ene 1, 6-di-nitrile

(4)



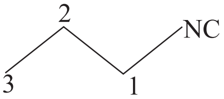
5-Aldo 3-hydroxy pent -3, 4 di-ene 1-nitrile

(2)



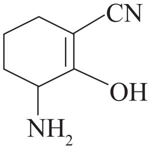
Propane 1,2,3-tri-carbonitrile

(5)



Propane Carbyl amine

(3)



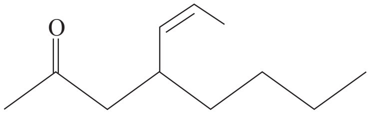
3-Amino 2-hydroxyl cyclo hexene 1-carbonitrile

(6) $C_6H_5CH_2NC$
Benzyl carbyl amine

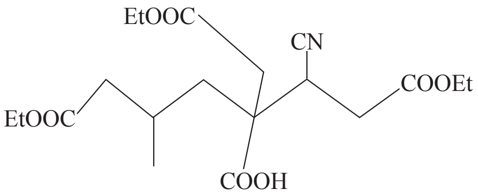
Problems

Give the IUPAC nomenclature to each of the following molecules:

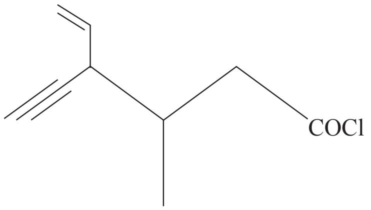
(i)



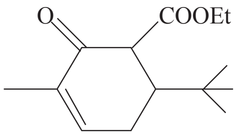
(ii)



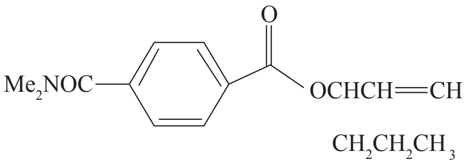
(iii)



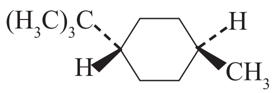
(iv)



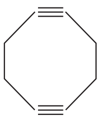
(v)



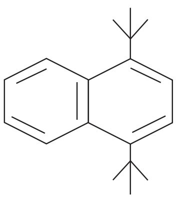
(vi)



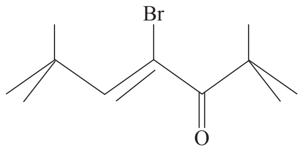
(vii)



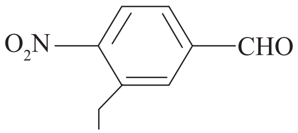
(viii)



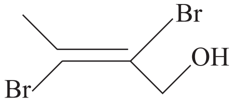
(ix)



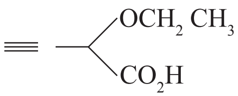
(x)



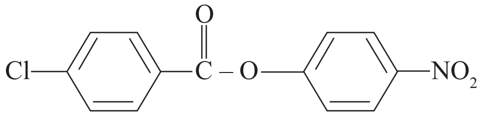
(xi)



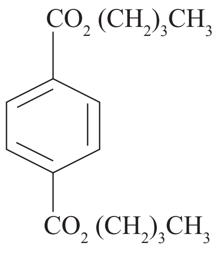
(xii)



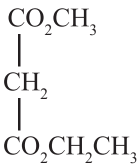
(xiii)



(xiv)

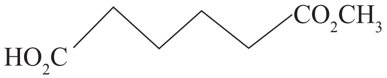


(xv)



$$\begin{array}{l} CO_2CH_3 \\ | \\ CH_2 \\ | \\ CO_2CH_2CH_3 \end{array}$$

(xvi)



Answers

(i) 4-Butylhept-5-en-2-one

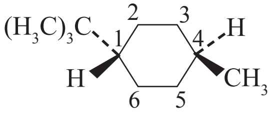
(ii) 4- Bromo-2-(2-carbethoxy-1- cyanoethy)-2-(1- carbethoxymethyl) -5-carbethoxypentan-oic acid

(iii) 2-Chloroformyl-3-ethynyl-pent-4-en-1-oic acid

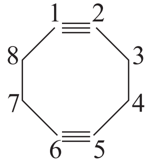
(iv) Ethyl 6[-1, 1-Dimethylethyl]-3-methyl-2-oxocyclohex-3-en-1-carboxylate

(v) 1 ‘-Propylprop-2’-enyl-4-N, N-dimethylcarbamoylbenzoate

(vi) trans-1-tert -butyl-4-methylcyclohexane



(vii) 1, 5-Cyclooctadiyne: Both triple bonds internal and endocyclic.



(viii) 1, 4-Di-tert-butylnaphthralene.

(ix) Z-4-bromo-2 ,2, 6, 6 -tetramethyl-4-hepten-3-one

(x) 3-iodo-4-nitrobenzaldehyde

(xi) trans-2, 3-dibromo -2-buten-1-ol

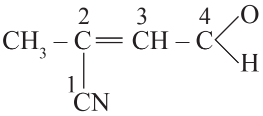
(xii) 2-ethoxy-3-butynoic acid

(xiii) 4 (or para)-nitrophenyl 4 (or para)-chlorobenzoate

(xiv) dibutyl tetraphthalate

(xv) ethyl methyl malonate

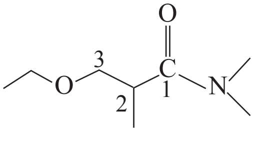
(xvi) methyl succinate



$$CH_3-\underset{\overset{1}{|}\atop CN}{\overset{2}{C}}=\overset{3}{C}H-\overset{4}{C}\genfrac{}{}{0pt}{}{O}{H}$$

2-Methyl-4-oxo-2-butenonitrile.

Methyl methyl propanedioate



2, N, N-trimethyl-3-ethoxy-propanamide.

ISOMERISM

The compounds which differ in their properties but have same molecular formula are called isomers and the phenomenon is known as isomerism.

TYPE OF ISOMERISM

Isomerism is of following three types:

- Structural or constitutional isomerism
- Stereo or configurational isomerism
- Conformational isomerism

STRUCTURAL OR CONSTITUTIONAL ISOMERISM

In this type of isomerism, compounds possessing same molecular formula differ in their properties due to the difference in the linkages of atoms inside the molecule, that is, due to the difference in their structures. Here isomers differ in the connectivity of carbon atoms that is, differ in structural formula. Structural isomers differ much in their physical as well as chemical properties.

For example, CH_3CH_2OH and CH_3OCH_3. Both have the molecular formula C_2H_6O but they differ in their structures.

Type of Structural Isomerism

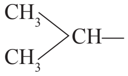
It is of following types:

Chain or Skeleton or Nucleus Isomerism In this type of isomerism, compounds possessing same molecular formula differ in their properties due to the difference in the arrangement of carbon chain present in them. The isomers differ in chain of carbon atoms that is, branched or unbranched chain. Here a chain of minimum 4 carbon atoms is necessary to show this isomerism.

For example,

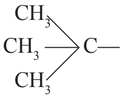
$CH_3 – CH_2 – CH_2 – CH_2 – CH_2 –$

Normal alkane



$$\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle CH—$$

Iso alkane



$$\left.\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\right\rangle C—$$

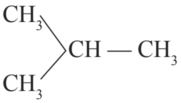
Neo alkane

For example, (1)

C_4H_{10}:

$CH_3 – CH_2 – CH_2 – CH_3$

n-butane



$$\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle CH — CH_3$$

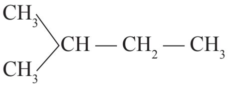
Isobutene (2-methyl propane)

For example, (2)

C_5H_{12}:

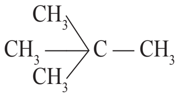
$CH_2 – CH_2 – CH_2 – CH_2 – CH_3$

n-pentane



$(CH_3)_2CH-CH_2-CH_3$

Isopentane



$(CH_3)_3C-CH_3$

Neopentane

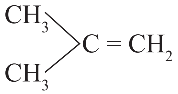
S. No.	*Molecular Formula*	*Number of isomers*
1	C_4H_{10}	2
2	C_5H_{12}	3
3	C_6H_{14}	5
4	C_7H_{16}	9
5	C_8C_{18}	18
6	C_9H_{20}	35
7	$C_{10}H_{22}$	75
8	$C_{15}H_{32}$	347

Ring Chain Isomerism Here in isomers mode of chain formation differs that is, open or close type of chain formation. Ring chain isomers are also functional isomers.

For example, (1) Alkene and cyclo alkane ($C_n H_{2n}$)

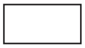
C_4H_8:

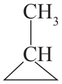
$CH_3-CH_2-CH=CH_2$



$(CH_3)_2C=CH_2$

$CH_3-CH=CH-CH_3$ [cis and trans]





For example, (2): Cyclo alkenes, alkynes and alkadienes **(C_nH_{2n-2})**

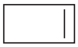
For example, (1)

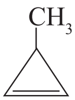
C_4H_6: Alkynes

$CH_3-C\equiv C-CH_3$, $H-C\equiv C-CH_2-CH_3$

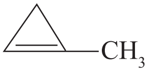
Alkadienes

$CH_2=CH-CH=CH_2$, $CH_3-CH=C=CH_2$





or



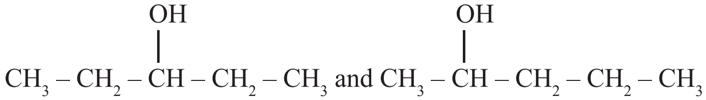
Position Isomerism In this type of isomerism, the compounds possessing same molecular formula differ in their properties due to the difference in the position of either the functional group or the multiple bond or the branched chain or the substituent attached to the main carbon chain.

For example, (1)

$$CH_3-CH_2-\overset{\overset{\large O}{\|}}{C}-CH_2-CH_3 \quad \text{and} \quad CH_3-CO-CH_2-CH_2-CH_3$$

Pentanone-3 Pentanone-2

For example, (2)



$$CH_3-CH_2-\overset{\overset{\large OH}{|}}{C}H-CH_2-CH_3 \text{ and } CH_3-\overset{\overset{\large OH}{|}}{C}H-CH_2-CH_2-CH_3$$

Pentanol-3 Pentanol-2

For example, (3)

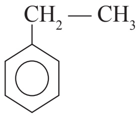
C_4H_8:

$CH_2=CH-CH_2-CH_3$ and $CH_3-CH=CH-CH_3$

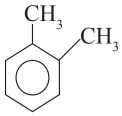
Butene-1 But-2-ene

For example, (4)

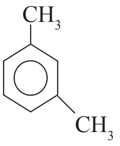
C_8H_{10}:



I



II



III

IV

- Here II, III and IV are positional isomers.

Functional Isomerism It is the type of isomerism in which the compounds possessing same molecular formula differ in their properties due to the difference in their functional groups.

For example,

(1) –CN (cyanide) and –NC (Isocyanide)

CH_3CN and CH_3NC

(2) $-NO_2$ (ntiro) and –ONO (Nitrite)

$C_2H_5NO_2$ (Nitro ethane) and C_2H_5ONO (Ethyl nitrite)

(3) primary (RNH_2), secondary (R_2NH) and tertiary amines (R_3N)

Metamerism It is the type of isomerism in which the compounds possessing same molecular formula differ in their properties due to the difference in the alkyl groups present in them that is, same functional group but different alkyl groups attached to it. It is shown by ether, thioether, ketones, esters, secondary amines, tertiary amines and alkenes

For example,

(1) $CH_3-COOCH_3$ and $HCOOC_2H_5$ are metamers.

(2) $C_2H_5-NH-C_2H_5$ and $CH_3-NH-CH_2CH_2CH_3$ are metamers.

(3) $C_2H_5-O-C_2H_5$ and $CH_3-O-CH_2CH_2CH_3$ Or $CH_3-O-CH(CH_3)_2$

(4) $C_2H_5-NH-C_2H_5$ and $CH_3-NH-CH_2CH_2CH_3$ Or $CH_3-NH-CH(CH_3)_2$

Some Molecular Formulas and Possible Isomers

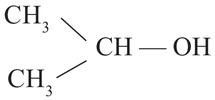
(i) **Alcohol and Ether ($C_n H_{2n+2} O$):** It has alcohols, ethers and the possible isomerisms are functional, positional , chain and metamerism

C_2H_6O:

$CH_3 – O – CH_3$ (Methoxy methane)
$CH_3 – CH_2 – OH$ (Ethanol)

C_3H_8O:

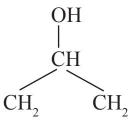
$CH_3 – O – CH_2 – CH_3$, $CH_3 – CH_2 – CH_2OH$

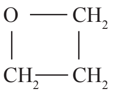


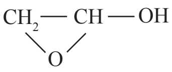
C_4H_8O: It has four alcohols and 3 ethers.(draw your self)

(5) **$C_n H_{2n} O$:** The isomers having this molecular formula are Aldehyde, Ketone, Cyclic alcohol, Cyclic ether, Unsaturated alcohol, Unsaturated Ether and Epoxyether. Here possible isomerisms are functional, position and chain.

For example, **C_3H_6O:**

- $CH_3 – CH_2 – CHO$, $CH_3 – CO – CH_3$
- $CH_2 = CH – CH_2 – OH$, $CH_2 = CH –O\ CH_3$
- 

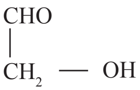




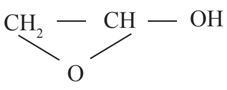
(6) **$C_n H_{2n} O_2$:** The isomers having this molecular formula are Acid, Ester, Aldehyde with –OH group, Ketone with –OH group and Cyclic ether with –OH group. Here possible isomerisms are functional, position and chain.

For example, **$C_2H_4O_2$:**

- $CH_3 — COOH$, $HCOOCH_3$



$$\begin{array}{l} CHO \\ | \\ CH_2 — OH \end{array}$$



$C_3H_6O_2$:

For example,

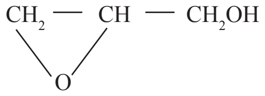
$CH_3 – CH_2 – COOH$

$CH_3 – COOCH_3$

$HCOOC_2H_5$

$CH_2OH – CH_2CHO$

$CH_2OH-COOCH_3$

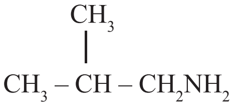


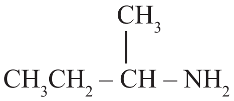
(7) **$C_nH_{2n+3}N$:** It has primary, secondary and tertiary amines and possible isomerisms are functional chain, position. and metamerism.

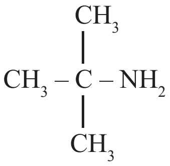
For example,

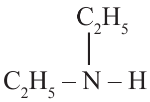
$C_4H_{11}N$ has 4-primary, 3-secondary and 1-tertiary amines that is, 8 isomers in all.

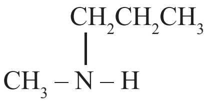
(i) $CH_3CH_2CH_2CH_2NH_2$

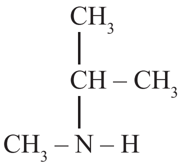
(ii)

$CH_3-\overset{\overset{\large CH_3}{|}}{CH}-CH_2NH_2$

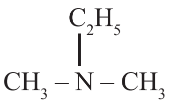
(iii)

$CH_3CH_2-\overset{\overset{\large CH_3}{|}}{CH}-NH_2$

(iv)

$CH_3-\underset{\underset{\large CH_3}{|}}{\overset{\overset{\large CH_3}{|}}{C}}-NH_2$

(v)

$C_2H_5-\overset{\overset{\large C_2H_5}{|}}{N}-H$

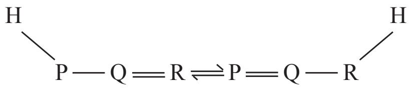
(vi)

$CH_3-\overset{\overset{\large CH_2CH_2CH_3}{|}}{N}-H$

(vii)

$CH_3-\overset{\overset{\overset{\overset{\large CH_3}{|}}{CH}-CH_3}{|}}{N}-H$

(viii)

$CH_3-\overset{\overset{\large C_2H_5}{|}}{N}-CH_3$

Tautomerism

Other Names: krytomerism, allelotropism, metrotropy, ketoenol isomerism. It was introduced by Conard Larr. It is the type of isomerism in which the two functional isomers exist together in a dynamic equilibrium and the two forms existing in the equilibrium are called tautomers. These forms are formed due to the migration of H^+ or proton (cation mainly) due to which bond position changes (Desmotropism). The migration of H^+ or proton is called cationtropism or prototropism. The least stable form is called labile form.

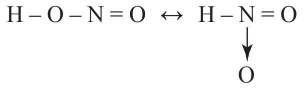


(shifting of 'H' from P to R)

The migration of cation is possible in following two ways:
Diad System Here H^+ (cation) migrates to next atom.

For example,

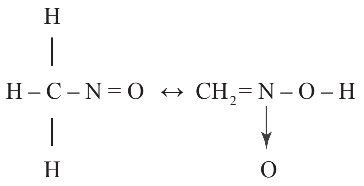
$$\mathrm{H-C\equiv N \leftrightarrow H-N \rightrightarrows C}$$



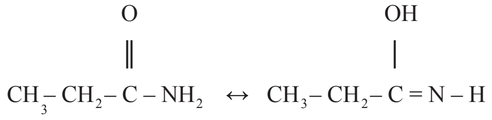
$$\mathrm{H-O-N=O \leftrightarrow H-\underset{\downarrow \atop O}{N}=O}$$

Triad System Here H^+ migrates to next alternate atom (3^{rd})

For example,

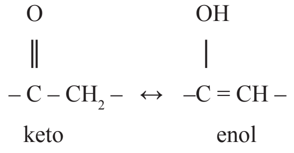


$$\mathrm{H-\overset{H}{\underset{H}{C}}-N=O \leftrightarrow CH_2=\underset{\downarrow \atop O}{N}-O-H}$$



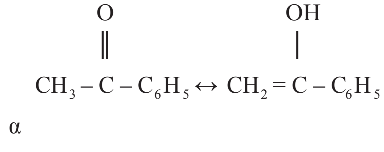
$$\mathrm{CH_3-CH_2-\overset{O}{\overset{\|}{C}}-NH_2 \leftrightarrow CH_3-CH_2-\overset{OH}{\overset{|}{C}}=N-H}$$

Keto-enol Isomerism It is the most common type of tautomerism in which the two tautomeric forms are keto and enol forms which are formed as a result of migration of α - hydrogen atom. The presence of α - hydrogen atoms is must here, however, α – C – atom must not be unsaturated.



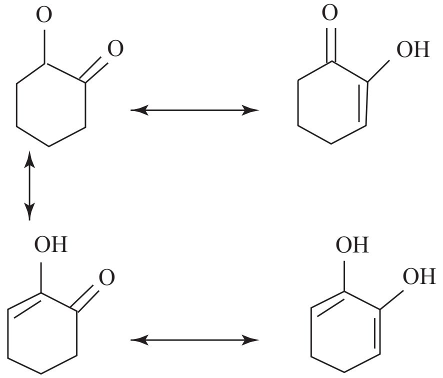
$$\mathrm{-\overset{O}{\overset{\|}{C}}-CH_2- \leftrightarrow -\overset{OH}{\overset{|}{C}}=CH-}$$

For example,

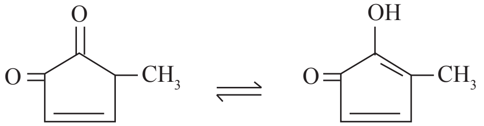


$$\mathrm{CH_3-\overset{O}{\overset{\|}{C}}-C_6H_5 \leftrightarrow CH_2=\overset{OH}{\overset{|}{C}}-C_6H_5}$$

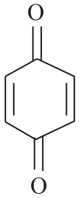
For example,

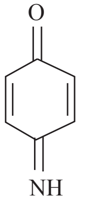


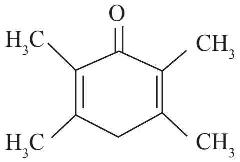
Unsaturated



For example,





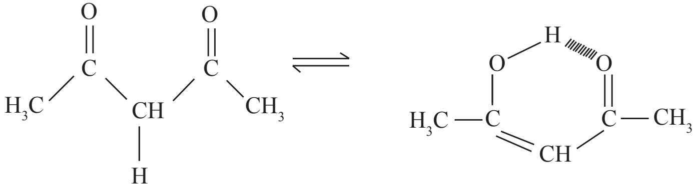


These cannot show tautomerism as all α-carbon atoms are unsaturated so migration of α-H-atom is not possible.

- Enol content $\propto$ (proportional) Number of α-H-atom
- Enol content $\propto$ (proportional) Acidic nature

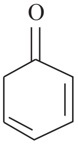
Enol content $\propto$ Number of carbonyl groups

In acyclic β-diketones generally enol content is higher

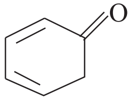
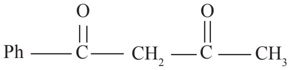
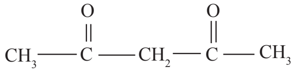
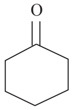
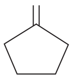
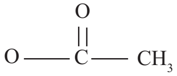
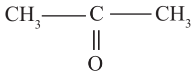


In this case, enol form is stabilized by extended conjugation and Intramolecular hydrogen bonding.

Enol Content in Decreasing Order



> $C_6H_5COCH_2COCH_3$ > $CH_3COCH_2COCH_3$ > $CH_3COCH_2COOC_2H_5$ > CH_3COCH_2CHO > CH_3COCH_3 > CH_3CHO

Compound	*% of enol content*
	99.99 %
EtOOCCH$_2$COOEt	7.7 × 10–3
 $Ph-\overset{O}{\overset{\Vert}{C}}-CH_2-\overset{O}{\overset{\Vert}{C}}-CH_3$	89 %
 $CH_3-\overset{O}{\overset{\Vert}{C}}-CH_2-\overset{O}{\overset{\Vert}{C}}-CH_3$	76 %
CH$_3$COCH$_2$COOEt	8.4
Ph$_2$CH – CHO	9.1
(CH$_3$)$_2$CHCHO	1.4 × 10^{-4}
Butanal	5.5 × 10^{-4}
	4 × 10^{-5}
CH$_3$CHO	6 × 10^{-5}
	1.0 × 10^{-6}
 $O-\overset{O}{\overset{\Vert}{C}}-CH_3$	
 $CH_3-\underset{O}{\underset{\Vert}{C}}-CH_3$	1.1 × 10^{-6}
	6 × 10^{-7}

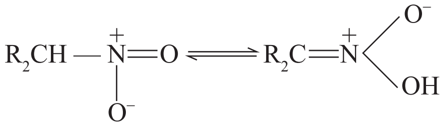
Some Specific Examples of Tautomerism

(i) Nitroso-oxime tautomerism

$R_2CH-N=4=O \rightleftharpoons R_2C=N-OH$

(nitroso) (oxime)

(ii) Nitro-acinitro tautomerism



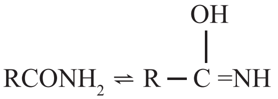
(nitro -Form) (aci- Form)

(iii) Imine-enamine tautomerism

$R_2CH-C(R)=NR \rightleftharpoons R_2C=C(R)-NHR$

(imine) (enamine)

(iv) Amide-imidol tautomerism



$$\mathrm{RCONH_2 \rightleftharpoons R-\overset{\displaystyle OH}{\overset{|}{C}}=NH}$$

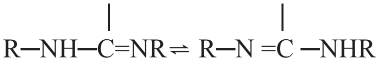
(amide) (imidol)

(v) Azo-hydrazone tautomerism

$\mathrm{R_2CH-N=N-R \rightleftharpoons R_2C=N-NHR}$

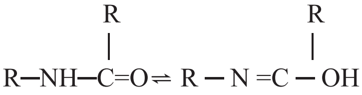
(azo-form) (hydrazone)

(vi) Amidine tautomerism



$$\mathrm{R-NH-\overset{|}{C}=NR \rightleftharpoons R-N=\overset{|}{C}-NHR}$$

(vii) Lactum-lactim tautomerism



$$\mathrm{R-NH-\overset{\displaystyle R}{\overset{|}{C}}=O \rightleftharpoons R-N=\overset{\displaystyle R}{\overset{|}{C}}-OH}$$

(lactum) (lactim)

STEREO ISOMERISM OR SPACE ISOMERISM

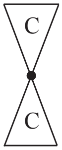
In this type of isomerism, the compounds possessing same molecular formula differ in their properties due to the difference in the arrangement in space of their atoms or groups in the molecule.

Types of Stereo Isomerism

It is of following types:

(1) Geometrical Isomerism

It is the type of isomerism in which the compounds possessing same molecular formula differ in their properties due to the difference in their geometry that is, due to the difference in the direction of attachment of same atoms or groups in their molecule. It is not shown by single bonded compounds like (C–C) due to free rotation.

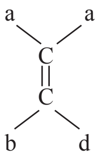


Head to head or free rotation is possible here so no geometrical isomerism is possible.

It is shown by [>C = C<], [>C = N –] [– N = N –] , cyclo alkanes.

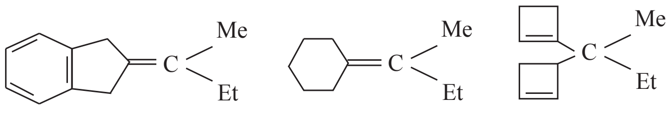
Geometrical Isomerism in Alkenes and Cyclo Alkanes

- Case I

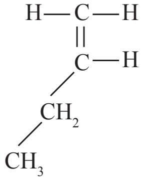


Same atoms or groups so no geometrical isomerism

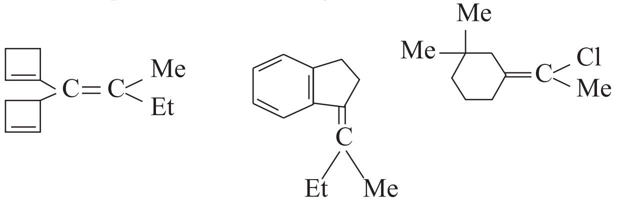
These compounds cannot exhibit geometrical isomerism.



Butene – 1 also does not show geomatrical isomerism.

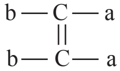


These compounds can exhibit geometrical isomerism.



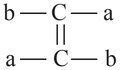
Compounds capable of exhibiting geometrical isomerism.

- Case II



$$\begin{array}{ccc} \mathrm{b} & \mathrm{—C—} & \mathrm{a} \\ & \| & \\ \mathrm{b} & \mathrm{—C—} & \mathrm{a} \end{array}$$

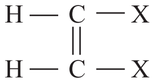
cis



$$\begin{array}{ccc} \mathrm{b} & \mathrm{—C—} & \mathrm{a} \\ & \| & \\ \mathrm{a} & \mathrm{—C—} & \mathrm{b} \end{array}$$

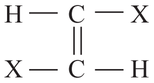
trans

For example, $C_2H_2X_2$



$$\begin{array}{ccc} \mathrm{H} & \mathrm{—C—} & \mathrm{X} \\ & \| & \\ \mathrm{H} & \mathrm{—C—} & \mathrm{X} \end{array}$$

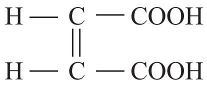
Cis



$$\begin{array}{ccc} \mathrm{H} & \mathrm{—C—} & \mathrm{X} \\ & \| & \\ \mathrm{X} & \mathrm{—C—} & \mathrm{H} \end{array}$$

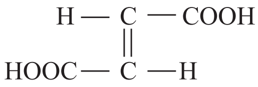
Trans

For example, $C_4H_4O_4$



$$\begin{array}{ccc} \mathrm{H} & \mathrm{—C—} & \mathrm{COOH} \\ & \| & \\ \mathrm{H} & \mathrm{—C—} & \mathrm{COOH} \end{array}$$

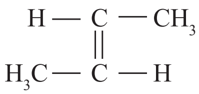
Cis
Maleic acid



$$\begin{array}{ccc} \mathrm{H} & \mathrm{—C—} & \mathrm{COOH} \\ & \| & \\ \mathrm{HOOC} & \mathrm{—C—} & \mathrm{H} \end{array}$$

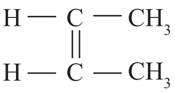
Trans
Fumeric acid

For example, 2-Butene



$$\begin{array}{ccc} \mathrm{H} & \mathrm{—C—} & \mathrm{CH_3} \\ & \| & \\ \mathrm{H_3C} & \mathrm{—C—} & \mathrm{H} \end{array}$$

Trans-2-butene



$$\begin{array}{ccc} \mathrm{H} & \mathrm{—C—} & \mathrm{CH_3} \\ & \| & \\ \mathrm{H} & \mathrm{—C—} & \mathrm{CH_3} \end{array}$$

Cis-2-butene

Difference between Cis and Trans Forms

Cis:

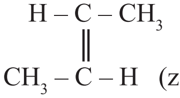
- Cis is more reactive but less stable form as the same species are on the same side so steric repulsion increases reactivity and decreases stability.
- The dipole moment of cis is more.
- It has less melting point as same groups are on same side.

- The boiling point of cis is more.
- The solubility, viscosity refractive index of cis is more.

Trans:

- It is more stable but less reactive form as same species are on the opposite sides.
- The dipole moment is mostly zero due to symmetry in case of symmetrical alkenes.

For example,

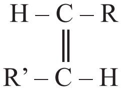


$$\begin{array}{c} H-C-CH_3 \\ \| \\ CH_3-C-H \end{array}$$

(zero)

Trans-2-butene

- In case of unsymmetrical alkenes, due to little unsymmetry there may be some dipole moment value also,

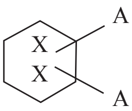


$$\begin{array}{c} H-C-R \\ \| \\ R'-C-H \end{array}$$

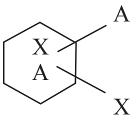
For example, trans-2-pentene has some dipole moment value but less than cis form.

- Have more melting point than cis.
- The boiling point of trans form is less.
- The solubility, viscosity refractive index are less than cis form.

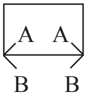
Geometrical Isomerism in Cyclo Alkanes



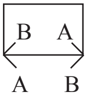
Cis



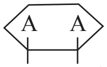
Trans



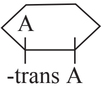
Cis



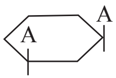
Trans



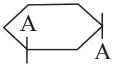
1, 2 - cis



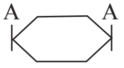
1, 2 -trans



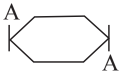
1, 3 - cis



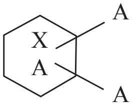
1, 3 - trans



1, 4 - cis

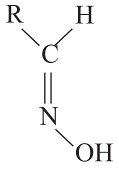


1, 4 - trans

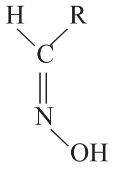


It cannot show geometrical isomerism as one carbon atom has two similar species ‘A’.

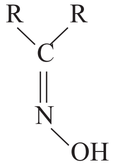
Geometrical Isomerism in Oximes and Azo Compounds



Syn



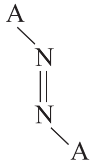
Anti-form



It cannot show geometrical isomerism as one carbon atom has two similar species (R).

- In azo compounds

syn



anti

Here, the attached groups may be differ also that is, A and B.

Calculation of Geometrical Isomer

(A) When Ends are Different

Number of geometrical isomers $= 2^n$

Here, n = number of double bonds

For example, $CH_3 - CH = CH - CH = CH - Cl$

$n = 2$

Number of geometrical isomers

$= 2^n = 2^2 = 4$

(B) When Ends are Same

(i) *When n is an even number*

Number of Geometric Isomers

$$= 2^{n-1} + 2^{n/2-1}$$

For example, $X - CH = CH - CH - CH = CH - CH = CH - CH = CH - X$

$n = 4$

Number of geometric isomers

$= 2^{4-1} + 2^{4/2-1}$

$= 2^3 + 2^1 = 10$

(ii) *When n is an odd number*

Number of geometric isomers

$$= 2^{n-1} + 2^{(n+1/2)} - 1$$

For example, $CH_3 - CH = CH - CH = CH - CH = CH - CH_3$

$n = 3$

Number of geometric isomers

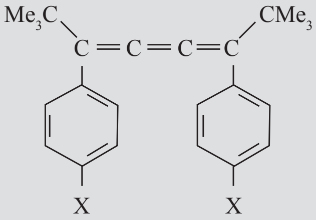
$= 2^{3-1} + 2^{(3+1)}/2 - 1$

$= 2^2 + 2^1 = 6$

REMEMBER

In comulated system, if compound contains odd number of double bond, it can show geometrical isomerism.

For example,



Stereomutation: The conversion of cis-from into trans-form and vice versa is known as stereomutation.

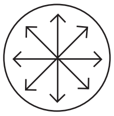
$$\text{Maleic acid} \xrightleftharpoons{\text{UV radiation}} \text{Fumaric acid}$$

OPTICAL ISOMERISM

It is the type of isomerism in which the compounds possessing same molecular formula differ in their direction of bringing the optical rotation or the extent of bringing the optical rotation.

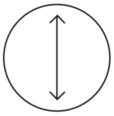
Plane Polarized Light

The light from an ordinary source is composed of waves vibrating in many different planes perpendicular to the plane of its propagation. When such a light is passed through a Nicol prism, the light coming through is found to be vibrating in only one plane. Such a light is called as plane polarized light and here Nicol prism is called Polaroid.



Simple light

Nicol prism or (calcite) $CaCO_3$



Plane Polarized Light (light with unidirectional vibration)

Optical Activity or Optical Rotation

The optically active substances rotate the plane polarized light clockwise or anti-clockwise that is, dextro and laevo rotation respectively at an angle θ this rotation is called optical rotation. Here, in both the rotations there is a same value of θ but with opposite signs that is, same in magnitude but opposite in direction.

Optical rotation is measured by polarometer in terms of specific rotation.

$$[\alpha]_{\lambda}^{t^\circ c} = \frac{\alpha\ (\text{observed})}{l \times c}$$

here α = specific rotation

α (observed) = observed value of rotation

l = length of solution
c = concentration of solution.

Specific Rotation Depends Upon

- Nature of solute and solvent.
- Wavelength of light during the experiment.
- Temperature during the experiment.
- Length and concentration of solution.

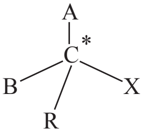
Reason of Optical Activity or Optical Isomerism

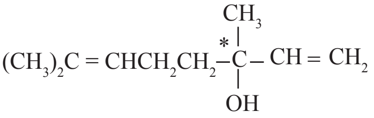
- The compound must be asymmetric or dissymmetric with a non-super imposable mirror image.

  For example, a hand in mirror.

  Ambulance in mirror.
- The asymmetric molecule does not have plane or central or axial axis of symmetry.

Chiral Center or Stereogenic Center



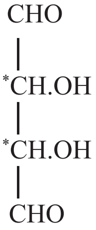


$$(CH_3)_2C=CHCH_2CH_2-\overset{CH_3}{\underset{OH}{\overset{*}{C}}}-CH=CH_2$$

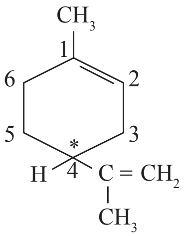
Linalool
(a pleasant smelling oil obtained from orange flowers)

For example, Lactic acid,
$CH_3\,.{}^{*}CH.OH\,.COOH$

For example,

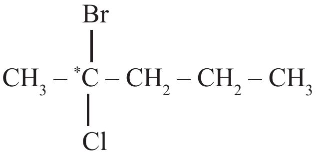


$$\begin{array}{c} CHO \\ | \\ {}^{*}CH.OH \\ | \\ {}^{*}CH.OH \\ | \\ CHO \end{array}$$

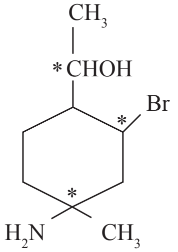


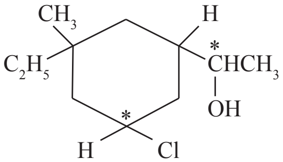
Limonene
(a constituent of lemon oil)

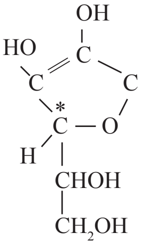
For example, 2-Bromo-2-chloro-pentane



$$CH_3-{}^{*}\overset{Br}{\underset{Cl}{C}}-CH_2-CH_2-CH_3$$

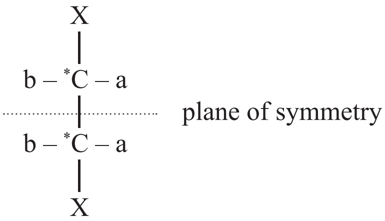






Types of Symmetry:

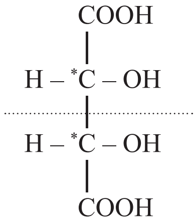
(A) Plane of Symmetry: For it, minimum two stereogenic centers are needed. Here, the molecule can be divided into two equal halves.



$$\begin{array}{c} X \\ | \\ b - {}^{*}C - a \\ | \\ b - {}^{*}C - a \\ | \\ X \end{array}$$

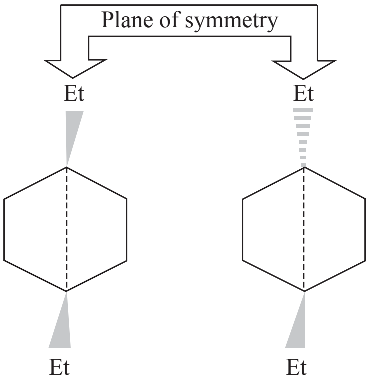
- It is an optically inactive form due to mutual cancellation (or) internal compensation.

For example,

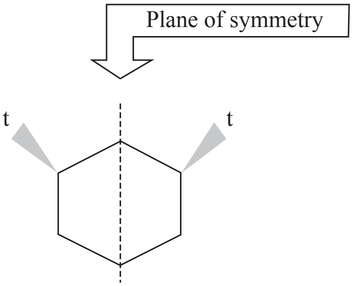


$$\begin{array}{c} COOH \\ | \\ H - {}^{*}C - OH \\ | \\ H - {}^{*}C - OH \\ | \\ COOH \end{array}$$

Meso tartaric acid

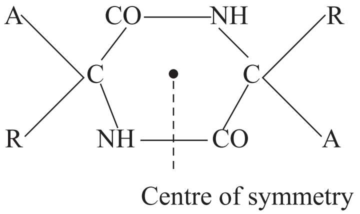


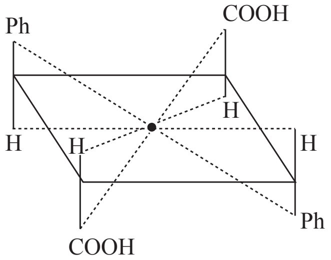
The cis and trans forms of 1, 4-dimethylcyclohexane are diastereomers of each other. Both compound are achiral.



cis-1, 3-dimethylcyclohexane has a plane of symmetry and is therefore achiral.

(B) Center of Symmetry

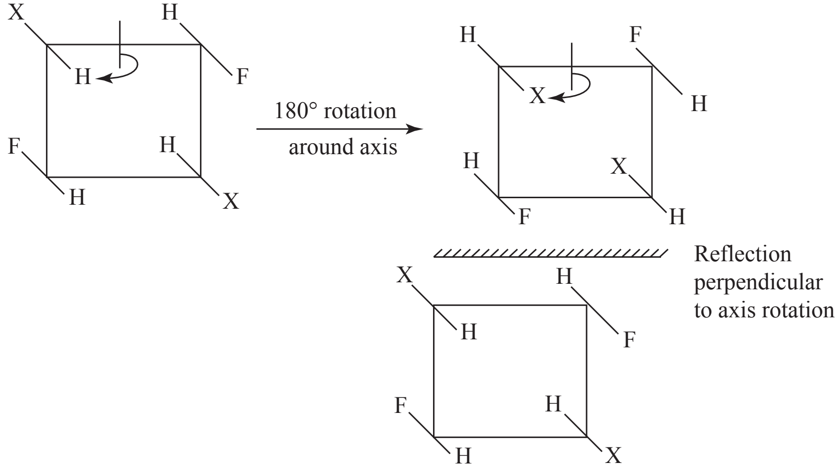




α-truxillic acid

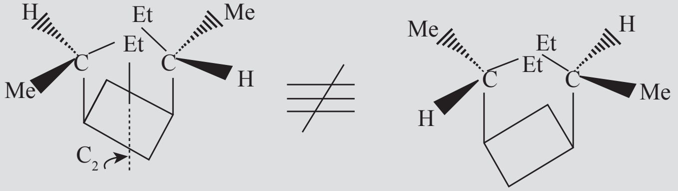
Alternating Axis Of Symmetry

Any molecule can have an alternating axis of symmetry if an orientation indistinguishable from the original is obtained when the molecule is rotated Q degree around an axis passing through the molecule and rotated molecule is reflected in a mirror that is perpendicular to the axis of rotation.



REMEMBER

- Molecule of the type as shown below would be optically active, even though they bear simple axis of symmetry.



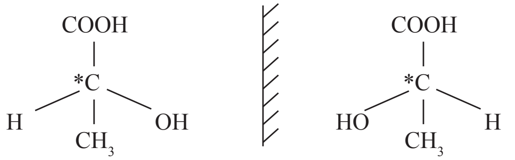
Structure (I) has a two-fold simple axis of symmetry (C_2), but its mirror image (II) is not superimposable on it. Thus, both I and II can show optical activity.

OPTICAL ISOMERS

Optical isomers differ in their optical activity that is, the rotation of plane polarized light.
Optical isomers are of following types:

1. **Optically Active Isomers** These can rotate the plane polarized light that is, show optical activity. For example, dextro and laeveo.

For example, Lactic acid



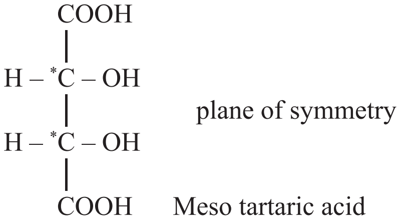
‘d’ ‘*l*’

- Dextro or d isomers show clockwise rotation of plane polarized light.
- Laeveo or *l* isomers show anti-clockwise rotation of plane polarized light.
- Both d and *l* isomers have same value of θ but with opposite signs.
- These are non-super imposable mirror images and called enantiomers or enantiomorphs or antimers.
- They have almost identical chemical properties and have nearly same physical properties.
- They have different biological property or activity.
- d, *l* form cannot be separated by simple distillation etc.
- For their separation, spectrographic methods, chromatography are used.
- They can be separated by converting them into their diastereomers which differ in their physical properties.

2. Optically Inactive Isomer or Meso Form

For the meso form, minimum two chiral centers are needed and there must be a plane of symmetry. The meso form is optically inactive due to mutual cancellation or internal compensation.

For example,

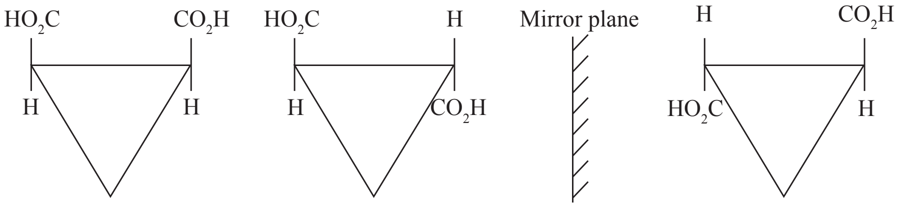


$$\begin{array}{c} COOH \\ | \\ H-{}^{*}C-OH \\ | \\ H-{}^{*}C-OH \\ | \\ COOH \end{array}$$

Meso tartaric acid

- Lactic acid has no mesoform as it has only one chiral center.
- Dextro or laeveo and meso forms are non-mirror images to each other and are called Diastereomers Diastereomers have different physical properties.

Stereoisomers of cyclopropane -1, 2- dicarboxylic acid



Meso-cis
(mp 139°C)

d- or ml -trans
(mp 175°C)
Specific rotation ± 84°

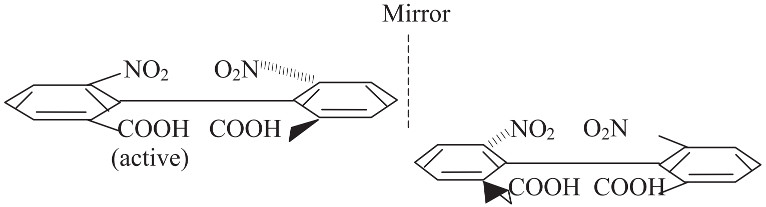
Racemic Mixture

It is an equimolecular mixture of (+) and (–) (that is, d- and l-) forms of an optically active compound. It is not able to rotate the plane polarized light because of the external compensation. The phenomenon is called as racemization. It is also written as dl or ± form.

Some Special Examples of Optical Isomerism

I. In case of Biphenyls

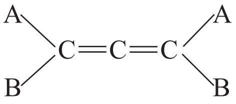
Here steric hinderance by bulky group makes rotation of C–C bond difficult and causes optical activity This stereo isomerism due to restricted C–C bond rotation is called Atropisomerism.



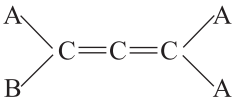
(enantiomeric pair)

II. In case of Allenes

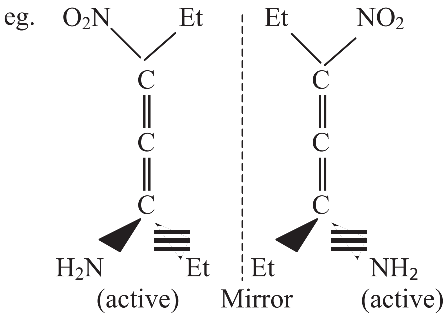
For example,



Optically active

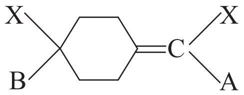


Optically inactive



(enantiomeric pair)

III. In case of Alkylidenes



To Find Number of Optical Isomers

Case I: When chiral molecule has no symmetry, that is, molecule is undivisible.

Optically active isomers (a) = 2^n

Here n = number of chiral center.

- Here there is no meso form.
- Racemic form = a/2
- Total optical isomers = a + m = a

For example, CH_3 . *CH . OH . COOH

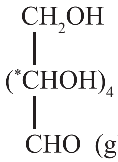
$n = 1$

$a = 2^1 = 2$

$m = 0$

$r = a / 2 = 1$

For example,



$CH_2OH-(^*CHOH)_4-CHO$ (glucose) $n = 4$

$a = 2^4 = 16$

$m = 0$

total = 16

Case II: When molecule has symmetry that is, molecule is divisible.

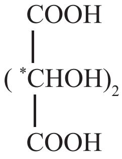
When n is an even Number

Optically active isomers (a) $= 2^{n-1}$

Meso form (m) $= 2^{2/n-1}$

Total optical isomers = a + m

For example,



$COOH-(^*CHOH)_2-COOH$

$n = 2$, $a = 2^{n-1} = 2^1 = 2$

$m = 2^{2/2-1} = 2^o = 1$

total = 3

When n is an odd Number

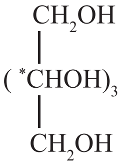
Optically active isomer (a)

$= 2^{n-1} + 2^{n-1/2}$

Meso form (m) $= 2^{n-1/2}$

Total optical isomers = a + m

For example,



$CH_2OH-(^*CHOH)_3-CH_2OH$

$n = 3$,

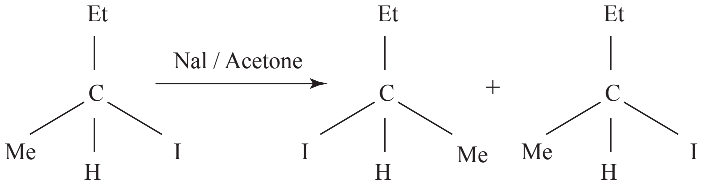
$a = 2^{3-1} + 2^{3-1/2} = 2^2 + 2^1 = 6$

$m = 2^{3-1/2} = 2^1 = 2.$

Total optical isomers = 6 + 2 = 8

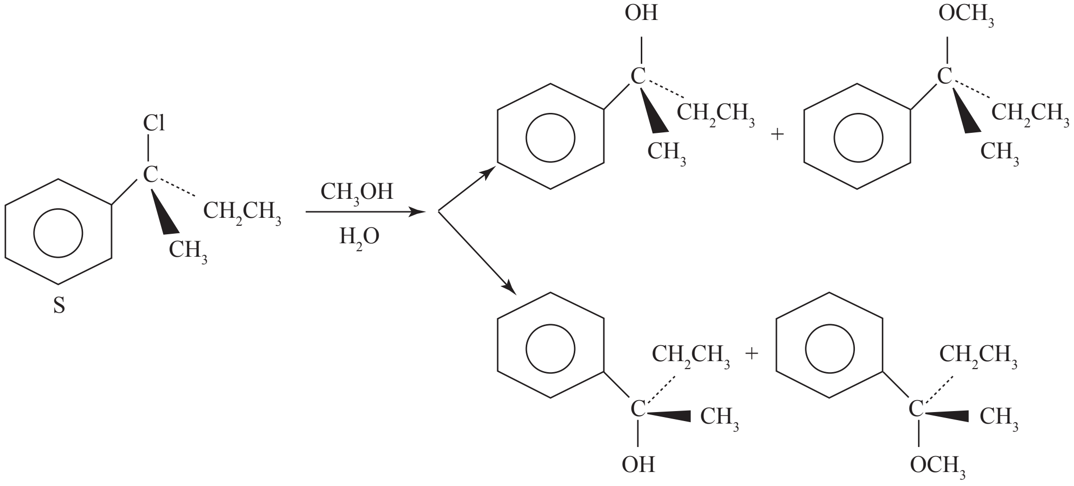
Racemization: It is the conversion of an optically active form into an optically inactive form by the action of light or heat or a chemical reagent. Here, the half part of the molecule changes into its enantiomer so the resulting product is optically inactive.

For example, (1)



2 - Iodo butane

Optical inactive



Resolution:

It is the conversion of a racemic mixture into dextro and laeveo forms. It is possible by following methods:

1. **Mechanical Separation Method:** It is possible as both forms have different crystal shapes.
2. **Bio chemical separation:** Penicillium glaucum separates dextro ammonium tartarate from laevo form.
3. By converting enantiomers into diastereomers as diastereomers differ in the physical properties.
4. By chromatography methods.
5. By salt formation method.

Asymmetric Synthesis

Here an optically inactive compounds is changed into an optically active compound.

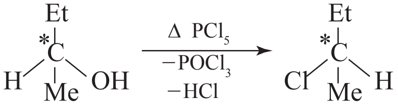
For example,

optically active
cyanohydrin

Walden or Optical Inversion

When as a result of a reaction, the product is optically active but its configuration is reverse from that of the reactant, the process is known as optical inversion or Walden inversion. It is the conversion of one optically active form into another optically active form with the help of strong reagents like PCl_5, KOH etc It involves SN^2 mechanism.

For example,



Conformation

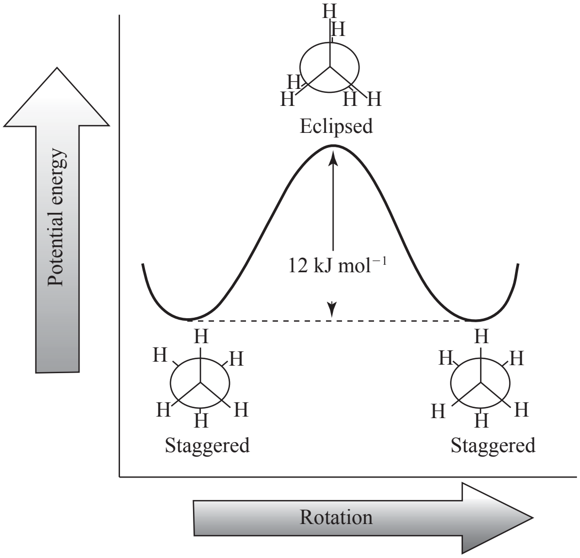
- These are formed by the rotation around C–C bond. The maximum number of conformations for an alkane is infinite.The conformers differ slightly in energy. After 360° rotation conformation is back.
- The main structural work was made by Sawhorse and Newmann. The conformers have a slight difference in their energies. The conformers cannot be separated. In staggered conformation, the angle between H – C – H is 60^{o} while in eclipsed it is less than 10^{o}.
- Staggered form is more stable but less reactive than eclipsed form. In staggered conformation the distance between H-nuclei is 2.55 Å but in eclipsed it is 2.29 Å only.
- The rotational barrier in staggered form is 0.6 Kcal/mole. The rotational barrier in staggered form is 2.9 Kcal/mole. For free rotation, energy barrier in 0.6 Kcal/mole. For restricted rotation, energy barrier is 0.6 – 16 Kcal/mole. The energy barrier between staggered and eclipsed is 2.9 Kcal/mole.

Stability Orders of Conformations

On case of Butane stability order is as follows:

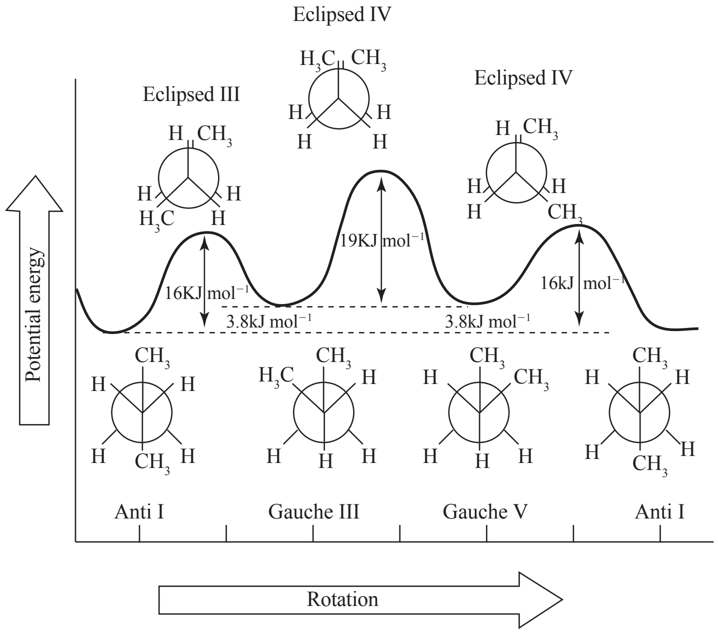
- Anti-staggered > staggered > gauche > partially eclipsed > fully eclipsed
- In case of cyclo hexane stability order is
  Chair > twist boat > boat > half chair
  Chair form is more stable than boat form due to torisonal strain or bond–bond repulsion in chair form and stearic repulsion in boat form.

Conformation of Ethane

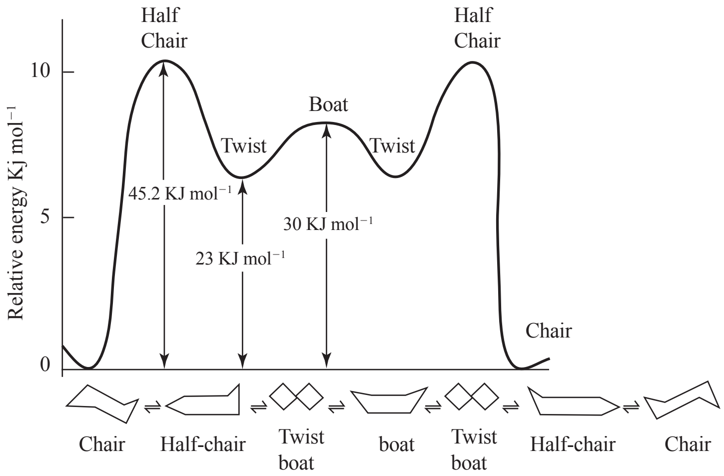


Potential energy changes that accompany rotation of groups about the carbon-carbon bond of ethane

Conformation of Butane

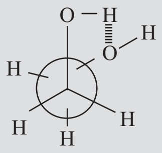


Conformation of Cyclohexane



REMEMBER

Gauche form of ethylene glycol is more stable due to H-bonding.



ENHANCE YOUR KNOWLEDGE

- **Isotopic Isomerism:** It arises due to the presence of different isotopes of an element in the compound.

  For example,

  (i) $\overset{12}{C}H_4$ and $\overset{14}{C}H_4$
  (ii) H_2O and D_2O

- **Double Bond Equivalent (D.B.E) or Index Number**
  By calculating D.B.E the problems on structural isomerism can be solved easily.

  $$\text{D.B.E} = \sum \frac{n(V-2)}{2} + 1$$

  Here n = Number of atoms
  V = Valency of the atom

  For example, In C_4H_6

  $$\text{D.B.E} = \frac{4(4-2)+6(1-2)}{2} + 1 = 2$$

  Here D.B.E is 2 which implies that molecule may have:

  (i) Two double (=) bond for one double bond
  (ii) One ring with one triple (≡) bond
  (iii) Two rings

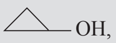
  Here we can say that the no structural isomers can be find out by D.B.E.

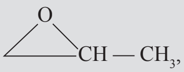
  For example, In case of C_3H_6O

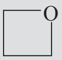
  $$\text{D.B.E} = \frac{3(4-2)+6(1-2)+1(2-2)}{2} + 1 = 1$$

  That is, isomers will have either a double bond or a ring. Its has 7 isomers as follows:

  $CH_3 - CH_2 - CHO$, $CH_2 = CH - OCH_3$,
  $CH_2 = CH - CH_2OH$, $CH_3 - CO - CH_3$,



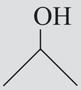




- **Homomers**: Homomers are identical representations of the same compounds that is, the molecular models of these representations are superimposable.
- Regiomers differ in the position of the functional groups.

  For example,

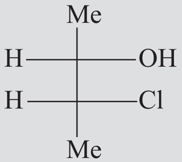
  and



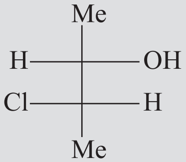
- Optical isomerism was first noted in Quartz. It is also shown by $KClO_3$, $NaClO_3$, $(HCOO)_2Ba$.
- D, L notation (system) was introduced by Emil Fischer. D, L form do not always represent optical isomers that is, clockwise or anti-clockwise rotation.

Erythro, Threo System: In erythro, two similar species are on the same side but in threo these are on opposite sides.

For example,



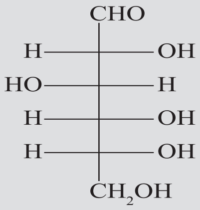
Erythro

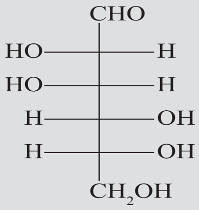


Threo

Epimers: These differ in configuration only at one chiral center or one stereogenic center.

For example,





- Here configuration differs at 2 carbon atom.

Absolute Configuration: The actual three dimensional arrangement of groups in a molecule containing asymmetric carbon is known as absolute configuration. It is a three dimensional arrangement of atoms of groups in space.

R, S System

It was introduced by Cohn, Ingold and Prelog.

R : Rectus (means clockwise rotation)

S : Sinister (means anti-clockwise rotation).

Rules

- First decide priority of groups attached to chiral center.

For example,

$$\underset{3}{CH_3}\,.\,\underset{4}{CH}\,.\,\underset{1}{OH}.\,\underset{2}{COOH}$$

To Decide Priority of Group

- It is decided by atomic number (α – atomic number) and atomic weight in case of isotopes.
- If first atom is same consider 2nd atom and so on.

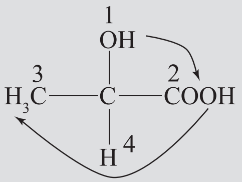
$$-\underset{8\;1}{OH} > \underset{6}{CH_3}-\underset{6}{CH_2}- \;>\; -\underset{6\;1}{CH_3}$$

Priority Order of Some Groups

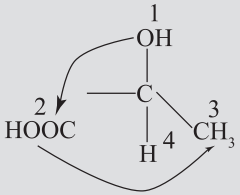
$I > Br > Cl > SO_3H > -S-R > -SH > F > -O-R > COOR > COOH$

$> COR > CHO > CN > C_2H_5 > CH_3 > D > H$

- Here the top priority must be at the top and 4 priority must be at bottom.

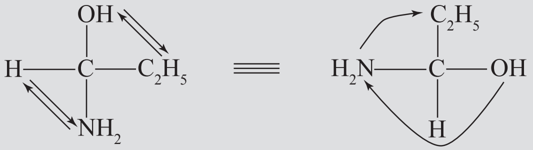


'R'



'S'

Switching Case: If 4 priority is not at bottom the positions are interchanged as given below.

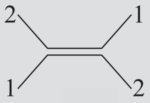


'R'

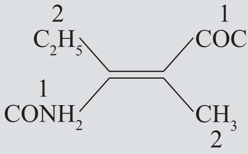
- In switching cases, the configuration is just reverse as it looks from the given configuration in most of the cases.

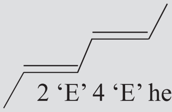
E, Z System: It is modern way to express geomatrical isomers
E: Entigegen means same priorities are on opposite side like in trans.

For example,



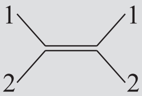
Example,



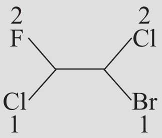


2 'E' 4 'E' hexa
2,4 di-ene

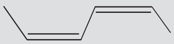
Z: Zussaman [means together] that is, same priorities are on same side like in cis.



For example,



It is Z



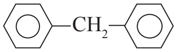
2 'Z' 4 'Z' hexa
2,4 di-ene

MULTIPLE-CHOICE QUESTIONS

Straight Objective Type Questions (Single Choice only)

1. Number of isomers which can be obtained theoretically on monochlorination of 2-methylbutane is
(a) 2
(b) 3
(c) 4
(d) 5

2. The molecular formula of diphenyl methane



is $C_{13}H_{12}$.

How many structural isomers are possible when one of the hydrogen is replaced by a chlorine atom?
(a) 4
(b) 6
(c) 7
(d) 8

3. Diastereomers are
(a) Stereisomers that are nonsuperimposable non - mirror images.
(b) Stereisomers that are nonsuperimposible mirror images.
(c) Isomers that only differ by rotations around single bonds.
(d) Isomers that only differ in the bonding arrangement of the atoms.

4. An organic compound C_4H_8O, is found to be optically active. Which of the following could it be?
(a) $CH_3 - CH_2 - CH_2 - CHO$
(b) $CH_2 - CO - CH_2 - CH_3$
(c) $CH_2 = CH - CH(OH) - CH_3$
(d) $(CH_3)_2\ CH - CHO$

5. How many structural (including stereoisomers) isomers could be obtained by replacing one hydrogen of propene with chlorine?
(a) 2
(b) 3
(c) 4
(d) 5

6. Which organic structure among the following is not an isomer of the compound?
$CH_3 - CO - CH_2CH_2CH_2CH_3$?
(a) $CH_3CH = CHCH_2CH_2CHO$
(b) $CH_3CH_2OCH = CHCH_2CH_3$
(c) $CH_3CH_2COCH_2CH_2CH_3$
(d) $(CH_3)_2CH - CO - CH_2CH_3$

7. The most stable conformation of ethylene glycol is
(a) anti
(b) gauche
(c) fully eclipsed
(d) partially eclipsed.

8. In the reaction,
$CH_3CHO + HCN \rightarrow CH_3CH(OH)CN$
a chiral centre is produced. This product would be
(a) racemic mixture
(b) meso compound
(c) dextrorotatory
(d) laevorotatory

9. Which of the following compounds will show metamerism?
(a) $CH_3 - O - C_2H_5$
(b) $CH_3 - O - CH_3$
(c) $CH_3 - CO - C_2H_5$
(d) $C_2H_5 - S - C_2H_5$

10. Fischer projection indicates:
(a) vertical substituents above the plane
(b) horizontal substituents above the plane
(c) both horizontal and vertical substituents above the plane
(d) both horizontal and vertical substituents below the plane

11. Which of the following has zero dipole moment?
(a) 1-butene
(b) cis-2-butene
(c) trans-2-butene
(d) 2 methyl-1-propene

12. The total number of isomers for C_4H_8 is
(a) 8
(b) 7
(c) 6
(d) 5

13. 2, 3-dimethyl hexane contains …. tertiary …. Secondary and ….. primary carbon atoms, respectively.
(a) 2, 4, 3
(b) 3, 2, 4
(c) 4, 3, 2
(d) 2, 2, 4

14. The number of enantiomers of the compound $CH_3CHBrCHBrCOOH$ is
(a) 1
(b) 2
(c) 3
(d) 4

15. In the boat conformation of cyclohexane, the most destabilizing interaction is
(a) eclipsing
(b) flagpole – flagpole
(c) 1,3-diaxial
(d) 1,3-diequatorial

16. Which of the following has zero dipole moment?
(a) 1,1-dichloromethane
(b) 1-chloroethane
(c) cis-1,2-dichloroethene
(d) trans-1,2-dichloroethene

17. The Baeyer's angle strain is expected to be maximum in
(a) cyclopentane
(b) cyclodecane
(c) cyclooctane
(d) cyclohexane

18. (+)-Mandelic acid has a specific rotation of + 158°. What would be the observed specific rotation of a mixture of 25 % (–)-mandelic acid and 75 % (+)-mandelic acid?
(a) + 79° (b) –118.5°
(c) –79° (d) +118.5°

19. The number of geometrical isomers of $CH_3CH = CH - CH = CH - CH = CHCl$ is
(a) 4 (b) 6
(c) 8 (d) 10

20. The number of isomers possible for C_7H_8O is
(a) 3 (b) 4
(c) 5 (d) 6

21. Number of stereoisomers of the compound, 2-chloro-4-methylhex-2-ene is
(a) 2 (b) 4
(c) 8 (d) 16

22. The number of stereoisomers for pent-3-en-2-ol is
(a) 2 (b) 3
(c) 4 (d) 5

23. How many isomers can C_5H_{12} have?
(a) 2 (b) 3
(c) 4 (d) 5

24. The number of possible alkynes with molecular formula C_5H_8 is
(a) 3 (b) 4
(c) 5 (d) 6

25. How many cyclic isomers of C_5H_{10} are possible?
(a) 3 (b) 4
(c) 5 (d) 6

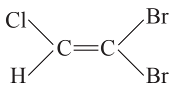
26. Which one of the following compounds is capable of existing in a meso form?
(a) 3-dibronopentane
(b) 3,3-dibromopentane
(c) 4-bromo-2-pentanol
(d) 2,4-dibromopentane

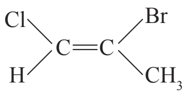
27. Consider the following organic compound,
1 2 3 4 5 6 7
$CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_3$
To make it a chiral compound, the attack should be on carbon
(a) 1 (b) 4
(c) 3 (d) 6

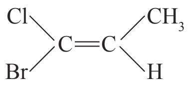
28. Which of the following will show geometrical isomerism?
(a) 1,2-dibromobutene (b) isobutylene
(c) 1-butene (d) propene

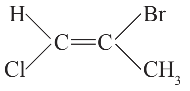
29. A compound with molecular formula C_7H_{16} shows optical isomerism, the compound will be
(a) 2-methylhexane
(b) 2,2-dimethylpentane
(c) 2,3-dimethylpentane
(d) none of these

30. Which is a pair of geometrical isomers?

I.


II.


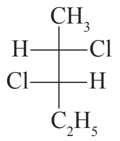
III.


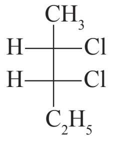
IV.


(a) I and III (b) II and IV
(c) III and IV (d) I and II

31. Which of the following does not show geometrical isomerism?
(a) 1,1-dichloro-1-pentene
(b) 1,2-dichloro-1-pentene
(c) 1,3-dichloro-1-pentene
(d) 1,4-dichlroro-2-pentene

32. The two optical isomers given below, namely





(a) enantiomers
(b) geometrical isomers
(c) structural isomers
(d) diastereomers

33. The number of optical isomers formed by hydrogenation of the compound, $(CH_3)_2C = CHCH_3$ are
(a) 0
(b) 1
(c) 2
(d) 3

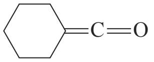
34. IUPAC name of the following compound is

(a) N-Cyclohexyl-N-phenylmethanamide
(b) N-Phenylcyclohexane carboxamide
(c) N-Cyclohexylbenzamide
(d) N-Phenyl-N-cyclohexylmethanamide

35. The IUPAC name to $[(CH_3)_2CH]_3COH$.
(a) 3-(2-methylethyl)-3(1-methylethyl) pentan-2-ol
(b) tris-(1-methylpropyl)methanol
(c) 2, 4-dimethyl-3 (1-methylethyl) pentan- 2-ol
(d) 3-(1-methylethyl)-2, 4-dimethylpentan-3-ol

36. The IUPAC name of $CH_3CH = CHCOOC_2H_5$ is
(a) Ethyl but-2-enoate (b) Ethyl prop-2-enoate
(c) Ethyl but-1-enoate (d) None of these

37. The IUPAC name of



is
(a) Cyclohexylmethanone
(b) Cyclohexanone
(c) Cyclohexylidenemethanone
(d) Oxycyclohexene

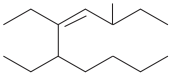
38. Which of the following have asymmetric carbon atoms?
1. $ClCH_2 - CH_2Br$
2. $CH_3 - CHCl_2$
3. $CH_3 - CH\,DCl$
4. $CH_2Br - CHOH - CH_3$

(a) 1, 2 ,3 (b) 1, 3, 4
(c) 2, 3 (d) 3, 4

39. The Cl – C – Cl angle in 1, 1, 2, 2-tetrachloroethene and tetrachloromethane will be about
(a) 120° and 109.5° (b) 90° and 109.5°
(c) 109.5° and 90° (d) 109.5° and 120°

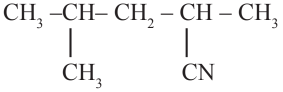
40. The compound with an isopropyl group is
(a) 2, 2, 3, 3-tetramethylpentane
(b) 2, 2-dimethylpentane
(c) 2, 2, 3-trimethylpentane
(d) 2-methylpentane

41. The IUPAC name of the compound



is
(a) 5, 6-Diethyl-8-methyldec-6-ene
(b) 5, 6-Diethyl-3-methyldec-4-ene
(c) 6-Butyl-5-ethyl-3-methylloct-4-ene
(d) 4, 5-Diethyl-8-methyldec-6-ene

42. IUPAC name of



$$\underset{\displaystyle CH_3}{CH_3-\underset{|}{C}H-}CH_2-\underset{\underset{\displaystyle CN}{|}}{CH}-CH_3$$

(a) 2-cyano- 4-methylpentane
(b) 2-methyl- 4-cyanopentane
(c) 2, 4-dimethyl pentane nitrile
(d) 2-dimethyl- 4-cyanopentane

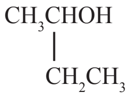
43. The IUPAC name of $CH_3COCH(CH_3)_2$ is
(a) 4-methyl isopropyl ketone
(b) 3-methylbutan-2-one
(c) isopropylmethyl ketone
(d) 2-methylbutan-3-one

44. An optically active compound is
(a) 1-Bromobutane
(b) β-Bromobutyric acid
(c) 2-Bromo-2-methylpropane
(d) 1-Bromo-2-methylpropane

45. Which of the following will exhibit cis-trans isomerism?
(a) $CBr_3 - CH_3$
(b) $CBr_2 = CH_2$
(c) $CHBr = CHBr$
(d) $CH_2Br - CH_2Br$

46. Following types of compounds as (I, II)

$CH_3CH = CHCH_3$



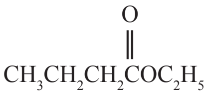
$$CH_3\underset{\underset{\displaystyle CH_2CH_3}{|}}{C}HOH$$

are studied in terms of isomerism in
(a) chain isomerism
(b) position isomerism
(c) conformers
(d) stereoisomerism

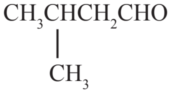
47. Among the following alkenes:
(I) 1-butene
(II) cis-2-butene
(III) trans-2-butene
the decreasing order of stability is
(a) III > I > II
(b) I > II > III
(c) II > I > III
(d) III > II > I

48. An organic molecule necessarily shows optical activity if it
(a) contains asymmetric carbon atoms
(b) is non-planar
(c) is non-superimposable on its mirror image
(d) is superimposable on its mirro image

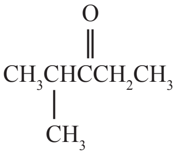
49. The incorrect IUPAC name is



(a) $CH_3CH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}OC_2H_5$
ethylbutanoate

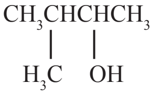


(b) $CH_3\underset{\underset{\displaystyle CH_3}{|}}{C}HCH_2CHO$
3-methyl butanal

(c) 

$CH_3\underset{\underset{CH_3}{|}}{CH}\overset{\overset{O}{\|}}{C}CH_2CH_3$

2-methyl-3-pentanone

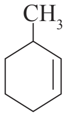
(d) 

$CH_3\underset{\underset{H_3C}{|}}{CH}\underset{\underset{OH}{|}}{CH}CH_3$

2-methyl-3-butanol

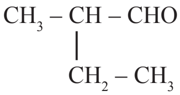
50. IUPAC name of 4-isopropyl-m-xylene is
(a) 1-Isopropyl-3, 5-dimethylbenzene
(b) 4-Isopropyl-3, 5-dimethylbenzene
(c) 4-Isopropyl-m-xylene
(d) 1-Isopropyl-2, 4-dimethylbenzene

51. The IUPAC name of



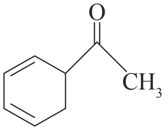
is

(a) 3-methyl cyclohexene
(b) 1-methyl cyclohex-2-ene
(c) 6-methyl cyclohexene
(d) 1-methyl cyclohex-5-ene.

52. The IUPAC name of  is

$CH_3-\underset{\underset{CH_2-CH_3}{|}}{CH}-CHO$

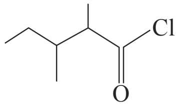
(a) butan-2-aldehyde
(b) 2-methylbutanal
(c) 3-methylisobutyraldehyde
(d) 3-methylbutanal

53. IUPAC name of  is

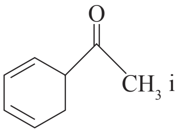
(a) 6-cyclohexa-1, 3-dienylethanone
(b) 1-cyclohexa-2, 4-dienylethanone
(c) acetylcyclohexadiene
(d) None of these

54. The IUPAC name of
$CH_3-CH=CH-C\equiv CH$ is
(a) Pent -3-en-1-yne (b) Pent-2-en-3-yne
(c) Pent-3-en-4-yne (d) Pent-2-en-4-yne

55. The IUPAC name of

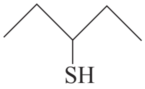


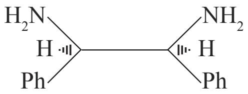
(a) 2-ethyl-3methylbutanoyl chloride
(b) 2, 3-dimethylpentanoyl chloride
(c) 3, 4-dimethylpentanoyl chloride
(d) 1-chloro-1-oxo-2, 3-dimethylpentane

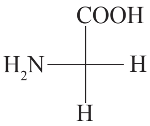
56. IUPAC name of  is

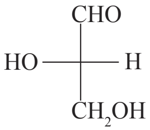
(a) 6-cyclohexa-1, 3-dienylethanone
(b) 1-cyclohexa-2, 4-dienylethanone
(c) acetylcyclohexadiene
(d) None of these

57. Which of the following molecules is expected to rotate the plane of plane polarized light?

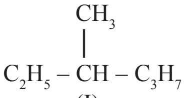
(a) 

(b) 

(c) 

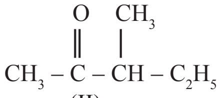
(d) 

58. Among the following four structures I to IV



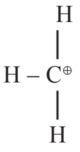
$C_2H_5-\overset{\overset{CH_3}{|}}{CH}-C_3H_7$

(I)



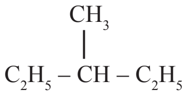
$CH_3-\overset{\overset{O}{\|}}{C}-\overset{\overset{CH_3}{|}}{CH}-C_2H_5$

(II)



$H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C^{\oplus}}}$

(III)

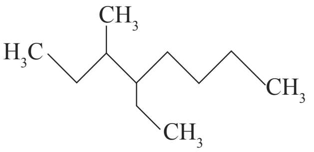


$C_2H_5-\overset{\overset{CH_3}{|}}{CH}-C_2H_5$

(IV)

it is true that
(a) all four are chiral compounds
(b) only I and II are chiral compounds
(c) only III is a chiral compound
(d) only II and IV are chiral compounds

59. Name of the compound given below is



(a) 3-methyl-4-ethyloctane
(b) 4-ethyl-3-methyloctane
(c) 2, 3-diethylheptane
(d) 5-ethyl-6-methyloctane

60. Which types of isomerism is shown by 2,3-dichlorobutane?
(a) diastereo
(b) optical
(c) geometric
(d) structural

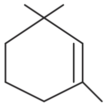
61. The compound having only primary hydrogen atoms is
(a) isobutene
(b) 2,3-dimethylbutene
(c) cyclohexane
(d) propyne

62. The correct decreasing order of priority for the functional groups of organic compounds in the IUPAC system of nomenclature is
(a) $–COOH, –SO_3H, –CONH_2, –CHO$
(b) $–SO_3H, –COOH, –CONH_2, –CHO$
(c) $–CHO, –COOH, –SO_3H, –CONH_2$
(d) $–CONH_2, –CHO, –SO_3H, –COOH$

63. Among the following, the most stable compound is
(a) cis-1, 2-cyclohexanediol
(b) trans-1, 2-cyclohexanediol
(c) cis-1, 3-cyclohexenediol
(d) trans-1,3-cyclohexanediol

64. Of the five isomeric hexanes, the isomer which can give two monochlorination compound is
(a) n-hexane
(b) 2,3-dimethylbutane
(c) 2,2-dimethylbutane
(d) 2-methylpentane

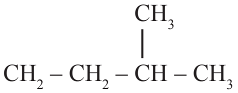
65. Give IUPAC name of the compound



(a) 1,1,5-Trimethylcyclohex-5-ene
(b) 1,3,3-Trimethylcyclohex-1-ene
(c) 1,1,3-Trimethylcyclohex-2-ene
(d) 2,6,6-Trimethylcyclohex-1-ene

66. Increasing order of stability among the three main conformations (that is, eclipse, anti, gauche) of 2-fluoroethanol is
(a) eclipse, gauche, anti
(b) gauche, eclipse, anti
(c) eclipse, anti, gauche
(d) anti, gauche, eclipse

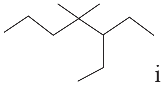
67. Amongst the following compounds the optically active alkane having lowest molecular mass is
(a) $CH_3 – CH_2 – CH_2 – CH_3$



(b) $CH_2 – CH_2 – \overset{\overset{\displaystyle CH_3}{|}}{C}H – CH_3$
(c) 2-cyclopropylbutane
(d) $CH_3 – CH_2 – C \equiv CH$

68. The reaction intermediate produced by homolytic cleavage of bond is called
(a) Carbanion (b) Carbocation
(c) Free radical (d) Carbene

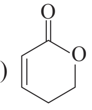
69. The IUPAC name of

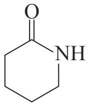


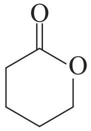
is
(a) 4, 4-dimethyl-5, 5-diethyl pentane
(b) 5, 5-diethyl-4, 4-dimethyl pentane
(c) 3-ethyl-4, 4-dimethyl heptane
(d) 1, 1-diethyl-2, 2-dimethyl pentane

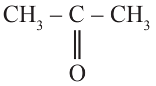
70. The IUPAC name of the following compound $CH_3 – C (CH_3)_2 – CH = C(CH_3)_2$ is
(a) 1, 1, 3, 3-Tetramethyl-but-1-ene
(b) 1, 3, 3-Trimethyl-pent-2-ene
(c) 2, 2, 4-Trimethylbut-4-ene
(d) 2, 4, 4-Trimethylpent-2-ene

71. Which one of the following compounds cannot show tautomerism?

(a)


(b)


(c)


(d)


$CH_3 – \underset{\underset{\displaystyle O}{\|}}{C} – CH_3$

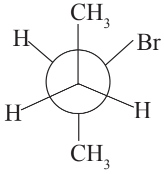
72. In a group of isomeric alkyl halides, the order of boiling points is
(a) Primary < secondary > tertiary
(b) Primary > secondary > tertiary
(c) Primary < secondary < tertiary
(d) Primary > secondary < tertiary

73. Which one of the following conformations of cyclohexane is chiral?
(a) Rigid (b) Chair
(c) Boat (d) Twist boat

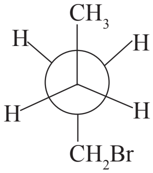
74. The formation of cyanohydrin from a ketone is an example of:

(a) Electrophilic substitution
(b) Nucleophillic addition
(c) Nucleophillic substitution
(d) Electrophillic addition

75. The pair the structure given below represents

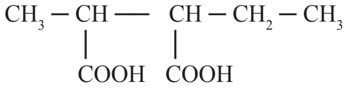


and



(a) Constitutional isomers
(b) Enantiomers
(c) Diastereoisomers
(d) Same compound

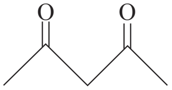
Brainteasers Objective Type Questions (Single choice only)

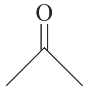
76. 
$CH_3-\underset{COOH}{CH}-\underset{COOH}{CH}-CH_2-CH_3$

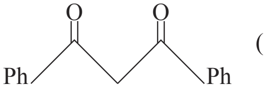
How many optical isomers are possible in this compound?

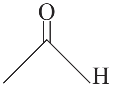
(a) 3 (b) 2
(c) 4 (d) Zero

77. Enol content is least in:

(a) 

(b) 

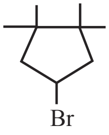
(c) 

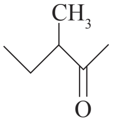
(d) 

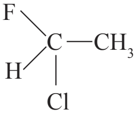
78. Which of the following molecules have stereognic C- atoms?

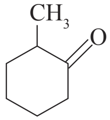
(a) 1,2- dibromobutane
(b) 1- bromo-2- methylcyclopentane
(c) 1,1,2- tribromopropane
(d) All of these

79. Consider the following compounds given below and select the correct statement.

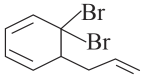
(I) 

(II) 

(III) 

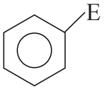
(IV) 

(a) except (I), all have stereogenic centre
(b) all have stereogenic centre
(c) all have plane of symmetry
(d) only II and III have stereogenic centre

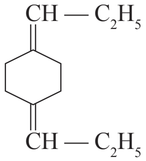
80. 

For the given structure, how many stereoisomers and how many racemic mixtures are possible?

(a) 2, 1
(b) 2, 0
(c) 4, 2
(d) 2, 4

81. In a compound  electrophilic substitution has occurred. The substituent –*E* are methyl, -CH$_2$Cl, -CCl$_3$, and –CHCl$_2$. The correct increasing order towards electrophilic substitution is

(a) – CH$_3$ < - CH$_2$Cl < - CHCl$_2$ < - CCl$_3$
(b) – CCl$_3$< - CH$_2$Cl < - CHCl$_2$ < - CH$_3$
(c) – CH$_3$ < - CHCl$_2$ < - CH$_2$Cl <- CCl$_3$
(d) – CCl$_3$ < - CHCl$_2$ < - CH$_2$Cl < - CH$_3$

82. 

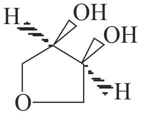
How many geometrical isomers of this compound are possible?

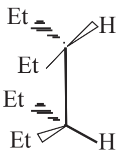
(a) 0 (b) 4
(c) 2 (d) 8

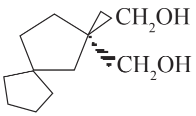
83. The number of possible open chain (acyclic) isomeric compounds for molecular formula C_5H_{10} would be

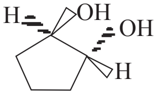
(a) 5 (b) 6
(c) 7 (d) 8

84. Which of the following structure represent meso compound?

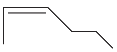
(a) 

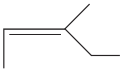
(b) 

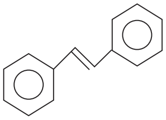
(c) 

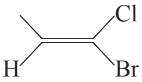
(d) 

85. Identify E and Z configuration of the following:

1. 

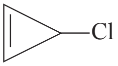
2. 

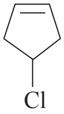
3. 

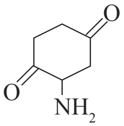
4. 

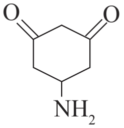
(a) 1 (E), 2 (Z), 3 (E), 4 (Z)
(b) 1 (Z), 2 (E), 3 (Z), 4 (E)
(c) 1 (Z), 2 (Z), 3 (E), 4 (E)
(d) 1 (Z), 2 (Z), 3 (E), 4 (Z)

86. Which of the following compounds has asymmetric centre?

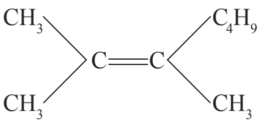
(a) 

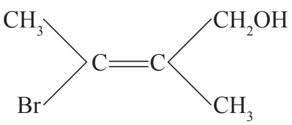
(b) 

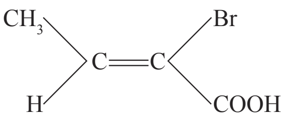
(c) 

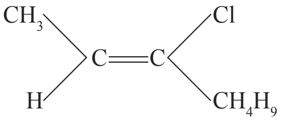
(d) 

87. Which of the following is an E isomer?

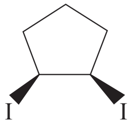
(a) 
$(CH_3)_2C{=}C(C_4H_9)(CH_3)$

(b) 
$(CH_3)(Br)C{=}C(CH_2OH)(CH_3)$

(C) 
$(CH_3)(H)C{=}C(Br)(COOH)$

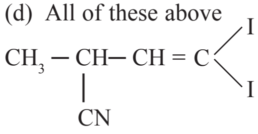
(d) 
$(CH_3)(H)C{=}C(Cl)(CH_4H_9)$

88. Consider the following compound:



Which of the following best describes this compound?

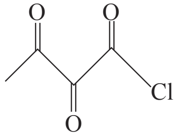
(a) It is a meso structure
(b) It is achiral
(c) It contains two stereogenic C atoms
(d) All of these above

89. 
$CH_3-\underset{\underset{CN}{|}}{CH}-CH=C\langle^{I}_{I}$

How many geometrical and optical isomers are possible in this compound?

(a) 0,2
(b) 0, 0
(c) 2, 0
(d) 2, 2

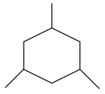
90. The IUPAC name of the compound



is

(a) 1-methyl-3-chloropropane-1,2,3-trione
(b) 2, 3-dioxobutanoyl chloride
(c) 1-chlorobutane-1,2,3-trione
(d) 1-chloro-3-methylpropane-1,2,3-trione

91. Total number of stereoisomer formed by the given compound is:

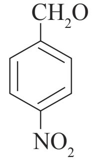


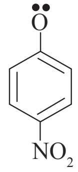
(a) 2
(b) 4
(c) 3
(d) Zero

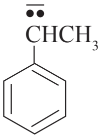
92. In terms of the resonance concept, which anion in each of the following pairs would be more stable relative to its protonated species?

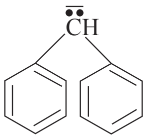
1. $CH_3\,\overset{\overline{\bullet\bullet}}{C}H\,CH_2\,CH=CH_2$

2. $CH_3\,\overset{\overline{\bullet\bullet}}{C}H\,CH=CHCH_3$

3. 

4. 

5. 

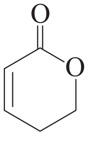
6. 

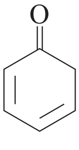
Select the correct answer using the code given below:

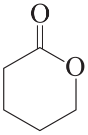
(a) 2, 4 and 5 (b) 2, 4 and 6

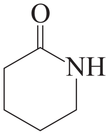
(c) 1, 4 and 6 (d) 2, 3 and 6

93. Which of the following can show Tauto merism here?

(I) 

(II) 

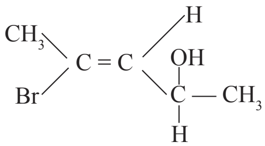
(III) 

(IV) 

(a) II, III (b) I, II

(c) II, III, IV (d) III, IV

94. The compound, whose stereochemical formula is written below, exhibits A-geometrical isomers and B-optical isomers

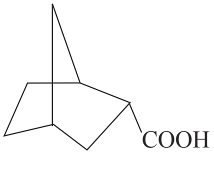


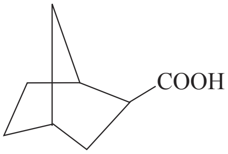
The value of A and B are:

(a) 4 and 4 (b) 4 and 2

(c) 2 and 4 (d) 2 and 2

95. Consider the following two molecules:





Which of the following best describes the relationship of these two molecules?

(a) Enantiomers

(b) Diastereomers

(c) Conformational isomers

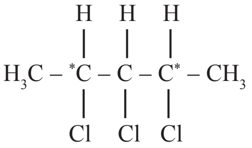
(d) No stereochemical relationship

96. How many chiral carbon atoms are present in 2, 3, 4-Trichloropentane?

(a) three (b) two

(c) one (d) four

[IIT 1990]



$$H_3C-{}^*\overset{H}{\underset{Cl}{C}}-\overset{H}{\underset{Cl}{C}}-\overset{H}{\underset{Cl}{C^*}}-CH_3$$

97. In the reaction

$CH_3CHO + HCN \longrightarrow CH_3CH(OH)CN$

$\xrightarrow{H^+ / H_2O} CH_3CH(OH)COOH$

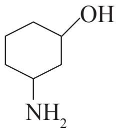
an asymmetric centre is generated. The acid obtained would be

(a) L-isomer

(b) D-isomer

(c) 20 % D + 80% L-isomer

(d) 50% D + 50 % L-isomer

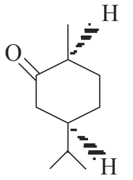


98. How many stereoisomers are possible in this compound?

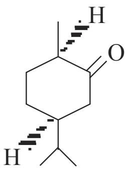
(a) 3 (b) 2

(c) 4 (d) Zero

99. The two compounds shown below are:



and



(a) enantiomers (b) Tautomers

(c) regiomers (d) epimers

100. Which one of the following compounds has the most stable enol form?

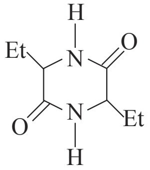
(a) CH_3-CHO

(b) $CH_3-CO-CH_2-COO-C_2H_5$

(c) $CH_3-CO-CH_2-CO-CH_3$

(d) $(Ph)_2\,CH-CO-CH_3$

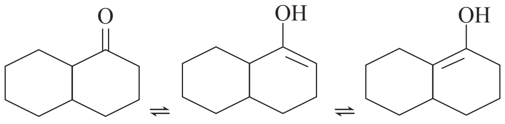
101. The number of stereoisomers formed by the compound is:



(a) 1 (b) 2

(c) 3 (d) 4

102.



(I) (II) (III)

Stability order among these tautomers is

(a) I > III > II (b) III > II > I

(c) II > I > III (d) II > III > I

103. Which of the following best describers the product of the reaction of (E)-2- butene and hydrogen chloride?

(a) The product is not optically active and contains one stereogenic C atom.

(b) The product is optically active and contains a stereogenic C atom.

(c) The product is optically active but contains no stereogenic C atom.

(d) The product is not optically active and contains no stereogenic C atom.

104. Which of the following compounds is isomeric with 2,2,4,4-tetramethylhexane?

(a) 4-ethyl-3-methyl-4-n-propyloctane

(b) 4,4-diethyl-3-methylheptane

(c) 4-isopropylheptane

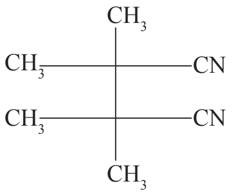
(d) 3-ethyl-2,2-dimethylpentane

105. How many stereoisomers does this molecule have? $CH_3CH = CHCH_2\ CHBrCH_3$

(a) 8 (b) 2

(c) 4 (d) 6

106. Consider the following structure.



Which of the following best describes this molecule?

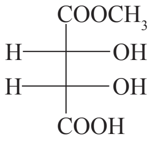
(a) This molecule has one stereogenic center but the molecule is achiral.

(b) This molecule has two stereogenic centers and is optically active.

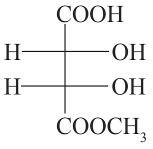
(c) This molecule has two stereogenic center but the molecule is achiral.

(d) None of these are correct

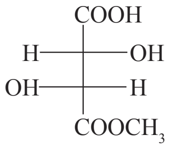
107. The correct statement about the compounds A, B and C



(A)



(B)



(C)

(a) A and B are identical

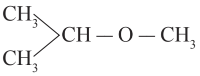
(b) A and B are diastereomers

(c) A and C are enantiomers

(d) A and B enantiomers.

108. (I) $CH_3 - CH_2 - CH_2 - OCH_3$

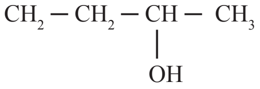
(II)



$(CH_3)_2CH - O - CH_3$

(III) $CH_3 - CH_3 - O - CH_2 - CH_3$

(IV)



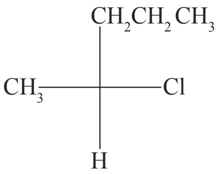
$CH_2 - CH_2 - \underset{\displaystyle OH}{\underset{|}{CH}} - CH_3$

(a) II only (b) III only

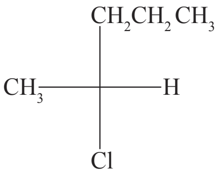
(c) both II and III (d) both III and IV

109. Consider the following structures.

(I)



(II)



Which of the following best describes the relationship of structures I and II?

(a) Enantiomers

(b) Diastereomers

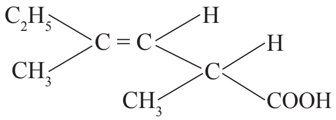
(c) Structural isomers

(d) No relationship between these structures

110. Acyclic stereoisomers having the molecular formula C_4H_7Cl are classified and tabulated. Find out the correct set of numbers

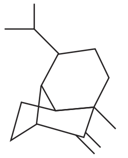
	Geometrical	*Optical*
A	6	2
B	4	2
C	6	0
D	4	0

111. The given compound can exhibit



(a) Geometrical isomerism
(b) Optical isomerism
(c) Geometrical and optical isomerism
(d) Conformational isomerism

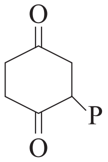
112. The structural formula of sativene is shown below. How many steregenic centers are presence in this molecule?



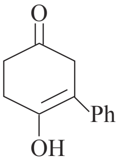
(a) 1 (b) 2
(c) 3 (d) 4

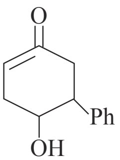
113. How many optically active stereomers are possible for butane-2, 3-diol?
(a) 3 (b) 2
(c) 10 (d) 8

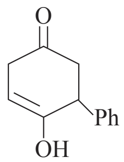
114. Which of the following has least hindered rotation about carbon-carbon bond?
(a) ethane
(b) ethylene
(c) acetylene
(d) hexachloroethane

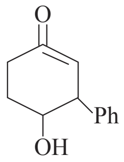
115.  $\xrightarrow{H^{\oplus}}$ Enol (Major)

The major enol should be:

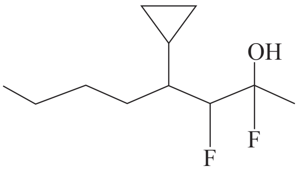
(a) 

(b) 

(c) 

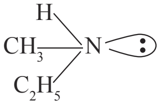
(d) 

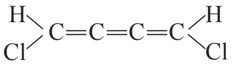
116. What is the IUPAC name for the following?



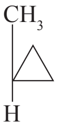
(a) 3- cyclopropyl -1, 2 - difluoro -1- methyl -1- heptanol
(b) 1- [1, 2- difluoro -2 - hydroxybutyl] -1 -butylcyclopropane
(c) 4- cyclopropyl -2, 3- difluoro-2- octanol
(d) 1, 2- difluoro -3- cyclopropaneheptanol

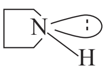
117. Which of the following can exhibit optical isomerism:

(1) 

(2) 

$\mathrm{HClC{=}C{=}C{=}CHCl}$

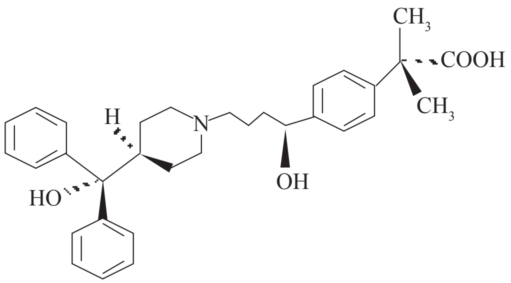
(3) 

(4) 

(a) 1 and 2 (b) 2 and 4
(c) 3 only (d) 2 only

118. An organic compound C_4H_8O is found to be optically active. Which of the following is correct structure of the given compound?
(a) $(CH_3)_2CHCHO$
(b) $CH_2 = CH - CH(OH)CH_3$
(c) $CH_3COCH_2CH_3$
(d) $CH_3CH_2CH_2CHO$

119. Allegra, a common prescription drug with the structure shown below, is given for the treatment of seasonal allergies. How many stereogenic carbon does Allegra possess?



(a) 2
(b) 1
(c) 3
(d) 5

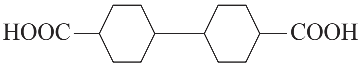
120. Which of the following compounds yields four monochloride products when it undergoes free radical chlorination?
(a) 2, 2- dimethylpropane
(b) pentane
(c) 2, 2- dimethylbutane
(d) 2- methylbutane

121. An optically pure substance is
(a) An optically inactive enantiomer.
(b) Optically inactive it is composed of a 50 : 50 mixture o enantiomers.
(c) An optically active racemic mixture.
(d) Optically active because it is composed of only one enantiomer.

122. If cyclopentane reacts with excess Cl_2 at a high temperature, how many dichloro- cyclopentanes would you except to obtain as products?
(a) 5
(b) 7
(c) 9
(d) 3

123. Which of the following produces two diastereomers when $Br_2(CCl_4)$ is added to the molecule?
(a) 3- methylcyclopentene
(b) methylenecyclopentene
(c) 4- methylcyclopentene
(d) 1- methylcyclopentene

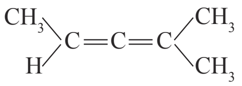
124.



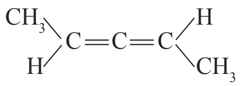
For this given compound how many stereoisomers and how many racemic- mixtures are possible?
(a) 3, 0
(b) 2, 4
(c) 4, 2
(d) 2, 0

125. Which of the following compounds are chiral?

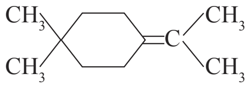
(1)



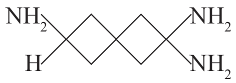
(2)



(3)



(4)

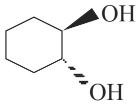


(a) 2 and 4
(b) 2 and 3
(c) 2, 3 and 4
(d) Only 2

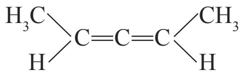
Decisive Thinking Objective Type Questions (One or more than one choice)

126. Which of the following compound can exhibit geometrical isomerism?

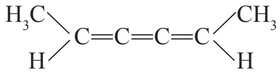
(a)



(b)



(c)

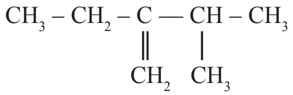


(d) $C_2H_5CH{=}CH{-}CH = CH - CH_3$

127. IUPAC names of some compounds are given. Which one of the following is/are correct?

(a) $CH_3 - C \equiv C - CH(CH_3)_2$
4-methyl-2-pentyne

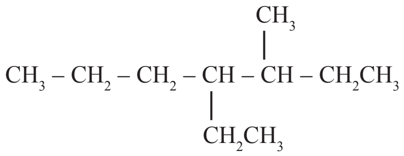
(b)



$CH_3 - CH_2 - \underset{\underset{CH_2}{\|}}{C} - \underset{\underset{CH_3}{|}}{CH} - CH_3$

2-ethyl-3-methyl-but-1-ene

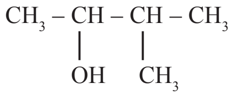
(c)



$CH_3 - CH_2 - CH_2 - \underset{\underset{CH_2CH_3}{|}}{CH} - \overset{\overset{CH_3}{|}}{CH} - CH_2CH_3$

3-ethyl-4-methylheptane

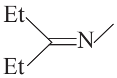
(d)

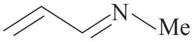


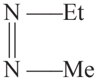
$CH_3 - \underset{\underset{OH}{|}}{CH} - \underset{\underset{CH_3}{|}}{CH} - CH_3$

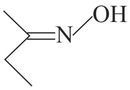
3-methyl-2-butanol

128. Which of these compound can exhibit geometrical isomerism?

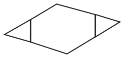
(a) 

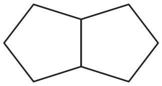
(b) 

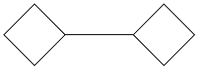
(c) 

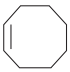
(d) 

129. Which of the compounds shown below, is/are isomers?

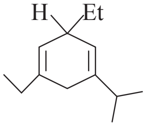
(a) 

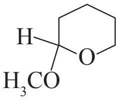
(b) 

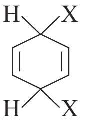
(c) 

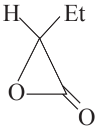
(d) 

130. Identify the compound, which has a stereocenter here.

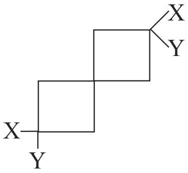
(a) 

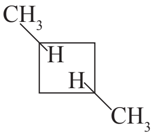
(b) 

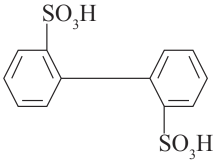
(c) 

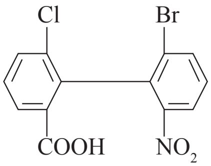
(d) 

131. Which of the following will show optical activity?

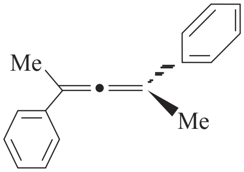
(a) 

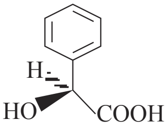
(b) 

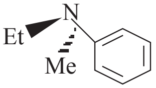
(c) 

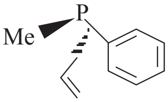
(d) 

132. Among the following, the optically active compound is/are

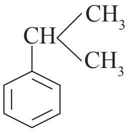
(a) 

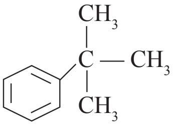
(b) 

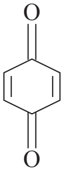
(c) 

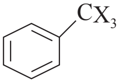
(d) 

133. Which of the following compounds cannot show hyperconjugation?

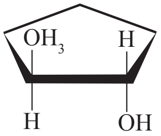
(a) 

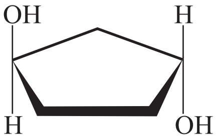
(b) 

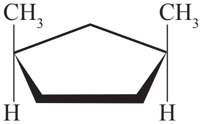
(c) 

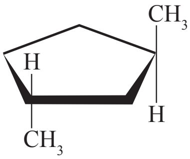
(d) 

134. Which of the following cyclopentane derivative is/are optically active?

(a) 

(b) 

(c) 

(d) 

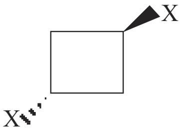
135. Which of the following alkenes can exhibit geometrical isomerism?

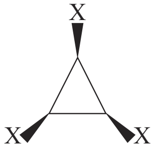
(a) $CH_3 - CH_2 - CH = CH_3$

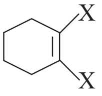
(b) $CH_3 - CH_2 - CH = CH - CH_2 - CH_3$

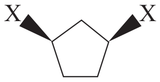
(c) $CH_3-CH_2-CH=CH-CH_3$
(d) $CH_3-CH_2-CH_2-CH=CH_2$

136. Which of the following compounds have non-zero dipole moment?

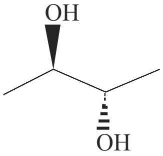
(a) 

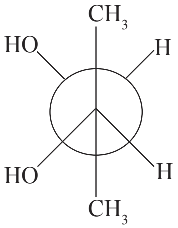
(b) 

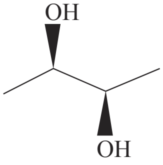
(c) 

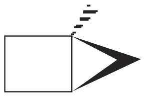
(d) 

137. Which of the following molecules are chiral?

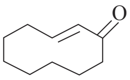
(a) 

(b) 

(c) 

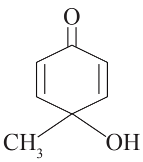
(d) 

138. Which of the following compounds can show geometrical isomerism as well as tautomerism here? (P. K)

(a) 

(b) $CH_3-CH=Ch-CH_2-NO_2$
(c) $(C_2H_5)_2C=N-OH$
(d) $Ph-N=N-OH$

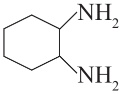
139. Which among these can exhibit tautomerism?
(a) $Ph-CH=N-NH-Ph$

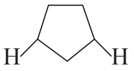
(b) 

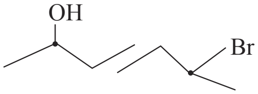
(c) CH_3NO
(d) $CH_3-COOC_2H_5$

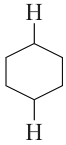
140. Which dimethylcyclobutane is/are optically inactive?
(a) Trans -1, 2
(b) trans -1, 3
(c) cis -1, 2
(d) cis -1, 3

141. Which of the following compounds has two similar asymmetric centres?

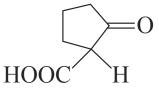
(a) 

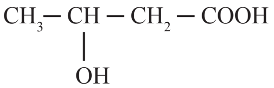
(b) 

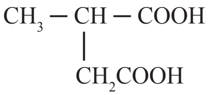
(c) 

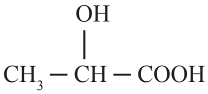
(d) 

142. The chirality is not lost on heating is case of

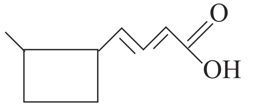
(a)  is heated

(b) 
$CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-COOH$ is heated

(c) 
$CH_3-\underset{\underset{CH_2COOH}{|}}{CH}-COOH$ is heated

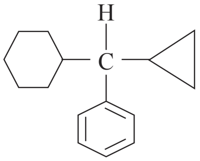
(d) 
$CH_3-\overset{\overset{OH}{|}}{CH}-COOH$ is heated.

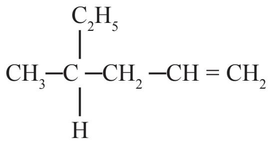
143. Which of the statement is/are corect for the following compound?

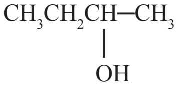


(a) It contains four lone pair of electrons
(b) It contains 19 sigma and 3 pi bonds
(c) It contains sp^3, sp^2 and sp hybrid carbon atom
(d) It contains sp^3 and sp^2 hybrid carbon atom

144. Which of the following can not show optical acitivity?

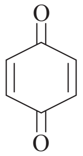
(a) 

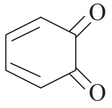
(b) 
$CH_3-\overset{\overset{C_2H_5}{|}}{\underset{\underset{H}{|}}{C}}-CH_2-CH=CH_2$

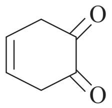
(c) 
$CH_3CH_2\underset{OH}{CH}-CH_3$

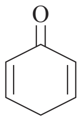
(d) $CH_3CH_2CH_2CH_2CHO$

145. Which can exhibit tautomerism here

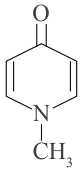
(a) 

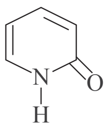
(b) 

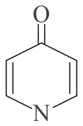
(c) 

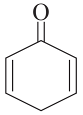
(d) 

146. Which can not exhibit tautomerism here

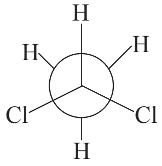
(a) 

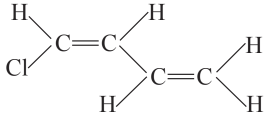
(b) 

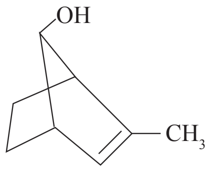
(c) 

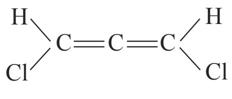
(d) 

147. Which of the following are chiral compounds? (P. K)

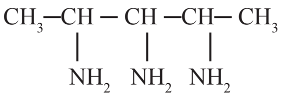
(a) 

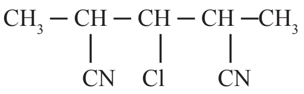
(b) 

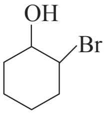
(c) 

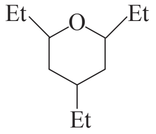
(d) 

148. Which of the following compounds has pseudoasymmetric centre?

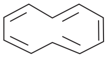
(a) 
$CH_3-\underset{NH_2}{CH}-\underset{NH_2}{CH}-\underset{NH_2}{CH}-CH_3$

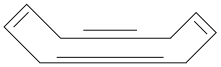
(b) 
$CH_3-\underset{CN}{CH}-\underset{Cl}{CH}-\underset{CN}{CH}-CH_3$

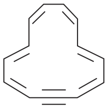
(c) 

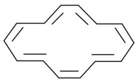
(d) 

149. Which of the following is/are aromatic?

(a) 

(b) 

(c) 

(d) 

150. Which of the following statements about conformers is/are correct?

(a) Conformation exist in a state of dynamic equilibrium.

(b) At equilibrium, population of more stable conformers will be more than that of less stable conformer.

(c) Conformers cannot be separated.

(d) Conformers different largely in energies.

Linked-Comprehension Type Questions

Comprehension 1

An organic compound having only C, H atoms has a molecular wt. **86.** By nature it is a liquid compound and it is capable of showing chain, position isomerisms. It can also show free radicle halogenation reaction also.

151. How many structural isomers of C_6H_{14} are possible?

(a) 3
(b) 4
(c) 5
(d) 6

152. How many of it's structural isomers is/are optically active?

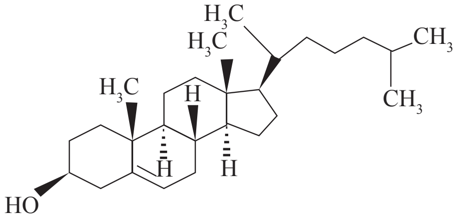
(a) Zero
(b) 1
(c) 2
(d) 3

153. Which of the following has all p°, s°, type of C-atoms?
(a) 2, 2 dimethyl butane
(b) 2, 3- dimethyl butane
(c) 3- methyl pentane
(d) n- hexane

154. Which of the following alkane on single mono chlorination can give 3- mono substituted products?
(a) 2- methyl pentane
(b) n- hexane
(c) 2,2- dimethyl butane
(d) both B and C

Comprehension 2

Cholesterol the principal sterol of animals. It is found in free and esterified forms in all parts of the body. It has a molecular formula $C_{27}H_{46}O$. It is capable of showing optical isomerism and its structure is as follows



Cholesterol

155. How many chirality centers does cholsesterol have?
(a) 4 (b) 6
(c) 8 (d) 10

156. What is the maximum number of stereisomers that cholesterol can have?
(a) 32 (b) 128
(c) 64 (d) 256

157. How many of these stereisomers are found in nature?
(a) 0 (b) 1
(c) 2 (d) 3

Comprehension 3

Compound having difference in structure due to difference in the manner of attachment of atoms are called structural isomers. They are further divided into chain, position, functional, metamers and tautomers. For example compounds having a molecular formula $C_nH_{2n+2}O$ can show chain, position, functional, metamerism, isomerisms.

158. How many structural isomers of alcohols of the molecular formula $C_5H_{12}O$ are possible?
(a) 5 (b) 8
(c) 10 (d) 7

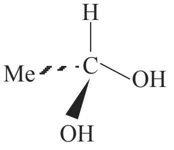
159. How many alcohols with molecular formula $C_5H_{12}O$ are capable of showing optical isomerism?
(a) 2
(b) 4
(c) 3
(d) 5

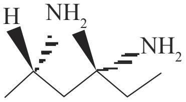
160. How many structural ether are possible for the mol. formula $C_5H_{12}O$?
(a) 4 (b) 6
(c) 5 (d) 8

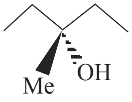
Comprehension 4

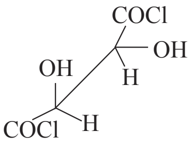
Optical isomerism arises due to difference in the rotation of plane polarized light that is, due to optical rotation by asymmetric or chiral molecules. A molecule having minimum one stereogenic centre, without any kind of symmetry and with a non-superimposable mirror image is capable to show optical isomerism. Stereoisomers that are non-superimposable mirror images are called enantiomers while non-mirror image ones are called diastereomers.

161. Which of the following are chiral here?

(1)


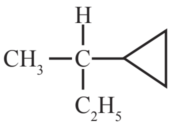
(2)


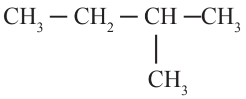
(3)


(4)


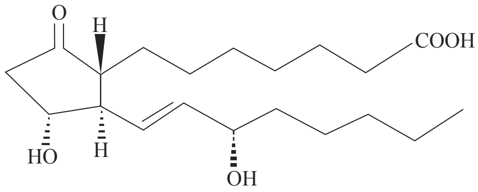
(a) 1, 3 (b) 2, 4
(c) 2, 3 (d) 1, 4

162. The lowest molecular weight alkane, which is optically active?

(a)

$CH_3-\underset{C_2H_5}{\overset{H}{C}}-\text{(cyclopropyl)}$

(b) $CH_3CH_2CH_2CH_3$
(c) $CH_3-CH=CH-CH_3$
(d)

$CH_3-CH_2-\underset{CH_3}{CH}-CH_3$

163. Prostaglandin E_1 is a compound generated by the body to regulate a number of phenomenons like fever blood, clothing etc. Which of the following is correct about it?



(a) It contains 4- chiral C- atoms
(b) The geometrical configuration at double bond in it is (E)
(c) It contains 5 sp^2 hybridized C- atoms.
(d) Both a and b

Assertion-Reason Type Questions

In the following question two statements (Assertion) A and Reason (R) are given. Mark

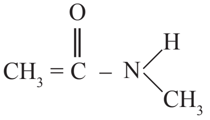
(a) if A and R both are correct and R is the correct explanation of A
(b) if A and R both are correct but R is not the correct explanation of A
(c) A is true but R is false
(d) A is false but R is true

164. (A): Compound possessing same molecular formulae but differing in their physical and chemical properties are called isomers.
(R): Rearrangement reactions produce isomers.

165. (A): Tetrahedral complexes show geometrical isomerism.
(R): The relative positions of the ligands attached to the central metal atom are same with respect to each other.

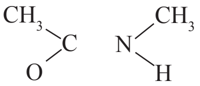
166. (A): Metamers can also be chain or position isomer.
(R): The term tautomerism was introduced to explain the reactivity of a substance according to two possible structures.

167. (A): There is evidence for the existence of N-methyl acetamide in two structural forms I and II and shown



$$CH_3=\overset{\overset{O}{\|}}{C}-N\begin{matrix}H\\CH_3\end{matrix}$$

(I)



$$\begin{matrix}CH_3\\O\end{matrix}C\;N\begin{matrix}CH_3\\H\end{matrix}$$

(II)

(R): Rotation about the carbon-nitrogen bond is restricted.

168. (A): Trans-1,2-dichloroethene has two-fold simple axis of relation
(R): The rotation of the molecular model through 180° about the axis passing through the geometrical centre and perpendicular to the plane of the molecule produces an arrangement which is in distinguishable from the original.

169. (A): cis-2-butene gives meso-2,3- butanediol with dilute alkene $KMnO_4$ solution.
(R): Dilute alkaline $KMnO_4$ solution gives trans addition with alkenes.

170. (A): Meso-tartaric acid is optically active.
(R): Optically active molecule is a molecule that cannot be superimposed on its mirror image.

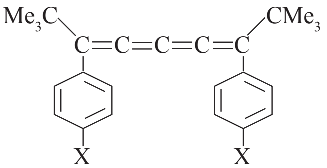
171. (A): Cyclohexanone exhibits keto-enol tautomerism.
(R): In cyclohexanone, one form contains the keto-group (C = O) while other contains enolic group (–C = C – OH)

172. (A): Enol form of cyclohexane-1,3,5 trione is more stable than its keto form.
(R): Enol form contains α-hydrogen atoms.

173. (A): 6, 6'-dinitrodiphenic acid shows enantiomerism.
(R): Enantiomers rotate the plane of polarized light in the opposite direction but to the same extent.

174. (A): Alkenes containing more than three carbons exhibit chain isomerism.
(R): All the carbon atoms in alkanes are sp^3-hybridized.

175. (A): When even number of cummulated bonds are present, the compound is optically active. For example



(R): It can show gerometrical isomerism also.

176. (A): Lactic acid shows geometrical isomerism.
(R): It has a chiral C-atom

177. (A): Cis-1,3-dimethylcyclo-hexane is achiral in its chair conformation.
(R): It has plane of symmetry passing through carbon-1 and carbon-4.

178. (A): Conformation are not different compound and true isomers.
(R): As in most cases they are interconvertable even at room temperature.

179. **(A):** Cyclobutane is less stable than cyclopentane.
(R): Presence of 'bent bond' causes loss of orbital overlap.

180. **(A):** Molecules that are not superimposable on their mirror images are chiral.
(R): All chiral molecules have chiral centre.

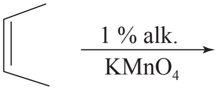
[IIT 1997]

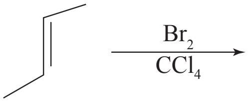
Matrix-Match Type Questions

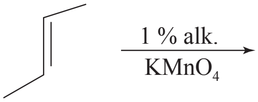
181. Match the following:

Column I

(a)


(b)


(c)


(d)


Column II

(p) cis- but 2- ene
(q) Meso product
(r) Racemic product
(s) Trans -but -2 -ene

182. Match the following:

Column I

(a) Enantiomers
(b) Diastereomers
(c) Meso compound
(d) Racemic modification
(E) stereoisomers that are not related as object and

Column II

(p) An optically inactive compound having plane of symmetry
(q) An equimolar mixture of enantiomers
(r) separation of a mixture of enantiomers
(s) stereoisomers that are not related as object and mirror image

183. Match the following:

Column I

(a) Lactic acid
(b) d- tartaric acid
(c) Meso- tartaric acid
(d) Glucose

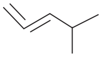
Column II

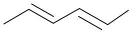
(p) 4- chiral C- atoms
(q) 2- chiral C- atoms
(r) one chiral C- atom
(s) plane of symmetry

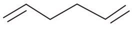
184. Match the following:

Column I

(a)


(b)


(c)


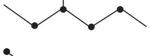
(d)


Column II

(p) one tertiary c- atom
(q) sp- hybridization
(r) geometrical isomerism
(s) 2- π- bonds

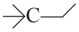
185. Match the following:

Column I

(a)


(b)


(c)

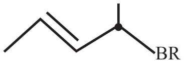

(d)


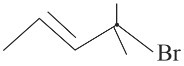
Column II

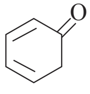
(p) one t° three s° -c- atoms
(q) one t°, two s°- c- atoms
(r) one chiral c- atom
(s) chain isomer of n- hexane
(t) one quarternary c- atom

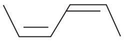
186. Match the following:

Column I

(a)


(b)


(c)


(d)


Column II

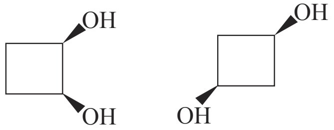
(p) Geometrical isomerism
(q) optical isomerism
(r) tautomerism
(s) resonance stabilization of enol form

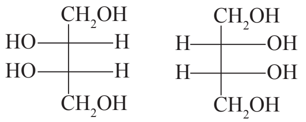
187. Match the following:

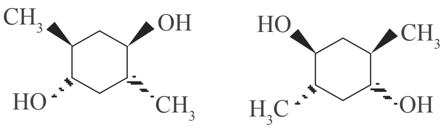
Column I

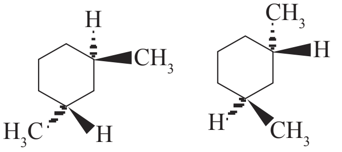
(a) Same compound
(b) Enantiomer
(c) Diastereomer
(d) Constitutional

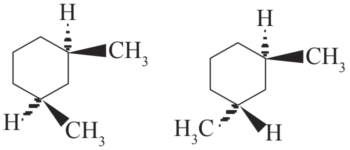
Column II

(p)


(q)


(r) 

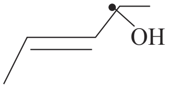
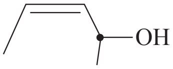
(s) 

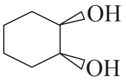
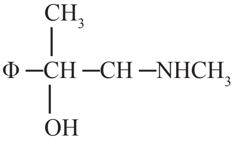


(t)

188. Match the following:

Column I

(a)  (b) 

(c)  (d) 

$\Phi-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}H-CH-NHCH_3$

Column II

(p) Z- geometrical isomer

(q) E- geometrical isomer

(r) cis - geometrical isomer

(r) One chiral C- atom

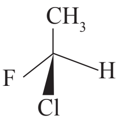
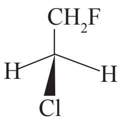
(t) 2- chiral C- atom

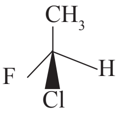
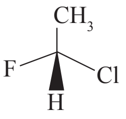
189. Match the following:

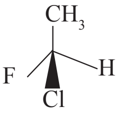
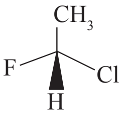
Column I (Isomer Type)

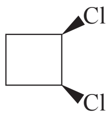
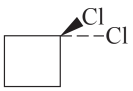
(a) Constitutional	(b) Enantiomer
(c) Identical	(d) Diastereomer

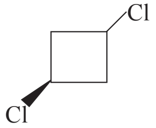
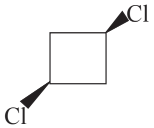
Column II

(p)  and 

(q)  and 

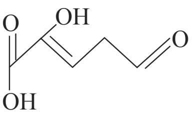
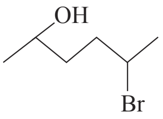
(r)  and 

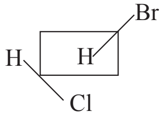
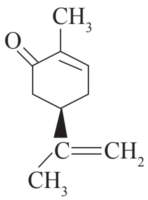
(s)  and 

(t)  and 

190. Match the following:

Column I

(a)  (b) 

(c)  (d) 

Column II

(p) can show geometrical isomerism

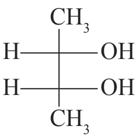
(q) can show optical isomerism

(r) 2- hydroxy 5- oxo -pent 2- enoic acid

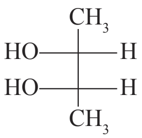
(s) 3- bromo butan 2- ol

(t) trans -1- bromo -3- chloro cyclobutane

Extra



$$\begin{array}{ccc} & CH_3 & \\ H & - & OH \\ H & - & OH \\ & CH_3 & \end{array}$$



$$\begin{array}{ccc} & CH_3 & \\ HO & - & H \\ HO & - & H \\ & CH_3 & \end{array}$$

The IIT-JEE Corner

191. How many optically active stereoisomers are possible for Butan-2, 3-diol?

(a) 1	(b) 2
(c) 3	(d) 4

[IIT 1997]

192. The number of possible enantiomeric pairs than can be produced during monochlorination of 2-Methyl butane is

(a) 2	(b) 3
(c) 4	(d) 1

[IIT 1997]

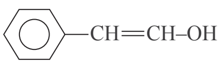
193. Which of the following compounds will show geometrical isomerism?

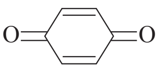
1. 2-butene
2. propene
3. 1-phenylpropene
4. 2-methylbut-2-ene

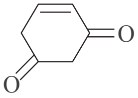
(a) 1, 2
(b) 3, 4
(c) 1, 2, 3
(d) 1, 3

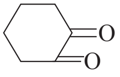
[IIT 1998]

194. Tautomerism is exhibited by:

1. 

2. 

3. 

4. 

(a) 1,2,3
(b) 1,3,4
(c) 1,2,4
(d) 1,2,3,4

[IIT 1998]

195. The optically active tartaric acid is named as D (+)-tartaric acid because it has a positive:

(a) optical rotation and is derived from D-glucose.
(b) pH in an organic solvent.
(c) optical rotation and is derived from D (+)-glyceraldehyde.
(d) optical rotation only when substituted by deuterium.

[IIT 1999]

196. Which of the following compounds will exhibit geometrical isomerism?

(a) 1-phenyl-2-butene
(b) 3-phenyl-1-butene
(c) 2-phenyl-1-butene
(d) 1,1-diphenyl-1-propene

[IIT 2000]

197. The number of isomers for the compound with molecular formula $C_2BrClFI$ is

(a) 3
(b) 4
(c) 5
(d) 6

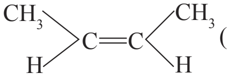
[IIT 2001]

198. Which of the following compounds exhibit steroisomerism?

(a) 2-methylbutene-1
(b) 3-methylbutyne-1
(c) 3-methylbutanoic acid
(d) 2-methylbutanoic acid

[IIT 2002]

199. Which of the following hydrocarbons has the lowest dipole moment?

(a) 
$\begin{matrix}CH_3 & & CH_3\\ & >C=C< & \\ H & & H\end{matrix}$

(b) $CH_3 - C \equiv C - CH_3$

(c) $CH_3CH_2CH = CH_2$

(d) $CH_2 = CH - C \equiv CH$

[IIT 2002]

200. On monochlorination of 2-methyl butane, the total number of chiral compounds is

(a) 2
(b) 4
(c) 6
(d) 8

[IIT 2004]

201. The IUPAC name of C_6H_5COCl is

(a) benzoyl chloride
(b) benzene chloro ketone
(c) benzene carbonyl chloride
(d) chloro phenyl ketone

[IIT 2006]

202. The number of stereoisomers obtained by bromination of trans-2-butene is

(a) 1
(b) 2
(c) 3
(d) 4

[IIT 2007]

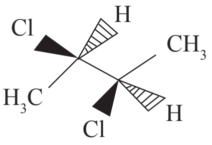
203. The number of structural isomers for C_6H_{14} is

(a) 6
(b) 5
(c) 4
(d) 3

[IIT 2007]

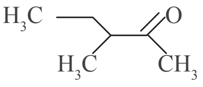
204. The correct statement(s) about the compound given below is/are

[IIT 2008]

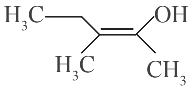


(a) The compound is optically active
(b) The compound possesses centre of symmetry
(c) The compound possesses plane of symmetry
(d) The compound possesses axis of symmetry

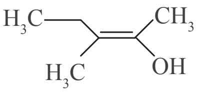
205. The correct statement(s) concerning the structures E, F and G is/are



(E)



(F)



(a) E, F and G are resonance structure
(b) E, F and E, G are tautomers
(c) F and G are geometrical isomers
(d) F and G are diastereomes

[IIT 2008]

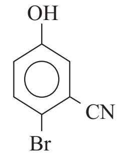
206. The correct statements about the compound $H_3C(HO)HC-CH = CH-CH(OH)CH_3(X)$ is/are

[2009]

(a) The total number of stereoismers possible for X is 6
(b) The total number of diastereomers possible for X is 3
(c) If the stereochemistry about the double in X is *trans*, the number of enatiomers possible for X is 4
(d) If the stereochemistry about the double in X is *cis*, the number of enatiomers possible for X is 2

207. The total number of cyclic structural as well as stereo isomers possible for a compound with the molecular formula C_5H_{10} is
(a) 4 (b) 6
(c) 3 (d) 7

208. The IUPAC name of the following compound is **[IIT 2009]**



(a) 4- Bromo 3cyanophenol
(b) 2- Bromo – 5-hydroxybenzonitrile
(c) 2-Cyano – 4- hydroxybromobenzene
(d) 6- Bromo – 3- hydroxybenzonitrile

ANSWERS

Straight Objective Type Questions

1. (c) **2.** (a) **3.** (a) **4.** (c) **5.** (c) **6.** (a) **7.** (b) **8.** (a) **9.** (d) **10.** (b)
11. (c) **12.** (c) **13.** (a) **14.** (d) **15.** (a) **16.** (d) **17.** (b) **18.** (a) **19.** (c) **20.** (c)
21. (b) **22.** (c) **23.** (b) **24.** (a) **25.** (d) **26.** (d) **27.** (c) **28.** (a) **29.** (c) **30.** (b)
31. (a) **32.** (d) **33.** (a) **34.** (b) **35.** (c) **36.** (a) **37.** (c) **38.** (d) **39.** (a) **40.** (d)
41. (b) **42.** (c) **43.** (b) **44.** (d) **45.** (c) **46.** (d) **47.** (d) **48.** (c) **49.** (d) **50.** (d)
51. (a) **52.** (b) **53.** (b) **54.** (a) **55.** (b) **56.** (b) **57.** (d) **58.** (b) **59.** (b) **60.** (b)
61. (b) **62.** (c) **63.** (d) **64.** (b) **65.** (b) **66.** (c) **67.** (b) **68.** (d) **69.** (c) **70.** (d)
71. (a) **72.** (b) **73.** (c) **74.** (b) **75.** (a)

Brainteasers Objective Type Questions

76. (c) **77.** (d) **78.** (d) **79.** (a) **80.** (c) **81.** (d) **82.** (c) **83.** (b) **84.** (a) **85.** (c)
86. (c) **87.** (b) **88.** (d) **89.** (a) **90.** (b) **91.** (a) **92.** (b) **93.** (c) **94.** (b) **95.** (b)
96. (b) **97.** (d) **98.** (c) **99.** (a) **100.** (c) **101.** (c) **102.** (c) **103.** (a) **104.** (c) **105.** (c)
106. (c) **107.** (d) **108.** (b) **109.** (a) **110.** (a) **111.** (c) **112.** (d) **113.** (a) **114.** (a) **115.** (a)
116. (c) **117.** (d) **118.** (b) **119.** (b) **120.** (d) **121.** (d) **122.** (b) **123.** (a) **124.** (a) **125.** (d)

Decisive Thinking Objective Type Questions

126. (a), (c), (d) **127.** (a), (b), (d) **128.** (b), (c), (d) **129.** (b), (c), (d) **130.** (a), (b), (d)
131. (a), (b), (d) **132.** (a), (b), (d) **133.** (b), (c) **134.** (a), (b), (d) **135.** (b), (c)
136. (b), (c) ,(d) **137.** (b), (c) , (d) **138.** (a), (b) **139.** (a), (c), (d) **140.** (b), (c), (d)
141. (a), (b), (c) **142.** (c), (d) **143.** (a), (b), (c) **144.** (a), (b), (d) **145.** (c), (d)
146. (a), (d) **147.** (a), (c) **148.** (a), (b), (d) **149.** (a), (d) **150.** (a), (b), (c) ,(d)

Linked-Comprehension Type Questions

151. (c) **152.** (b) **153.** (c) **154.** (d) **155.** (c) **156.** (d) **157.** (b) **158.** (b) **159.** (c) **160.** (b)
161. (b) **162.** (a) **163.** (d)

Assertion-Reason Type Questions

164. (b) **165.** (d) **166.** (b) **167.** (d) **168.** (a) **169.** (c) **170.** (d) **171.** (a) **172.** (b) **173.** (b)
174. (c) **175.** (b) **176.** (d) **177.** (c) **178.** (a) **179.** (a) **180.** (c)

Matrix-Match Type Questions

181. (a) - (p, r), (b) - (p, q), (c) - (q, s), (d) - (r, s)
182. (a) - (r), (b) - (s), (c) - (p), (d) - (q)
183. (a) - (r), (b) - (q), (c) - (q, s), (d) - (p)
184. (a)- (p, q, s), (b) - (p, q, s), (c) - (r, s), (d) - (s)
185. (a) - (p, r), (b) - (q, s), (c) - (q, s), (d) - (s, t)
186. (a) - (p, q), (b) - (p), (c) - (r, s), (d) - (p)
187. (a) - (r), (b) - (q, s), (c) - (t), (d) - (p)
188. (a) - (q, s), (b) - (p, s), (c) - (r), (d) - (t)
189. (a) - (p, s), (b) - (q), (c) - (r), (d) - (t)
190. (a) - (p, r), (b) - (q, s), (c) - (p, t), (d) - (p, q)

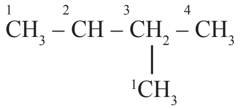
The IIT-JEE Corner

191. (b) **192.** (a) **193.** (d) **194.** (b) **195.** (c) **196.** (a) **197.** (d) **198.** (d) **199.** (b) **200.** (a)
201. (c) **202.** (a) **203.** (b) **204.** (a),(d) **205.** (b), (c),(d) **206.** (a),(d) **207.** (d) **208.** (b)

HINTS AND EXPLANATIONS

Straight Objective Type Questions

1.



$$\overset{1}{C}H_3 - \overset{2}{C}H(\overset{1}{C}H_3) - \overset{3}{C}H_2 - \overset{4}{C}H_3$$

has four types of H-atoms and gives four isomeric monochloro derivatives.

2. Three in the ring and the fourth on CH_2.

3. A diastereomers are stereoisomers that are nonsuperimposable nonmirror images. Cis- trans isomers are examples of diastereomers.

4. $CH_2 = CH - {}^*CH(OH) - CH_3$ has a chiral carbon atom.

6. Structures (B), (C) and (D) have the same molecular formula ($C_6H_{12}O$) as that of $CH_3COCH_2CH_2CH_2CH_3$ and are all isomers. The molecular formula of structure (A) is $C_6H_{10}O$ and it is not an isomer.

8. As during the reaction, a chiral carbon is created and further since the CN^- ion can attack the planar aldehyde group both from the top and the bottom face of the aldehyde group with equal ease, therefore, a 50 : 50 mixture of the two enantiomers, that is, a racemic mixture is obtained.

9. Only $C_2H_5 - S - C_2H_5$. The two metamers are $CH_3 - S - CH_2CH_2CH_3$ and $C_2H_5 - S - C_2H_5$.

10. In fischer projections, horizontal substituents are above the plane.

11. Trans-2-butene has zero dipole moment.

12. Six These are:
1-butene, trans-2-butene, cis-2-butene, 2-methyl propene, cyclobutane and methyl-cyclopropane.

14. The compound $CH_3\ {}^*CHBr\ {}^*CHBrCOOH$ contains two dissimilar chiral carbon atoms and hence $2^2 = 4$ enantiomers are possible.

15. Boat conformation of cyclohexane has two types of destabilizing interactions, that is, eclipsing and flagpole-flagpole. Out of these eclipsing interactions are the most destabilizing.

16. Trans-1,2-dichloroethene has zero dipole moment.

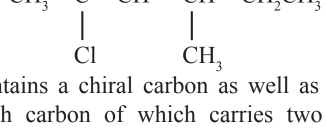
17. As the size of the ring increases, the internal angle increases accordingly. As a result, the derivation from the tetrahedral angle and the angle strain increases as the size of the ring increases. Thus, planar cyclodecane is expected to have the maximum angle strain.

18. Specific rotation of the mixture
$= (75/100)\ (+158^o) + (25/100)\ (-158^o) = +79^o$

19. As both the carbon atoms of each of the three double bonds are differently susbstituted, therefore, $2^3 = 8$ geometrical isomers are possible.

20. These are: benzyl alcohol, anisole, o- , m- and p-cresols (that is, methylphenols)

21. 2-chloro-4-methylhex-2-ene that is,



$$CH_3 - C(Cl) = CH - {}^*CH(CH_3) - CH_2CH_3$$

contains a chiral carbon as well as a double bond each carbon of which carries two different substituents, therefore, it shows optical as well as geometrical isomerism. Since each geometrical isomer has a pair of enantiomers, therefore, in all, 2 x 2 = 4 stereoisomers are possible.

22. Pents-3-en-2-ol that is,

$$CH_3 - {}^*CH(OH) - CH = CH - CH_3$$

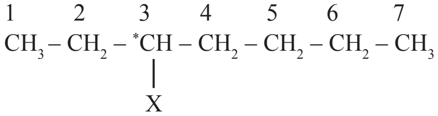
shows both geometrical as well as optical isomerism and hence in all four stereoisomers are possible.

24. These are:
$CH_3CH_2CH_2C \equiv CH$, $CH_3CH_2C \equiv CCH_3$, and $(CH_3)_2CHC \equiv CH$.

25. These are: Cyclopentane, methyl-cyclobutane, ethylcyclopropane,
1,1-dimethyl-cyclohexane, 2-dimethyl-cyclopropane, 2-dimethyl-cyclopropane.

26. 2, 4 –dibromopentane contains two similar asymmetric carbon atoms and any compound with two or more asymmetric carbon atoms but also having a plane of symmetry is called *meso*-compound.

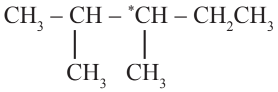
27. Putting a substituent at position 3 will make the molecule chiral



$$\overset{1}{CH_3} - \overset{2}{CH_2} - \underset{X}{\overset{3}{{}^*CH}} - \overset{4}{CH_2} - \overset{5}{CH_2} - \overset{6}{CH_2} - \overset{7}{CH_3}$$

28. 1,2-dibromobutene has different substituents on each C-atom of the double bond and shows geometrical isomerism.

29.



$$CH_3 - \underset{CH_3}{CH} - \underset{CH_3}{{}^*CH} - CH_2CH_3$$

2,3-dimethylpentane has a chiral carbon and hence is optically active.

30. II and IV and cis-trans-isomers.

31. 1,2-dichloro-1-pentene
$C.(Cl)_2 = CHCH_2CH_2CH_3$ does not show geometrical isomerism since it has two identical atoms that is, Cl on C_1.

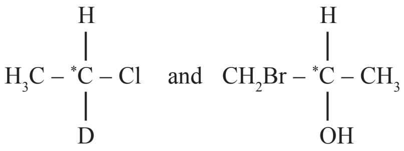
32. The two stereoisomers are not mirror images and hence are diastereomers.

33. $(CH_3)_2C = CHCH_3 \xrightarrow{H_2} (CH_3)_2CH - CH_2CH_3$
the reduced product does not contain a chiral carbon atom and hence is optically inactive.

34.

IUPAC name of this compound is
N-Phenylcyclohexane carboxamide.

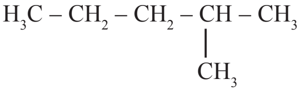
38.



$$H_3C - \underset{D}{\overset{H}{{}^*C}} - Cl \quad \text{and} \quad CH_2Br - \underset{OH}{\overset{H}{{}^*C}} - CH_3$$

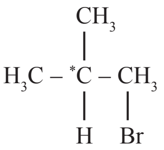
39. Sp^2 hybridization (120°) and sp^3 hybridization (109° 28')

40.



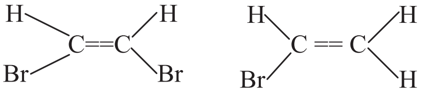
$$H_3C - CH_2 - CH_2 - \underset{CH_3}{CH} - CH_3$$

44. 1-Bromo-2-methylpropane has one chiral carbon.



$$H_3C - \underset{H}{\overset{CH_3}{{}^*C}} - \underset{Br}{CH_3}$$

45. Due to restricted rotation about double bond, the alkene shows geometrical isomerism that is, *cis-trans* isomerism.

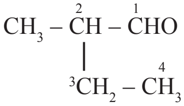


Cis form *trans* form

Besides this the same group should not be attached to the single carbon.

48. Disymmetry is essential condition for optical activity.

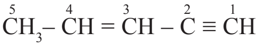
52.



$$CH_3 - \underset{\overset{3}{C}H_2 - \overset{4}{C}H_3}{\overset{2}{CH}} - \overset{1}{CHO}$$

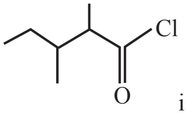
2-Methylbutanal

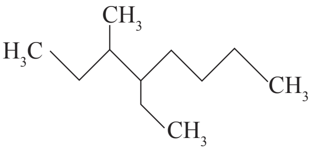
54.

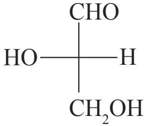


$$\overset{5}{CH_3} - \overset{4}{CH} = \overset{3}{CH} - \overset{2}{C} \equiv \overset{1}{CH}$$

Pent -3-ene-1-yne

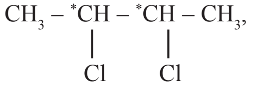
55. The IUPAC name of  is 2, 3-dimethylpentanoyl chloride.



57. The plane of polarized light is rotated by optically active compound that is, it should be chiral. Therefore  has chiral C-atom, so it is optically active.

59. The name of this compound is 4-ethyl-3-methyloctane.

60. Due to presence of two asymmetric carbon atoms in 2,3-dichlorobutane,

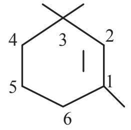


$CH_3 - {}^*CH(Cl) - {}^*CH(Cl) - CH_3$,

It exhibits optical isomerism

62. The correct decreasing order is as follows:
$-SO_3H$, $-COOH$, $-CONH_2$, $-CHO$

65.



1,3, 3-Trimethylcyclohex-1-er

73. Twisted boat is chiral as it does not have plane of symmetry.

Brainteasers Objective Type Questions

78. All of the molecules listed, A, B and A, have chiral C atoms.

81. Chlorine atoms are strongly negative (show-I effect). They deactivate the ring to towards electrophillic reaction.

83. Six. These are:
1-pentene, cis-2-pentene , trans-2-pentene,
2-methyl-1-butene, 3-methyl-1-butene,
2-methyl-2-butene.

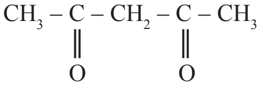
87. The E - isomer is the transisomer, which means that the high - priority groups are on opposite side of the double bond. The Br atom is the higher priority group on one side, and the CH_2OH group is the higher priority group on the other side.

88. All of the above are correct. This molecule, cis -1, 2- dibromocyclobutane, has two stereogenic centers but also has a plane of symmetry, Which makes the mirror image superimposible. This means it is a meso compound.

95. These molecules are diastereomers because they are non - mirror - image molecules that only differ in the arrangement of their atoms in space.

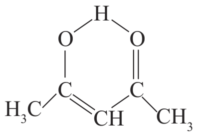
97. A racemic mixture is always produced whenever a new chiral carbon atom is generated in a reaction. Thus, 50 per cent D and 50 per cent L isomers are produced.

100. The active methylene group of the compound



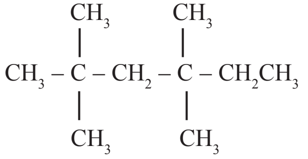
$CH_3 - C(=O) - CH_2 - C(=O) - CH_3$

can tautomerise with the two carbonyl groups more readily and the enol formed is stabilized by intramolecular H-bonding.



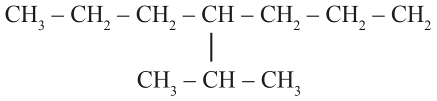
103. The product, 2- chlorobutane, is not optically active because a racemic mixture results. The second C atom in 2- chlorobutane is stereogenic center because it has four different groups attached.

104.



$CH_3 - C(CH_3)_2 - CH_2 - C(CH_3)_2 - CH_2CH_3$

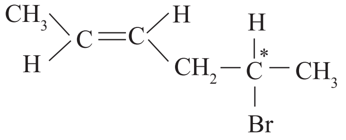
2,2,4,4-tetramethylhexane has the molecular formula $C_{10}H_{22}$. The molecular formula of 4-isopropylheptane



$CH_3 - CH_2 - CH_2 - CH(CH_3 - CH - CH_3) - CH_2 - CH_2 - CH_2$

is also $C_{10}H_{22}$ and hence the two are isomers.

105. Given compound
$CH_3CH = CHCH_2\ CHBrCH_3$
may also be written as follows:

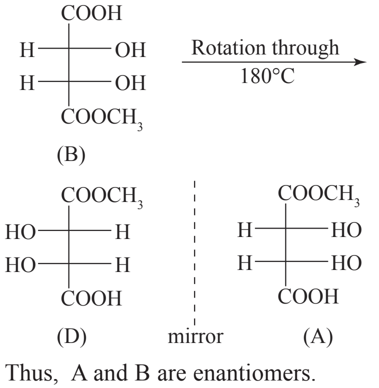


Both geometrical isomerism (cis-trans form) and optical isomerism is possible in this compound

Number of optical isomer = $2^n = 2^1 = 2$
(Here n = number of asymmetric carbon)
Therefore, total number of stereoisomers
= 2 + 2 = 4

106. This molecule has two chiral centers, but the molecule is achiral because it is meso structure.

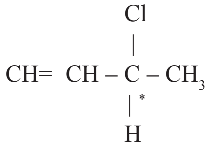
107. Rotation of B through 180° within the plane of paper gives D which is an enantiomer of A.



Thus, A and B are enantiomers.

109. Structure I and II are enantiomers because they are nonsuperimposible mirror - image molecules.

110. Acyclic stereo isomers having molecular formula C_4H_7Cl



$$CH{=}\ CH - \underset{\overset{|^{*}}{H}}{\overset{\overset{Cl}{|}}{C}} - CH_3$$

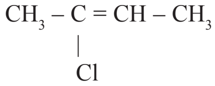
One asymmetric carbon

Therefore, number of optical isomers

$= 2^n = 2^1 = 2$

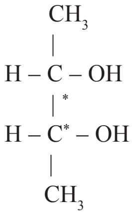
Two geometrical isomers of each compound are possible for the following structures:

$ClHC = CH - CH_2 - CH_3$, $ClHC- CH = CH - CH_3$ and



$$CH_3 - \underset{\underset{Cl}{|}}{C} = CH - CH_3$$

113.



$$\begin{array}{c} CH_3 \\ | \\ H - C - OH \\ |^{*} \\ H - C^{*} - OH \\ | \\ CH_3 \end{array}$$

Butane-2,3-diol

Number of asymmetric or chiral carbon = 2

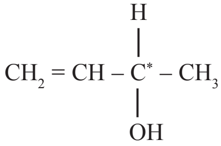
Therefore no. of optical isomers = $2^n = 2^2 = 4$

No. of optically active stereomers = 4 – 1 = 3; because meso compound is optically inactive due to internal compensation.

114. Ethylene and acetylene have hindered rotation around C = C and C ≡ C bond. Ethane and hexachloroethane both have C – C bonds and have less hindered rotation but the latter has more hindered rotation because of bigger size of Cl atoms.

116. 4- Cyclopropyl 1-2, 3- difluoro -2- octanol is the correct name because the longest chain has eight C atoms. Bonded to the fourth C atom is a cyclopropyl group. Bonded to the second and third C atoms are F atoms. Finally, the OH group is bonded to the second C atom of the longest chain (Alcohol nomenclature)

118. The compound $CH_2 = CH - CH(OH)CH_3$,



$$CH_2 = CH - \underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C^{*}}} - CH_3$$

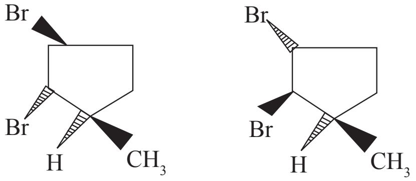
has non super imposable image, due to the presence of one asymmetric carbon atom.

120. 2- Mehtylbutane produces 1- chloro -2- mehtylbutane, 2- chloro-2- methyl butane, 2- chloro -3- methylbutane, and 1- chloro -3- methylbutane. (Halogenation of alkanes).

121. An optically pure substance is optically active because it is composed of only one enantiomer. It is 100% of either the R or S form of an enantiomer.

122. Seven dichlorocyclopentanes would be obtained as products. Only one isomer is possible for the 1,1- dichloro compound. The 1,2 -and 1,3- dichloro compounds have two chirality centers. Each has three stereoisomers-the cis isomer is a meso compound and the trans isomer is a pair of enantiomers.

123. 3- Methylcyclopentene produces the following two diastereomers.



Methylenecyclopentene only produces one product. Both 1- methylcyclopentene and 4- methylcyclopentene produces enantiomeric products.

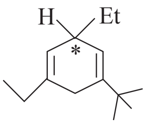
Decisive Thinking Objective Type Questions

126. As alkenes with odd number of olefinic carbons (= bonded) usually do not show geometrical isomerism.

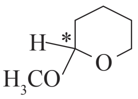
127. As the correct name should be 4-ethyl-3-methylheptane.

130. Compound C is optically inactive here due to plane of symmetry and does not have carbon atom with four different group attached. While these are optically active ones.

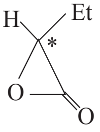
(a)



(b)

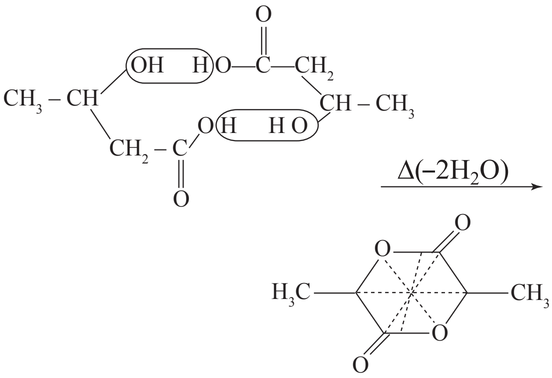


(d)



133. As they don't have any α - H- atom

142.



Optically inactive due to point of symmetry.

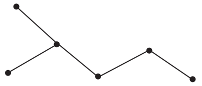
147. Compounds (A) an s (C) have one stereogenic center and does not contain any S_n symmetry element so they are optically active.

149. Cyclooctatetraene, [14]- annulene are not aromatic, due to lack of planarity.

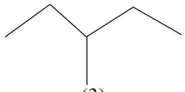
Linked-Comprehension Type Questions

151.

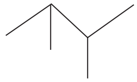
(1)



(2)



(3)



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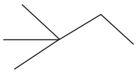
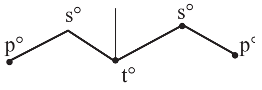
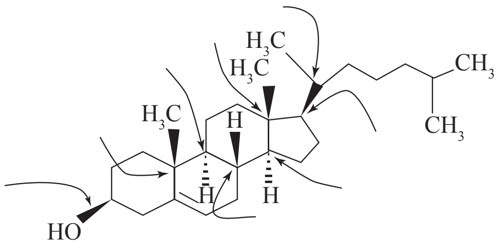


(5)

153.



155.

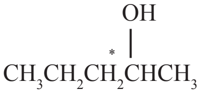


It contains 8 chiral atoms as indicated by the arrows.

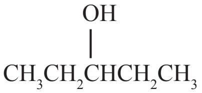
156. Number of stereoisomers = $2^8 = 256$

158. $CH_3CH_2CH_2CH_2CH_2OH$

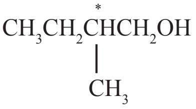
Pentan -1- ol


$CH_3CH_2CH_2\overset{\overset{OH}{|}}{\overset{*}{C}}HCH_3$

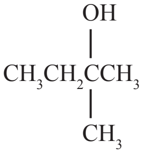
Pentan -2- ol


$CH_3CH_2\overset{\overset{OH}{|}}{C}HCH_2CH_3$

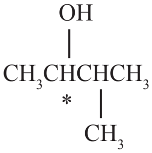
Pentan -3- ol


$CH_3CH_2\underset{\underset{CH_3}{|}}{\overset{*}{C}}HCH_2OH$

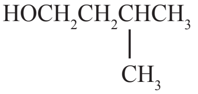
2- Methylbutan-1-ol


$CH_3CH_2\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}CH_3$

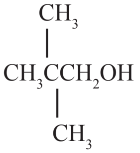
2- methylbutan -2-ol


$CH_3\overset{\overset{OH}{|}}{\underset{*}{C}}H\underset{\underset{CH_3}{|}}{C}HCH_3$

3- Methylbutan-2-ol


$HOCH_2CH_2\underset{\underset{CH_3}{|}}{C}HCH_3$

3- methylbutan-1-ol


$CH_3\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}CH_2OH$

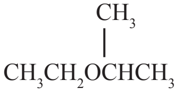
2,2-dimethylpropan-1-ol

Here out of 8 of the alcohols only pentan -2-ol, 2- methylbutan -1-ol, and 3- methylbutan -2-ol are chiral and capable to show optical isomer.

159.

$CH_3CH_2OCH_2CH_2CH_3$

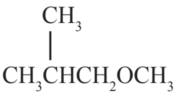
Ethyl propyl ether


$CH_3CH_2O\overset{\overset{CH_3}{|}}{C}HCH_3$

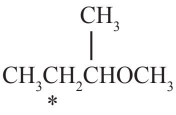
Ethyl isopropyl ether

$CH_3CH_2CH_2CH_2OCH_3$

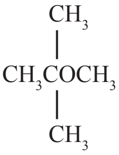
Butyl methyl ether


$CH_3\overset{\overset{CH_3}{|}}{C}HCH_2OCH_3$

Isobutyl methyl ether


$CH_3CH_2\overset{\overset{CH_3}{|}}{\underset{*}{C}}HOCH_3$

sec- Butyl methyl ether


$CH_3\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}OCH_3$

tert- Butyl methyl ether

Only sec -butyl methyl ether is chiral.

163. As it has 4 sp^2 hybridized C- atoms.

Assertion-Reason Type Questions

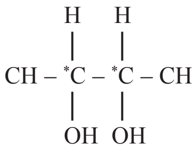
169. Dilute alkaline $KMnO_4$ solution gives is addition with alkenes.

170. Meso-tartaric acid possesses a plane of symmetry and is consequently optically inactive. This optically inactive form is said to be internally compensated. (optical rotation of one asymmetric carbon is cancelled by that of the other).

172. Enol form of cyclohexane-1,3,5-trione that is, phloroglucinol is stabilized by resonance that is, aromatic character.

The IIT-JEE Corner

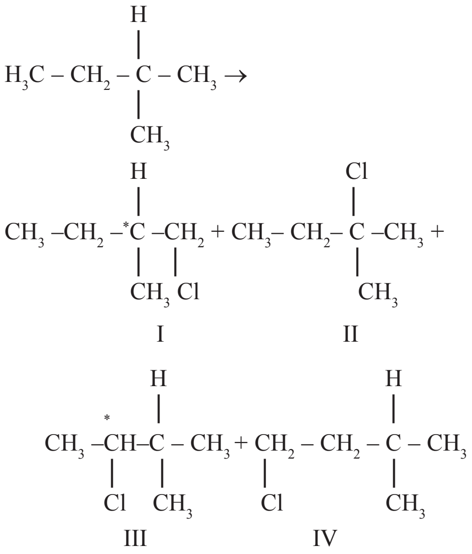
191.



$$CH-{}^{*}\overset{\overset{H}{|}}{\underset{\underset{OH}{|}}{C}}-{}^{*}\overset{\overset{H}{|}}{\underset{\underset{OH}{|}}{C}}-CH$$

has two similar chiral carbon atoms. Therefore, it has three stereoisomers d, l and meso form. Out of these, only two (d- and l-) are optically active.

192.



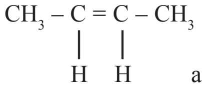
$$H_3C-CH_2-\overset{\overset{H}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3\rightarrow$$

$$\underset{\text{I}}{CH_3-CH_2-{}^{*}\overset{\overset{H}{|}}{\underset{\underset{CH_3}{|}}{C}}-\underset{\underset{Cl}{|}}{CH_2}}+\underset{\text{II}}{CH_3-CH_2-\overset{\overset{Cl}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3}+$$

$$\underset{\text{III}}{CH_3-\overset{*}{\underset{\underset{Cl}{|}}{CH}}-\overset{\overset{H}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3}+\underset{\text{IV}}{\underset{\underset{Cl}{|}}{CH_2}-CH_2-\overset{\overset{H}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3}$$

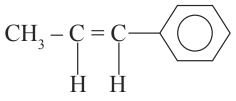
I and III exists as enantiomers.

193.



$$CH_3-\underset{\underset{H}{|}}{C}=\underset{\underset{H}{|}}{C}-CH_3$$

and



have two different groups attached to each carbon atom of the double bond.

194. (a) shows tautomerism because aldehydes are more stable than vinyl alcohols.

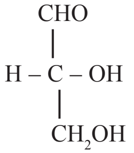
$C_6H_5-CH=CH-OH \leftrightarrow$
$C_6H_5-CH_2-CH=O$

(b) does not show tautomerism due to absence of α–hydrogen.

(c) shows tautomerism because enol form is stabilized by aromatic nature.

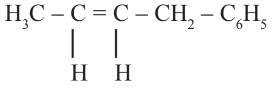
(d) shows tautomerism because enol form is stabilized by hydrogen bonding.

195. (+) sign is used for positive optical rotation. Symbol D is derived from D (+)-glyceraldehyde that is, orientation of the OH group at the second carbon of tartaric acid is the same as in D (+) – glyceraldehydes that is, towards right.



$$\begin{array}{c}CHO\\|\\H-C-OH\\|\\CH_2OH\end{array}$$

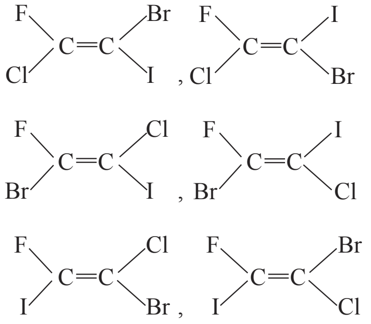
196.



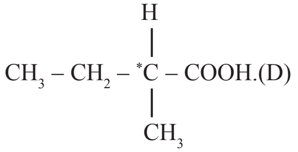
$$H_3C-\underset{\underset{H}{|}}{C}=\underset{\underset{H}{|}}{C}-CH_2-C_6H_5$$

In this, both the carbons of the double bonds carry different substituents and hence it show geometrical isomerism.

197. Six isomers are



198.

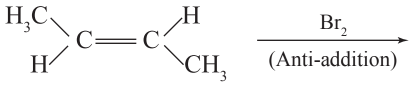


$$CH_3-CH_2-{}^{*}\overset{\overset{H}{|}}{\underset{\underset{CH_3}{|}}{C}}-COOH.(D)$$

exhibits stereoisomerism (optical isomerism) because it contains one asymmetric carbon and is nonsuperimposable on its mirror image.

199. Linear symmetrical structures have zero dipole moment.

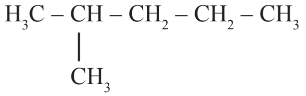
202.



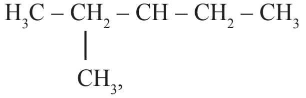
Meso Product

203. C_6H_{14} has 5 structural isomers.

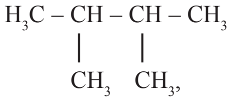
$H_3C - CH_2 - CH_2 - CH_2 - CH_2 - CH_3$,



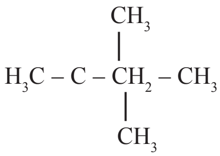
$H_3C - \underset{|}{CH}(CH_3) - CH_2 - CH_2 - CH_3$



$H_3C - CH_2 - CH(CH_3) - CH_2 - CH_3$,

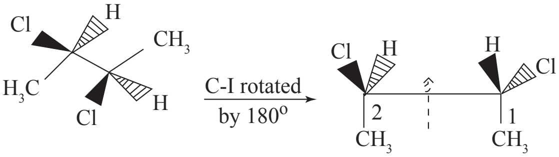


$H_3C - CH(CH_3) - CH(CH_3) - CH_3$,



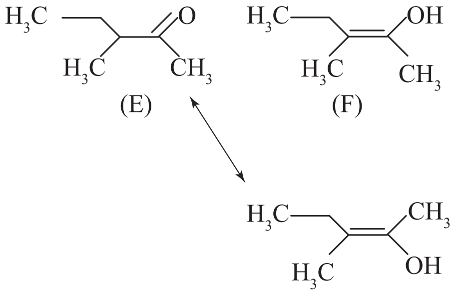
$H_3C - C(CH_3)_2 - CH_2 - CH_3$

204. The compound is optically active as it possesses two chiral centres.



The compound possesses axis of symmetry perpendicular to the C-C bond.

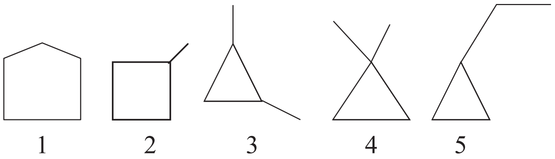
205.



E – F and E- G are tautomers to each other.

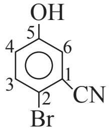
F and g are geometrical isomers as their methyl group can be cis and trans position to each other. Also all geometrical isomers are diastereomers to each other.

207. Cyclic C_5H_{10}



For the 3D structure, 2 cis -trans and 1 optical isomer are possible. Total 7 isomers.

208.

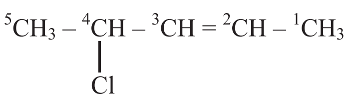


2-Bromo 5-hydroxy benzonitrile

SUBJECTIVE SOLVED EXAMPLES

1. Write the structural formula of 4-chloro-2-pentene.

Solution

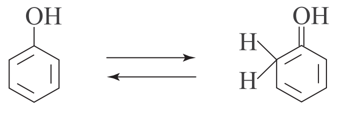


$^5CH_3 - {}^4\underset{\displaystyle Cl}{\underset{|}{CH}} - {}^3CH = {}^2CH - {}^1CH_3$

2. Write tautomeric forms for phenol.

[IIT 1992]

Solution



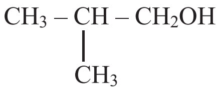
3. Write structural formulae for all the isomeric alcohols having the molecular formula $C_4H_{10}O$.

Solution

$C_4H_{10}O$ represents 4-isomeric alcohols:

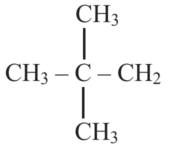
$CH_3CH_2CH_2CH_2OH$ Butanol-1

$CH_3CH_2CHOHCH_3$ Butanol-2



$CH_3 - \underset{\displaystyle CH_3}{\underset{|}{CH}} - CH_2OH$

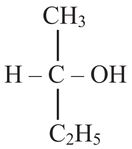
2-methyl-propanol-1



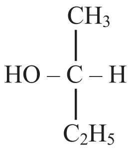
$CH_3 - \overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}} - CH_2$

2-methyl-propanol-2

Here butanol-2 shows optical isomerism, as it has one asymmetric carbon atom and it exists into these two optically active forms:



d-form

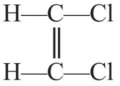


l-form

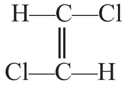
4. Write the structure of all the possible isomers of dichloroethene. Which of them will have zero dipole moment

Solution

Dichloro ethene exists in two geometrical isomers as follows:

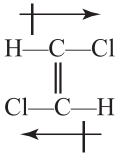


(cis-form)

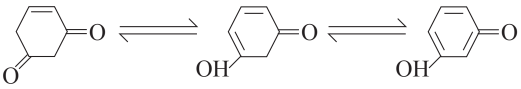


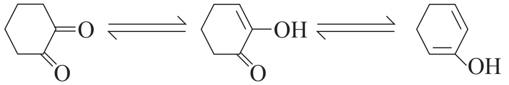
(trans -form)

trans -isomer has zero dipole moment



(dipole moment = 0)





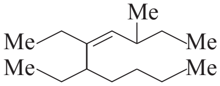
5. (i) Write the IUPAC name of:

$CH_3CH_2CH = CHCOOH$

Solution

Pent-2-en-1-oic acid or 2-Pentenoic acid

(ii) Give the IUPAC name of the following compound:



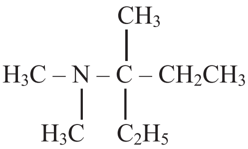
Here Me = Methyl

[IIT 1990]

Solution

5,6-diethyl-3-methyl dec-4-ene.

(iii) Write the IUPAC name for the following:



[IIT 1991]

Solution

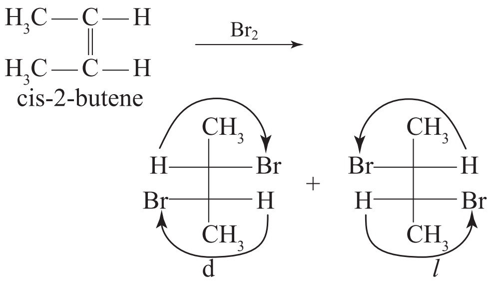
3-(N,N-dimethyl amino)-3-methyl pentane.

6. Write down the structures of the stereoisomers formed when cis-2-butene is reacted with bromine.

[IIT 1995]

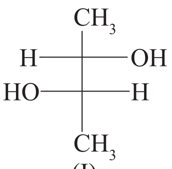
Solution

As in case of cis-Alkenes addition of bromine is anti-addition so here racemic mixture will be formed as follows:.

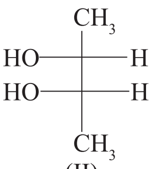


2,3-dibromobutane
(Racemic mixture)

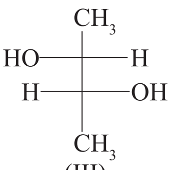
7. Identify the pairs of enantiomers and diastereomers from the following compounds I, II and III



(I)



(II)



(III)

[IIT 2000]

Solution

Here I and III are enantiomers while I and II as well as II and III are diastereomers.

8. (i) $\mu_{obs} = \sum_i \mu_i x_i$

Here μ_i is the dipole moment of a stable conformer of the molecule, $Z - CH_2 - CH_2 - Z$ and x_i is the mole fraction of the stable conformer.

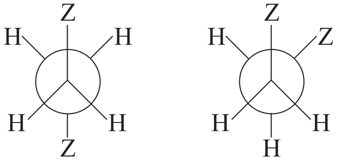
Given: $\mu_{obs} = 1.0$ D and x (anti) = 0.82
Draw all the stable conformers of $Z - CH_2 - CH_2 - Z$ and calculate the value of μ (gauche).

(ii) Draw the stable conformer of $Y - CHD - CHD - Y$ (meso form), when Y = CH_3 (rotation about $C_2 - C_3$) and Y = OH (rotation about $C_1 - C_2$) in Newmann projection.

[IIT 2005]

Solution

(i) Mole fraction of anti form = 0.82



$\mu_{obs} = 1$

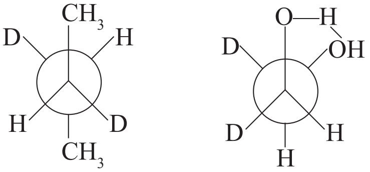
$1 = \mu_{(anti)} \times 0.82 + \mu_{(gauche)} \times 0.18$

As $\mu_{(anti)} = 0$

So $1 = \mu_{(gauche)} \times 0.18$

$$\mu_{(gauche)} = = \frac{1}{0.18} = 5.55 \text{ D}$$

(ii)

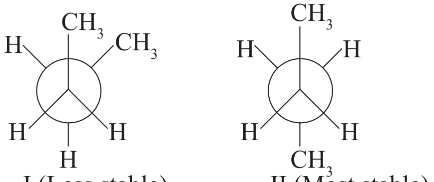


9. Draw Newmann projection of relatively less stable staggered form of n-butane. The reason of low stability of this form is Van der Waal's repulsion, torsional strain, or both.

[IIT 2004]

Solution

Newmann projection formulae II is the most stable as the bulky groups (CH_3) are at maximum possible distance from each other. Structure I is relatively less stable as the two CH_3 groups are close to each other leading to Van der Waal's repulsion between the two methyl groups.



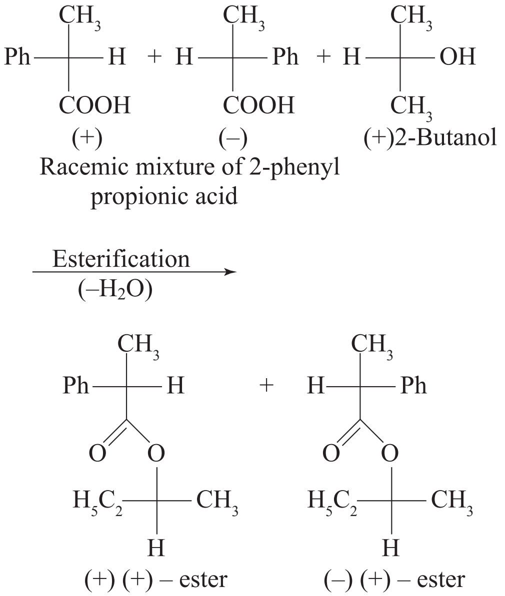
I (Less stable) II (Most stable)

Staggered conformations of n-butane

10. A racemic mixture of (±)2-phenylpropanoic acid on esterification with (±)2-butanol gives two esters. Mention the stereochemistry of the two esters produced.

[IIT 2003]

Solution



The bonds attached to the chiral asymmetric carbon atom in both molecules are not broken during the esterification reaction.

With racemic mixture (+) acid reacts with (+) alcohol to give (+) (+) ester while (–) acid reacts with (+) alcohol to give (+) (–) ester. So in the esterification reaction neither bonds are breaked nor optical activity of the molecules are changed both esters are diastereo isomers i.e., both are neither enantiomers nor superimpose to each other.

GENERAL ORGANIC CHEMISTRY-2

(CONCEPTS OF ORGANIC CHEMISTRY)

CHAPTER 2

CHAPTER CONTENTS

Hybridization of carbon; Sigma and pi- bonds; Shapes of simple organic molecules; Hydrogen bonds; definition and their effects on physical properties of alcohols and carboxylic acids; Inductive and resonance effects on acidity and basicity of organic acids and bases; Polarity and inductive effects in alkyl halides; Reactive intermediates produced during homolytic and heterolytic bond cleavage. Formation, structure and stability of carbocations, carboanion and free radicals and various levels of multiple-choice questions.

HYBRIDIZATION

Pauling and Slater introduced it to explain the shape of molecules which can be explained by VBT. It is the intermixing or re-distribution of energy among two or more half filled or full filled or incomplete or empty orbitals of comparable energy to form same number of hybrids. Hybrids have identical energies and similar shapes.

FACTS ABOUT HYBRIDIZATION

- Number of atomic orbitals taking part in hyrbridization is equal to number of hybrids formed.
- Electrons do not undergo hybridization.
- A hybrid bond is always a sigma bond.
- A hybrid bond is always stronger than a non-hybrid bond.
- Hybridization occurs at the time of bond formation.
- Hybridization α overlapping (for enough over lapping orbitals must be fairly apart that is, neither very close nor very far).
- Hybridization is for increasing stability and decreasing reactivity and energy.
- Hybridization is of central atom in a molecule (NH_3, H_2O, CH_4).
- Hybridization is not meant for isolated atoms but for bonded atoms.

TYPES OF HYBRIDIZATION

(1) sp hybridization

Here one s and one p orbital form two sp hybrids after intermixing. Shape of molecule is linear and bond angle is 180°.

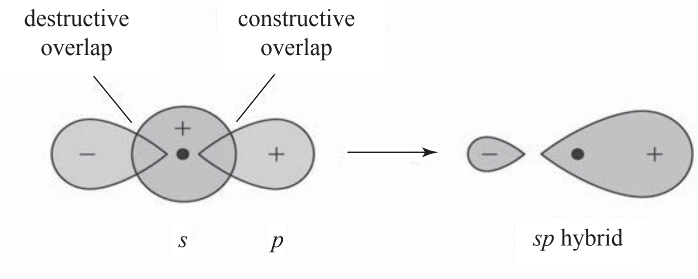
Example, X – M – X
sp
(M = Be, Zn, Hg)
H – C ≡ C – H
sp sp

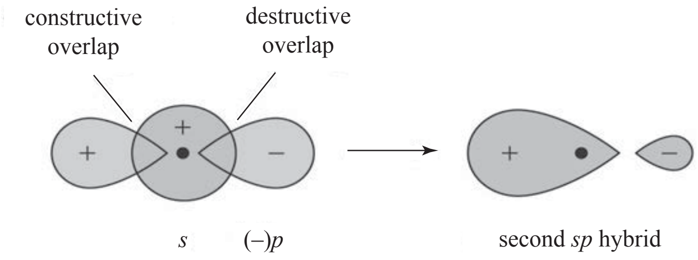
Some other examples are CO_2, CS_2 $BeCl_2$,$ZnCl_2$ etc.

Characteristic of sp-Hybrid Orbitals →

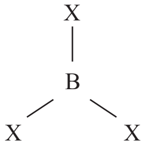
(i) Shape of sp-hybrid orbital is oval.
(ii) Its relative power of overlapping is 1.93 with respect to s orbital.
(iii) Both sp-hybrid orbitals are completely equivalent and symmetrical.
(iv) These two sp-hybrid orbitals are collinear, i.e., angle between the hybrid orbitals is 180°.]
(v) Energy of sp-hybrid orbital is more than s-orbital but less than the p-orbital.

In sp-hybrid orbital, one lobe is bigger while other lobe is small. The bigger lobe is very large with respect to p-orbital, hence it has higher degree of overlapping. So it forms stronger bond. For example, in the formation of acetylene. In acetylene, hybridization of carbon is sp. One 2s orbital blends with only one 2p orbital to form two sp-hybrid orbitals. In this case, two unhybridized orbitals remain, each with ne electron.



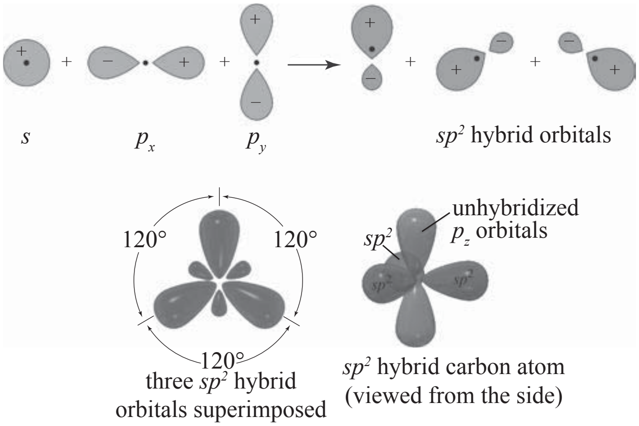


(2) **sp^2 hybridization** Here one s and two p orbital intermix to form three new sp^2 –hybrids. Shape of the species is trigonal or co-planar and bond angle is 120°

Example, 

, CH_3^+

,CH_3^+



Characteristics

(i) These hybrid orbitals are planar with bond angle 120°.

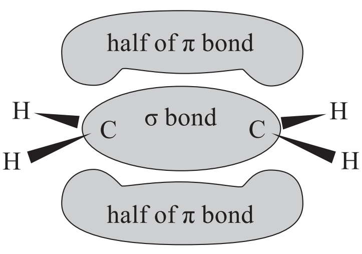
(ii) These sp^2-hybrid orbitals are completely equivalent and symmetrical.

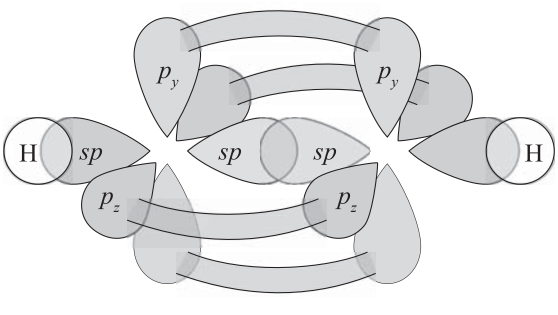
(iii) These are stronger than s and p orbitals. Its relative power of overlapping is 1.99 with respect to s-orbital.

(iv) As in this hybridization contribution of p-orbitals is more hence it is less oval than sp-hybrid orbitals. In this case, one lobe is bigger and one lobe is smaller and its forms stronger bond.

When carbon is bonded to another atom by a double bond, the carbon atom is in the sp^2-hybrid state. Example is ethylene. In order to form sp^2 bonding orbitals, carbon hybridizes its 2s orbital with only two of its orbitals. one p-orbital remains unhybridised on the carbon atom. In ethylene two sp^2 carbons are joined by a sigma bond formed due to the overlap of one sp^2 orbital from each carbon atom.

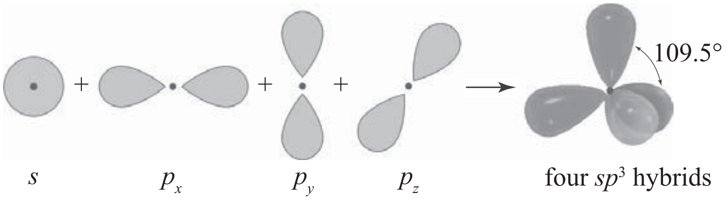
Both carbon atoms also have unhybridized p-orbitals, which can be oriented parallel to each other and thereby overlap. Both lobes of the p-orbitals merge above and below the sigma bond forming a π MO. Thus double bond is composed of a σ bond and a π bond. The ethylene molecules are completed when σ bonds are formed between the overlapping sp^2 orbitals of carbon and the s-orbitals of the hydrogens.





(3) sp^3 hybridization Here one s and three p orbitals intermix to give four new sp^3 hybrids. Shape of the species is tetrahedral and bond angle is 109° 28’.

Example, C_2H_6, CX_4, SiX_4, NH_4^+, BX_4^-, NH_3, PH_3, H_2O, H_2S,



Characteristics

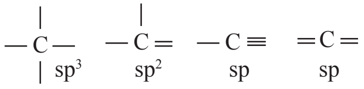
(i) These orbitals are directed towards the four corners of a regular tetrahedron and the angle between each pair of them is 109°28’ or 109.5°.

(ii) All the four sp^3 hybrid orbitals are completely equivalent and symmetrical.

(iii) As in sp^3 hybridization the contribution of p-orbitals is 75 per cent, its shape is almost same as that of the parent p-orbitals except that the bigger lobe in sp^3-orbital is somewhat more spread and shorter in length than the pure p-orbitals.

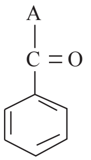
Their relative power of overlapping is 2.00 with respect to s-orbital. This shows that sp^3-orbitals are stronger than sp^2 which is stronger than sp-orbitals.

To find Hybridization in organic compound:



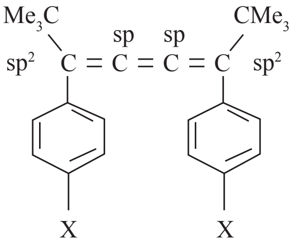
$$\underset{sp^3}{-\overset{|}{\underset{|}{C}}-} \qquad \underset{sp^2}{-\overset{|}{C}=} \qquad \underset{sp}{-C\equiv} \qquad \underset{sp}{=C=}$$

In it, all carbon atoms are sp^2 hybridized.

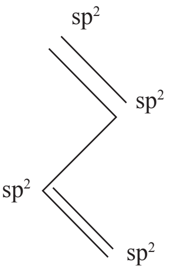


Example,

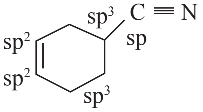
(1)



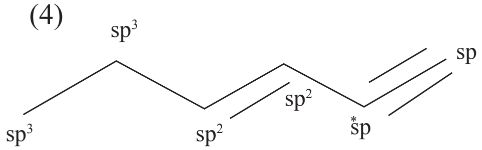
(2)



(3)

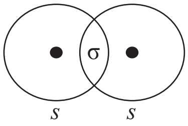


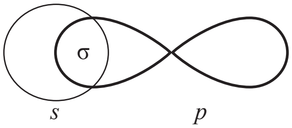
(4)

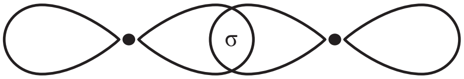


SIGMA AND PI BONDS

Sigma (Σ) Bond

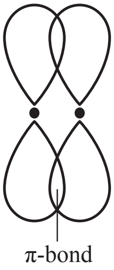






- It is formed by axial or head to head or linear overlapping between two s-s or s-p or p-p orbitals.
- Sigma bond is stronger but less reactive due to more effective and stronger over lapping than the pi bond.
- The minimum and maximum number of sigma bond is between two bonded atoms is one.
- Stability α number of sigma bonds.
- Reactivity α 1/σ
- In sigma bond free rotation is possible.
- Sigma bond determines the shape of molecule.

Pie (π) Bond



- It is formed by lateral or sidewise overlapping between two p orbitals.
- It is a weak or less stable bond but more reactive due to less effective overlapping.
- Minimum and maximum number of pi bonds between two bonded atoms is 0 and 2 respectively.
- Stability α 1/number of pi bonds.
- Reactivity α number of pi-bonds.

- In case of a pi bond free rotation is not possible.
- It does not decide shape of molecule but shortens bond length.

Strength of σ- and π-Bonds

The strength of a bond depends upon the extent of overlapping of half filled atomic orbitals. The extent of overlapping between two atoms is always greater when there is end-to-end overlapping of orbitals. There fore a σ-bond is always stronger than π-bond.

To find sigma and pi bonds in a molecule

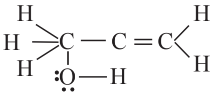
(–) = 1 σ

(=) = 1σ, 1π

(≡) = 1σ, 2π

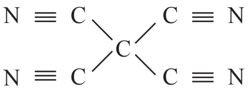
Example, Enolic form of acetone

(1)



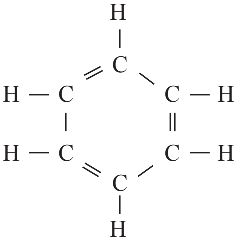
It has 9σ, 1π and 2 lone pair of electrons.

(2) $C_2(CN)_4$ (Tetracyanoethylene):



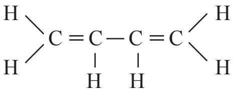
It has 9σ, 9π and 4 lone pair of electrons.

(3)



Benzene has 12σ and 3π bonds.

(4) Buta-1,3-diene:

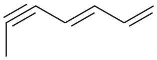


It has 9σ and 2π bonds.

(5) CaC_2 or $Ca^{2+}[C \equiv C]^{2-}$

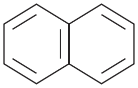
It has 1σ, 2π-bonds.

(6)



Hept 1, 3, dr-en 5-yne

It has 15σ, 4π-bonds.



(7) Napthalene

It has 19s, 5p-bonds.

HYDROGEN BONDING

It was introduced by Latimer and Rodebush. It is a weak interaction shown by dotted (---) lines between hydrogen and highly electronegative and small size atoms like F, O and N when hydrogen atom is covalently bonded to any of these. It's nature is dipole, ion or dipole induced dipole interaction.

- H-bond strength order is

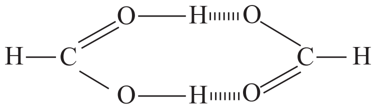
  $HF > H_2O > NH_3$

  10 7 2 Kcal per mole.

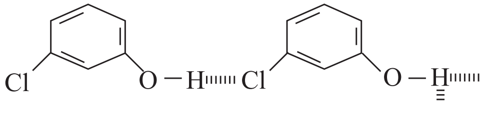
TYPE OF HYDROGEN BONDING It is of the following two types:

Intermolecular H-Bonding

It is formed between two or more different molecules of the same or different types.
Example, HF, H_2O, NH_3, R – OH, R – COOH, R-NH_2, R_2NH (secondary amine) and carbohydrates like glucose, fructose etc.



Hydrogen bonding in formic acid (dimerisation)



Hydrogen bonding in m-chlorophenol

Effects Due to intermolecular hydrogen bonding B.P. M.P, solubility , thermal stability, viscosity and surface tension increase and liquid nature is observed as molecules get associated more closely.

- Alcohols are highly soluble in water in any proportion and have higher boiling points than ethers which are very less soluble in water.

- Glycerol is highly viscous with higher boiling point due to more extent of H-bonding.

  Glycerol > Glycol > Ethanol

  $\longrightarrow$

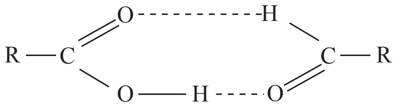
  Viscosity and b.p. decreases as extent of H-bonding decreases

- Ethers are also slightly soluble in water due to hydrogen bonding with water molecules
- Acids have higher boiling point, solubility in water etc. than corresponding acid derivatives.

  Example, $CH_3COOH > CH_3COCl >$ ..... .

- Acids can dimerise due to intermolecular hydrogen bonding.

  Example, acetic acid dimerises in benzene.

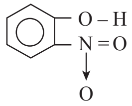


- Acids have more value of boiling point than alcohols also due to more extant of hydrogen bonding.
- Carbohydrates like Glucose, Sucrose etc. are also soluble in water due to hydrogen bonding.
- In DNA and RNA bases and In nucleic acid the proteins are held together by intermolecular H-bonding.

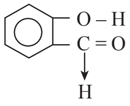
Intramolecular H-Bonding or Chelation

This type of hydrogen bond is formed within a molecule and here a six membered cyclic ring is formed so it is called chelation also.

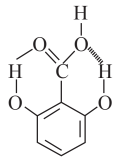
Example,

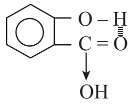


o-nitrophenol



o-hydroxybenzaldehyde



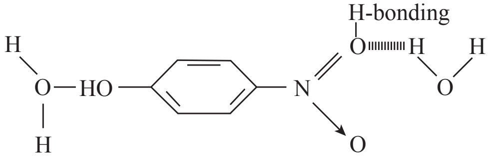


o-Hydroxybenzoic acid

Some other examples are Pyridine 2-carbonaldoxime, o-hydroxybenzioc acid etc.

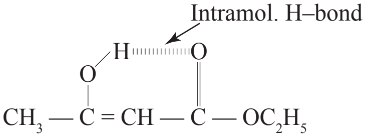
Effects

- Due to it boiling point, acidic nature, solubility etc. decrease but volatile nature increases.
- o'-nitro phenol has less boiling point and acidic nature but more volatile nature than p-nitrophenol (which has intermolecular H-bonding). These are separated by steam distillation method.
- o-Hydroxy benzaldehyde has intramolecular hydrogen bonding so it is less solid while para hydroxyl benzaldehyde is more solid due to intermolecular hydrogen bonding.
- p- nitrophenol is quite soluble in water due to hydrogen bonding on the other hand ortho nitro phenol is less soluble in water.

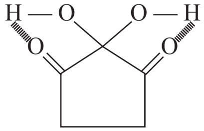


Hydrogen bonding between p- nitrophenol and water

- It also increases enol content and stability of hydrates.



'Enol form'



BOND FISSION

It is the breaking of covalent bonds present in organic molecules.It occurs in two ways as follows:

HOMOLYTIC FISSION OR HOMOLYSIS Here the bond fission occurs symmetrically and free radicals are formed.It is possible in presence of light, peroxide or temperature more than 500°C Here less energy is needed for bond fission

$$A\text{o} \underset{\text{Homolysis}}{\text{———}} \text{x}A \rightarrow A^{o} + {}^{x}A$$

- Example,

  $Clo - xCl \rightarrow Cl^{o} + {}^{x}Cl$

  $CH_3o - xCH_3 \rightarrow CH_3^{o} + {}^{x}CH_3$

- Photochlorination of methane involves homolytic fission. When in ethane homolysis occurs CH_3^{o} free radicals are formed in which C-atom is sp^2 hybridized.

HETEROLYTIC FISSION OR HETEROLYSIS Here the bond fission occurs un-symetrically and ions are formed however here more energy is needed for fission.

Example,

$$\mathrm{CH_3} \overset{x}{\underset{o}{\text{———}}} \mathrm{X} \longrightarrow \underset{\text{carbocation}}{\overset{+}{\mathrm{CH_3}} + \mathrm{X}^{-}\,{}^{x}_{o}}$$

$$\mathrm{CH_3} \overset{x}{\underset{o}{\text{———}}} \mathrm{H} \longrightarrow \underset{\text{carbanion}}{\mathrm{CH_3^{-}}\,{}^{x}_{o}} + \mathrm{H}^{+}$$

- The cleavage of bond becomes easier if electro negativity difference between the atoms is more
- Example, In case of C_2H_5OH the easiest cleavage is of – O – H bond and order or ease of cleavage is – O – H > C – O > C – H > C – C.

ELECTROPHILE OR ELECTROPHILLIC SPECIES

- These are electron deficient species which take electrons that is, act as lewis acids.
- These are of following types:

Positively Charged H^+, X^+, R^+, N^+O_2, N^+O, S^+O_3H

Exception M^+ (IA), M^{2+} (IIA), Al^{+3}, $\overset{+}{S}R_2$ NH_4^+, NR_4^+ (as all have octet state)

Neutral Electrophiles It is of following types

(a) Incomplete Octate State Here the central atom is electron deficient that is, does not have octet state.

Example, BeX_2, $ZnCl_2$, BH_3, BX_3, AlX_3, FeX_2,

$\dot{\mathrm{C}}\mathrm{H_3}$,$\ddot{\mathrm{C}}\mathrm{H_2}$

(b) Extended Octate State Due to presence of vacant d-orbital the central atom can extend its octet state.
Example, $SnCl_4$, PCl_5, IF_7

(c) Central Metal Atom with Two or More Electronegative Atoms Example, CO_2, SO_2, CS_2,

Classification of Electrophiles

Electrophiles have been classified in three categories:

(a) Hard electrophiles: These are small in size and the valence e cannot be easily excited,
Example, $H^{\oplus}$, Li^+, $K^{\oplus}$, Na^+ , Mg^{2+}, Cr^{3+}, Ca^{2+}, Al^{3+}, Me_3Al, $AlCl_3$, AlH_3, BF_3, CO_2, SO_3.

(b) Soft electrophiles: These are large in size and the valence e can be easily excited,
Example, I_2, Fe^{2+}, Fe^{3+}, Ag^+, Hg^{2+}, Cu^{3+}, Pd^{2+}, Pt^{2+}, BH_3, $GaCl_3$, $:CH_2$, Br_2

(c) Border line acids: Fe^{2+}, Co^{2+}, Cu^{2+}, Sn^{2+}, Sb^{3+}, Zn^{2+}, Bi^{3+}, BMe_3, SO_2, $R_3\overset{\oplus}{C}$, $N\overset{\oplus}{O}$ and $C_6\overset{\oplus}{H}_5$

NUCLEOPHILE OR NUCLEOPHILIC REAGENTS

These are electron efficient species with lone pair of electrons to donate i.e., act as lewis base.
It is of two types:

1 Negatively Charged H^-, OH^-, $R–O^-$, $\bar{C}^-H_3$, X^-, SH^-, $R – S^-$.

2 Neutral The central atom with lone pair of electron to donate: Example,
$\rightarrow\!\ddot{\mathrm{N}}$, (NH_3, RH_2 etc.)

$-\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}}-$ (H_2O, HOR, R – O – R) $-\overset{\bullet\bullet}{\underset{\bullet\bullet}{S}}-$ (R – SH, R – S – R, H_2S)

Ambident Nucleophile

Such nucleophiles have two nucleophillic centers one of which is negatively charged and one is neutral.

For example, $\bar{C}\equiv\overset{\bullet\bullet}{N}$, $\bar{O}-\overset{\bullet\bullet}{N}=O$,

Classification of Nucleophiles

(a) Hard nucleophile: In them the electronegativity of donor atom is high however oxidation is difficult,

Example, H_2O, NH_3, RNH_2, OH^-, SO_4^{2-}, R_2O, F^-, RO^-, $CH_3CO\overset{\ominus}{O}$,

(b) Soft nucleophile: In them the electronegativity of donor atom is low however oxidation is easy,

For example, CO, C_2H_4, R_2S, RSH, CN^-, I^-,

(c) Broder line Basis: Example, $C_6H_5NH_2$, C_5H_5N, NO_2^-, Br^-.

REMEMBER

■ A species can behave both like Electrophile and Nucleophile. If Carbon atom has multiple bonds with (O, N, S)

Example, R – CHO, R – C ≡ N, RCOR, RCOOH, RCOCl

■ H_2, CH_4, NH_4^+, NR_4^+ can not act like electrophile and nucleophile.

REACTION INTERMEDIATES

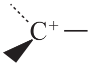
Those species which are formed during reactions but can not be isolated as they destroy at once during the completion of the reaction. The reaction intermediates are highly reactive but very unstable and short lived.

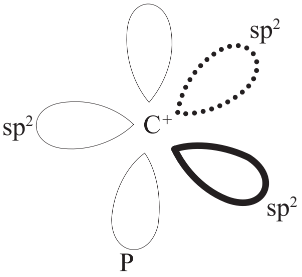
Types of Reaction Intermediates

(1) Charged Reaction Intermediates

(A) Carbocation or Carbonium Ion

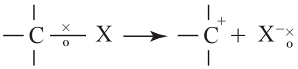
Carbo stands for 'Carbon' and Onium stands for positive charge. It has at least one carbon atom with positive charge and 6 electrons. It is sp^2 hybridized with trigonal coplanar shape. It is diamagnetic in nature. It acts as an electrophile and give rise to the formation of Racemic Mixture.





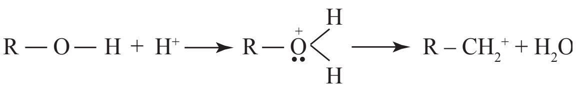
Preparation of Carbocation:

1 **By Heterolytic Fission**:



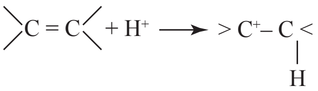
$$-\overset{|}{\underset{|}{C}}\overset{\times}{\underset{\circ}{-}}X \longrightarrow -\overset{|\,+}{\underset{|}{C}} + X^{-\overset{\times}{\circ}}$$

2 **By Protonation of Alcohols**:



$$R-O-H + H^+ \longrightarrow R-\overset{+}{\underset{\bullet\bullet}{O}}\langle^{H}_{H} \longrightarrow R-CH_2^+ + H_2O$$

3 **By Protonation of Alkene**:



$$>C=C< + H^+ \longrightarrow >C^+-\underset{H}{\underset{|}{C}}<$$

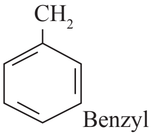
Types of Carbocation

(a) *Non- Classical Carbocation:* Here positive charged is delocalized.

Example,

$CH_2 = CH\ 2\,\overset{1}{C}H_2$

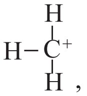
Allyl carbocation



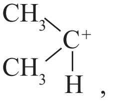
Benzyl

(b) *Classical Carbocation:* Here positive charge is localized.

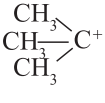
Example,



$H-\overset{H}{\underset{H}{C^+}}$,



,

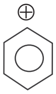


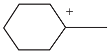
Order of Stability of Carbocation

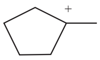
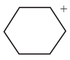
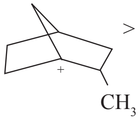
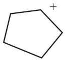
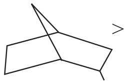
- The stability of carbocation is decided by resonance, hyperconjugation, +I effect or electron releasing groups.

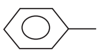
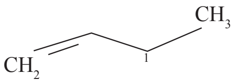
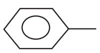
Stability α Resonance, Hyperconjugation, +I.effect, Number of alkyl groups.
Some Stability Orders and Their Reasons

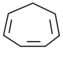
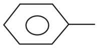
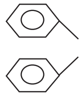
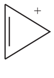
$(Ph)_3C^+ > (Ph)_2C^+H > \underset{t^o}{R_3C^+} > PhC^+H_2 > CH_3-CH=C^+H_2 > \underset{s}{R_2C^+H} > \underset{p}{RC^+H_2}$

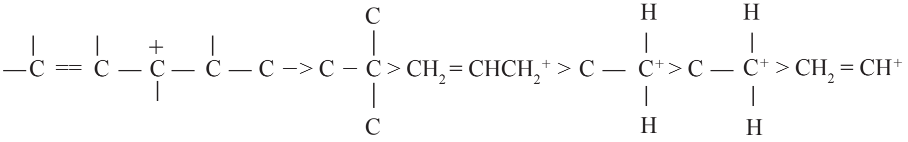
$> C^+H_3 > CH_2 = C^+H >$ 

(I) $(CH_3CH_2)_3C^+ > (CH_3CH_2)_2{+}CCH_3 >$  $> CH_3CH_2C^+(CH_3)_2 > (CH_3)_3C^+ >$

(II)  >  >  > $CH_3CHCH_2CH_3$ >  >  >

(III)  $C^+(CH_3)_2 > (CH_3)_2\overset{+}{C}H$  =  $CH-CH_3 > CH_3CH_2\overset{+}{C}H_2 >$

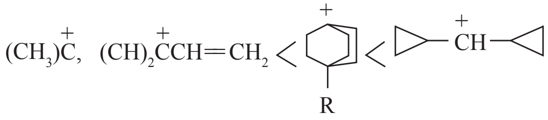
(IV)  >  $\overset{+}{C}H_2$ >  $\overset{+}{C}-CH_3 > CH_3\overset{+}{C}H_2 >$  $> CH_3^+$

(v) 

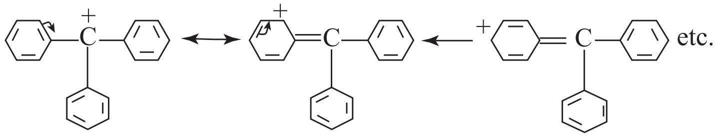
$$-\overset{|}{C}=\overset{|}{C}-\overset{+}{\underset{|}{C}}-\overset{|}{C}-C\ {-}{>}\ C-\overset{C}{\underset{C}{C}}>CH_2=CHCH_2^+>C-\overset{H}{\underset{H}{C^+}}>C-\overset{H}{\underset{H}{C^+}}>CH_2=CH^+$$

Substituted allylic > 3° > Ally1 > 2° > 1° > Vinyl

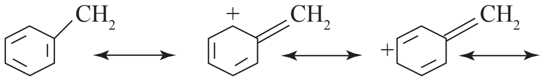
(vi)



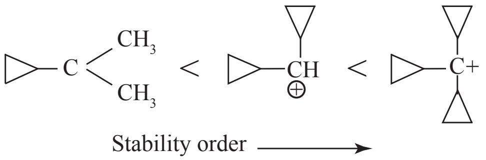
- Greater stability of the triphenylmethyl cations is attributed to effective resonance. The central positively charged carbon is attached with three phenyl rings,



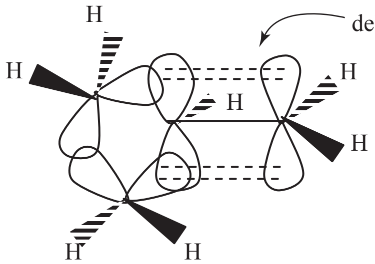
(triphenylmethyl cation)



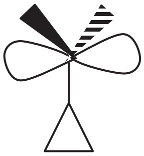
(benzyl cation; resonance stabilized)



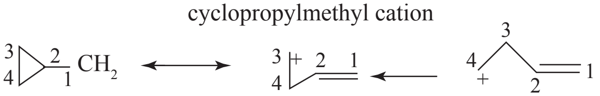
- Cyclopropylmethyl cations get stability as a result of conjugation between the bent orbitals of the cyclopropyl ring and the vacant p orbital of the cationic carbon the vacant p orbital lies parallel to the C_2 - C_3 bond of the ring.



(cyclopropylmethyl cation)



cyclopropylmethyl cation

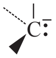


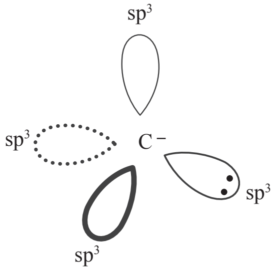
Reactions of Carbocation: Carbocations are reaction intermediates in following reactions.

- SN^1 (Nucleophillic substitution unimolecular)
- E^1 reaction (uni molecular elimination)
- Electrophillic addition
- Molecular rearrangements like pinacole-pinacolone etc

(B) Carbanion or Carbanium Ion

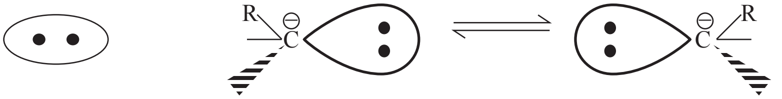
It is anion having a negatively charged carbon atom with 8 electrons.





- It is formed by heterolytic fission.
- $CH_3 \overset{x}{\underset{o}{—}} H \longrightarrow CH_3^{-}\overset{x}{o} + H^+$
- $CH_3 \overset{x}{\underset{o}{—}} H \longrightarrow C\overline{H}_3\overset{x}{o} + H^+$

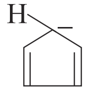
Features:

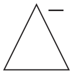


- It is sp^3 hybridized with pyramidal shape. It is diamagnetic in nature. It quickly undergoes pyramidal inversion that is Umbrella effect.

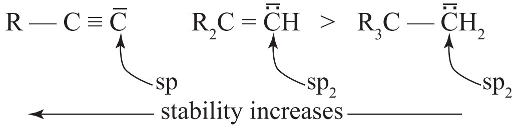
Stability of carbanion: It is stabilized by resonance, hyperconjugation and electron attracting groups (-I effect) however de-stabilized by electron releasing groups like alkyl groups.

Stability Order

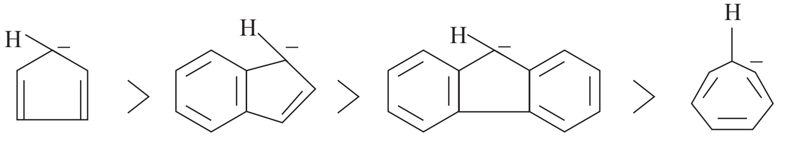
 $> Ph_3\overline{C} > HC \equiv \overline{C} > Ph - \overline{C}H_2 > Me_2Ph\overline{C}H_2 > Me_3Si\overline{C}H_2 > Cl - \overline{C}H_2 >$

$\overline{P}h > CH_2 = \overline{C}H >$  $> \overline{C}H_3 > CH_3 - \overline{C}H_2\text{:} > (CH_3)_2\overline{C}H\text{:} > (CH_3)_3\overline{C}\text{:}$

- Stability of carbanion α s per cent (s character)

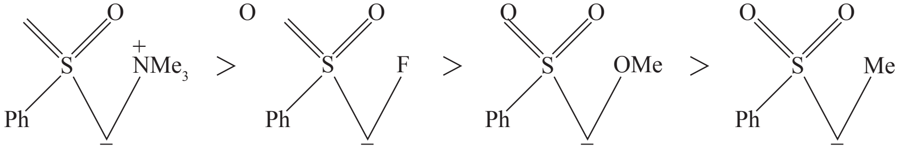


- With aromaticity is the factor for stability, few carbanions and their stability order is:

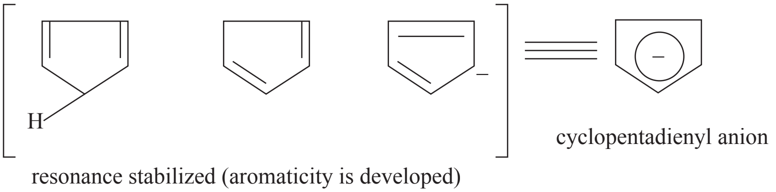


Aromatic Anti -aromatic

- Electrton withdrawing substituents can also inductivity stabilize negative charge no bearby carbons.

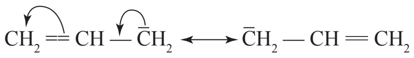


Stabilization of carbanions due to resonance:

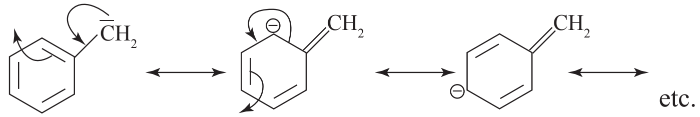


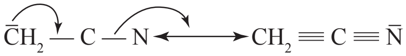
cyclopentadienyl anion

resonance stabilized (aromaticity is developed)



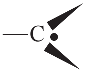
$\mathrm{CH_2 = CH - \bar{C}H_2 \longleftrightarrow \bar{C}H_2 - CH = CH_2}$

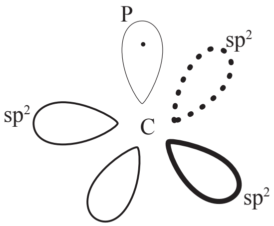




$\mathrm{\bar{C}H_2 - C \equiv N \longleftrightarrow CH_2 = C = \bar{N}}$

FREE RADICALS





- These are atoms or groups with a free or odd electron. which are neutral in nature, highly reactive and very short lived.

FORMATION

(1) Homolytic Fission Free radicals are the result of homolytic fission. The presence of sun-light or heat is needed to prepare them.

$\mathrm{A - A \longrightarrow A^o + {}^oA}$

Example,

$\mathrm{Cl - Cl \xrightarrow{sun\ light} Cl^o + {}^oCl}$

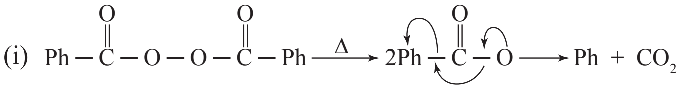
$\mathrm{C_2H_5 - C_2H_5 \xrightarrow{sun\ light} C_2H_5^o + {}^oC_2H_5}$

$\mathrm{C_2H_5 - Br^o \xrightarrow{sun\ light} C_2H_5^o + HBr}$

$\mathrm{CH_2 - CH_2 - CH_3 \xrightarrow{hv} CH_3 - {}^oCH - CH_3 + H^o}$

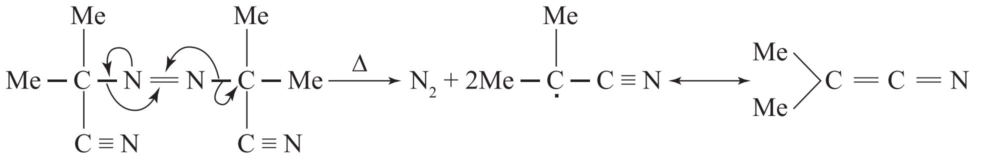
(2) Thermolysis Subjection of any organic molecule to a high enough temperature in the gas phase results in the formation of free radicals.

Example,



$\mathrm{(i)\ Ph - \overset{O}{\overset{\|}{C}} - O - O - \overset{O}{\overset{\|}{C}} - Ph \xrightarrow{\Delta} 2Ph - \overset{O}{\overset{\|}{C}} - O \longrightarrow Ph + CO_2}$

Due to the small bond energy of the O - O bond (30 kcal/mol). Peroxides generate free radicals when heated to 80° to 100°C.

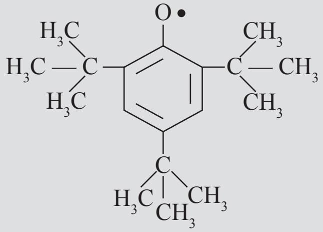
(ii) 

(AIBN)
(azobisisobutyronitrile)

Resonance : Stabilized free radicals

REMEMBER

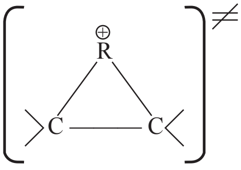
Generally, the free radicals can not be isolated from the reaction mixture, but 2,4,6 -tri -tert , butyl phenoxyl radical is most stable and has been isolated.



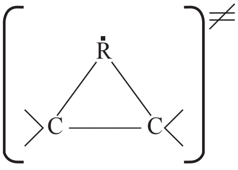
Features

- It has one unpaired electron so it is paramagnetic in nature.
- It may be sp^2 hybridized with flat or trigonal coplanar structure.
- Free radical shows disproportion reaction.

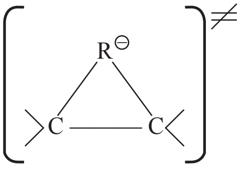
  $C_2H_5^o + C_2H_5 \rightarrow C_2H_4 + C_2H_6$
- Free radical does not have enantiomorphs due to continuous reversible exchange (that is, umbrella and it's reversal).
- The free radicals can act as electrophiles, which attack at the site of high electron density on the substrate. Free radicals have very less or no tendency to rearrange to give a more stable radical.



Carbocation T.S.

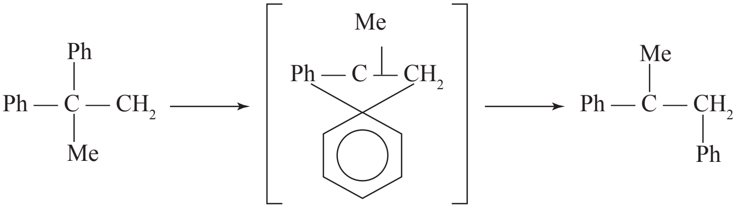


Radical T.S.



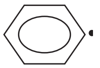
Carbanion T.S.

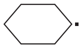
Here more than 2e in rearrangement go to antibonding orbital (like radical, carbanion) in T.S. which is unstable and need more energy. Therefore rearrangement in radical and carbanion do not occur frequently, but in some cases it can be observed. For example,

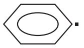


Here the Ph shift makes the radical more stable in the reaction.

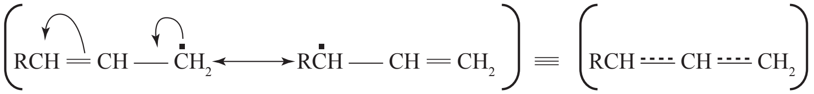
Stability of Free Radicals Stability α resonance, hyperconjugation, electron releasing groups

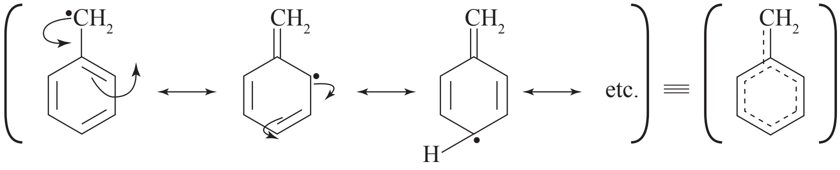
$(Ph)_3\overset{o}{C} > (Ph)_2\overset{o}{C}H > \overset{o}{P}hCH_2 >$ Allyl $> \overset{o}{t} > \overset{o}{s} > \overset{o}{p} >$ vinyl free radical > 

$N \equiv C - CH_2 > CH_2 = CH - \dot{C}H_2 > H - \overset{O}{\overset{\|}{C}}{}^{\bullet} > Ph - \dot{C}H_2 > CH_3 - \overset{O}{\overset{\|}{C}} - \dot{C}H_2 >$ 

$> (CH_3)_3\dot{C} > (CH_3)_2\dot{C}H > Cl_3\dot{C} > CH_3\dot{C}H_2 > \dot{C}H_3 > CH_2 = \dot{C}H > \dot{C}F_3 >$  $> CH \equiv \dot{C}$

Stabilization of free radical due to resonance:

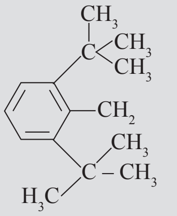


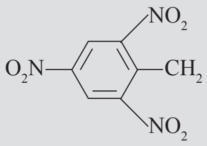


REMEMBER

Stability of free radicals is enhanced by the presence of at the radical center of both an electron - donating and an electron withdrawing group. This effect is known as push-pull or captodative effect. Captodative effect arises from increased resonance of sterichindrence.

Example,





are more stable than a simple benzyl free radical.

CARBENE

It is a special form of carbon in which carbon atom is bivalent with two free or odd electrons.

$-\ddot{C}-$ OR $-\dot{\underset{\bullet}{C}}-$

Example, (1) Methylene

$H - \ddot{C} - H$ OR $H - \dot{\underset{\bullet}{C}} - H$ OR $CH_2{:}$

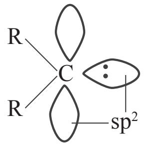
(2) Chloro Methylene

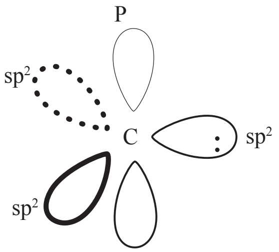
$Cl - \ddot{C} - Cl$ OR $Cl - \dot{\underset{\bullet}{C}} - Cl$ OR $CCl_2{:}$

TYPES OF CARBENE

Carbene is of two types:

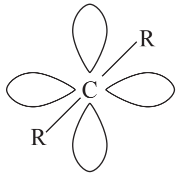
(a) Singlet Carbene

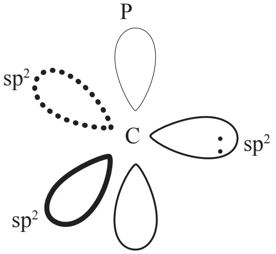




- It has two un-shared electrons with opposite spins present in one orbital.
- It is less stable but have more energy and reactivity.
- It is sp^2 hybridized with bent shape.
- It shows similarity to carbocation.

(b) Triplet Carbene





- It has two electrons with the same spin but in different orbitals making it a free di-radical.
- It is sp hybridized with linear shape.
- It is more stable and have less energy.
- It is just like free di radical.

FORMATION OF CARBENES Carbenes are prepared as follows:

(1) From diazo methane

$$\underset{\text{diazomethane}}{H_2C-\overset{+}{N}=\overset{-}{N}} \xrightarrow[-N_2]{hv} :CH_2$$

(2) From ketene

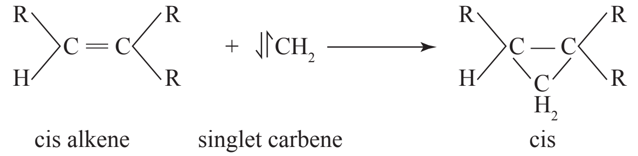
$$CH_2=C=O \xrightarrow{hv} :CH_2 + CO\uparrow$$

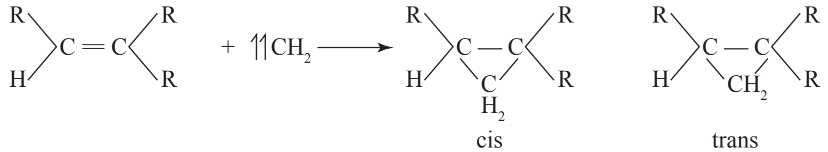
(3) From haloforms

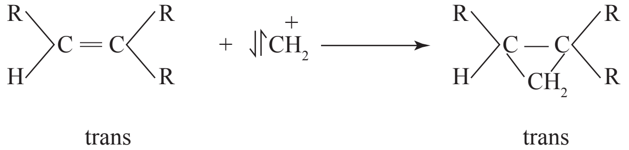
$$\begin{tikzcd}
CHX_3 \arrow[r, "\Delta alc.\ KOH"] & \overset{-}{C}X_3 + H^+ \arrow[d] \\
 & \underset{\text{Halo carbene}}{\ddot{C}X_2 + \overline{X}}
\end{tikzcd}$$

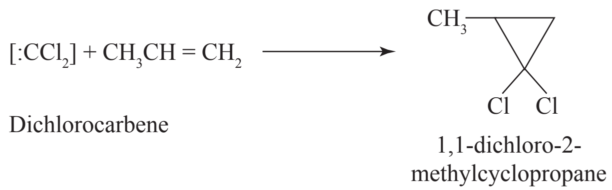
REACTIONS OF CARBENE Carbene show following reactions:

1 Addition with Alkene

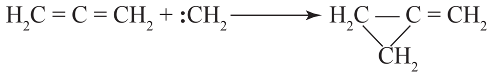








2 Addition of Carbene at 1,2 Position in Dienes



$$H_2C=C=CH_2 + :CH_2 \longrightarrow \underset{CH_2}{H_2C - C} = CH_2$$

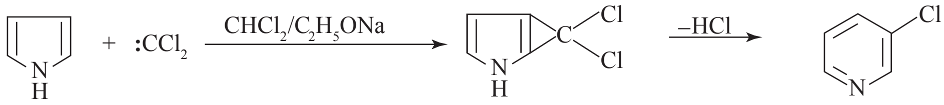
3 Insertion Reaction

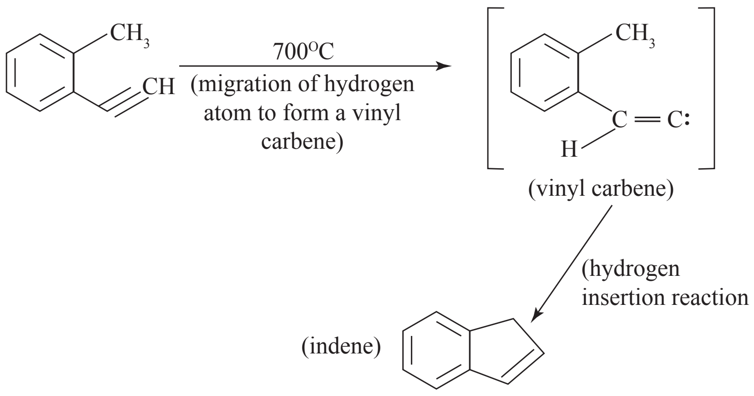
Here carbene inserts in the chain to increase chain length.

$$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-H + :CH_2 \longrightarrow -\overset{|}{\underset{|}{C}}-CH_2-\overset{|}{\underset{|}{C}}-$$

4 Ring Expansion Reaction

(addition of halogen carbene) Example,





CARBENE AS REACTION INTERMEDIATES Carbene is the reaction intermediate in following reactions.

Example, Carbyl Amine reaction, Reimer-Tiemann reaction, Witting reaction, Wolf rearrangement.

Stability of Carbenes:

$$\overset{\bullet\bullet}{C}H_2 > \overset{\bullet\bullet}{C}F_2 > \overset{\bullet\bullet}{C}Cl_2 > \overset{\bullet\bullet}{C}Br_2 > \overset{\bullet\bullet}{C}I_2$$

$$\xrightarrow{\text{Stability decreases}}$$

Nitrene:

- It is a neutral monovalent ~~species of~~ nitrogen which is just like carbene shown as given below:

  Alkyl or aryl nitrene, $R-\ddot{N}\colon$ or $Ar-\ddot{N}\colon$,

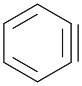
  Acyl nitrene, $R-CO-\ddot{N}\colon$, $Ar-CO-\ddot{N}\colon$

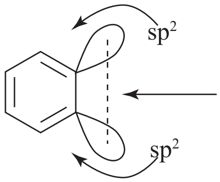
Preparation:

$$R-\underset{\bullet\bullet}{N}=\overset{+}{N}=\underset{\bullet\bullet}{\overset{-}{N}}\colon \xrightarrow{hv} R-\underset{\bullet\bullet}{N}\colon + N\equiv N$$

Alkyl or aryl nitrene

BENZYNE (1,2 DI DEHYDRO BENZENE)

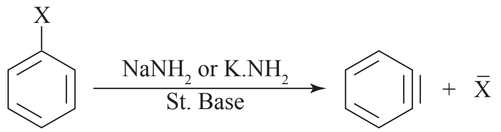


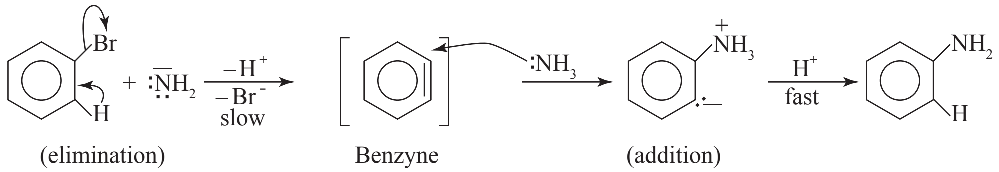


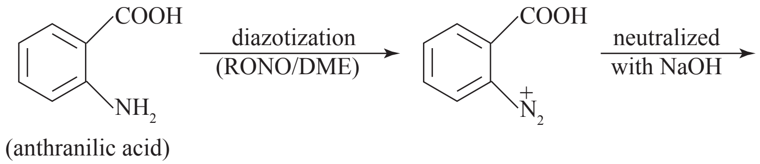
abnormal π-bond formed due to overlap between two sp^2 hybridized orbitals

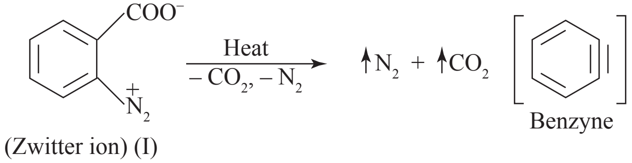
- Here the triple bond is partial due to poor overlapping of p orbitals as p orbitals are outside the plane of the ring in benzyne so these are not properly aligned for over lapping.

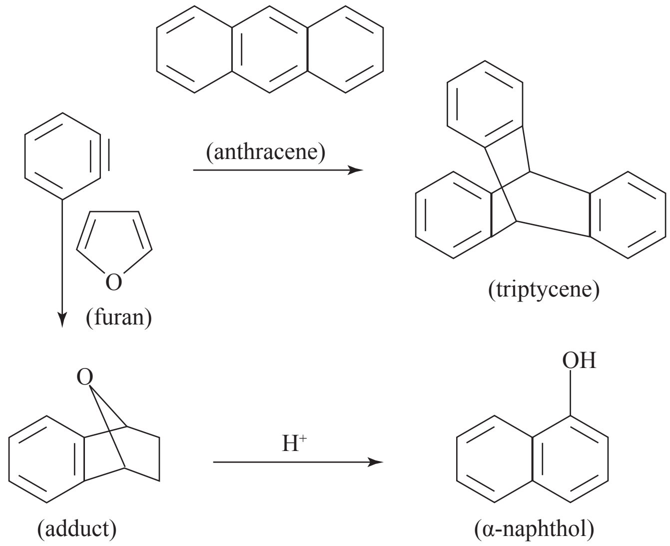
Formation











ELECTRON DISPLACEMENT EFFECTS

These are of the following types:

INDUCTIVE EFFECT

It is a permanent effect involving displacement of σ electrons towards more electronegative species. It is a weak effect. It can be transmitted through a chain of C-atoms. (negligible at C-atom 4.)

$$\mathrm{C - \overset{+\delta\delta\delta}{C} \rightarrow\!\!>\!\!>\!\!> \overset{+\delta\delta}{C} \rightarrow\!\!>\!\!> \overset{+\delta}{C} \rightarrow\!\!> \overset{-\delta}{X}}$$

↓

negligible here

Types of Inductive Effect It is of two types.

– I Effect It is shown by electron attracting or withdrawing species. Here sigma electrons are displaced away from the carbon atom towards this species.

$$\overset{+\delta}{\mathrm{C}} \longrightarrow\!\!> \overset{-\delta}{\mathrm{X}}$$

e⁻ attracting species

−I Effect Showing Groups in Decreasing Order

$: \overset{+}{N}R_3 > -NO_2 > -CN > -SO_3H > -COOH > F > -COOR > -CHO >$
$-COR > X\ (Cl, Br, I) > -NH_2 > -OH > -OR > Ph$ etc.

- It increases acidic nature, stability of carbanion but decreases basic nature, stability of carbocation.

+I Effect It is shown by electron releasing species. Here sigma electrons are displaced away from this species and towards carbon atom.

$$\overset{-\delta}{\mathrm{C}} \longleftarrow\!\!< \overset{+\delta}{\mathrm{Y}}$$

e⁻ releasing group

+I Effect Showing Groups in Decreasing Order

$O^- > COO^-$ > tertiary alkyl gp. > secondary alkyl gp. > primary alkyl gp. > hydrogen

- It increases basic nature and stability of carbocation but decreases acidic nature and stability of carbanion.
- Inductive effect is responsible for high melting point, boiling point and dipole moment also as it causes polarity in the compound.

Application of Inductive Effect

(1) Stability of Carbocation

Stability α +I effect

Stability α 1/ –I effect

Order of stability t > s > p carbocations

Example 1

$(CH_3)_3C^+ > (CH_3)_2\ CH^+ > CH_3CH_2^+ > CH_3^+$

Example 2

$CH_3CH_2^+ > CH_2^+ - CH_2 - C_6H_5 > CH_2Cl - CH_2^+ > CH_2NO_2CH_2^+$

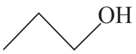
Example 3

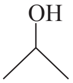
$CH_3CH^+OCH_3 > CH_3C^+HCH_3 > CH_3CH^+COCH_3 >$

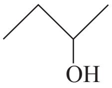
Properties Related to Stability of C^+:

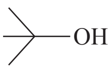
- Reactivity of –OH group in alcohol α stability of carbocation.

Example,

(I) 

(II) 

(III) 

(IV) 

IV > III > II > I

- Dehydration of alcohol α Stability of carbocation. that is, t > s > p
- Reactivity of 'X'(halogen) in R – X α Stability of carbocation. that is, t > s > p

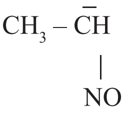
(2) Stability of Carbanion

Stability α $\frac{1}{+I\ \text{effect}}$.

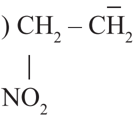
Stability α –I effect

Example, $\overline{C}H_3 > CH_3 - \overline{C}H_2 > (CH_3)_2 - \overline{C}H > (CH_3)_3\overline{C}$

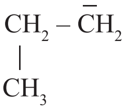
- Here +I effect increases reactivity so decreases stability of carbanion.

Example, (1) 

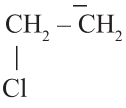
$CH_3 - \overline{C}H(NO_2)$

(2) 

$CH_2(NO_2) - \overline{C}H_2$

(3) 

$CH_2(CH_3) - \overline{C}H_2$

(4) 

$CH_2(Cl) - \overline{C}H_2$

1 > 2 > 4 > 3

- **Some More Orders**

Acidic nature of R – OH
or
Ester formation of R – OH α Stability of alkoxide ion or α $\frac{1}{+I\ \text{effect}}$.
or
Reactivity of H^- atom in R – OH

Example,

$CH_3 - OH > CH_3 - CH_2 - OH > (Me)_2CHOH > (Me)_3C - OH$

Basic Nature of Aliphatic Amines

Basic nature of amines α +I effect

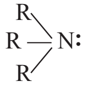
Basic nature of amines α $\frac{1}{-I\ \text{effect}}$.

If R is Methyl

Basic nature of amines decreases as

$2^o > 1^o > 3^o > NH_3 > C_6H_5 - NH_2 > \ldots$

- The reason of less stability of t-Amines is the steric hinderance caused by 3 bulky alkyl groups to donate electron by nitrogen atom and moreover poor salvation effect also decreases basic nature in it.



If 'R' is other than Methyl group

$2^o > 3^o > 1^o > NH_3 \ldots\ldots$

Example,

$(Pr)_2NH > (Pr)_3N > Pr.NH_2 > NH_3$

- Electron donating groups like (—R, —OR, —OH) increase basic nature.
- Electron attracting groups like (—NO, —CN, —I) decrease basic nature.

Example, $CH_3 - CH_2 - NH_2 > NH_3 > Cl - NH_2$

- Basic nature α Stability of conjugate acid formed

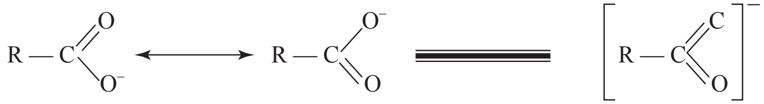
Acidic Nature of Carboxylic Acids Carboxylic acids is acidic in nature as it can release H^+ due to following reasons.

(a) Carboxylic acid and carboxylate ion undergo resonance .

(b) Due to resonance oxygen atom in carboxylic acids acquires partial positive charge which facilitates release of proton.

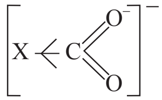
(c) Carboxylic ion is more stable than carboxylic acid, because in carboxylic acid charge separation takes place, whereas negative charge is dispersed over two oxygen atoms in carboxylate ion. Greater the dispersal of negative charge more is the stability.

Therefore, carboxylic acid easily loses a proto to form carboxylate ion, which explains the acidic nature of carboxylic acids.



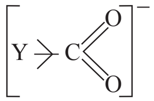
Resonance stabilized (Hybrid)

- **Effect of −I (Electron Withdrawing Groups on Acidic Nature):**



X (electron attracting groups) disperses more negative charge to increase its stability and acidic nature.

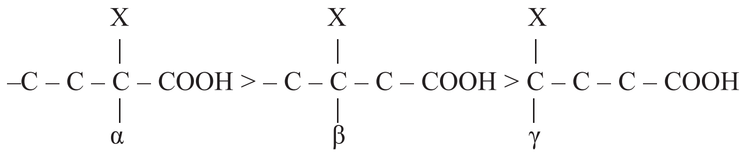
- **Effect of +I (Electron Releasing Groups on Acidic Nature)**:



Y (electron releasing groups) disperses less negative charge to decrease its stability and acidic nature.

Example,

- $X - CH_2 - COOH > CH_3COOH > CH_3 - CH_2 - COOH > CH_3 - CH_2 - CH_2 - COOH$
- $CH_2FCOOH > CH_2ClCOOH > CH_2BrCOOH > CH_2ICOOH$
- $CF_3COOH > CCl_3COOH > CBr_3COOH$
- $CCl_3COOH > CHCl_2COOH > CH_2ClCOOH$
- **In case of α, β, γ Substituted Acids**:



$$-C - C - \underset{\alpha}{\overset{X}{C}} - COOH > - C - \underset{\beta}{\overset{X}{C}} - C - COOH > \underset{\gamma}{\overset{X}{C}} - C - C - COOH$$

- At high temperature, $CH_3COOH > CCl_3COOH$

  It is due to thermodynamic reason as

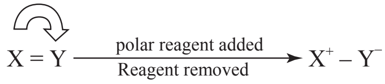
  Δ G is 1.5 kJ for CH_3COOH

  Δ G is 27 kJ for CCl_3COOH

- $HCOOH > C_6H_5COOH > C_6H_5 - CH_2 - COOH > CH_3COOH$
- $COOH - COOH > COOH - CH_2 - COOH > HCOOH > CH_3COOH > C_2H_5COOH$
- Acidic nature α s per cent (s character)

  $\underset{sp}{CH \equiv C - COOH} > \underset{sp_2}{CH_2 = CH - COOH} > \underset{sp_3}{CH_3\ CH_2COOH}$

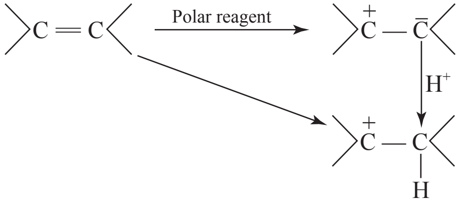
Electromeric Effect



$$X = Y \xrightarrow[\text{Reagent removed}]{\text{polar reagent added}} X^+ - Y^-$$

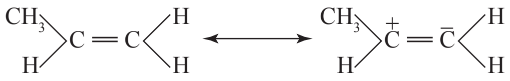
- It is a temporary but more powerful effect than inductive effect.
- It involves the transfer of π e^- by the demand of attacking reagent towards more electronegative species.
- It is shown by (↷).
- It always fascilates the reaction and does not inhibit it.
- It is shown by compounds having $> C = C <$, $>C = O$, $-C \equiv N$.
- It is shown by E (+E or –E)

+E Effect: Here the transfer of π electrons occur towards the attacking reagent.



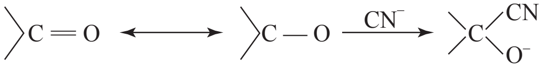
- If both the groups are same it can be from any side.
- If both the groups are different it is favoured by +I effect favouring direction.

Example,

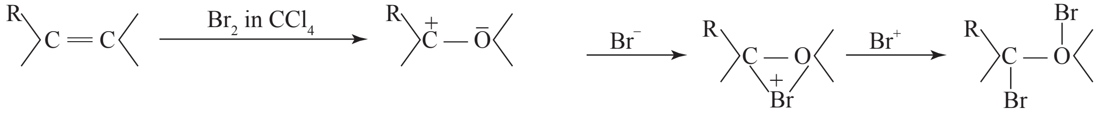


It is possible as (+I) favour it.

- **–E Effect**: Here the transfer to π electrons take place away from the attacking reagent.



Example,



cyclic bromonium ion

- As Br^+ is large in size and have lone pair of electrons so cyclic brominium ion is possible.
- Electromeric effect is helpful to explain the mechanism of electrophillic and nuelcophillic addition reactions.

Resonance

- When all the properties of a molecule can not be explained by a single structure than such a molecule is shown by many structures that is, canonical structures or contributing or resonating structures.
- Resonance is the process in which a single compound is considered to be a hybrid of two or more canonical structures. It is the delocalization of π electrons.
- The canonical structures have difference in electron distribution only. The canonical structures are shown (↔) by this arrow. The canonical structures have same arrangement of atoms. The canonical structures should be planar or nearly planar. Total number of paired and unpaired electrons are also same in canonical structures. The position and arrangement of atoms are same in canonical structures.

Example,

(1)

$$CH_2 = CH - \overset{..}{\underset{..}{Cl}}\!: \longleftrightarrow \bar{C}H_2 - CH = \overset{+}{\underset{..}{Cl}}\!:$$

(2)

$$\begin{tikzcd}
CH_2 = CH - CH = CH_2 \arrow[d, leftrightarrow] \\
CH_2^{+} - CH = CH - CH_2^{-} \arrow[d, leftrightarrow] \\
CH_2^{-} - CH = CH - CH_2^{+}
\end{tikzcd}$$

Criteria of Resonance

- Change in Bond length: Resonance changes bond length for example, in benzene. C – C = 1.39 Å that is, intermediate value between [C – C = 1.54 Å, C = C = 1.34 Å]
- **Resonance Energy**

  Resonance Energy = Energy of most stable Canonical structure – Resonance hybrid energy. (or actual molecule)
- Resonance Energy α Number of Canonical structure

  Resonance Energy α Stability

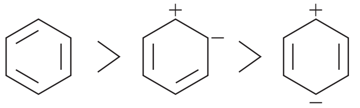
  Resonance Energy α $\frac{1}{\text{Reactivity}}$.

  Resonance Energy = Expected heat of hydrogenation – Actual heat of hydrogenation.
- Due to high resonance energy benzene is quite stable and gives electrophillic substitution reactions while does not give addition reaction although it has 3(=) bonds. (due to delocalisation of π electrons or resonance).
- Benzene has 36 K.cal/mole resonance energy.
- CO_2 has 154.9 kJ/mole resonance energy.
- Resonance differs from tautomerism as in tautomerism arrangement of atoms is different but in resonance arrangement of atoms is same.

Stability of Different Canonical Structure

(1) A non-polar structure is always more stable a polar structure.

Example,



charges are apart so less stable

- For polar structures apply these rules:
  - (I) Greater the number of covalent bonds, greater will be the stability.

    Example,

    $CH_3 - C \equiv \overset{+}{O} > CH_3 - \overset{+}{C} = O$

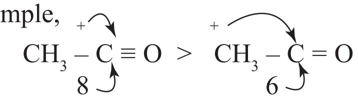
    More covalent bonds
  - (II) The canonical structure in which positive charge in on positive atom and negative charge on negative atom is more stable.

    Example,

    $R_2\overset{+}{C} - \overset{-}{O} > R_2\overset{-}{C} - \overset{+}{O}$
  - (III) The canonical structure in which each atom has octet state is more stable one.

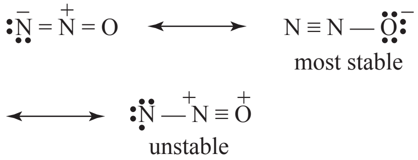
    Example,

    $CH_3 - \underset{8}{\overset{+}{C}} \equiv O > CH_3 - \underset{6}{\overset{+}{C}} = O$

(IV) If the same charges are closer, structure will be unstable.

For example,



Types of Resonance

Isovalent Resonance: When same number of bonds and same type of charges are present.

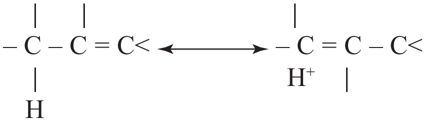
Example, SO_2, NO_2, CO_3^{-2}

Heterovalent Resonance: When different number of bonds and charges are present.

Example, Buta 1, 3 di ene, Vinyl cyanide.

Hyper Conjugation

- It was introduced by Baker and Nathan. It is also called No-Bond resonance or σ-π conjugation or Secondary resonance. "Alkyl groups with atleast one α-H-atom attached with an unsaturated C – atom will be able to released electrons like electromeric effect.



$$-\underset{\underset{H}{|}}{\overset{|}{C}}-\overset{|}{C}=C< \longleftrightarrow -\underset{H^+}{\overset{|}{C}}=C-\underset{|}{C}<$$

Hyperconjugation α Number of α-H-atoms

So,

$CH_3– > CH_3–CH_2 > (CH_3)_2CH– > (CH_3)_3C–$

3α-H -atoms 2α-H-atoms 1 α-H-atom no α-H-atom

- Hyperconjugation like +I effect releases electron however the magnitude is in opposite direction The magnitude of effect of hyperconjugation is smaller than resonance so it is also called Secondary resonance. Hyperconjugation increases the stability in alkenes by decreasing heat of hydrogenation.

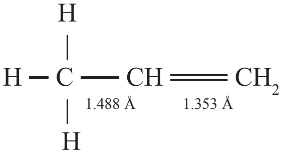
Example 1, Pent-2-ene is more stable than pent -1- ene

Example 2,

But -2 ene or Isobutene is more stable than Butene-1

- Hyperconjugation changes bond length like resonance.

Example,



- Stability of carbocation and free radical α Hyperconjugation α Number of α-H-atom

  Example, $(CH_3)_3\overset{+}{C}- > (CH_3)_2\overset{+}{C}H- > \overset{+}{C}H_3CH_2 > \overset{+}{C}H_3$

  $(CH_3)_3\overset{o}{C}- > (CH_3)_2\overset{o}{C}H- > CH_3\overset{o}{C}H_2 > \overset{o}{C}H_3$

Mesomeric Effect

- It is just like resonance but in conjugate system. It involves complete transfer of pi electrons or lone pair of electrons towards more electronegative species. It is of two types +M and –M.

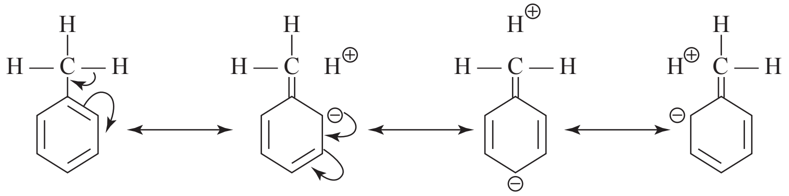
M Effect

- Here the electrons are transferred towards the conjugate system by electron releasing (+M) groups. Here in the +M group key-atom or central atom has lone pair of electrons to donate.

  Example,

  $-OH, -OR, -NH_2, -NHR, -NR_2, -O-, CO-R, X-$ (Cl, Br, I)

- When such groups are attached to benzene ring they increase the rate of electrophillic substitution that is, they are ring activating and ortho, para-directing groups as they increase electron density at ortho and para positions as shown below:



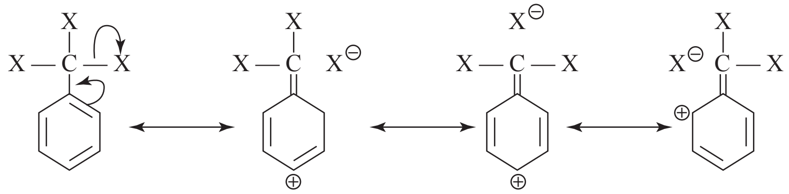
–M Effect

- Here the electrons are attracted from conjugate system by the electron withdrawing –M group. Here in the –M group key-atom or central atom is electron deficient and surrounded by more electronegative atoms with multiple bonds.

  Example,

  $-NO_2, -SO_3H, -CN, -CX_3, -COOR, -COOH, -CO-$ etc.

- When such groups are attached to benzene ring they decrease the rate of electrophillic substitution i.e., they are ring deactivating and meta-directing groups as they decrease electron density at ortho and para positions as shown below:



- Here at meta-position electron density is not affected so electrophilic substitution can take place here only.
- **Effects of Mesomeric Effect**: It explains stability of aryl carbocation, aryl carbanion, basic nature of aromatic amines, acidic nature of phenol and acidic nature of substituted benzoic acid.

SOME ORDERS

(1) **Stability of Substituted Benzyl Carbocations**: The stability of a substituted benzyl carbocation depends on the nature of the group present in the benzene ring. This group may be +I, –I , +R or –R.

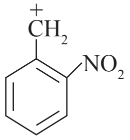
■ **Case-I: In case of –I and –R groups**

As –I group withdraws electrons, increases the magnitude of positive charge so decreases stability.

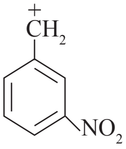
As –R group (when present at o- or p-position) withdraws electrons, increases magnitude of positive charge so decreases stability.

$$\xrightarrow[\text{Decreasing order of stability}]{\text{m-derivative > p-derivative > o-derivative}}$$

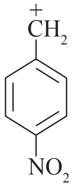
Example,



(1)



(2)



(3)

Reason

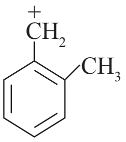
(1) (i) Increase in the magnitude of positive charge by –I and –R effect
(ii) –I and –R power is maximum.

(2) Increase in positive charge only by –I effect.

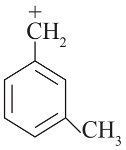
(3) (i) Increase in positive change by –I and –R effect.
(ii) –I and –R power is maximum.

■ **Case-II : In case of +I and +R groups**

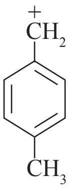
$$\xrightarrow[\text{Decreasing order of stability}]{\text{o-derivative > m-derivative > p-derivative}}$$



(1)



(2)



(3)

Reason

(1) Positive charge is decreased by +I and +R group or stabilized by +I and +R group and +I and +R power is maximum.

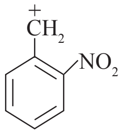
(2) Stabilized by +I group only.

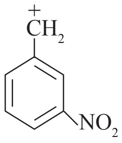
(3) Stabilized by +I and +R effect and +I and +R power is minimum.

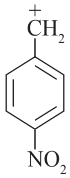
- **Case III: In case of +R and –I group**

p-derivative > o-derivative > m-derivative

$$\xrightarrow[\text{Decreasing order of stability}]{}$$


(1)


(2)


(3)

Reason

(1) Stabilized by +R effect, destabilized by –I effect, -I power is maximum (due to distance)

(2) Destabilized by –I effect

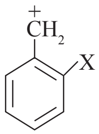
(3) Stabilized by +R effect, destabilized by –I effect, -I power is minimum (due to distance)

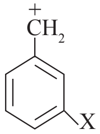
- **In case of halo derivatives–**It depends only on –I power of the group.

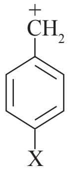
p-derivative > m-derivative > o-derivative

$$\xrightarrow[\text{Decreasing order of stability}]{}$$

Example,







$$\xrightarrow[\text{Stability in increasing order}]{}$$

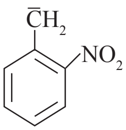
(2) **Stability of Substituted Benzyl Carbanions:** The stability of a substituted benzyl carbanion depends on the nature of the group present in the benzene ring. This group may be +I, –I , +R or –R.

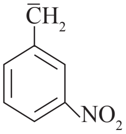
- **Case I: In case of –R and –I group**

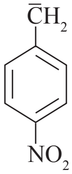
o-derivative > p-derivative > m-derivative

$$\xrightarrow[\text{Decreasing order of stability}]{}$$

For example,





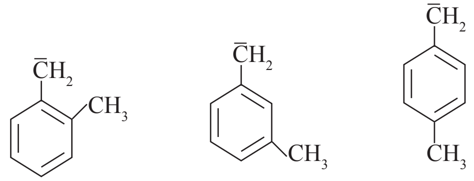


- **Case II: In case of +R and +I group**

m-derivative > p-derivative > o-derivative

$$\xrightarrow[\text{Decreasing order of stability}]{\hspace{12em}}$$

For example,



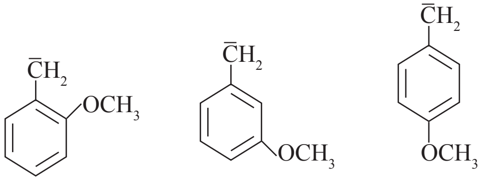
- **Case III: In case of +R and –I group**

m-derivative > o-derivative > p-derivative

$$\xrightarrow[\text{Decreasing order of stability}]{\hspace{12em}}$$

For example,

Decreasing order of stability

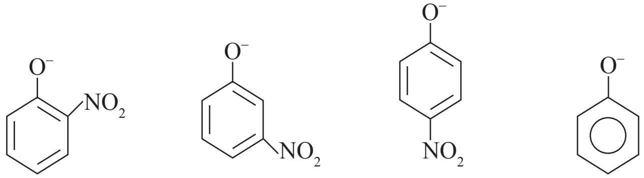


(3) Acidic Nature of Phenol: Phenol is weakly acidic in nature due to the formation of phenoxide ion which is resonance stabilized i.e., more is the stability of phenoxide ion more will be the acidity of phenol.

$C_6H_5OH \longrightarrow C_6H_5O^{\oplus} + H^{\ominus}$

Acidity of Substituted Phenols: It depends on the stability of the phenoxide ion as acidity is the function of the stability of acid anion.

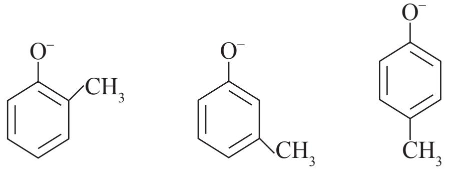
- **Case I: In case of –R and –I group**



p-derivative > o-derivative > m-derivative > phenol

$$\xrightarrow[\text{Acidity in decreasing order}]{\hspace{16em}}$$

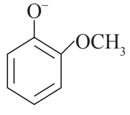
- **Case II: In case of +R and +I group**

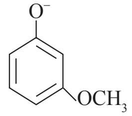


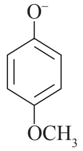
Phenol > m-derivative > p-derivative > o-derivative

$$\xrightarrow[\text{Acidity in decreasing order}]{\hspace{16em}}$$

- **Case III: In case of +R and –I group**







- **In case of halo group (except fluoro):** Acidity order is as follows based on –I effect only:
  o-derivative > m-derivative > p-derivative > phenol
  $\xrightarrow[\text{Acidity in decreasing order}]{\hspace{20em}}$

- **In case of fluoro group**. Acidity order is as follows:
  m-derivative > p-derivative > o-derivative > phenol
  $\xrightarrow[\text{Acidity in decreasing order}]{\hspace{20em}}$

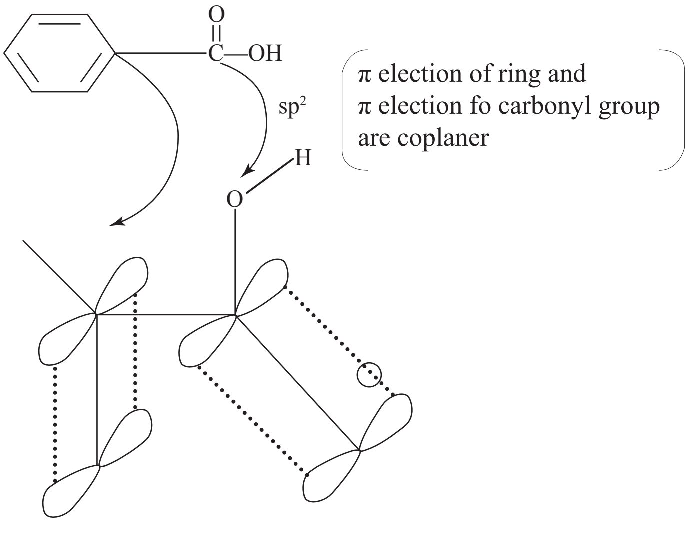
S. No.	*Compound name*	*pKa*
1	2,4,6 -Trinitrophenol	0.4
2	P- nitrophenol	7.2
3	O- nitrophenol	7.2
4	P-nitrophenol	8.4 or 10.1
5	O- Chlorophenol	8.6
6	m- methoxy phenol	9.1
7	P- Chlorophenol	9.4
8	m- Methoxy phenol	9.6
9	O- methoxy phenol	10
10	P -methoxy phenol	10.2

(4) Acidity of monosubstituted Benzoic acid derivatives: It is increased by electron withdrawing groups which stabilize $C_6H_5COO^-$ ion while electron releasing group decrease acidity by decreasing the stability of $C_6H_5COO^-$.

ORTHO EFFECT

Irrespective of the polar type, nearly all the O- substituted benzoic acid are stronger than benzoic acid. The effect that operates from ortho position of benzoic acid and increases acidic strength is called as ortho effect. Benzoic acid is a resonance hybrid, so the carbonyl group is coplanar with the ring. An O- substituent tends to prevent this coplanarity. As a result, resonance is diminished, so the O atom of the OH group has a greater positive charge, resulting in increased acid strength.

Ortho effect can be understand by the structure of benzoic acid as follows:



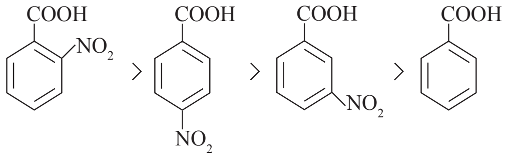
π election of ring and
π election fo carbonyl group
are coplaner

By this structure one can say that here both the carbon are sp^2 hybridized and coplanar with each other having perpendicular II- orbital from the plane,. Now such structure shows that benzene exerts both + R and -I effect and combined effect of both + R, -I is what we call is +I effect. Now if any group attached at O- position tends to prevent this coplanarity like shown in figure will block + R effect, and benzene now exert only -I effect. It means acidic strength increases.

- **Case I: In case of –R and –I group**

$$\xrightarrow[\text{Acidity in decreasing order}]{\text{o-derivative > p-derivative > m-derivative > benzoic acid}}$$

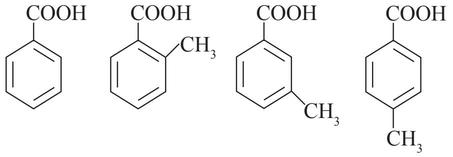
Example,



- **Case II: In case of +R and +I group**

$$\xrightarrow[\text{Acidity in decreasing order}]{\text{Benzoic acid > o-derivative > m-derivative > p-derivative}}$$

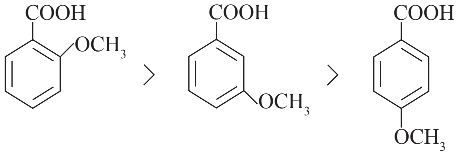
Example,



- **Case III: In case of +R and –I group**

$$\xrightarrow[\text{Acidity in decreasing order}]{\text{o-derivative > m-derivative > p-derivative > benzoic acid}}$$

Example,



- **In case of halo group:** Acidity order is as follows based on –I effect only:

$$\xrightarrow[\text{Acidity in decreasing order}]{\text{o-derivative > m-derivative > p-derivative > benzoic acid}}$$

Value of pKa for carboxylic acid

S. No.	*Structure*	*pKa*
1	$F_3C-COOH$	0.23
2	$Cl_3C-COOH$	0.64
3	O_2N-CH_2COOH	1.68

(Continued)

S. No.	*Structure*	*pKa*
4	$O-NO_2C_6H_5COOH$	2.17
5	FCH_2COOH	2.59
6	$BrCH_2COOH$	2.90
7	$O-FC_6H_5COOH$	3.27
8	$HC\equiv CCH_2COOH$	3.32
9	$P-NO_2C_6H_5COOH$	3.43
10	m- $NO_2C_6H_5COOH$	3.49
11	HCCOH	3.75
12	$HOCH_2COOH$	3.83
13	$m-FC_6H_5COOH$	3.87
14	$O-Me-C_6H_5COOH$	3.91
15	$P-FC_6H_5COOH$	4.14
16	C_6H_5COOH	4.19
17	$m-Me-C_6H_5COOH$	4.27
18	$P-Me-C_6H_5COOH$	4.37
19	$ClCH_2CH_2CH_2COOH$	4.52
20	CH_3COOH	4.74
21	$CH_3(CH_2)_2COOH$	4.82
22	CH_3-CH_2COOH	4.87

BASICITY OF NITROGEN CONTAINING COMPOUNDS

It is determined by the relative availability of the non bonding electrons on the nitrogen atom to a proton donor or Lewis acid and by the stabilization of the positively charged nitrogen atom by solvation or, in some special cases by resonance.

- **Basicity of Aliphatic Amines**: It is measured by the position of equilibrium in reaction with water. The further the reaction goes to the right, the greater is the basic strength.

$$>\ddot{N} + HOH \rightleftharpoons \underset{\text{Ammonium ion}}{>\overset{\oplus}{N}-H} + \overset{\ominus}{O}H$$

that is, Basicity α Stability of ammonium ion

Stability of amine cation depends on two factors:

(1) Magnitude of positive charge on nitrogen atom.

↓

Less is the magnitude of positive charge, more will be the stability.

↓

Basicity α +I power of group

$$\text{Basicity } \alpha \ \frac{1}{-\text{I power of group}}.$$

According to this, basicity order will be as follows:

Tertiary amine > secondary amine > primary amine > NH_3

(2) Degree of Solvation: It always increases stability of cation

Basicity α stability of cation

α degree of solvation

Degree of solvation of ammonia, 1^o-amine and 2^o-amine is almost the same but degree of solvation of 3^o-amine is very-very less, i.e., almost zero. According to this, 3^o-amine is least basic. In a solution, basicity order of aliphatic amines is as follows:

$$\xrightarrow[\text{Basicity of aliphatic amines in decreasing order}]{\text{Secondary amine > primary amine > tertiary amine > } NH_3}$$

REMEMBER

- In gas phase
  Tertiary amine > secondary amine > primary amine
- In aqueous medium
  $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$
- In aqueous medium
  $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$

- **Basicity of Aromatic Amines**: Basicity of aromatic amines depends or electron density on nitrogen, more is the electron density on nitrogen, more will be basicity.

  In aromatic amines, lone pair of electrons present on nitrogen is delocalized, hence electron density decreases due to resonance.

$$\text{Basicity } \alpha \ \frac{1}{\text{Number of resonating structures}}.$$

$C_6H_5NH_2 > (C_6H_5)_2NH > (C_6H_5)_3N$
4 7 10 Resonating structures No.

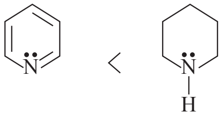
- **Basicity of Other Nitrogen Containing Compounds**: Basicity depends on the following factors

(1) Electronegativity of Nitrogen

$$\text{Basicity } \alpha \ \frac{1}{\text{Electronegativity of nitrogen.}}.$$

Example,

(1)

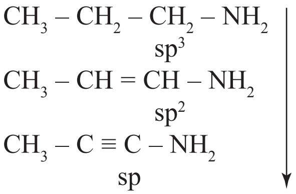


(2) $\underset{sp^3}{R-NH_2}$ $\underset{sp^2}{R-CH=NH}$ $\underset{sp}{R-C\equiv N}$

$$\xrightarrow[\hspace{6cm}]{}$$

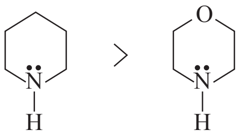
Electronegativity in increasing order

Basicity in decreasing order

(3) 

$$\left.\begin{array}{l} CH_3-\underset{sp^3}{CH_2}-CH_2-NH_2 \\ CH_3-CH=\underset{sp^2}{CH}-NH_2 \\ CH_3-C\equiv \underset{sp}{C}-NH_2 \end{array}\right\downarrow$$

Electronegativity of carbons attached to amino group is in increasing order hence basicity is in decreasing order.

(4) 

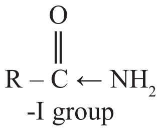
- **Inductive Effect**:

Basicity α +I power of the group on nitrogen

$$\text{Basicity } \alpha \ \frac{1}{\text{-I power of the group on nitrogen}}.$$

$\underset{\text{+I group}}{R-NH_2} \quad > \quad \underset{\text{–I group}}{NH_2-OH}$

Thus amines are more basic than hydroxyl amines.



$\underset{\text{-I group}}{R-\overset{\overset{\displaystyle O}{\|}}{C}\leftarrow NH_2} \quad < \quad \underset{\text{+I group}}{R-NH_2}$

- **Resonance**: Delocalization of lone pair of electrons present on nitrogen decreases basicity.

Lone pair delocalized — Lone pair is not delocalized

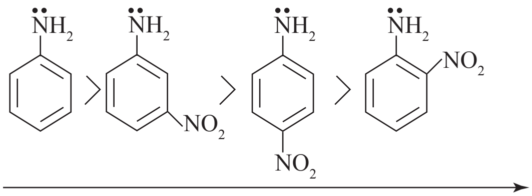
Basicity of Substituted Anilines: A para substituted aniline is more basic than ortho substituted aniline and this effect is called para effect.

- **Case I: In case of –R and –I group.**

aniline > m-derivative > p-derivative > o-derivative

$\xrightarrow[\text{Basicity in decreasing order}]{\hspace{12em}}$

Example,

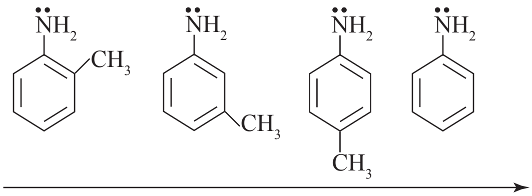


Basicity in decreasing order

- **Case II: In case of +R and +I group.**

$$\xrightarrow[\text{Basicity in decreasing order}]{\text{p-derivative > o-derivative > m-derivative > aniline}}$$

Example,

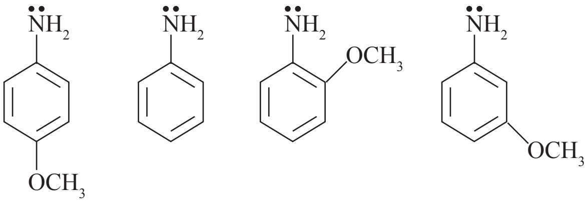


Basicity in decreasing order

- **Case III: In case of +R and –I group.**

$$\xrightarrow[\text{Basicity in decreasing order}]{\text{p-derivative >aniline > o-derivative > m-derivative}}$$

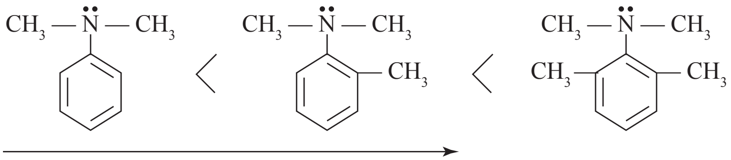
Example,



Basicity in decreasing order

Here Basicity of para isomer is more due to para effect also.

- **Stearic Effect on Basicity**: Bulky groups present at ortho position inhibits delocalization of lone pair of electrons present on nitrogen, hence increases basicity.



Basicity in increasing order

- Basicity of some nitrogen compounds in decreasing order:

$$\xrightarrow[\text{Basicity in decreasing order}]{\text{Guanidine > Aliphatic amines > }NH_3\text{ > Aromatic amines > Imine > Amide > Cyanide}}$$

REACTION MECHANISM

ORGANIC REACTION It involves the breaking and forming of covalent bonds.

Types of Organic Reactions

Organic reactions are of following types:

- Substitution
- Addition
- Elimination
- Rearrangement
- Pyrolysis and decomposition

(1) SUBSTITUTION OR DISPLACEMENT REACTION

Here one atom or group is substituted by another atom or group. For example,
$A - B + C \rightarrow A - C + B$
Here B is substituted by C.

Types of Substitution Reactions

(A) Free Radicle Substitution

- It is shown by the compounds having at least one H-atom on sp^3 hybridized carbon-atom that is, in saturated compounds. Here substitution is due to a free radical this means a weak free radical substituent is substituted by a stronger one. It takes place in presence of sun light or heat ($\geq 500^{o}C$).

$$R - H + X_2 \xrightarrow{\text{Sun Light}} R - X + HX$$

Mechanism

$X - X \longrightarrow X^{o} + {}^{o}X$ Initiation

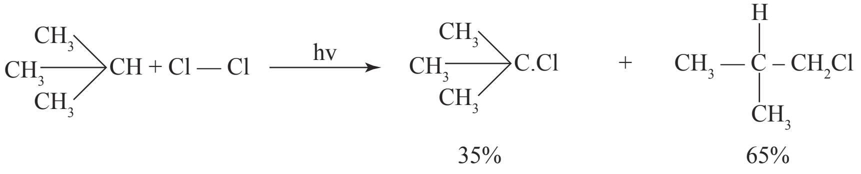
$R - H \xrightarrow{X^{o}} R^{o} + H^{o} - X$ Propogation

$R^{o} + X_2 \longrightarrow R - X + X^{o}$

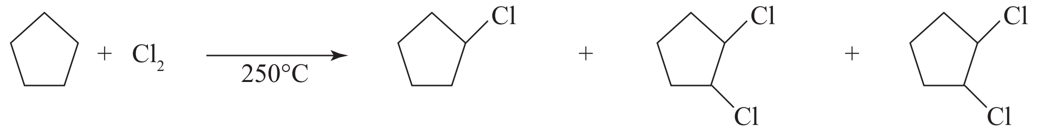
$R^{o} + R^{o} \longrightarrow R - R$ Termination

- Order of Reactivity for Halogenation:
  $F_2 > Cl_2 > Br_2 > I_2$
- Order of Reactivity of Alkanes: The order of substitution of H-atom in alkanes is decided by the stability of free radicles that is,
  Benzyl > Allyl > $3^{o} > 2^{o} > 1^{o} > CH_3^{o}$

Example,



When a large excess of cyclopentane is heated with chlorine at $250^{o}C$, chlorocy -clopentane is formed, along with small amounts of dichlorocyclopentanes.



cyclopentane

chlorocyclopentane 95%

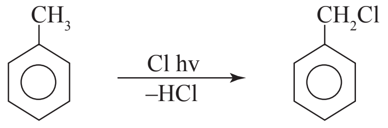
1, 2-dichloro-cyclopentane 4%

1, 3-dichloro-cyclopentane 1%

In case of chlorination, **Reactivity α $\frac{1}{\text{Selectivity}}$.**

- The reaction rate of formation of alkyl radicle by a Cl° is

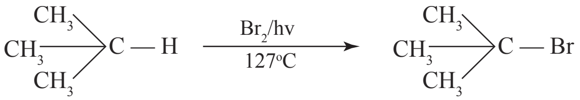
t	>	s	>	p
5		3.8		1

- 

Toluene

Benzyl chloride

- Some chlorinating reagents are Cl_2, SO_2Cl_2, $(CH)_3COCl$
- Some brominating reagents are Bromine, N-Bromosuccinamide
- Bromination is possible only in case of benzyl , Allyl group compounds.



Isobutane

Tertiary butyl bromide

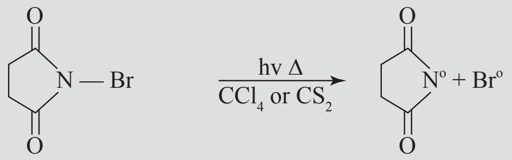
- N-bromosuccinamide (NBS) is used for bromination at allylic position in case of alkenes as follows:

Example,

$$\underset{\text{Propene}}{CH_3 - CH = CH_2} \xrightarrow[CCl_4]{NBS/hv} \underset{\text{Allyl bromide}}{CH_2Br - CH = CH_2 + HBr}$$

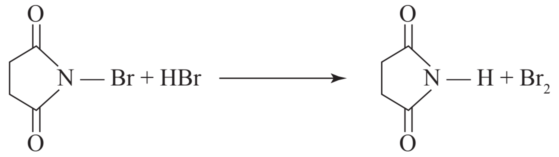
Mechanism

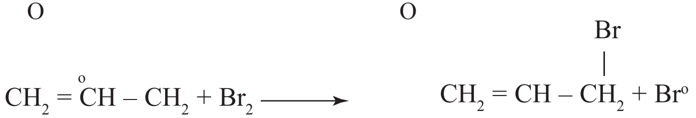
The mechanism of the above example can be given as follows:



N-bromosuccinamide

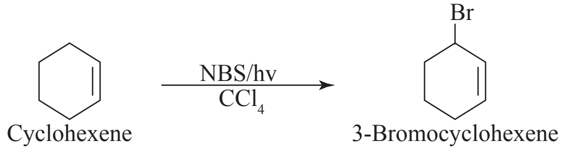
$$\underset{\text{Propene}}{CH_2 = CH - CH_3} \xrightarrow[-HBr]{Br^{o}} \underset{\text{Allyl free radical}}{CH_2 = CH - \overset{o}{C}H_2}$$





$$CH_2=\overset{o}{C}H-CH_2+Br_2\longrightarrow CH_2=CH-\overset{\overset{Br}{|}}{C}H_2+Br^{o}$$

Example,



(B) Electrophillic Substitution

- It is a two step process proved by isotopic tracer technique. Here substitution is by an electrophile [positively charged species like NO_2^+, X^+ etc.]
- **Activating Groups:** These groups increase electron density at ortho- and para- positions that is., these groups are ortho-para directing and highly ring activating so rate of electrophilic substitution is very fast.

Some Activating Groups in Decreasing Order

$-NH_2$, $-NHR$, $-NR_2$, $-OH$, $-OR$, -NHCOR, ϕ, $-R$

Deactivating Group:

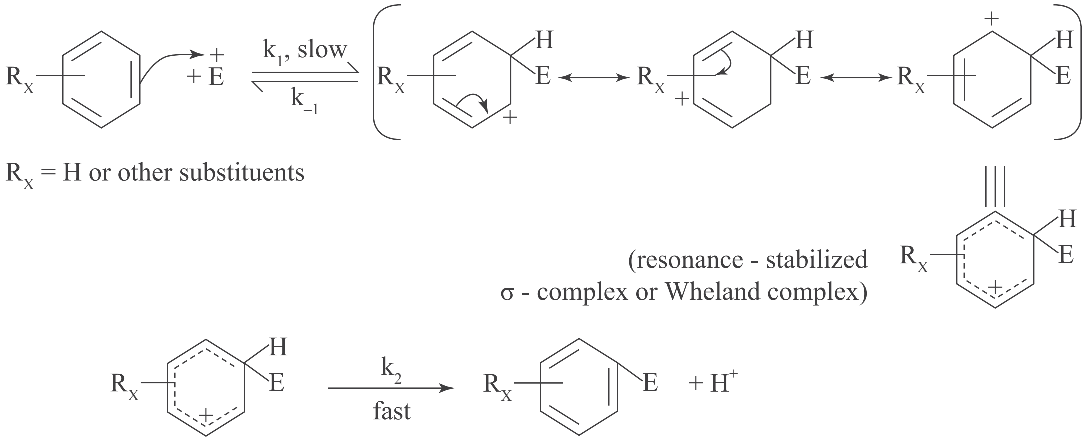
These groups are meta-directing and deactivate benzene ring that is, decrease electron density at ortho- and para- positions so electrophilic substitution is slower and occurs only at the meta position.

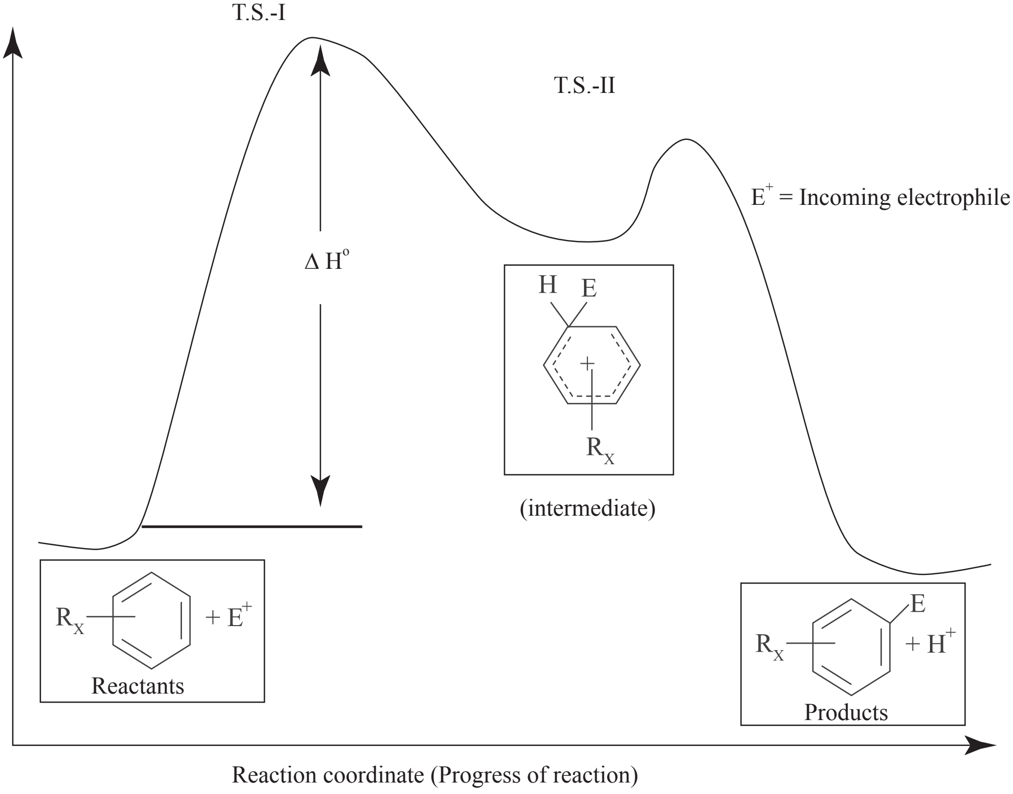
Some Deactivating Groups in Decreasing Order

$-NR_3$, $-NO_2$, $-CN$, $-COOH$, $-COOR$, $-SO_3H$, $-CHO$, $-COR$

Table

	Activating	*Weakly Deactivating*	*Deactivating*	
increase ↑	$-\ddot{\underset{..}{O}}:^-$	$-\ddot{\underset{..}{F}}:$ $-\ddot{\underset{..}{Cl}}:$ $-\ddot{\underset{..}{Br}}:$ $-\ddot{\underset{..}{I}}:$ $-\ddot{N}=\ddot{O}:$	$-NR_3^+$	increase ↑
	$-\ddot{\underset{..}{O}}H$ $-\ddot{N}H_2$ $-\ddot{N}R_2$		$-NO_2$ $-CF_3$ $-CCl_3$	
	$-\ddot{N}H\underset{\underset{O}{\|}}{C}R$ $-\ddot{\underset{..}{O}}R$		$-CN$ $-SO_3H$	
	$-R$ C_6H_5- $-\overset{\vert}{C}=\overset{\vert}{C}-$		$-\underset{\underset{O}{\|}}{C}OH$ $-\underset{\underset{O}{\|}}{C}OR$ $-\underset{\underset{O}{\|}}{C}H$ $-\underset{\underset{O}{\|}}{C}R$	



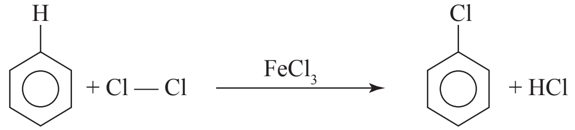


Energy Profile diagram for an aromatic electrophilic substitution reaction involving σ- complex as the reaction intermediate

Type of Electrophillic Substitution

(1) Halogenation Here substituent or electrophile is X^+ that is, H-atom of benzene ring is substituted by X^+.The reaction occurs in cold dark or in presence of halogen carriers like Fe, $FeCl_3$, $SnCl_4$, ICl etc.

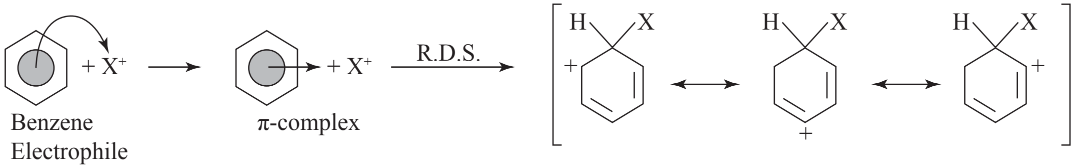
Example,



Mechanism of Halogenation:

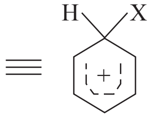
$$X - X \quad + \quad FeX_3 \rightarrow X^+ + FeX_4^-$$

Halogen Halogen carrier Electrophile

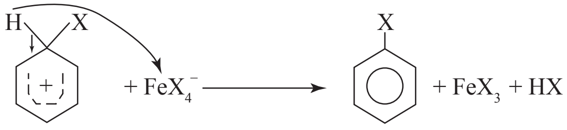


Benzene Electrophile

π-complex



σ-complex (Resonance hybrid)

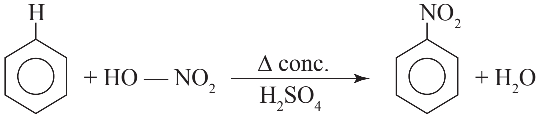


σ-complex Base

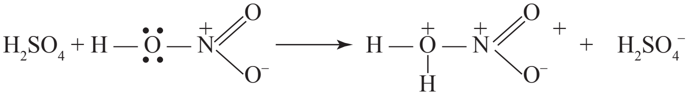
Chlorobenzene (substitution product)

- Here $AlCl_3$, anhy. $ZnCl_2$ can also be used as halogen-carriers to polarize the attacking molecules (X_2).
- In case of phenol, aniline etc there is no need for halogen carrier because OH, NH_2 groups are highly ring activating groups.

(2) ***Nitration*** Here electrophile is NO_2^+ and nitrating mixture is $HNO_3 + H_2SO_4$ or $HNO_3 + (CH_3CO)_2O$

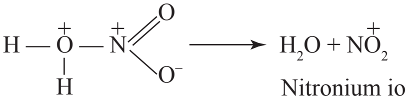


Mechanism of Nitration:



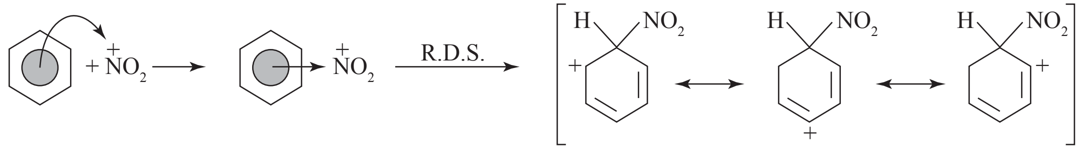
$$H_2SO_4 + H - \ddot{O} - \overset{+}{N}(=O)O^- \longrightarrow H - \overset{+}{O}(H) - \overset{+}{N}(=O)O^- + H_2SO_4^-$$

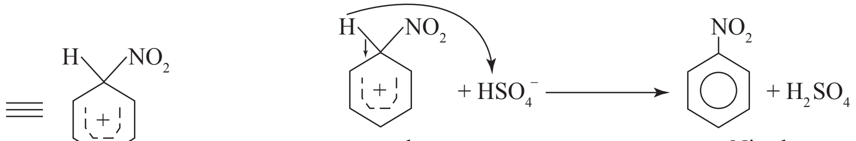
Protonated nitric acid Base



$$H - \overset{+}{O}(H) - \overset{+}{N}(=O)O^- \longrightarrow H_2O + \overset{+}{N}O_2$$

Nitronium ion (electrophile)



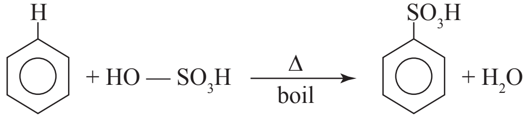


σ-complex

σ-complex

Nitrobenzene
(substitution product)

(3) ***Sulphonation*** Here electrophile is SO_3. It is catalysed by the presence of $HgSO_4$ or I_2. Here H_2SO_4 is the main sulphonating agent, however $ClSO_3H$ in CCl_4 can also be used in some cases

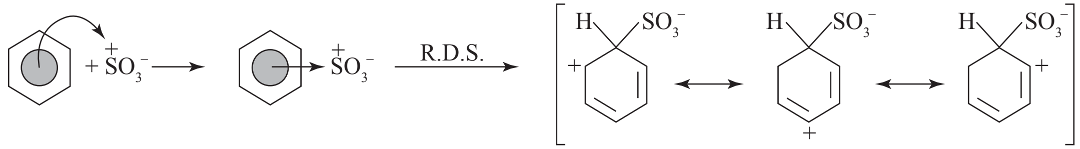


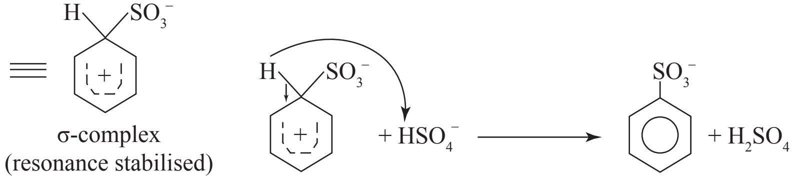
Mechanism of Sulphonation

Conc. sulphuric acid releases a molecule of SO_3.

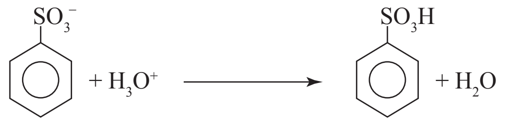
$$H_2SO_4 + H_2SO_4 \rightleftharpoons H_3O^+ + HSO_4^- + SO_3$$

The electrophile attacks on benzene ring to form a σ-complex.





σ-complex
(resonance stabilised)

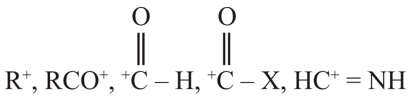


Benzene sulphonic acid
(substitution product)

- Kinetic isotopic effect occurs here C_6H_6 and C_6D_6 and abstraction of H^+ is rate determining step here.

(4) ***Freidal–Craft Reaction***

Here the electrophiles are

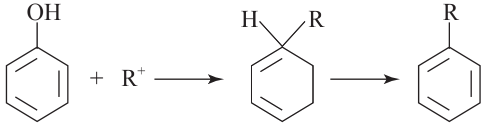


$$R^+, RCO^+, \overset{\displaystyle O}{\overset{\|}{{}^+C}} - H, \overset{\displaystyle O}{\overset{\|}{{}^+C}} - X, HC^+ = NH$$

- This reaction is mainly catalysed by anhydrous $AlCl_3$ however $FeCl_3$, $SnCl_4$, BF_3, $ZnCl_2$ can also be used and the decreasing order of these are as follows:

  $AlCl_3 > FeCl_3 > BF_3 > TiCl_3 > ZnCl_2 > SnCl_4$

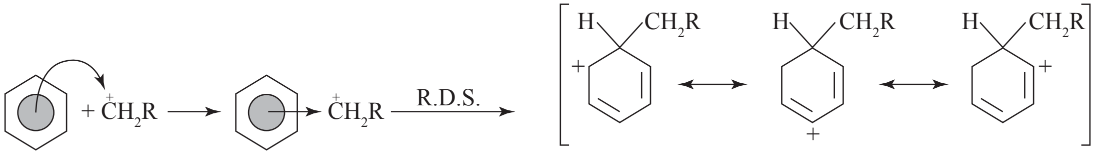
(a) Alkylation Here the electrophile is R^+.

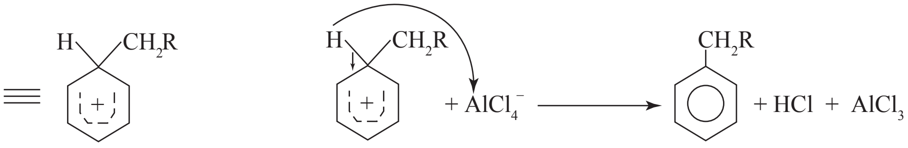


Friedal-Crafts Alkylation

$RCH_2Cl + AlCl_3 \rightarrow RCH_2^+ + AlCl_4^-$

Alkyl halide Lewis acid Electrophile Base



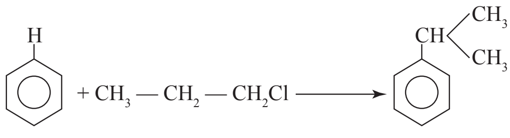


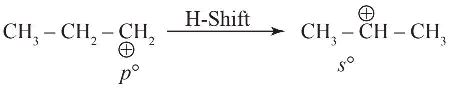
σ-complex (resonance stabilized) σ-complex Base Alkyl benzene (substitution product)

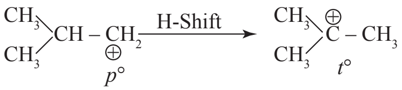
- Here rearrangement must be done if needed to form more stable carboca tion that is. t > s > p
- R^+ is obtained from $R - X$, $RCH = CHR$, $R - OH$ etc.

  Example,

Example,

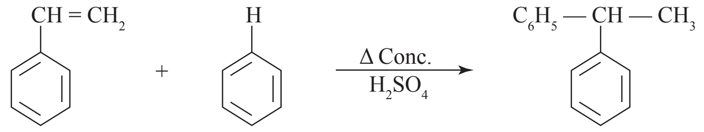


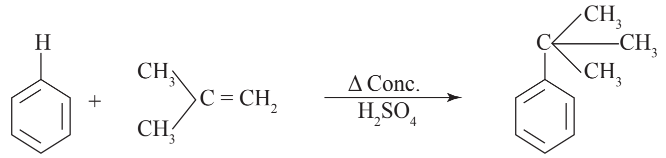


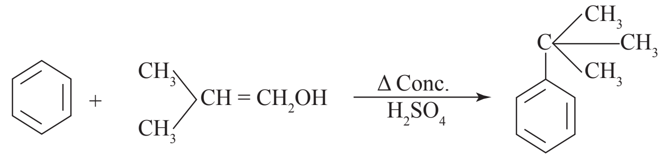


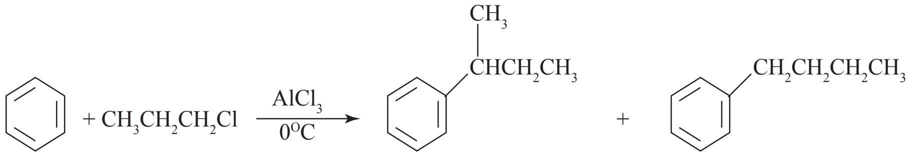
- From Alkene (In presence of H_2SO_4):

Example,





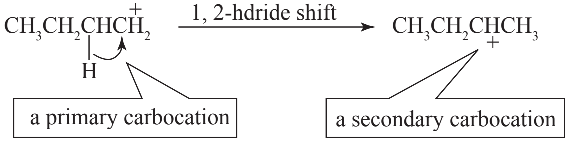




1-chlorobutane

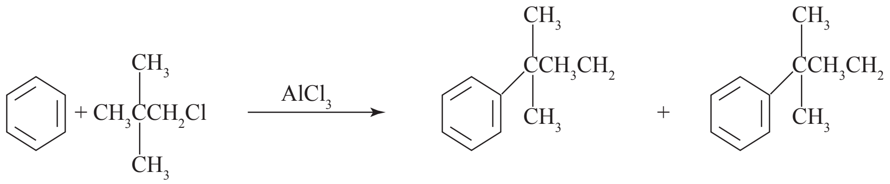
2-phenylbutane
rearranged alkyl
substituent 65%

1-phenylbutane
unarranged alkyl
substituent 35%



a primary carbocation

a secondary carbocation



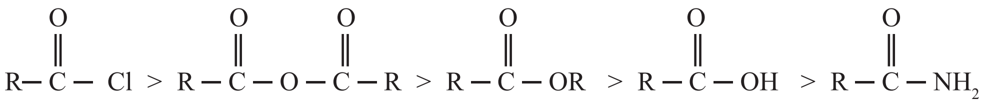
1-chloro-2,
2-dimethylpropane

2-methyl-2-phenylbutane
rearranged alkyl
substituent 100%

2, 2-dimethyl-2-
phenylpropane
unarranged alkyl
substituent 0%

(b) **Acylation** In acetylation electrophile is CH_3CO^+ and in benzylation electrophile is $C_6H_5CO^+$. Both these are combinedly termed under process acylation.

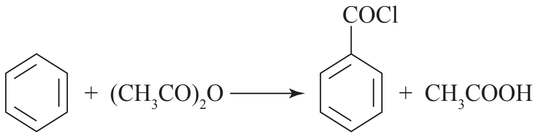
Decreasing Order for Acylation



$$R-\overset{O}{\overset{\|}{C}}-Cl > R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R > R-\overset{O}{\overset{\|}{C}}-OR > R-\overset{O}{\overset{\|}{C}}-OH > R-\overset{O}{\overset{\|}{C}}-NH_2$$

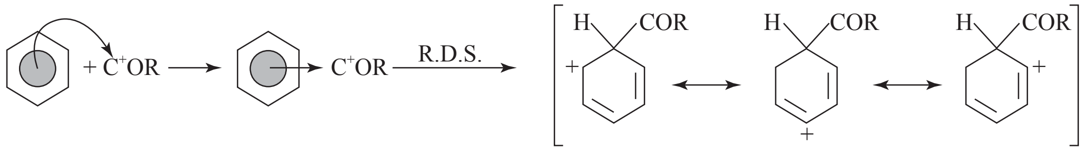
Example (1)

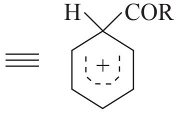
(2)



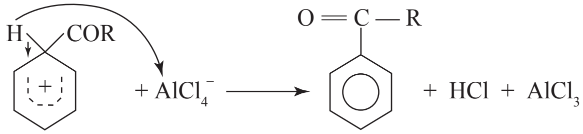
Mechanism of Acylation

$R - CO - Cl + AlCl_3 \rightarrow R - C^{+}O + AlCl_4^{-}$





σ-complex
(resonance stabilized)

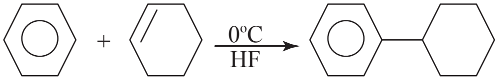


σ-complex Base

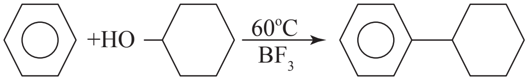
Specific example,

$$2\ \Phi - H + CH_2Cl_2 \xrightarrow[AlCl_3]{anhy.} (\Phi)_2CH_2 + 2HCl$$

$$3\ \Phi - H + CHCl_3 \xrightarrow[AlCl_3]{anhy.} (\Phi)_3CH + 3HCl$$



Cyclohexene Cyclohexylbenzene
(62%)



Cyclohexanol Cyclohexylbenzene
(56%)

(c) Nucleophillic Substitution Here substitution is due to a nucleophile that is, a weak nucleophile is substituted by a stronger nucleophile.

$R - X + OH^- \rightarrow R - OH + X^-$

Types: It is of two types: SN^1 and SN^2

(i) SN^1 or Nucleophillic Substitution First Order or Unimolecular:

- It is a first order reaction that takes place in two steps and the first step is the rate determining step.

$R - X \xrightarrow[\text{Slow step}]{\text{heterolytic}} R^+ + X^-$ [ionization]

$R^+ + Y^- \xrightarrow{\text{Fast step}} R - Y$

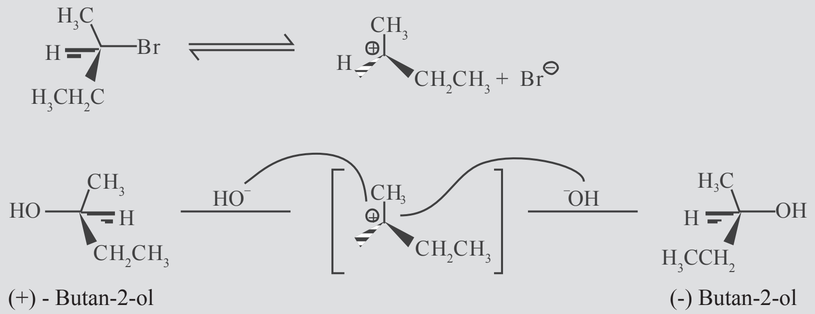
More strong
Nucleophile

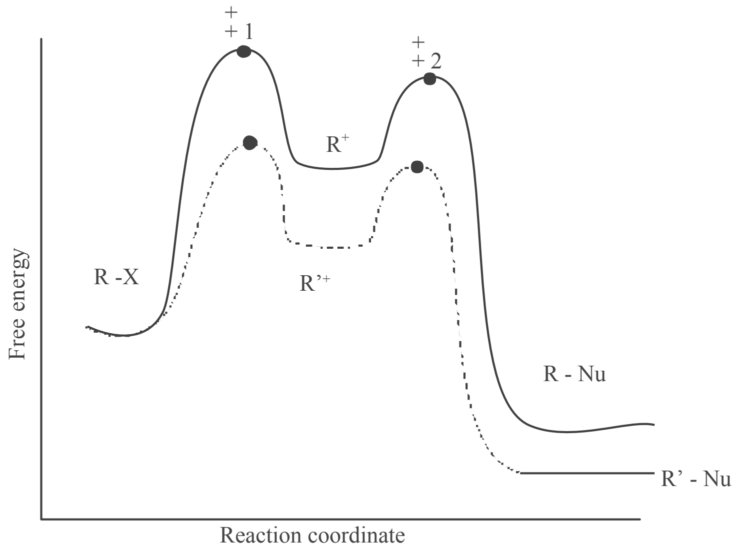
As rate is given by the slow step only so

$\frac{-dx}{dt}\ \alpha\ [R - X]^1$

that is, first order or unimolecular reaction.

Mechanism





The reaction profile for an S_N1 reaction. The dashed curve involves the more stable carbocation (R'^+).

Important Facts About SN^1

- No inversion takes place here.
- Here Nucleophile can attack the carbon atom of substrate from both back and front sides.
- The order of reactivity of alkyl halides towards SN^1 reaction is

  $3^o > 2^o > 1^o > CH_3X >$ vinyl

  The following decreasing order is observed for reactivity towards S_N1 reaction, (where Z = RCO, HCO, ROCO, NH_2CO , NC)

  $(C_6H_5)_3CX,\ (C_6H_5)_3CHX,\ ROCH_2X,\ RSCH_2X,\ R_2NCH_2X,\ R_3CX,\ C_6H_5CH_2X,$

  $-\overset{|}{C}=\overset{|}{C}-CH_2X,\ R_2CHX,\ RCH_2X,\ -\overset{|}{C}=\overset{|}{C}-X,\ ZCH_2X$

  Decreasing order of reactivity

- It is favoured by mild nucleophiles of low concentration and by the solvent of high polarity like H_2O.

  The relative order of nucleophilicity in protic solvent is as follow

  $\overset{\ominus}{SH} > \overset{\ominus}{CN} > \overset{\ominus}{I} > \overset{\ominus}{OH} > \overset{\ominus}{N_3} > \overset{\ominus}{Br} > CH_3CO\overset{\ominus}{O} > \overset{\ominus}{Cl} > \overset{\ominus}{F} > H_2O$

  And

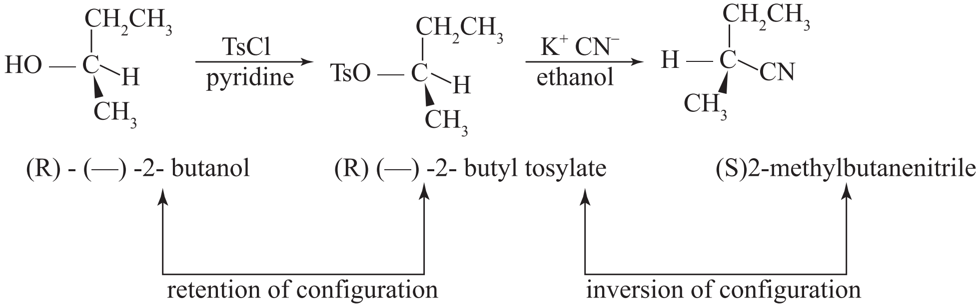
  $\overset{\ominus}{N}H_2 > R\overset{\ominus}{O} > \overset{\ominus}{O}H > R_2NH > Ar\overset{\ominus}{O} > NH_3 >$ pyridine $> \overset{\ominus}{F} > H_2O > \overset{\ominus}{Cl}O_4 > R_3\overset{\ominus}{C} > R_2\overset{\ominus}{N} > R\overset{\ominus}{O} > F$

- It is catalysed by Lewis acids like Ag^+, $AlCl_3$, $ZnCl_2$ etc.
- In case of optically active halides partial racemization is possible, also retention due to planar geometry of reaction intermediates.
- During SN^1 reaction the leaving group leaves the molecule before the incoming group attached to the molecule so that a carbocation is formed.
- Carbocation is the reaction intermediate here and it can go one time rearrangement only for more stability.
- A primary alkyl halide may also undergo SN^1 reaction in aqueous formic acid.
- The product of SN^1 reaction is almost racemic.
- The leaving group tendency order of nucleophiles in increasing order.

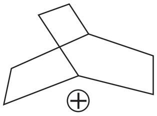
  $OH^-, NH^-, OR^-, F^-, Cl^-, Br^-, I^-, ToSo^-$

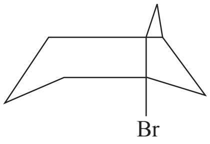
Example,

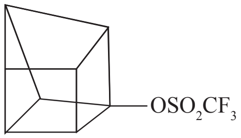
$(CH_2)_3C - Br + NaOH \rightarrow (CH_3)_3COH + NaBr$

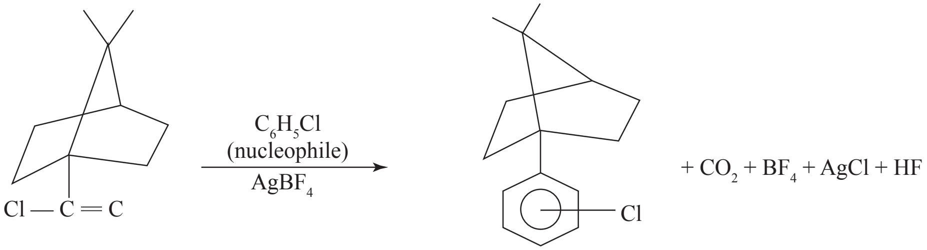


S_N1 reactions can tak place if the rings are large enough. Example, following compounds undergo hydrolysis:









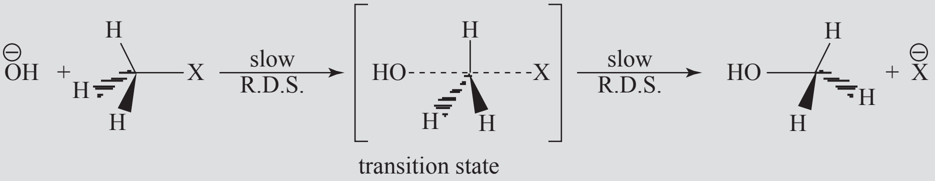
(ii) SN² (Nucleophillic Substitution Bimolecular):

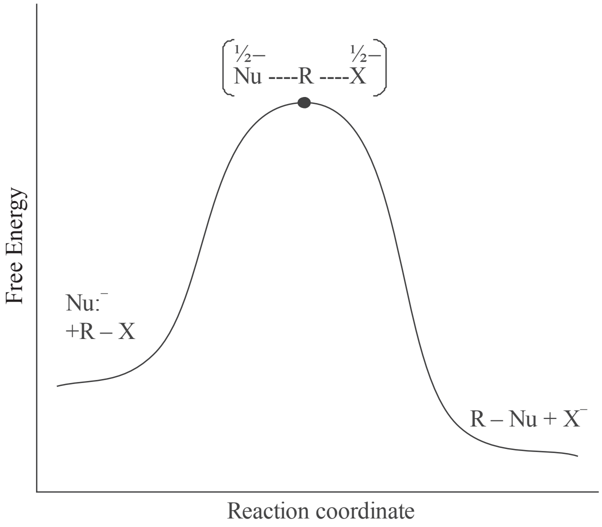
S : Substitution

N : Nucleophillic

2 : Bimolecular (II nd Order)

Mechanism





Corresponding energy profile diagram

Important Facts About SN^2

- It is a bimolecular and a second order reaction.

  $$\frac{-dx}{dt} \alpha \ [R - X]^1 \ [Nu]^1$$

- Here the reaction intermediate is unstable transition state which is formed before product formation.
- Here the stronger nucleophile can attack only from the back side.
- Here reaction occurs in presence of polar aprotic solvent like acetone, D.M.F and D.M.S.O. (which favours formation of transition state).
- Here configuration changes that is, optical inversion occurs in case of optically halides.
- Here the rate determining factor is Steric Hinderance.
- The order of reactivity of alkyl halide:

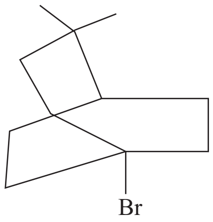
  $CH_3 - X > p^o > s^o > t^o$

  $R - I > R - Br > RCl > R - P$

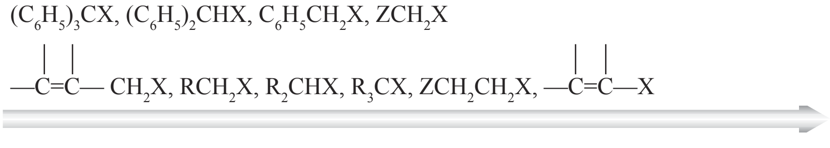
- In case of SN^2 reactions the ses as follows:

  $RS^- > ArS^- > CN^- > OH^- > N_3^- > Br^- > ArO^- > Cl^- > CH_3COO^- > H_2O$

- No S_N2 reaction occurs at bridge carbon atom, Example,



- The groups in decreasing order of reactivity towards S_N2 reaction is as follows

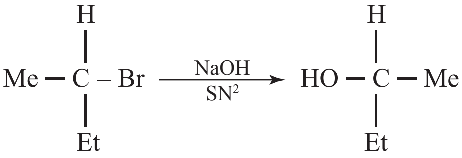


$(C_6H_5)_3CX, (C_6H_5)_2CHX, C_6H_5CH_2X, ZCH_2X$

$\overset{|\ \ |}{—C{=}C—}\ CH_2X, RCH_2X, R_2CHX, R_3CX, ZCH_2CH_2X, \overset{|\ \ |}{—C{=}C}—X$

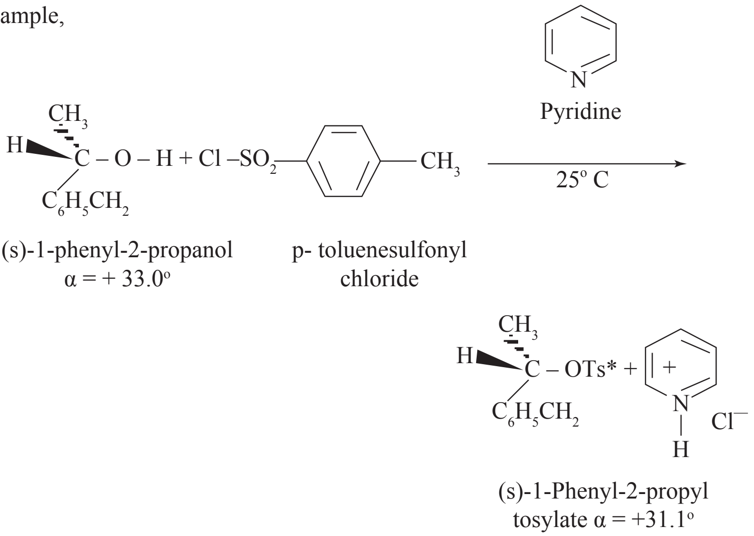
Decreasing order of reactivity

Example,



$$Me - \underset{Et}{\overset{H}{C}} - Br \xrightarrow[SN^2]{NaOH} HO - \underset{Et}{\overset{H}{C}} - Me$$

For example,

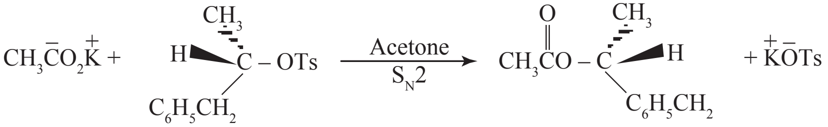


(s)-1-phenyl-2-propanol α = + 33.0°

p- toluenesulfonyl chloride

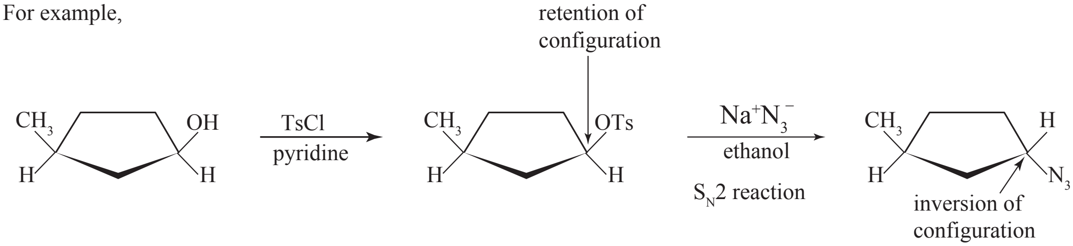
(s)-1-Phenyl-2-propyl tosylate α = +31.1°

For example,



(R)-1-Phenyl-2-propyl acetate α = -7.06°

For example,

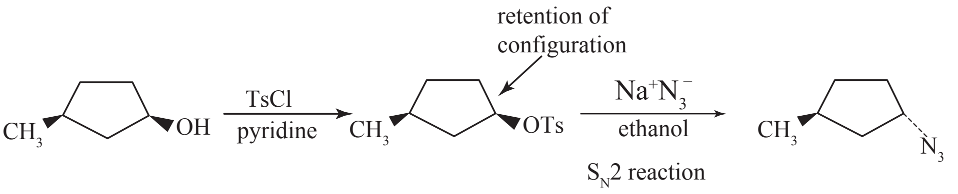


cis -3- methyl -1 cyclopentanol

cis -3- methyl -1 cyclopentyl tosylate

trans -1- azido -3- methylcyclopenane

Example,



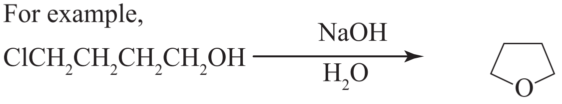
cis -3- methyl -1 cyclopentanol

cis -3- methyl -1 cyclopentyl tosylate

trans -1- azido -3- methylcyclopenane

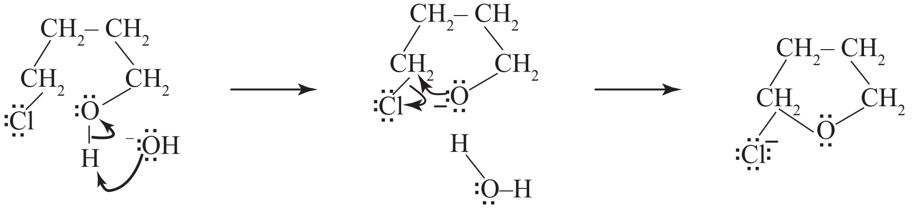
Intramolecular S_N2 Reaction

For example,



$$ClCH_2CH_2CH_2CH_2OH \xrightarrow[H_2O]{NaOH}$$

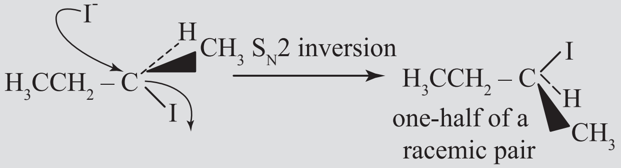
4- chloro -1- butanol Tetrahydrofuran (95 %)



deprotonation intramolecular attack by nucleophile

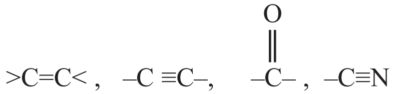
REMEMBER

The S_N2 reaction of optically active 2- iodobutane with iodide ion leads to racemization rather than inversion as the product of each displacement is the enantiomer of the substrate, and this product, together with another substrate molecule, constitutes a racemic pair.



(2) ADDITION REACTIONS

- It is given by unsaturated compounds having π-bonds like



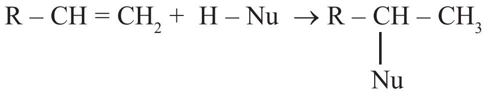
$$>C=C< ,\quad -C\equiv C-,\quad -\overset{\overset{O}{\|}}{C}- ,\quad -C\equiv N$$

- Here loss of one π-bond and gain of two σ- bonds take place.Here a less stable compound changes into a more stable product.

Type of Addition Reaction Addition reactions are of following types:

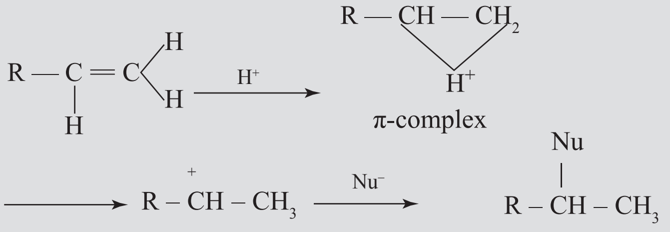
(A) Electrophilic Addition

It is given by alkene and alkynes. (>C = C< , –C ≡C–) It is a two step reaction in which the attacking reagent is an electrophile. If the reagent is a weak electrophile the reaction is catalysed by the strong acids like concentrated H_2SO_4



$$R-CH=CH_2 + H-Nu \rightarrow R-\underset{\displaystyle Nu}{\underset{|}{CH}}-CH_3$$

Mechanism



- If carbocation is less stable one time rearrangement is also possible.

Some Examples of Electrophillic Addition

(i) With HX:

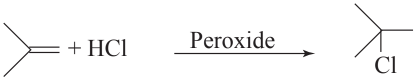
Order of reactivity for HX

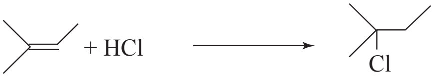
HF > HBr > HCl

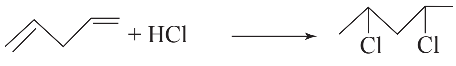
Addition According to Markownikoff's Rule:

In case of un-symmetrical alkenes or alkynes addition takes place according to Markoni Koff's rule that is, negative part of the attacking reagent is added to the unsaturated carbon atom having least number of H-atoms.

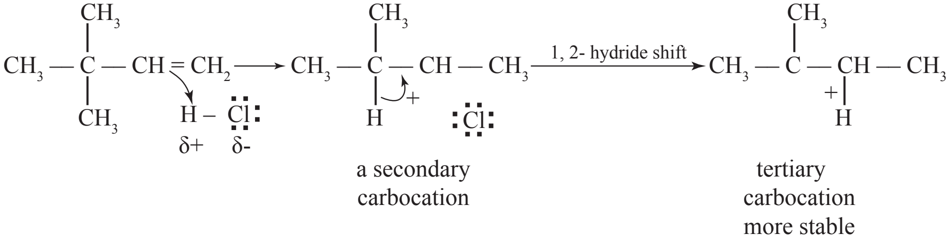
Example,

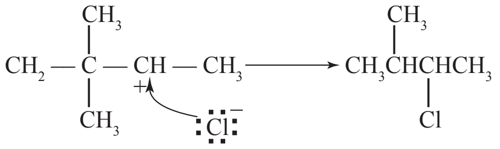




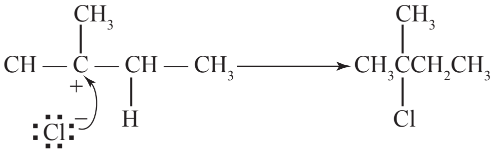


1, 2- Hydride Shift Case



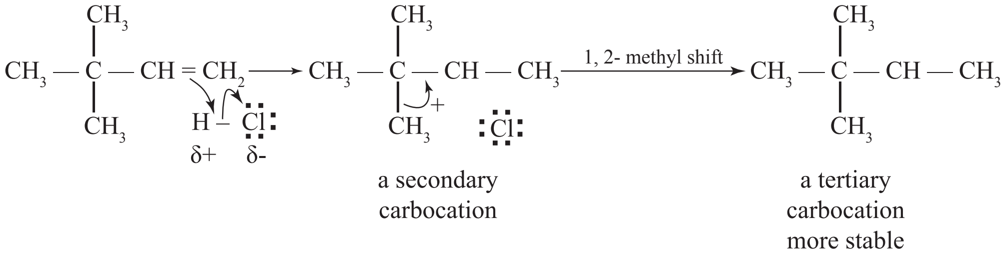


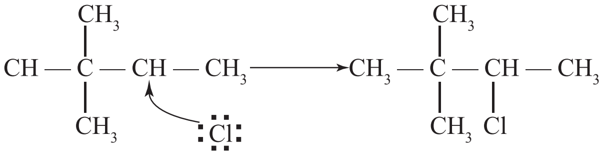
2- chloro -3- methylbutane
product from unrearranged
aecondary carbocation



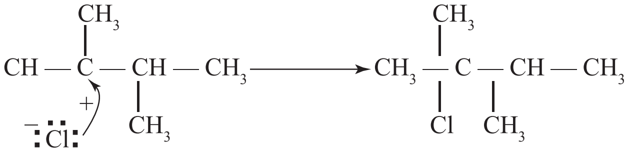
2- chloro -2- methylbutane
product from rearrangement
tertiary carbocation

1, 2- Alkyl Shift Case





3- Chloro -2,2- dimethylbutane
product from unrearranged (Secondary carbocation)



2- chloro -2, 3- dimethylbutane product from
rearranged tertiary carbocation

Peroxide Effect or Khrash Effect or Addition According to AntiMarkowniKoff Rule

- In case of un-symmetrical alknes, alkynes during addition with HBr in presence of peroxide or peroxy acids addition takes place according to Antimarkoni Koff's rule that is, negative part of the attacking reagent will be added to the unsaturated carbon atom having more H-atoms.
- It involves free radical addition mechanism.
- HF, HCl have larger bond energy so no such effect is possible in their cases as energy is not sufficient for this mechanism.HI being very reactive forms I_2 in place of I^o so no such effect is possible in this case.

$RCH = CH_2 + HBr \xrightarrow{\text{peroxide}} RCH_2CH_2Br$

Mechanism

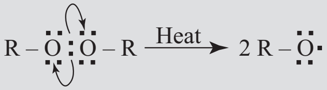
$$R - O - O - R \longrightarrow 2RO^{o}$$

$$R - O^{o} + H - Br \longrightarrow R - OH + Br^{o}$$

$$R - CH = CH_2 + Br^{o} \longrightarrow \underset{s^{o}\text{ more stable}}{R - {}^{o}CH - CH_2Br} \xrightarrow{H^{o}} R - CH_2 - CH_2Br$$

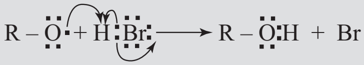
Mechanism

Step 1



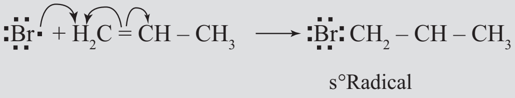
Heat brings about homolytic cleavage of the weak oxygen - oxygen bond.

Step 2



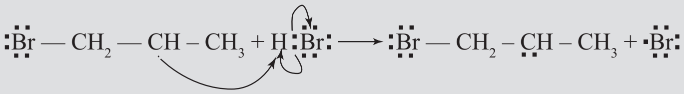
The alkoxyl radical abstracts a hydrogen atom from HBr, producing a bromine atom.

Step 3



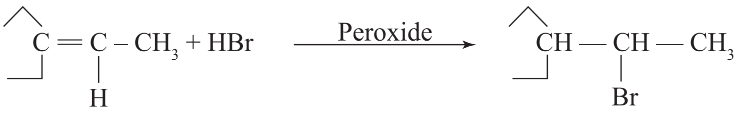
The bromine atom adds to the double bond to produce the more stable s°free radical

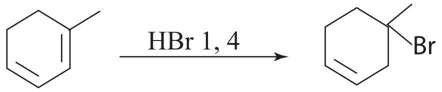
Step 4



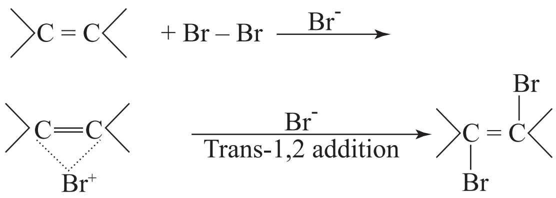
The s°radical abstracts a hydrogen atom from HBr. Which leads to the product and regenerates a bromine atom.

Example,





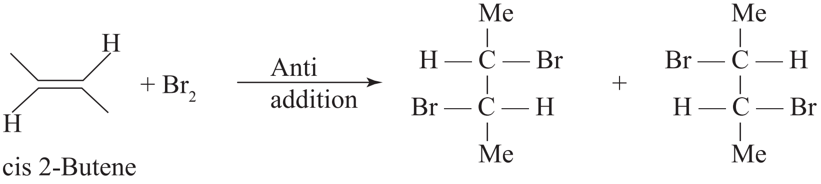
(ii) Addition of X_2:

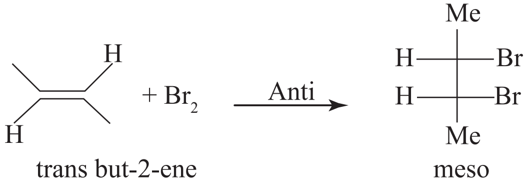


Points of Great Attention

- Cis alkene + syn addition → meso product
- Trans alkene + anti addition → meso product
- Cis alkene + anti addition → racemic prodcuct
- Trans alkene + syn addition → racemic product

Example,

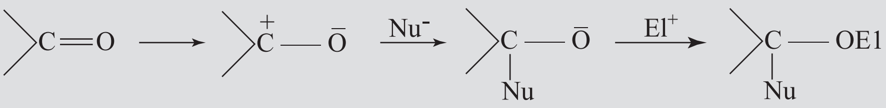




(B) Nucleophillic Addition Reaction

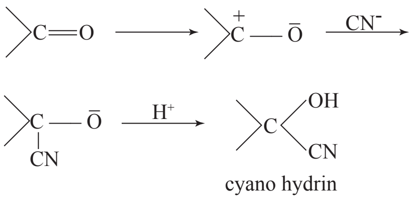
- It is given by carbonyl compounds (>C=O) mainly.Here the attacking reagent is a nucleophile that is, the nuclephile will be added first during addition.

Mechanism



Example,

(1) With HCN or Cyanohydrin formation:

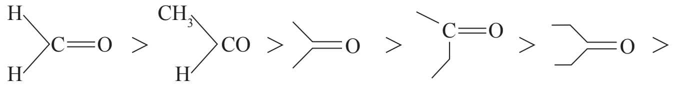


- Reactivity of carbonyl compounds:

  More the positive charge on ($> C^+ - O^-$) more is the reactivity that is,

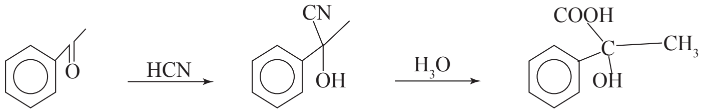
  Reactivity α 1/ +I effect.

  so



… $(CH_3)_3CO(CH_3)_3$
unreactive due to
steric hinderance

Example,



(3) ELIMINATION REACTION

- It is shown by the compounds having leaving groups such as X, OH, OR, N^+R_3 etc. Here due to removal of atoms or groups in the form of small molecules like H_2O, NH_3, HX etc., multiple bonds are formed. (that is, just reverse to addition reaction).
- It is mostly endothermic and possible on heating and here less stable product is obtained. It involves loss of 2σ bonds and gain of 1π bond.

Types of Elimination Reaction

(1) α-Elimination or 1,1, Elimination Reaction

- It is a very rare reaction and here both the species are removed from the same carbon atom.It is shown by Gem dihalides or Tri halides with alcoholic bases like KOH to give carbenes.

  Example,

$$CHX_3 \xrightarrow[\text{Alc. KOH}]{\Delta} \ddot{C}X_2 + X^- + H^+$$

$$CH_2X_2 \xrightarrow[\text{Alc. KOH}]{\Delta} \underset{\text{carbene}}{\ddot{C}HX} + X^- + H^+$$

(2) α – β or 1, 2 Elimination Reaction

Here atoms or groups are eliminated from α, β positions as follows

$$CH_3 - CH_2 - CH_2 - L \longrightarrow CH_3 - \overset{\beta}{CH} = \overset{\alpha}{CH_2} + H^+ + L^-$$

Types: It is of following types:

E_1: Elimination unimolecular and first order.

E_{1cb}: Elimination unimolecular with conjugation base.

E_2: Elimination bi molecular or second order.

(i) E_1 Type

Here elimination is acid catalysed and a carbocation is formed with one time rearrangement if carbocation is less stable. (that is, just like SN^1).

Rate α $[\text{subtract}]^1$

- The reaction occurs in presence of polar protic solvents.

Example,

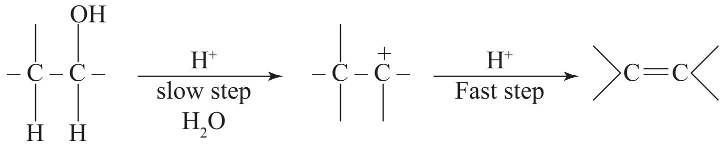
(1) Dehydration of Alcohol

Dehydration of alcohol is decided by the stability of carbocation that is, t > s > p.

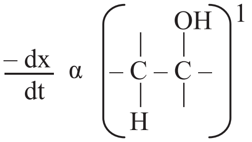
- Dehydrating reagents:
  Some common dehydrating agents are Anhy. PCl_5, conc. H_2SO_4, $KHSO_4$, Anhy. Al_2O_3, Anhy, $ZnCl_2$, P_2O_5 etc.

Mechanism

$$H_2SO_4 \longrightarrow H^+ + HSO_4^-$$



As rate is given by the slowest step so

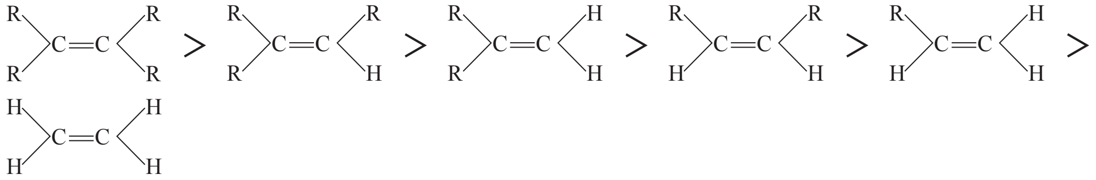


$$\frac{-dx}{dt} \; \alpha \left(-\overset{|}{\underset{\underset{H}{|}}{C}} - \overset{\overset{OH}{|}}{\underset{|}{C}} - \right)^1$$

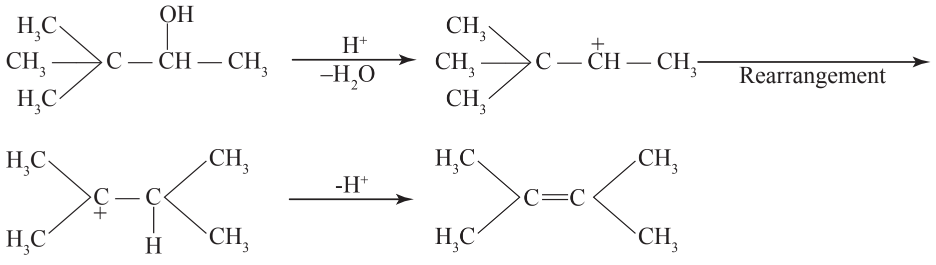
Saytzeff Rule

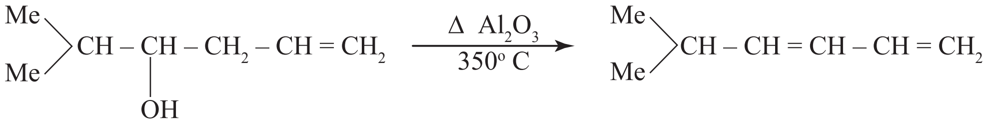
- According to it, “The removal of β-H-atom is from β-carbon atom having less number of H-atoms so that a more stable alkene is formed”.

Stability of alkene in decreasing order



For example,

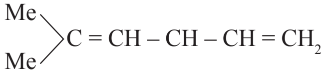




$$Me_2CH-CH(OH)-CH_2-CH=CH_2 \xrightarrow[350^o C]{\Delta\ Al_2O_3} Me_2CH-CH=CH-CH=CH_2$$

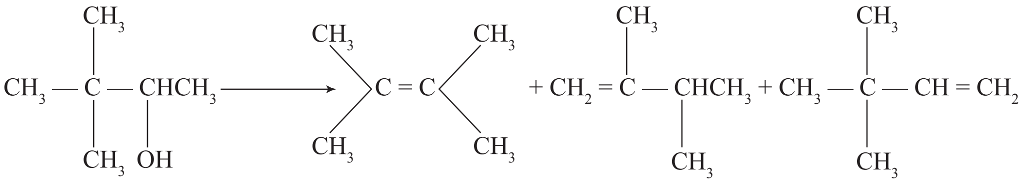
As it is conjugated diene so more stable hence it is the major product

or



$$Me_2C=CH-CH-CH=CH_2$$

Neglect it as it is less stable



$$CH_3-C(CH_3)_2-CH(OH)CH_3 \longrightarrow (CH_3)_2C=C(CH_3)_2 + CH_2=C(CH_3)-CHCH_3 + CH_3-C(CH_3)_2-CH=CH_2$$

3,3-dimethyl -2- butanol

2,3-dimethyl-2- butene (61%)

2,3-dimethyl-1- butene (31%)

3,3-dimethyl-1- butene (3%)

(ii) E_2 Type

- It is base catalysed and here an unstable intermediate transition state is formed like in SN^2

  Here rate of reaction is given as:

  $$\frac{-dx}{dt} \ \alpha \ (R-X)^1 (Base)^1$$

  that is, Reaction is of second order

  Rate of reaction α Leaving group power

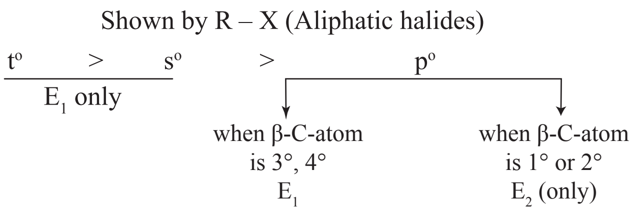
- The leaving group should be antiperiplanar (180º in same plane but Anti-conformation).

  Example,

  $$CH_3-CH_2-CH_2-Br + C_2H_5\bar{O} \rightarrow CH_3-CH=CH_2 + C_2H_5OH + Br^-$$

- **Dehydrohalogenation Reaction**

  Shown by R – X (Aliphatic halides)



Conditions Favouring E_1 and E_2 Reactions

E_1 Favouring Conditions

Alkyl Group - $3^o > 2^o > 1^o$

Base Strength

Weak bases like $\xrightarrow[\Delta]{NaOH}, \xrightarrow[\Delta]{KOH}, \xrightarrow[\Delta]{C^2H^5O^-}$

Catalyst-Lewis acid like $AlCl_3$

E_2 Favouring Conditions:

Alkyl Group - $1^o > 2^o > 3^o$

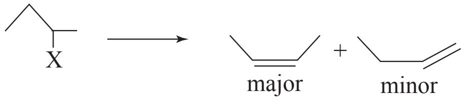
Base Strength

Strong bases like alc. KOH , $(CH_3)_3COOK$

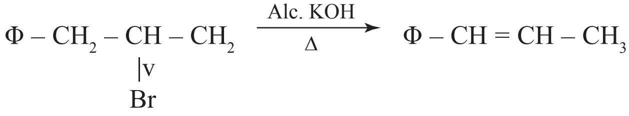
Catalyst-phase transfer catalyst

Example 1 Based on E_1 Concept:

Example 2

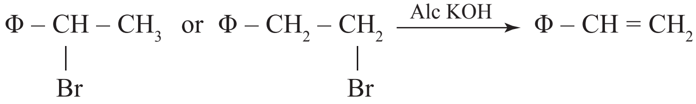


Example 3



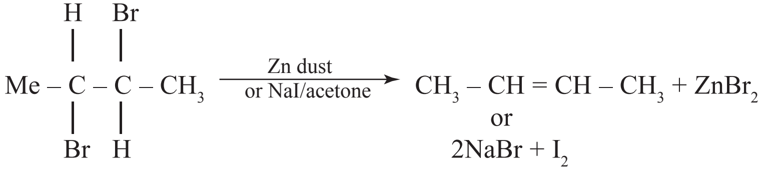
$$\Phi - CH_2 - \underset{\substack{|v\\Br}}{CH} - CH_2 \xrightarrow[\Delta]{Alc. KOH} \Phi - CH = CH - CH_3$$

Example 4

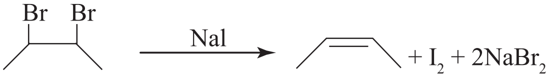


$$\Phi - \underset{\substack{|\\Br}}{CH} - CH_3 \text{ or } \Phi - CH_2 - \underset{\substack{|\\Br}}{CH_2} \xrightarrow{Alc KOH} \Phi - CH = CH_2$$

Examples Based on E_2 Concept:



$$Me - \overset{\substack{H\\|}}{\underset{\substack{|\\Br}}{C}} - \overset{\substack{Br\\|}}{\underset{\substack{|\\H}}{C}} - CH_3 \xrightarrow[\text{or NaI/acetone}]{\text{Zn dust}} \begin{matrix} CH_3 - CH = CH - CH_3 + ZnBr_2 \\ \text{or} \\ 2NaBr + I_2 \end{matrix}$$



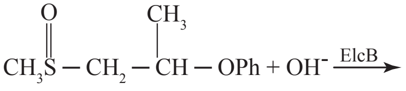
(iii) E_{1cb} Reaction:

- It occurs only when β-C-atom has strong electron attracting groups like >C =O, $-NO_2$, –CN, $-SO_3H$.
- When leaving group is very weak so that carbanion is easily formed.
- β -hydrogen atom should be strongly acidic. (For easy removal)

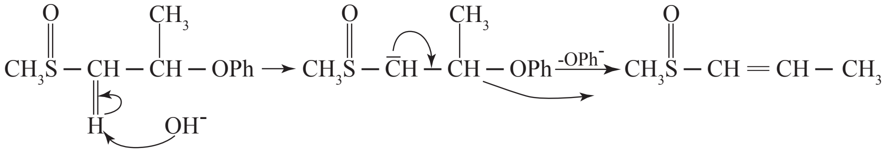
Example,

$$CF_3 - CHCl_2 \xrightarrow{C_2H_5O^-} F_2C = CCl_2$$

$$\Phi - CH_2 - CH_2F \xrightarrow{C_2H_5O^-} \Phi - CH = CH_2$$



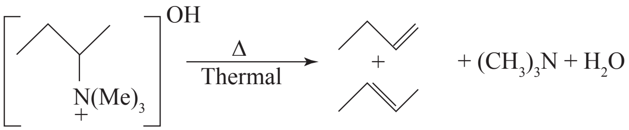
$$CH_3\overset{\overset{O}{\|}}{S} - CH_2 - \overset{\overset{CH_3}{|}}{C}H - OPh + OH^- \xrightarrow{ElcB}$$



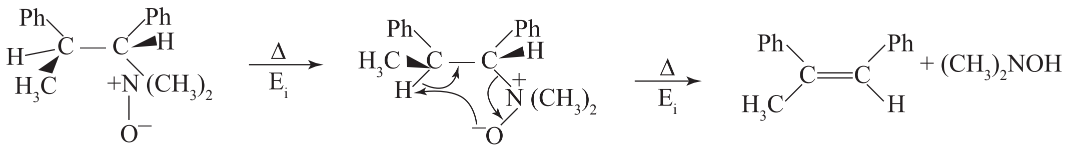
$$CH_3\overset{\overset{O}{\|}}{S} - \underset{\underset{H}{|}}{C}H - \overset{\overset{CH_3}{|}}{C}H - OPh \longrightarrow CH_3\overset{\overset{O}{\|}}{S} - \overset{-}{C}H - \overset{\overset{CH_3}{|}}{C}H - OPh \xrightarrow{-OPh^-} CH_3\overset{\overset{O}{\|}}{S} - CH = CH - CH_3$$

As the sulfonyl (S=O) group is a strong electron-withdrawing group, and will stabilize the carbanion formed in the first step.

Hoffmann Rule: According to Hoffmann rule the removal of β-H-atom is from β-C-atom with more H-atoms it is possible when leaving group is very bulky like N^+R_3 , S^+R_2

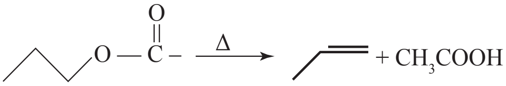


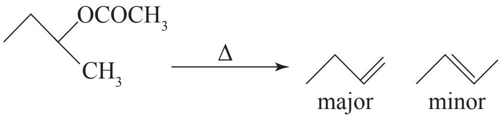
Here butene-1 is major product



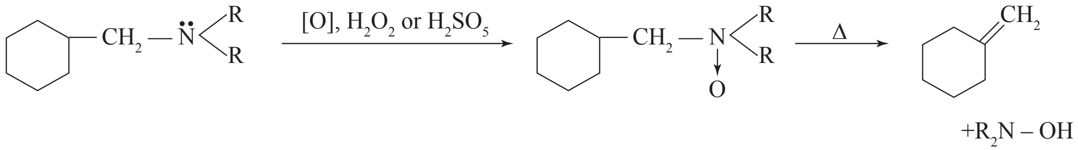
Thermal Or Pyrolytic Elimination:

It is according to Hoffmann Rule

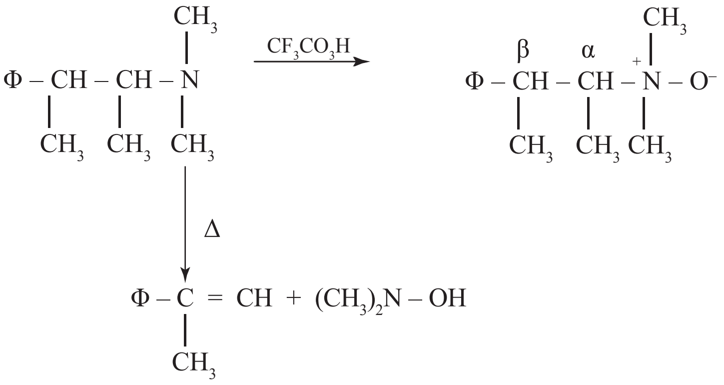




- **Cope Reaction:** Here a tertiary amine oxide is converted into alkene by heating and following α-β-elimination reaction.

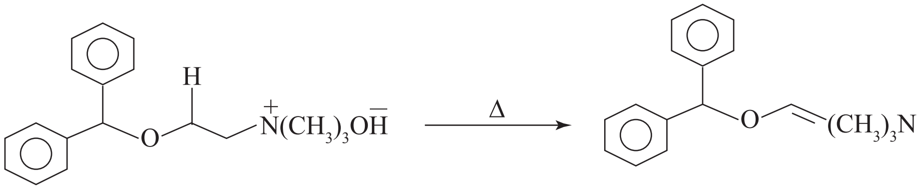


Example, (2)



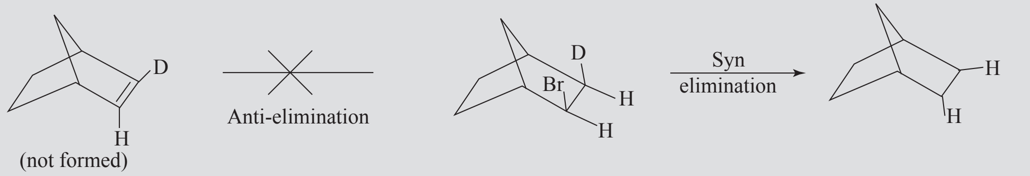
$$\Phi-\underset{CH_3}{CH}-\underset{CH_3}{CH}-\underset{CH_3}{\overset{CH_3}{N}} \xrightarrow{CF_3CO_3H} \Phi-\underset{CH_3}{\overset{\beta}{CH}}-\underset{CH_3}{\overset{\alpha}{CH}}-\underset{CH_3}{\overset{CH_3}{\overset{+}{N}}}-O^-$$

$$\xrightarrow{\Delta}\ \Phi-\underset{CH_3}{C}=CH+(CH_3)_2N-OH$$

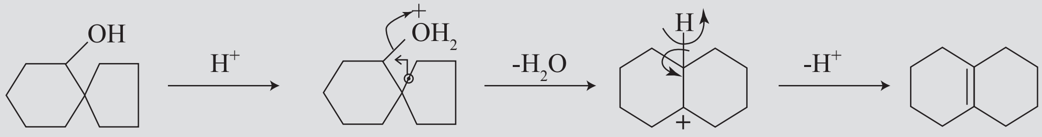


REMEMBER

When the leaving groups cannot achieve anti coplanar relationship they prefer to undergo syn-elimination



In some cases even a C - C bond migrates during elimination.



ENHANCE YOUR KNOWLEDGE

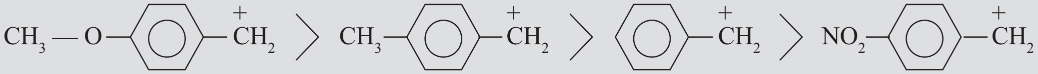
In case of same nucleophillic centre the basicity increases however nucleophilicity decreases as the size of the Nu^- approaching the substrate increases.

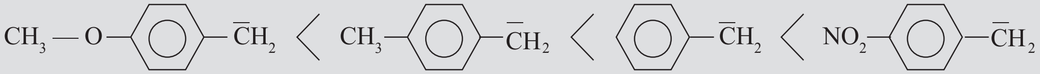
$MeO^- < Me_2CHO^- < Me_3CO^-$
(Basicity increases)

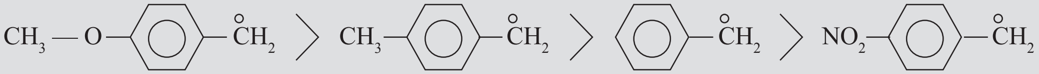
$Me_3CO^- < Me_2CHO^- < MeCH_2O^-$
(Nucleophilicity increases)

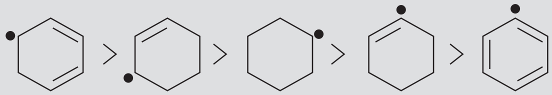
- $CH_3O^- > HO^- > CH_3COO^- > H_2O$
(Nucleophilicity, basicity decreases)

- **Some stability Orders**:

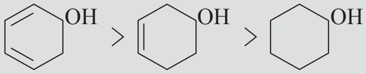






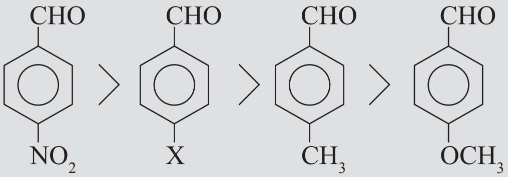


- **Decreasing Order of Dehydration**:



- **Decreasing order of >C =O towards nucleophillic addition.**

$CCl_3CHO > HCHO > CH_3CHO > CH_3-CH_2-CHO > CH_3COCH_3 > CH_3COC_6H_5 > C_6H_5COC_6H_5 > \ldots\ldots$



Characteristics of Common Substitution and Elimination Mechanisms

Mechanism	***S_N2***	***S_N1***	***E2***	***E1***	***E1cB***	***E_i***
Substrate Preference	Methyl $>1^o>2^o$	3^o or resonance stabilized $>2^o$; good leaving groups	Accessible β -hydrogen	Same as SN1; must have a β -hydrogen	Must have acidic β - hydrogen	Must have internal base located near β -hydrogen
Number of steps (intermediate)	1 (none)	2(carbocation)	1 (none)	2 (carbocation)	2 (carbanion)	1 (none)
Rate law	k[RX][Nu]	k[RX]	k[RX][B]	k[RX]	[RX][B]	k[RX]
Stereochemistry	Inversion at reaction center	Racemization at reaction center	Anti elimination	—	—	Syn elimination
Regiochemistry	—	—	Depends on lateness of transition state	Most stable alkene	—	Often gives least hindered alkene
Preferred Temperature	Low	Low	High	High	High	High
Preferred Solvent	basic	High ionization power	basic	High ionization power	Basic	Little or no effect

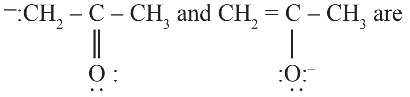
MULTIPLE-CHOICE QUESTIONS

Straight Objective Type Questions (Single Choice Only)

1. The kind of delocalization involving sigma bond orbitals is called
(a) inductive effect
(b) hyperconjugation effect
(c) electromeric effect
(d) mesomeric effect

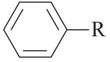
2. The order of effectiveness of o- and p- directing groups is
(a) $OH > NR_2 > NH.COCH_3 > Cl > CH_3$
(b) $OH > Cl > CH_3 > NR_2 > NH.COCH_3$
(c) $OH > NH.COCH_3 > Cl > NR_2 > CH_3$
(d) $OH > CH_3 > NH.COCH_3 > Cl > NR_2$

3. Which of the following is a correct statement regarding the effect of a Cl atom bonded to the C atom adjacent to a carbocation C?
(a) It has no effect on the stability of the carbocation.
(b) It helps stabilize the carbocation.
(c) It helps destabilize the carbocation.
(d) none of these

4. 

$\overset{-}{:}CH_2 - \underset{\ddot{O}:}{\overset{}{C}} - CH_3$ and $CH_2 = \underset{:\ddot{O}:^-}{C} - CH_3$ are
(a) tautomers
(b) optical isomers
(c) geometrical isomers
(d) resonating structures

5. In the following benzyl/allyl system

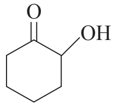
$R - CH = CH_2$ or 

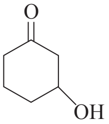
(R is alkyl group)
decreasing order of inductive effect is
(a) $(CH_3)_3C- > (CH_3)_2CH- > CH_3CH_2-$
(b) $CH_3CH_2- > (CH_3)_2CH- > (CH_3)_3C-$
(c) $(CH_3)_2CH- > CH_3CH_2- > (CH_3)_3C-$
(d) $(CH_3)_3C- > CH_3CH_2- > (CH_3)_2CH-$

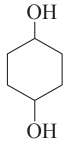
6. Which of the following species is attacked by benzene in the electrophilic nitration reaction?
(a) NO^+ (b) NO_2
(c) NO_2^+ (d) HNO_3

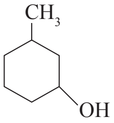
7. Which of the following compounds is least reactive in the nucleophilic aromatic substitution reaction with NaOH?
(a) m-nitrochlorobenzene
(b) o-nitrochlorobenzene
(c) p-nitrochlorobenzene
(d) 2, 4-dinitrochlorobenzene

8. Maximum dehydration takes place that of

(a) 

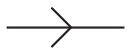
(b) 

(c) 

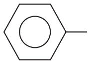
(d) 

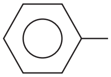
9. Which of the following is the best choice of reagents to effect the electrophilic iodination of an aromatic ring?
(a) I_2, HNO_3 (b) KI, acetone
(c) I_2, CH_3CN (d) KI, HNO_3

10. SN^1 reaction is feasible in

(a)  Cl + KOH ⟶

(b)  Cl + KOH ⟶

(c)  Cl + KOH ⟶

(d)  $CH_2CH_2Cl + KOH \longrightarrow$

11. In which of the following compounds, the underlined carbon has sp^3 – hybridization?
(a) $CH_3 - \underline{C}H = CH_2$ (b) $CH_3\underline{C}ONH_2$
(c) $CH_3 - \underline{C}H_2 - OH$ (d) $CH_3\underline{C}OOH$

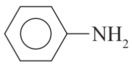
12. The most stable carbonium ion is
(a) $(CH_3)_2CH^+$ (b) $CH_3CH_2^+$
(c) $(CH_3)_3C - CH_2^+$ (d) $(CH_3)_3C^+$

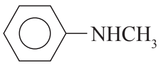
13. Which of the following is the strongest activating group in electrophillic aromatic substitution reactions?
(a) $-N(CH_3)_2$ (b) $-NO_2$
(c) $-CO_2CH_3$ (d) $-OCH_3$

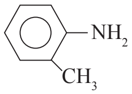
14. Which of the following compounds possesses the C – H bond with the lowest bond dissociation energy?
(a) n-pentane (b) toluene
(c) benzene (d) 2, 2-dimethylpropane

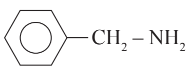
15. Which of the following intermediate has the complete octet around the carbon atom?
(a) free radical (b) carbene
(c) carbanion (d) carbonium ion

16. Which of the following is the strongest base?

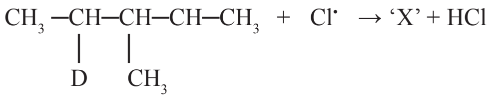
(a) 

(b) 

(c) 

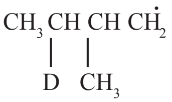
(d) 

17. Consider the following reaction

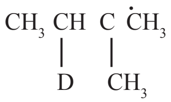


$CH_3-\underset{\substack{|\\ D}}{CH}-\underset{\substack{|\\ CH_3}}{CH}-CH-CH_3 + Cl^{\bullet} \rightarrow$ 'X' + HCl

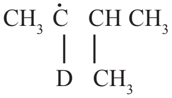
Identify the structure of the major product 'X' .

(a) 

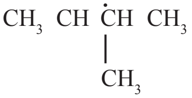
$CH_3\,\underset{\substack{|\\ D}}{CH}\,\underset{\substack{|\\ CH_3}}{CH}\,C\dot{H}_2$

(b) 

$CH_3\;CH\;\underset{\substack{|\\ D}}{C}\;\underset{\substack{|\\ CH_3}}{\dot{C}H_3}$

(c) 

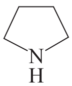
$CH_3\,\underset{\substack{|\\ D}}{\dot{C}}\;\underset{\substack{|\\ CH_3}}{CH}\,CH_3$

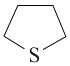
(d) 

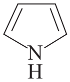
$CH_3\;CH\;\underset{\substack{|\\ CH_3}}{\dot{C}H}\;CH_3$

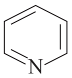
18. Among the following the strongest nucleophiles is
(a) C_2H_5SH (b) CH_3COO^-
(c) CH_3NH_2 (d) $NCCH_2^-$

19. Among the following compounds, the most basic compound is

(a) 

(b) 

(c) 

(d) 

20. The strongest dichlorobutanoic acid is
(a) 2, 3-dichlorobutanoic acid
(b) 2, 2-dichlorobutanoic acid
(c) 3, 4-dichlorobutanoic acid
(d) 4, 4-dichlorobutanoic acid

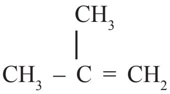
21. In the electrophilic aromatic substitution reactions, a $-CO_2H$ substituent on the aromatic ring is
(a) A deactivator and an o, p-director
(b) A deactivator and a m-director
(c) An activator and an o, p-director
(d) An activator and a m-director

22. The major product obtained on treatment of $CH_3CH_2CH(F)CH_3$ with CH_3O^-/CH_3OH is
(a) $CH_3CH_2CH(OCH_3)CH_3$
(b) $CH_3CH = CHCH_3$
(c) $CH_3CH_2CH = CH_2$
(d) $CH_3CH_2CH_2CH_2OCH_3$

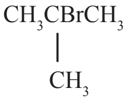
23. Among the following which one does not act as an intermediate in Hoffmann rearrangement?
(a) RNCO (b) $RCO\ddot{N}$
(c) $RCO\ddot{N}HBr$ (d) RNC

24. Among the following acids which has the lowest pKa value?
(a) CH_3COOH
(b) HCOOH
(c) $(CH_3)_2CH-COOH$
(d) CH_3CH_2COH

25. The reaction of HBr with

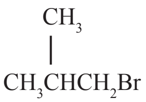


$CH_3-\overset{\substack{CH_3\\ |}}{C}=CH_2$ in the presence of peroxide will give

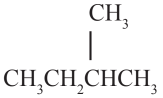
(a) 

$CH_3\underset{\substack{|\\ CH_3}}{C}BrCH_3$

(b) $CH_3CH_2CH_2CH_2Br$

(c) 

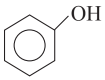
$CH_3\overset{\substack{CH_3\\ |}}{C}HCH_2Br$

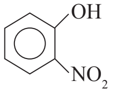
(d) 

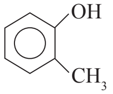
$CH_3CH_2\overset{\substack{CH_3\\ |}}{C}HCH_3$

26. Which of the following undergoes nucleophillic substitution exclusively by SN^1 mechanism?
(a) ethyl chloride
(b) isopropyl chloride
(c) chlorobenzene
(d) benzyl chloride

27. Which one of the following compounds is most acidic?
(a) $Cl-CH_2-CH_2-OH$

(b) 

(c) 

(d) 

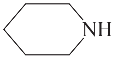
28. At pH 4.5, which of the following acids would be most dissociated?
(a) Hexanoic acid (pKa = 4.88)
(b) p-Nitrobenzoic acid (pKa = 3.41)
(c) Octanoic acid (pKa = 4.89)
(d) Acetic acid (ethanoic acid) (pKa = 4.74)

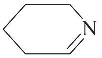
29. Which of the following compounds will undergo Friedel-Crafts alkylation with $(CH_3)_3CCl$, $AlCl_3$ most rapidly?
(a) Acetophenone
(b) Iodobenzene
(c) Toluene
(d) Benzenesulphonic acid

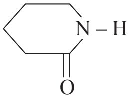
30. What effect does doubling the concentration of HCl have on the rate of the reaction of t- butyl alcohol and HCl?
(a) It has no effect on the reaction rate.
(b) It quadruples the rate of the reaction.
(c) It decreases the rate to one- half.
(d) It doubles the rate of the reactions.

31. 3-phenylpropene on reaction with HBr gives (as a major product)
(a) $C_6H_5CH_2CH(Br)CH_3$
(b) $C_6H_5CH(Br)CH_2CH_3$
(c) $C_6H_5CH_2CH_2CH_2Br$
(d) $C_6H_5CH(Br)CH = CH_2$

32. Consider the following and select the decreasing order of basic nature:

(1)


(2)


(3)


(a) 1 > 3 > 2 (b) 1 > 2 > 3
(c) 3 > 1 > 2 (d) 2 > 3 > 1

33. Amongst the following, the most basic compound is
(a) benzylamine
(b) aniline
(c) acetanilide
(d) p-nitroaniline

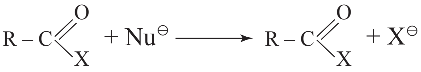
34. Which of the following is the strongest acid?
(a) Acetic acid
(b) Chloroacetic acid
(c) Trichloroacetic acid
(d) Dichloroacetic acid

35. Pyridine is less basic than triethylamine because:
(a) pyridine has aromatic character.
(b) nitrogen in pyridine is sp^2 hybridized.
(c) pyridine is a cyclic system.
(d) in pyridine, lone pair of nitrogen is delocalized.

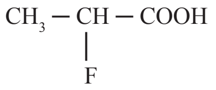
36. 2-methylbutane on reacting with bromine in the presence of sunlight gives mainly
(a) 1-bromo-2-methylbutane
(b) 2-bromo-2-methylbutane
(c) 2-bromo-3-methylbutane
(d) 1-bromo-3-methylbutane

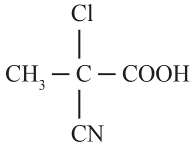
37. What intermediate is believed to occur in the elimination-addition nucleophilic aromatic substitution mechanism?
(a) Quinone (b) Benzyne
(c) Radical anion (d) Radical cation

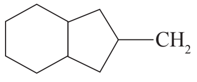
38. The reaction

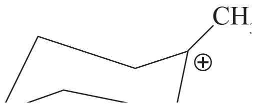


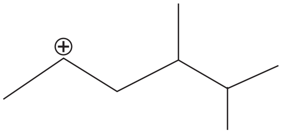
is fastest when X is
(a) Cl
(b) NH_2
(c) OC_2H_5
(d) OCOR

39. Which of these acids has the highest value of pK_a?
(a)

$CH_3-\underset{\underset{F}{|}}{CH}-COOH$

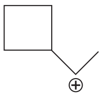
(b) CH_3-CH_2-COOH
(c) $F-CH_2-CH_2-COOH$
(d)

$CH_3-\overset{\overset{Cl}{|}}{\underset{\underset{CN}{|}}{C}}-COOH$

40. The most stable carbocation among the given below is
(a)


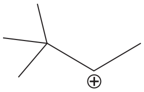
(b) $\overset{\oplus}{C}H_3$
(c)


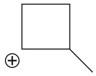
(d)


41. Which of the following is most likely to undergo a favourable hydride shift?

(a) 

(b) 

(c) 

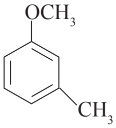
(d) 

42. Elimination of bromine from 2-bromobutane results in the formation of:
(a) equimolar mixture of 1 and 2-butene
(b) predominantly 2-butene
(c) predominantly 1-butene
(d) predominantly 2-butyne

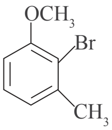
43. Which of the following is the strongest acid?
(a) $O_2NCH_2CO_2H$
(b) $CH_3OCH_2CO_2H$
(c) $(CH_3)_2CHCO_2H$
(d) $PhCH_2CO_2H$

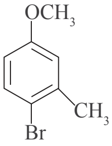
44. Which of the following compounds is the strongest acid?
(a) m-methoxybenzoic acid
(b) p-bromobenzoic acid
(c) p-nitrobenzoic acid
(d) m-methylbenzoic acid

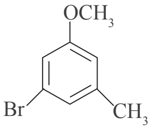
45. The major product obtained on the monobromination (with Br_2/ $FeBr_3$) of the following compound A is

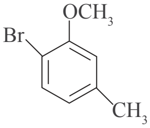


(A)

(a) 

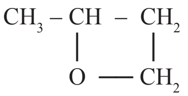
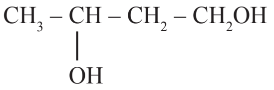
(b) 

(c) 

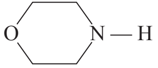
(d) 

46. The major product formed in the following reaction is

$CH_3CH(Cl)CH_2-CH_2OH \xrightarrow{\text{aq. KOH}}$

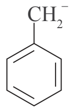
(a) $CH_3CH=CH-CH_2OH$
(b) $CH_2=CH-CH_2-CH_2OH$
(c) 
$\begin{array}{lll} CH_3-CH & - & CH_2 \\ \qquad\quad | & & \;\;| \\ \qquad\quad O & - & CH_2 \end{array}$
(d) 
$\begin{array}{l} CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2-CH_2OH \end{array}$

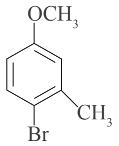
47. The total number of lone pair of electrons in the molecule given below are

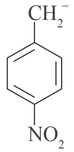


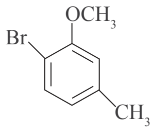
(a) 1 (b) 2
(c) 3 (d) 4

48. The most stable carbanion among the following is

(a) 

(b) 

(c) 

(d) 

49. The correct increasing order of the reactivity of halides for SN_1 reaction is
(a) $CH_3-CH_2-X < (CH_3)_2CH-X < CH_2=CH-CH_2-X < PhCH_2-X$
(b) $(CH_3)_2CH\text{-}X < CH_3-CH_2-X < CH_2=CH-CH_2-X < PhCH_2-X$
(c) $PhCH_2-X < (CH_3)_2CH-X < CH_3-CH_2-X < CH_2=CH-CH_2-X$
(d) $CH_2=CH-CH_2-X < PhCH_2-X < (CH_3)_2CH-X < CH_3-CH_2-X$

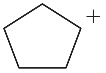
50. Which of the following are strongly hydrogen bonded in the liquid phase?
(a) Esters
(b) Secondary amides
(c) Acid chlorides
(d) Tertiary amides

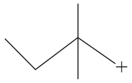
51. The nitrogen atom of trimethylamine is _____ hybridized which is reflected in the CNC bond angle of _____.
(a) sp, 108° (b) sp^2, 180°
(c) sp^3, 108° (d) sp^2, 120°

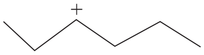
52. The increasing order of the rate of HCN addition to compounds A – D is
(a) HCHO (b) CH_3COCH_3
(c) $PhCOCH_3$ (d) PhCOPh

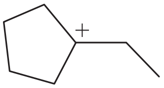
(a) a < b < c < d
(b) d < b < c < a
(c) d < c < b < a
(d) c < d < b < a

53. Consider the following carbocations and decide Which is the most stable one?

(a) 

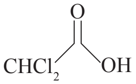
(b) 

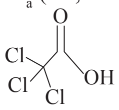
(c) 

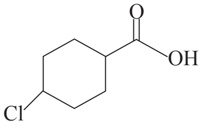
(d) 

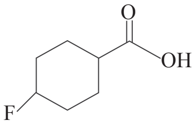
54. Reaction of trans-2-phenyl-1-bromocyclopentane on reaction with alcoholic KOH produces
(a) 4-phenylcyclopentene
(b) 2-phenylcyclopentene
(c) 1-phenylcyclopentene
(d) 3-phenylcyclopentene

55. Select the acid with the highest K_a (i.e., lowest pK_a)?

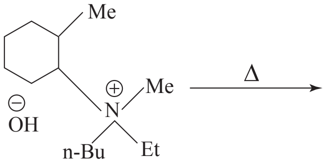
(a) 

(b) 

(c) 

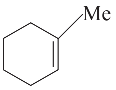
(d) 

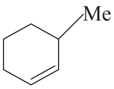
56. The alkene formed as a major product in the given elimination reaction is



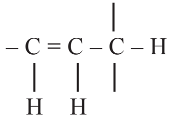
(a) 

(b) $CH_2 = CH_2$

(c) 

(d) 

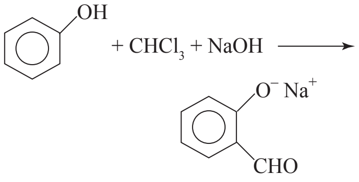
57. Which hydrogen atom can be abstracted easily from the given compound?



$$-\underset{\mathrm{H}}{\underset{|}{C}}=\underset{\mathrm{H}}{\underset{|}{C}}-\underset{|}{\overset{|}{C}}-H$$

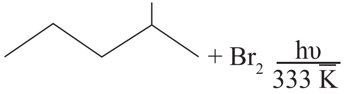
(a) α
(b) β
(c) γ
(d) Cannot be said

58. The electrophile involved in the given reaction is



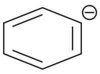
(a) dichloromethyl cation ($^{\oplus}CHCl_2$)
(b) dichlorocarbene ($:CCl_2$)
(c) trichloromethyl anion ($^{\ominus}CCl_3$)
(d) formyl cation ($^{\oplus}CHO$)

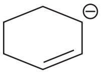
59. Which of the following is the major product of the following reaction?

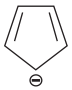


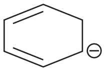
(a) 2- bromo -2- methylpentane
(b) 1 - bromo - 2- methylpentane
(c) 4- bromo -2- methylpentane
(d) 3- bromo -2- methylpentane

60. Negative charge of which of the following carbanions can not be resonance stabilized?

(a) 

(b) 

(c) 

(d) 

61. The increasing order of stability of the following free radicals is

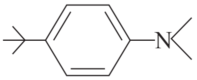
(a) $(CH_3)_2\dot{C}H < (CH_3)_3\dot{C} < (C_6H_5)_2\dot{C}H < (C_6H_5)_3\dot{C}$

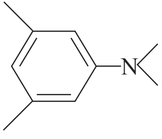
(b) $(C_6H_5)_3\dot{C} < (C_6H_5)_2\dot{C}H < (CH_3)_3\dot{C} < (CH_3)_2\dot{C}H$

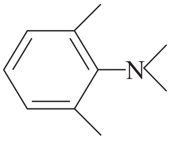
(c) $(C_6H_5)_2\dot{C}H < (C_6H_5)_3\dot{C} < (CH_3)_3\dot{C} < (CH_3)_2\dot{C}H$

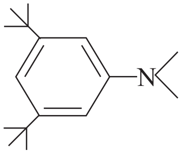
(d) $(CH_3)_2\dot{C}H < (CH_3)_3\dot{C} < (C_6H_5)_3\dot{C} < (C_6H_5)_2\dot{C}H$

62. Steric inhibition of resonance can be expected in:

(a) 

(b) 

(c) 

(d) 

63. Which one of the following resonating structures of 1-methoxy-1,3-butadiene is least stable?

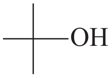
(a) $\overset{\ominus}{C}H_2 - CH = CH - CH = \overset{\oplus}{O} - CH_3$

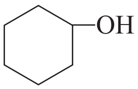
(b) $CH_2 = CH - \overset{\ominus}{C}H - CH = \overset{\oplus}{O} - CH_2$

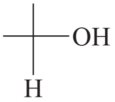
(c) $\overset{\ominus}{C}H_2 - \overset{\oplus}{C}H - CH = CH - O - CH_3$

(d) $CH_2 = CH - \overset{\ominus}{C}H - \overset{\oplus}{C}H - O - CH_3$

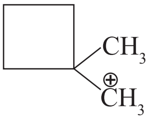
64. Which of the following will undergo dehydration most rapidly?

(a) 

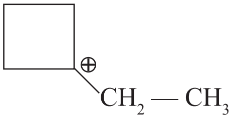
(b) 

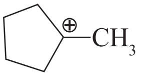
(c) 

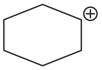
(d) 

65. 

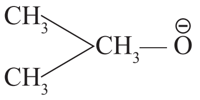
Rearrangement in this carbocation predominantly leads to:

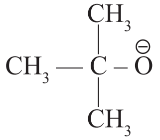
(a) 

(b) 

(c) 

(d) Both A and B

66. (I) $CH_3-\overset{\ominus}{O}$ (II) 

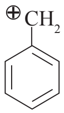
(III) 

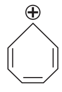
$CH_3 - \overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}} - \overset{\ominus}{O}$

Which of the following orders is correct for basic strength among these anions?

(a) III > II > I (b) I > II > III
(c) I > III > II (d) II > I > III

67. Which of the following represents the correct order of stability of the given carbocation?

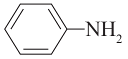
(I) 

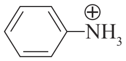
(II) 

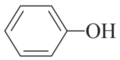
(III) 

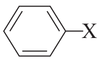
(a) II > III > I (b) I > II > III
(c) II > I > III (d) I > III > II

68. In which of the following, the resonance effect is not present?

(a) 

(b) 

(c) 

(d) 

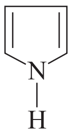
69. Amides are less basic than amines because:

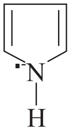
(a) The nitrogen has a full positive charge.
(b) The nitrogen does not have a lone pair of electrons.
(c) The carbonyl group withdraws electrons by resonance.
(d) The carbonyl group donates electrons by resonance.

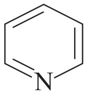
70. How many transition states and reaction intermediate are involved in S_N2 reactions respectively?

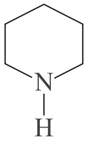
(a) 2, 1 (b) 1, 0
(c) 1, 1 (d) 0, 1

71. Which of the following is the strongest base in water?

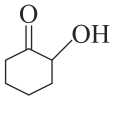
(a) 

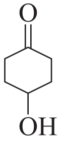
(b) 

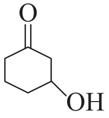
(c) 

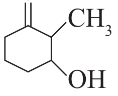
(d) 

72. Which is dehydrated to a maximum extent using conc. H_2SO_4?

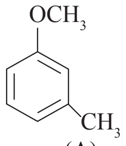
(a) 

(b) 

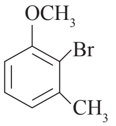
(c) 

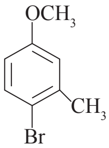
(d) 

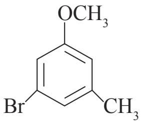
73. The major product obtained on the monobromination (with Br_2/ $FeBr_3$) of the following compound A is

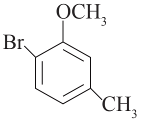


(A)

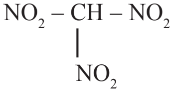
(a) 

(b) 

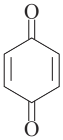
(c) 

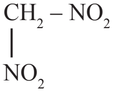
(d) 

74. Which of the following is having most acidic α-hydrogen?

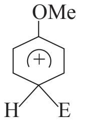
(a) 
$NO_2-\underset{\displaystyle NO_2}{\underset{|}{CH}}-NO_2$

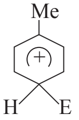
(b) CH_3NO_2

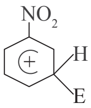
(c) 

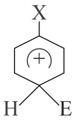
(d) 
$\underset{\displaystyle NO_2}{\underset{|}{CH_2}}-NO_2$

75. Which of the following complexes generated by the attack of an electrophile on benzene ring has lowest energy?

(a) 

(b) 

(c) 

(d) 

Brainteasers Objective Type Questions (Single choice only)

76. Consider the following structures

I. $CH_2=\overset{+}{C}H$ II. $CH_3-\overset{+}{C}H_2$

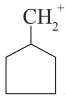
III. $CH_2=CH-\overset{+}{C}H_2$ IV. $C_6H_5-\overset{+}{C}H-C_6H_5$

The correct sequence of these carbocations in the decreasing order of their stability is

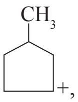
(a) I, II, III, IV (b) I, III, II, IV

(c) IV, II, III, I (d) IV, III, II, I

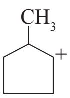
77. Arrange the following carbocations in order of increasing stability



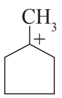
(A)



(B)



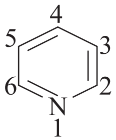
(C)



(D)

(a) A < B < C < D (b) D < B < C < A

(c) A < C < B < D (d) D < B < A < C

78. 

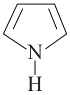
In pyridine electron density is maximum on

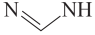
(a) 2 only (b) 3 and 4

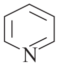
(c) 2 and 3 (d) 3 and 5

79. Acid strength of the conjugate acids of the following are:

(I) 

(II) 

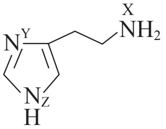
(III) 

(IV) 

(a) II > III > I > IV (b) II > IV > I > III

(c) II > I > III > IV (d) II > IV > I > III

80. The following compound has 3 types of nitrogens notified as X, Y and Z . Identify the most basic nitrogen.



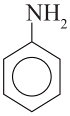
(a) X

(b) Y

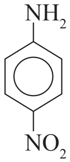
(c) Z

(d) all are equally basic.

81. Arrange the following in decreasing order of basicity

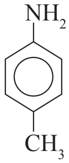


I



II

III



IV

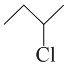
(a) IV > I > III > II

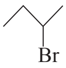
(b) IV > I > II > III

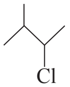
(c) IV > III > I > II

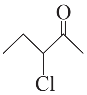
(d) I > II > III > IV

82. Arrange these compounds in order of increasing SN^2 reaction rate

(1) 

(2) 

(3) 

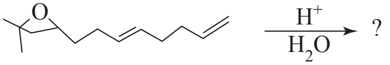
(4) 

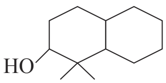
(a) $3 < 1 < 2 < 4$
(b) $3 < 2 < 1 < 4$
(c) $4 < 3 < 1 < 2$
(d) $2 > 3 > 1 > 4$

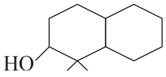
83. The correct order of increasing basic nature for the bases NH_3, CH_3NH_2, and $(CH_3)_2NH$ is

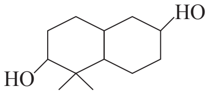
(a) $CH_3NH_2 < NH_3 < (CH_3)_2NH$
(b) $(CH_3)_2NH < NH_3 < CH_3NH_2$
(c) $NH_3 < CH_3NH_2 < (CH_3)_2NH$
(d) $CH_3NH_2 < (CH_3)_2NH < NH_3$

84. Select the product formed in this reaction



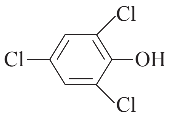
(a) 

(b) 

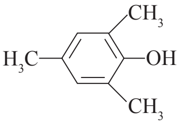
(c) 

(d) none of these

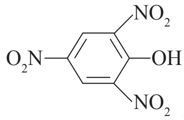
85. Rank the following compounds in order of increasing acidity



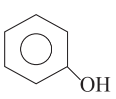
(1)



(2)



(3)



(4)

(a) $2 < 3 < 1 < 4$
(b) $1 < 2 < 3 < 4$
(c) $3 < 1 < 2 < 4$
(d) $2 < 4 < 1 < 3$

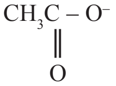
86. Consider the acidity of the carboxylic acids

(i) PhCOOH
(ii) o-$NO_2C_6H_4COOH$
(iii) p-$NO_2C_6H_4COOH$
(iv) m-$NO_2C_6H_4COOH$

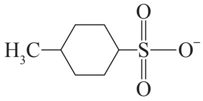
which of the following order is correct?

(a) i > ii > iii > iv
(b) ii > iv > iii > i
(c) ii > iv > I > iii
(d) ii > iii > iv > i

87. The decreasing order of nucleophilicity among the nucleophiles

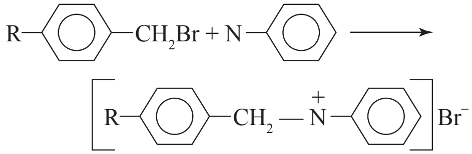
(1) 

$CH_3\underset{\underset{O}{\|}}{C}-O^-$

(2) CH_3O^-
(3) CN^-
(4) 

(a) 1, 2, 3, 4
(b) 4, 3, 2, 1
(c) 2, 3, 1, 4
(d) 3, 2, 1, 4

88. The reaction,



is influenced by the hyperconjugative effect of group R. Now if R sequentially is

I. CH_3
II. C_2H_5
III. $(CH_3)_2CH$
IV. $(CH_3)_3C$

The increasing order of speed of the above reaction shall be in the sequence

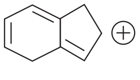
(a) I, IV, II, III
(b) I, II, III, IV
(c) I, III, II, IV
(d) IV, I, II, III

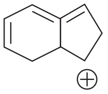
89. The correct order of decreasing acidity of the acids given below is

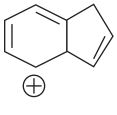
1. $Cl_3CCH = CH - CH_2 - COOH$
2. $H_3CCH = CH - CH_2 - COOH$
3. $Cl_3CCH = CH - COOH$
4. $H_3CCH_2CH_2CH_2COOH$

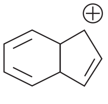
(a) $1 > 3 > 2 > 4$
(b) $3 > 1 > 2 > 4$
(c) $3 > 4 > 1 > 2$
(d) $3 > 1 > 4 > 2$

90. Which carbocation is the most stabilized?

(a) 

(b) 

(c) 

(d) 

91. $CH_3Br + Nu^- \rightarrow CH_3 - Nu + Br^-$

The decreasing order of the rate of the above reaction with nucleophiles (Nu^-) a to d is

[Nu^- =
(a) PhO^-
(b) AcO^-
(c) HO^-
(d) CH_3O^-]

(a) d > c > a > b
(b) d > c > b > a
(c) a > b > c > d
(d) b > d > c > a

92. Consider the dehydration of 2- methyl -1- propanol. Which of the following carbocations results when a hydride shift occurs in this mechanism?

(a) $(CH_3)_2C^+CH_3$
(b) $CH_3CH_2CH^+CH_3$
(c) $(CH_3)_2CHCH_2^+$
(d) none of these

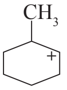
93. The correct order of increasing acid strength of the compound

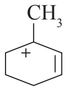
(a) CH_3O_2H
(b) $MeOCH_2CO_2H$
(c) CF_3CO_2H
(d) $(Me)_2 – CO_2H$

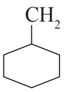
is

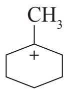
(a) b < d < a < c
(b) d < a < c < b
(c) d < a < b < c
(d) a < d < c < b

94. Consider the following carbocations

(I)


(II)


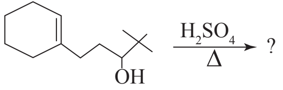
(III)


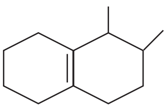
(IV)


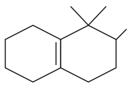
Which of the following is the correct ranking from least stable to most stable?

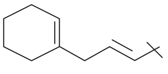
(a) II < IV < I < III
(b) III < I < II < IV
(c) III < I < II < IV
(d) I < II < III < IV

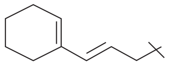
95. Here the major product for the reaction is?=



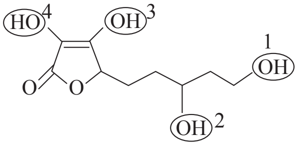
(a)


(b)


(c)


(d)


96.

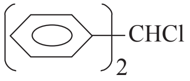


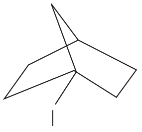
Which of these - OH groups is most acidic?

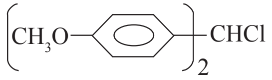
(a) OH 1
(b) OH 2
(c) OH 3
(d) OH 4

97. The following substrates with respect to their reactivity toward S_N1 in decreasing order can be given as:

(I) $(CH_3)_3 C – Cl$,

(II)


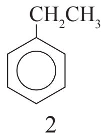
(III)


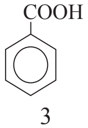
(IV)


(a) III > I > II > IV
(b) IV > II > I > III
(c) II > III > IV > I
(d) I > II > III > IV

98. Which will undergo Friedal–Craft alkylation reaction?


1

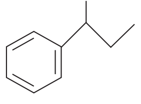

2

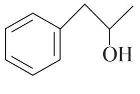

3

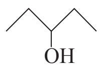

4

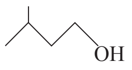
(a) 1 and 3
(b) 2 and 4
(c) 1 and 2
(d) 1,2 and 4

99. Four structures (1) – (4) of different alcohols are given below:

(1)


(2)


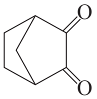
(3)


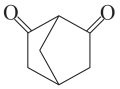
(4)


The order of facility, from fastest to slowest, of acid catalysed dehydration will be

(a) 2 > 1 > 3 > 4
(b) 1 > 2 > 3 > 4
(c) 4 > 3 > 2 > 1
(d) 2 > 3 > 4 > 1

100. Which of the following compound would you expect to be strongest carbon acid?

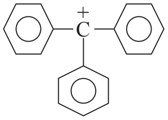
(a) 

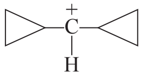
(b) 

(c) $CH_2(CO_2Et)_2$

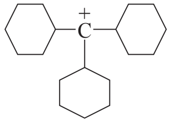
(d) $CH_3COCH_2COOC_2H_5$

101. Which one among the following carbocation has the longest half -life?

(a) 

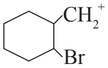
(b) 

(c) $(CH_3)_2\overset{\oplus}{C}H$

(d) 

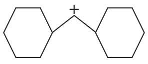
102. The correct decreasing order of stability of the following carbocations is given as

$F_3CCH_2^+$ (1)



(2)

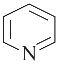
$Cl_3C\overset{+}{C}HCH_3$ (3)

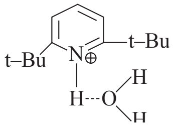


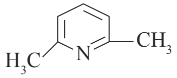
(4)

(a) 4 > 3 > 2 > 1
(b) 4 > 2 > 3 > 1
(c) 3 > 4 > 2 > 1
(d) 3 > 2 > 4 > 1

103. Which of the following is least basic?

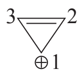
(a) 

(b) 

(c) 

(d) $(CH_3)_2NH$

104.



In this cation, π electron densiy is more

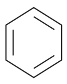
(a) C3
(b) C2
(c) C1
(d) π - electron -density is same on each C- atom.

105. Arrange these groups in decreasing order of their electron - donating power in resonance

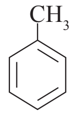
- OH (I), $-O-CO-CH_3$ (II), $-NH_2$ (III), NO_2 (IV)

(a) III > I > II > IV
(b) II > I > III > IV
(c) III > II > I > IV
(d) I > III > II > IV

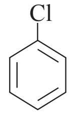
106. Identify the correct order of reactivity in electrophilic substitution reactions of the following compounds:



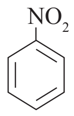
I



II



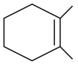
III



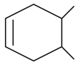
IV

(a) I > II > III > IV
(b) IV > III > II > I
(c) II > I > III > IV
(d) II > III > I > IV

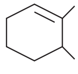
107.



(I)



(II)

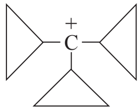


(III)

Which of the following orders is correct for the ease of electrophile addition on these alkenes?

(a) III > II > I
(b) I > II > III
(c) III > I > II
(d) I > III > II

108. Consider the following carbocations and arranged them in the increasing order of their stability:

(1) 

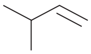
(2) $CH_3-\overset{+}{C}H-CH_3$

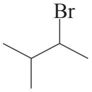
(3) $C_6H_5-\overset{+}{C}H_2$

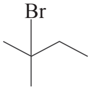
(4) $C_6H_5-\overset{+}{C}H-C_6H_5$

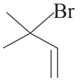
(5) $CH_3-CO-\overset{+}{C}H_2$

(a) 5 < 2 < 3 < 4 < 1
(b) 5 < 3 < 2 < 4 < 1
(c) 5 < 1 < 2 < 4 < 3
(d) 3 < 2 < 4 < 1 < 5

109.  $\xrightarrow{HBr}$? The product are

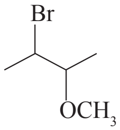
(a) 

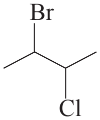
(b) 

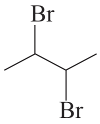
(c) 

(d) Both A and B

110. 

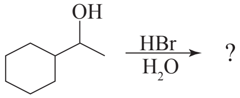
(a) 

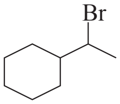
(b) 

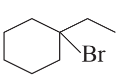
(c) 

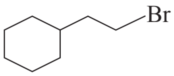
(d) All of these

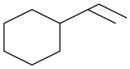
111. When 1- cyclohexlethanol is treated with concentrated aqueous HBr, the major product is



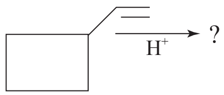
(a) 

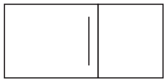
(b) 

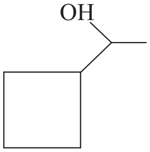
(c) 

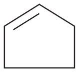
(d) 

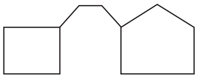
112. The major product of the reaction is

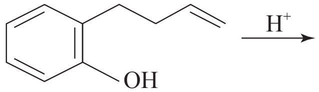


(a) 

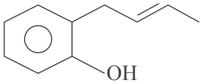
(b) 

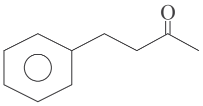
(c) 

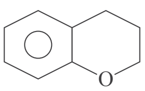
(d) 

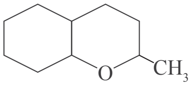
113. 

P; then P is

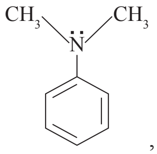
(a) 

(b) 

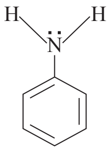
(c) 

(d) 

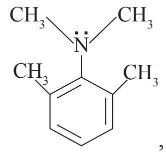
114. Arrange the following amines in the order of their decreasing basicity. Justify your answer.



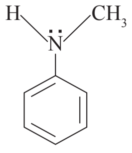
, (1)



, (2)

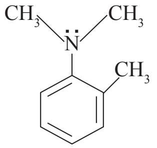


, (3)



(4)

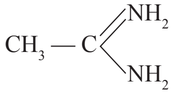
and



(5)

(a) 3 > 1 > 5 > 4 > 2 (b) 3 > 5 > 1 > 4 > 2
(c) 3 > 4 > 1 > 5 > 2 (d) 3 > 1 > 5 > 2 > 4

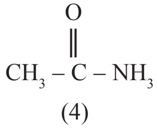
115. The correct order of basicity of the following compound is



(1)

$CH_3CH_2NH_2$
(2)

$(CH_3)_2NH$
(3)

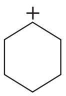


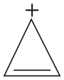
$CH_3-\overset{\overset{O}{\|}}{C}-NH_3$
(4)

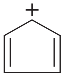
CH_5CN
(5)

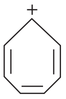
(a) 2 > 1 > 3 > 4 > 5 (b) 1 > 3 > 2 > 4 > 5
(c) 3 > 1 > 2 > 5 > 4 (d) 1 > 3 > 2 > 5 > 4.

116. The stability of the following carbocations decreases in the order

(1) 

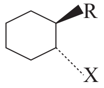
(2) 

(3) 

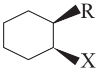
(4) 

(a) 4 > 1 > 2 > 3 (b) 4 > 2 > 3 > 1
(c) 4 > 3 > 2 > 1 (d) 4 > 2 > 1 > 3

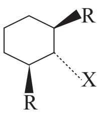
117.



(I)



(II)

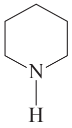


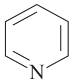
(III)

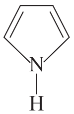
Ease of β-dehydrobromination among these substrates under the treatment of strong base will be in the order as

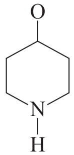
(a) I > II > III (b) III > II > I
(c) II > I > III (d) II > III > I

118. In the following compounds, the order of basicity is:


(I)

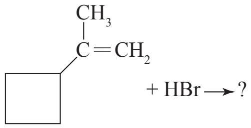

(II)

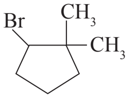

(III)

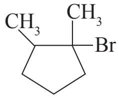

(IV)

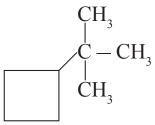
(a) I > IV > II > III (b) II > I > IV > III
(c) III > I > IV > II (d) IV > I > III > II.

119. The major product are



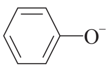

(a)


(b)


(c)

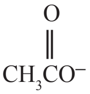
(d) Both a and b

120. Which of the following order of decreasing nucleophilcity in an aqueous solution?


(1)

CH_3OH (2)

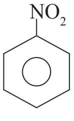
HO^- (3)

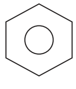

$CH_3\overset{\overset{\displaystyle O}{\|}}{C}O^-$ (4)

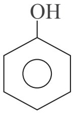
CH_3S^- (5)

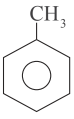
(a) 1 > 2 > 3 > 4 > 5 (b) 5 > 4 > 3 > 2 > 1
(c) 5 > 3 > 1 > 4 > 2 (d) 5 > 1 > 3 > 2 > 4

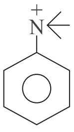
121. Arrange the following compounds in the order of increasing tendency to undergo electrophillic substitution.


(1)


(2)

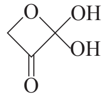

(3)

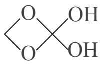

(4)

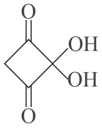

(5)

(a) 5 < 1 < 2 < 4 < 3 (b) 3 > 2 > 1 > 4 > 5
(c) 1 > 2 > 5 > 3 > 4 (d) 5 < 1 < 4 < 2< 3

122.


(I)

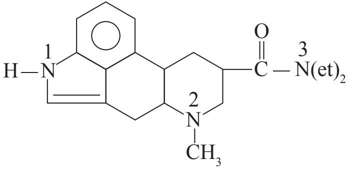

(II)


(III)

Ease of dehydration among these compounds will be in the order as:

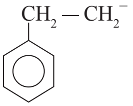
(a) II > I > III (b) I > II > III
(c) II > III > I (d) I > III > II

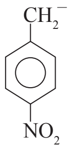
123. Which nitrogen atom in LSD is most basic?

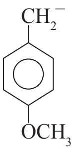


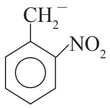
(a) 1 (b) 3
(c) 2 (d) All are equally basic

124. Arrange the following carbanions in the increasing order of stability.


(1)

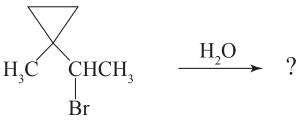

(2)

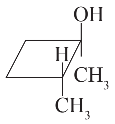

(3)

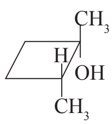

(4)

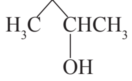
(a) 4 > 2 > 3 > 1 (b) 4 > 3 > 2 > 1
(c) 4 >1 > 2 > 3 (d) 4 > 2 > 1 > 3

125. Write the major products for the following reaction:



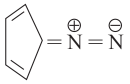

(a)


(b)

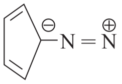

(c)

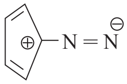
(d) Both a and b

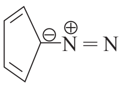
126.

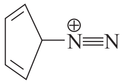


The most stable canonical structure of this molecule is

(a) 

(b) 

(c) 

(d) 

127. Consider the following carbanions:

(1) $CH_3—\overset{\ominus}{C}H_2$ (2) $CH_3{=}\overset{\ominus}{C}H$

(3) $CH{\equiv}\overset{\ominus}{C}$

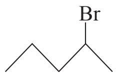
Correct order of stability of these carbanions in decreasing order is

(a) 1 > 2 > 3 (b) 2 > 1 > 3

(c) 3 > 2 > 1 (d) 3 > 1 > 2

128. Dehydrobromination (-HBr) of the following in increasing order is

(1) 

(2) 

(3) 

(a) 1 < 2 < 3 (b) 3 < 2 < 1

(c) 2 = 3 < 1 (d) 3 < 1 < 2

129. Arrange the following compounds in the order of increasing tendency to undergo electrophilic substitution

(1) Nitrobenzene (2) Benzene

(3) Phenol (4) Toluene

(5) Trimethyl phenyl ammonium ion

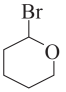
(a) 5 < 1 < 2 < 4 < 3

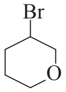
(b) 3 > 2 > 1 > 4 > 5

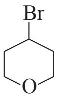
(c) 1 > 2 > 5 > 3 > 4

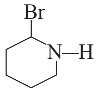
(d) 5 < 2 < 4 < 1 < 3

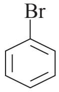
130.


(I)


(II)


(III)


(IV)


(V)

Ease of SN1 reactions among these compounds upon treatment with aq. NaOH will be in the order as:

(a) IV > I > III > II > V

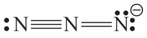
(b) I > II > III > IV > V

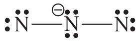
(c) I > IV > III > II > V

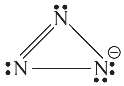
(d) V > IV > III > II > I

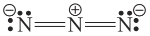
Decisive Thinking Objective Type Questions (One or more than one choice)

131. Which of the following Lewis structures are valid resonating structures for the azide ion?

(a) 
$:N{\equiv}N{=}\overset{\ominus}{\ddot{N}}:$

(b) 
$:\ddot{N}—\overset{\ominus}{\underset{..}{\ddot{N}}}—\ddot{N}:$

(c) 

(d) 
$\overset{\ominus}{:\ddot{N}}{=}\overset{\oplus}{N}{=}\overset{\ominus}{\ddot{N}}:$

132. Which of the following is/are polar?

(a) tert-Butyl free radical

(b) tert-Butyl carbocation

(c) tert-Butyl carbanion

(d) allyl cabanion

133. Which is/are correct about SN^1 reaction?

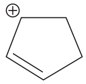
(a) Here reaction intermediate is carbocation.

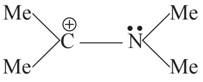
(b) It is favoured by polar solvents.

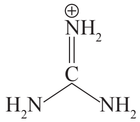
(c) It is favoured by stability of carbocation.

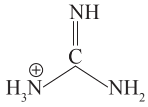
(d) Here complete inversion occurs.

134. In which of the following molecules positive charge is/are delocalized because of resonance?

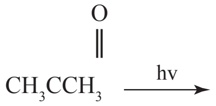
(a) 

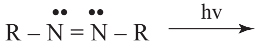
(b) 

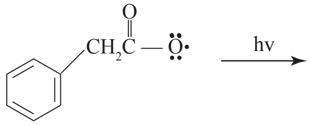
(c) 

(d) 

135. In which cases, free radicals can be formed by hemolytic fission?

(a) 
$CH_3\overset{\overset{\textstyle O}{\|}}{C}CH_3 \xrightarrow{hv}$

(b) 
$R-\ddot{N}=\ddot{N}-R \xrightarrow{hv}$

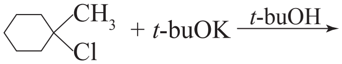
(c) 

(d) in all cases

136. In which case, the intermediate involved is/are correct?

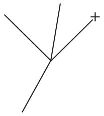
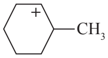
(a) Pinacol – pinacolone rearrangement – carbocation
(b) Hofmann's bromamide reaction – Nitrene
(c) Aldol condensation – carbocation
(d) Anti Markonikoff's addition of HBr to propene – Free radical.

137. Which of the given statement is/ are correct for the following reaction given below?

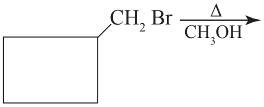


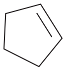
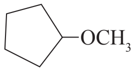
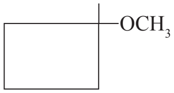
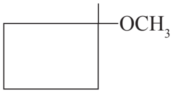
(a) Product is exocyclic alkene formed according to Hofmann.
(b) Product is endocyclic alkene formed according to Hofmann.
(c) Product is endocyclic alkene formed according to Saytzeff.
(d) Product is exocyclic alkene formed according to Saytzeff.

138. Which of the following carbocations rearrange to a more stable carbocation?

(a) 
(b) 
(c) 
(d) $C_6H_5CH_2^+$

139.

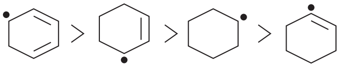
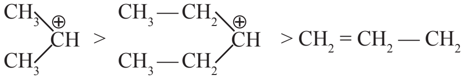


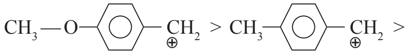
(a) 
(b) 
(c) 
(d) 

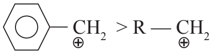
140. When a methyl radical is formed from CH_3Cl, select the correct statement:
(a) bond angle of 109°28' is retained
(b) number of sigma bonds is three
(c) carbon undergoes geometric change from tetrahedral to planar
(d) hybridization changes sp^3 to sp^2

141. Which of the following is/are not true about the cycloheptatrienyl free radical?
(a) It is an isolatable stable free radical.
(b) It is 4n + 2π electrons.
(c) It is an aromatic free radical.
(d) It is paramagnetic in nature.

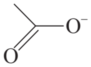
142. Which is /are the correct order /s of stability?

(a) 
(b) $CH_3-O-\dot{C}H_2 > CH_3-\dot{C}H_2 > CH_3-CO-\dot{C}H_2$
(c) 



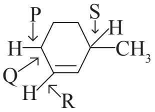
(d) 

143. Which of the following statements are correct?
(a) $\overset{-}{N}H_2$ is better nucleophile than NH_3 but latter (NH_3) is better nucleophile than NH_4^+
(b) $C_6H_5O^-$ is better nucleophile than



(c) OH^- is better nucleophile than SH^- and H_2O, but H_2O is better nucleophile than H_3O^+
(d) ClO^- is weaker nucleophile than ClO_4^-

144. Which of the following σ- bonds can participate in hyperconjugation?

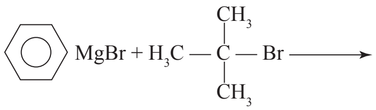
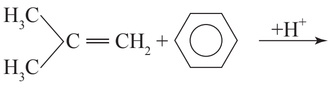


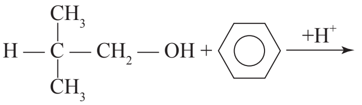
(a) P (b) Q
(c) R (d) S

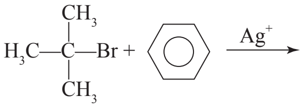
145. $-CX_3$ group is associated with
(a) Meta- directing
(b) Ring deactivation
(c) Increasing acidic
(d) Increase of stability of carbocation

146. Which of the followign group can participate in resonance with any group?
(a) $-\overset{\oplus}{N}H_3$ (b) $-\overset{\oplus}{C}H_2$
(c) –NO (d) $-\overset{\oplus}{N}-\overset{\ominus}{O}$

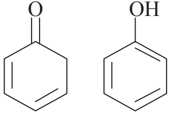
147. Which of the following reactions can be used to prepare t-butylbenzene?

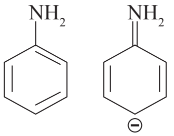
(a) 
(b) 

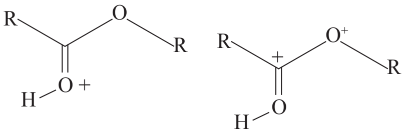
(c) 

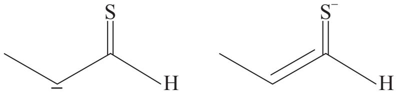
(d) 

148. Which of the following is/are incorrect relation between given pairs?

(a)  = Tautomers

(b)  = Resonance

(c)  = Tautomers

(d)  = Resonance

149. Which is/are correctly linked here?

List I	**List II**
(a) E_1Cb	Carbanion formation
(b) E_2	Stereo specific
(c) S_N1	Presence of non -polar solvents
(d) E_1	Carbocation formation

150. Anti-Markownikoff's rule is/are not followed in:

(a) $(CH_3)_2C= C(CH_3)_2 \xrightarrow{\text{HBr /peroxide}}$

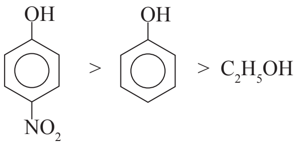
(b) $CH_3CH = C(CH_3)_2 \xrightarrow{\text{HBr /peroxide}}$

(c) $PhCH =CHCH_3 \xrightarrow{\text{DBr /peroxide}}$

(d) $(CH_3)_2C =CH_2 \xrightarrow{\text{DBr /peroxide}}$

151. Which of the following correctly represent the acidic strength of given acids?

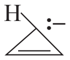
(a) $H_2O > CH_3OH > C_2H_5OH$

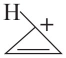
(b) 

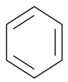
(c) $CH_2FCOOH > CH_2NO_2COOH$

(d) $CH_3COOH > CH_3CH_2OH$

152. In which of the following compounds resonance lead to stability of the compound?

(a) 

(b) 

(c) 

(d) $CH = CH – CH = CH_2$

153. Correct order of basic strength of given amines is

(a) $Me_3N > Me_2NH > Me–NH_2 > NH_3$ (Gas phase)

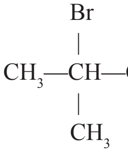
(b) $MeNH_2 > \Phi - NH_2 > \Phi_2 NH > (Me)_2NH$

(c) $Me_2NH > MeNH_2 > Me_3N > NH_3$ (Protic solvent)
2° 1° 3°

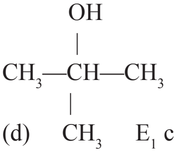
(d) $Et_2NH > Et_3H > EtNH_2 > NH_3$ (Protic solvnt)
2° 3° 1°

154. Which of the following is/are incorrectly matched

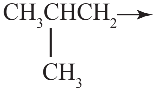
(a) $CH_3 – CH_2 – CH_2– {}^{\oplus}N(CH_3)_3\ {}^{\ominus}OH$.$E_2$ reaction

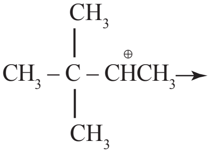
(b)  $CH_3\underset{CH_3}{\overset{Br}{CH}}CH_3$ E_2 reaction

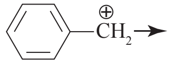
(c) $CH_3 – CH_2 – CH_2OH$, E_1 reaction

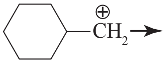
(d)  $CH_3\underset{CH_3}{\overset{OH}{CH}}CH_3$ E_1 cb reaction

155. In which cases free energy may decrease, if there can be some intramolecular rearrangement?

(a)  $CH_3\underset{CH_3}{CH}\overset{\oplus}{C}H_2 \rightarrow$

(b)  $CH_3 - \underset{CH_3}{\overset{CH_3}{C}} - \overset{\oplus}{C}HCH_3 \rightarrow$

(c) 

(d) 

156. Reaction involving carbanion formation is/are

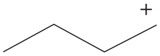
(a) Addition reaction of Grignard reagent

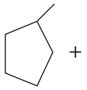
(b) Cannizaro's reaction

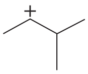
(c) Perkin's reaction

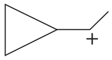
(d) Beckmann's rearrangement

157. Which of the following can rearrange to a more stable form?

(a) 

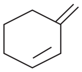
(b) 

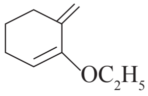
(c) 

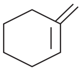
(d) 

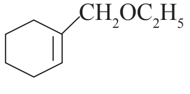
158. When 1 bromomethylcyclohexene undergoes solvolysis in ethanol, the major products formed are

1- bromomethylcyclohexene

(a) 

(b) 

(c) 

(d) 

159. The statements which are true among the following is

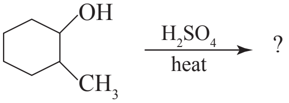
(a) The hybrid orbitals have a different shape from the orbitals from which they have been hybridized.

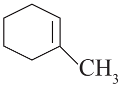
(b) The π-bond is stronger than a σ-bond as there are two regions of electron cloud, one above and one below the line joining the nuclei.

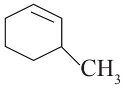
(c) σ-bond orbitals can be formed by the linear overlap of s- and p-orbitals, p- and p-orbitals.

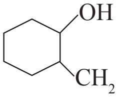
(d) Formation of covalent bonds by the overlap of orbitals is accompanied by the release of energy.

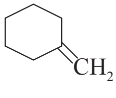
160. Which of the following alkenes are formed here?



(a) 

(b) 

(c) 

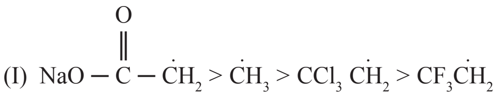
(d) 

Linked-Comprehension Type Questions

Comprehension 1

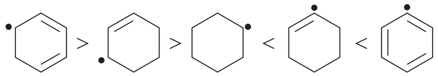
There are a number of reaction and rearrangement which involve reaction intermediate like free radical, carbocation , carbanion. These species are highly reactive but very unstable and short lived. The stability of carbocations and free radicales is enhanced by the resonance and hyper conjugation effect . Carbanion's stability is enhanced by resonance , electro withdrawing groups (-M, -I effects) while it decrease by electron realizing groups (+ N, +I effects).

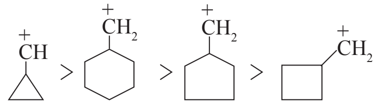
161. Which of the following represents the correct decreasing order of stability?

(I) 

$\mathrm{NaO-\overset{\overset{\displaystyle O}{\|}}{C}-\dot{C}H_2 > \dot{C}H_3 > CCl_3\dot{C}H_2 > CF_3\dot{C}H_2}$

(II) $\mathrm{CH_3{-}\dot{C}H_2 > CH_2=\dot{C}H > HC\equiv\dot{C}}$

(III) 

(IV) 

(a) I, II , III (b) I, II , IV
(c) II, III, IV (d) I, II, III, IV

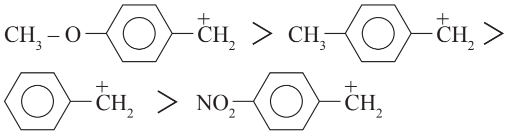
162. Which of the following is not correctly matched here?

Reaction Reaction	Intermediate Involved
(1) Favorskii Rearrangement	Carbanion
(2) Perkin's reaction	Carbacation
(3) Claisen condensation	Carbanion
(4) Pinacolpinacolone rearrangement	Carbocation
(5) Cannizaro's reaction	Carbocation

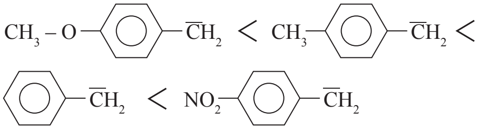
(a) 1, 5 (b) 2, 5
(c) 2, 3 (d) 1,3

163. Which of the following represents the correct decreasing order of stability?

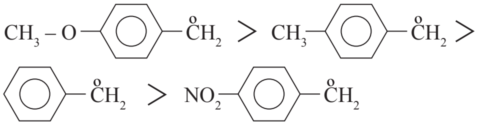
(I)



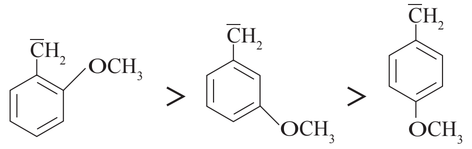
(II)



(III)



(IV)

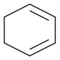


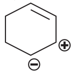
(a) I, II, III	(b) II, III, IV
(c) I, II , IV	(d) I, II, III, IV

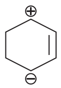
Comprehension 2

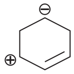
The various structures of a compound or ion having same arrangement of atoms but different electronic distribution are called resonating or canonical or contributing structures. The structures have same number of paired or unpaired electrons however the differ in their stabilities. A non polar structure is more stable than a polar structure. In case of polar structures stability is decided on the basis of number of covalent bonds, proper distribution of charges, octate state of atoms etc.

164. Which of the given structures does not represent resonance form of cyclo hexa 1,3 di- ene here?

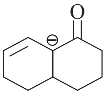
(a) 

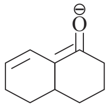
(b) 

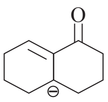
(c) 

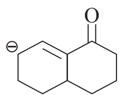
(d) 

165. Which of the following are resonating structures of each other?

(I) 

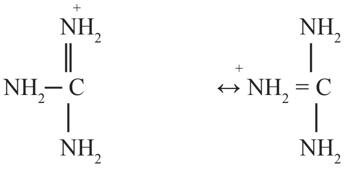
(II) 

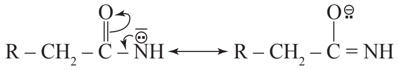
(III) 

(IV) 

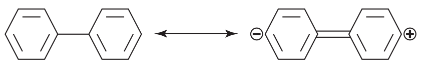
(a) I , II	(b) II, III
(c) I, II, III	(d) I, II, IV

166. Which of the following resonating structures are correct here?

(I) 

(II) 

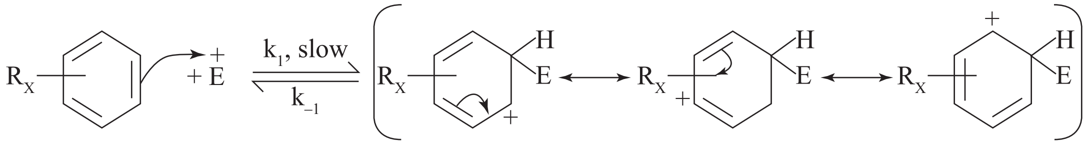
(III) 

(IV) 

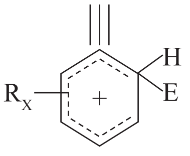
(a) I, II, III	(b) I, II, IV
(c) I, III, IV	(d) II, III, IV

Comprehension 3

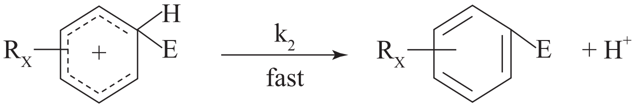
Aromatic compounds can easily show electrophilic substitution reactions due to the presence of pie electron clouds above and below the plane of aromatic ring. This ring can be easily attached by electrophiles due to high electro density. The mechanism of these reaction is common in general which can be given as follows:



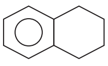
R_X = H or other substituents

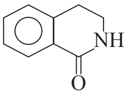


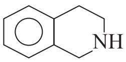
(resonance - stabilized
σ - complex or Wheland complex)

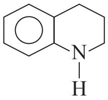


167. In which of the following compounds the rate of electrophillic substitution (Halogenation) is fastest?

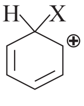
(a) 

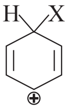
(b) 

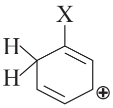
(c) 

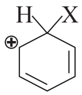
(d) 

168. Which of the following resonance structures is not a contributor to the cyclo hexa dienyl cation intermediate in the halogenation of benzene?

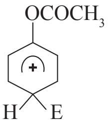
(a) 

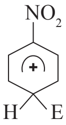
(b) 

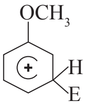
(c) 

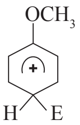
(d) 

169. Which of the following σ - complexes generated by the attack of an electrophile of benzene ring has lowest energy?

(a) 

(b) 

(c) 

(d) 

Comprehension 4

Nucleophilic substitution reactions occur with the attack of stronger nucloephile. The two main mechanisms for nucleoophilic substitution of alkyl halides are S_N1 and S_N2. These represent the extreme mechanisms of nucleophillic substitution, and some reactions involve mechanisms which lie somewhere in between the two. In both S_N1 and S_N2 reactions, the mechanisms involve the loss of the halide anion (X^-) from RX.

170. Which of the following are correctly linked with S_N1 reactions.

(1) Reactivity order for R — X is t° > s° > p°
(2) Occurs with complete inversion of configuration
(3) Rearrangement may take place.
(4) Strength of Na^- is important in determining rate
(5) Rate is affected by solvent polarity

(a) 1, 2, 5
(b) 1, 3, 5
(c) 1, 3, 4, 5
(d) 1, 2, 4, 5

171. For the reaction given below $(CH_3)_3CX + C_2H_5OH \rightarrow (CH_3)_3COC_2H_5$
If the concentration of C_2H_5OH is doubled while concentration of t°- butyl halide is kept constant by what factor will the rate of the reaction change?

(a) Decreases by a factor of 2
(b) Increases by a factor of 2
(c) Increases by a factor of 4
(d) Remains the same

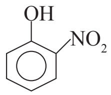
172. Which of the reagent will give more amount of substitution on reaction with 1- chloro propane?

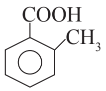
(a) $(CH_3)_3COK$ in DMSO
(b) CH_3CH_2OK in DMSO
(c) $(CH_3)_3COK$ in water
(d) CH_3CH_2OK in water

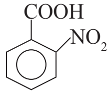
Comprehension 5

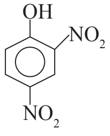
The acidic nature of carboxylic acids, phenol and basic nature of amines can be decided by considering the magnitudes of inductive and mesomeric effects caused by atoms or group attached to these species. Electron withdrawing groups (-I, -M) increase acidic nature but reduces basic nature while electron releasing groups (+I, +M) have just opposite trends.

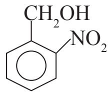
173. Which of the following is the correct decreasing order of acidic strength for following?

(1) 

(2) 

(3) 

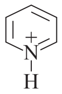
(4) 

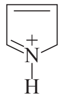
(5) 

(a) 3 > 4 > 2 > 1 > 5
(b) 3 > 2 > 4 > 1 > 5
(c) 3 > 4 > 1 > 2 > 5
(d) 3 > 5 > 4 > 2 > 1

174. Which of the following is the correct order of acidic nature?

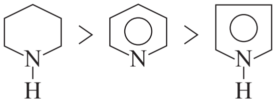
(I) H_2O
(II) H_3O^+

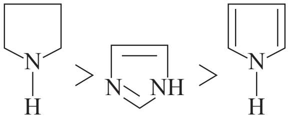
(III) 

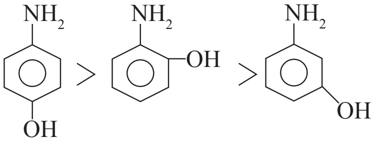
(IV) 

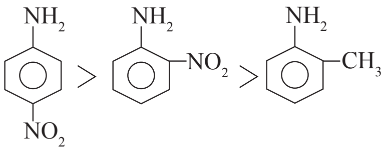
(a) II > IV > III > I
(b) IV > III > II > I
(c) IV > II > III > I
(d) II > III > IV > I

175. Which of the following order is not correct for basic nature?

(a)


(b)


(c)


(d)


Assertion-Reason Type Questions

In the following question two statements (Assertion) A and Reason (R) are given Mark

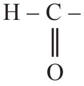
- (a) if A and R both are correct and R is the correct explanation of A;
- (b) if A and R both are correct but R is not the correct explanation of A;
- (c) A is true but R is false;
- (d) A is false but R is true,
- (e) A and R both are false;

176. (A): Tropylium cation is more stable than $(CH_3)_3C^{\oplus}$
(R): It is stabilized by both resonance effect and inductive effect.

177. (A): Solvolysis of $CH_2 = CHCH_2Cl$ is much faster compared to $(CH_3)_2CHCl$
(R): In $CH_2 = CHCH_2Cl$, solvolysis occurs through SN^2 mechanism.

178. (A): In SN^1 mechanism, the product with inversion of configuration is obtained in higher amount compared to the product with the retention of configuration.
(R): Front side attack of nucleophile is hindered due to the presence of leaving group in the vicinity.

179. (A): Benzene reacts with CO and HCl in presence of $AlCl_3$ to give benzaldehyde.
(R): The electrophillic reagent formed is



$H-\underset{\underset{O}{\|}}{C}-Cl$ and it is an electrophillic substitution reaction.

180. (A): Neopentyl chloride undergoes SN^2 reaction easily.
(R): It is a primary alkyl halide.

181. (A): Pyrrole is weaker base than its hydrogenated product pyrrolidine.
(R): Lone pairs of electrons on nitrogen are delocalized in pyrrole.

182. (A): The hydrogen of the $-CH_2$ group of 1,3-cyclopentadiene are acidic and this hydrocarbon is nearly 10^{30} times more acidic than ordinary alkanes.
(R): In cyclopentadienyl anion, all five carbons are equivalent as demonstrated by labeling experiments.

183. (A): PH_3 is stronger nucleophile than NH_3:
(R): PH_3 is stronger base than NH_3:

184. (A): In the transition state of SN^2 reaction the central carbon atom with three non reacting groups. Nucleophile and the leaving group remain approximately in the same plane.
(R): Back side attack of the nucleophile to substrate brings out this geometry.

185. (A): Phenoxide ion $(C_6H_5^- O^{\ominus})$ is more reactive than phenol towards electrophiles.
(R): Phenoxide ion is more stable than phenol.

186. (A): The Friedal craft alkylation of nitrobenzene gives meta alkylated nitrobenzene.
(R): Nitro groups are meta directing.

187. (A): $HC \equiv C^-$ is more stable than $H_2C = C^-$.
(R): $HC \equiv C^-$ has more s-character than $H_2C = C^-$.

188. (A): $\overset{\oplus}{C}F_3$ is more stable than $CF_3-\overset{|}{\underset{|}{C}}{}^{\oplus}$
(R): In $\overset{+}{C}F_3$ due to smaller size of F^- atom P – P overlaping shifts lone towards Gatom and Cf_3 group is highly electron withdrawing also.

189. (A): Pyrrole is a relatively non basic amine.
(R): In pyrrole, nitrogens is sp^3 hybridised.

190. (A): The carbocation $CF_3 - {}^{\oplus}CH_2$ is less stable than ${}^{\oplus}CF_3$.
(R): In case of $CF_3 - {}^{\oplus}CH_2$, CF_3 is strong electron withdrawing, therefore increases +ve charge whereas in ${}^{\oplus}CF_3$, lone pair of 'F' overlap with vacant p-orbital of carbon reducing +ve charge by pπ-pπ bonding or back bonding.

191. (A): In contrast to the six equivalent bonds in benzene, the C – C bonds naphthalene come in two lengths: $C_1 – C_2$ is considerably shorter than $C_2 – C_3$ bond.

(R): Out of the resonating structures of naphthalene $C_1 – C_2$ bond is double in two of the structure while $C_2 – C_3$ is double in one.

192. (A): CH_3OH is a nuclophile.

(R): CH_3OH forms sodium methoxide on reaction with NaH.

193. (A): The acidic strength of the following is $HF > H_2O > NH_3 > CH \equiv CH$

(R): More stable the conjugate base, of the corresponding acid, more the acidic strength.

194. (A): $C_6H_5N^{\oplus}(CH_3)_3$ undergoes 100% meta nitration although amino group is ortho para directing.

(R): Withdrawal of electrons from an aromatic ring always favours meta substitution.

195. (A): Heterolytic fission of propane forms ethyl carbocation and $^{\ominus}CH_3$ carbanion.

(R): Ethyl carbocation is stabilized by inductive effect and $^{\ominus}CH_3$ is most stable carbanion.

196. (A): Tertiary carbonium are generally formed more easily than primary carbonium ions.

(R): Hyperconjugative as well as inductive effect due to additional alkyl group stabilize tertiary carbonium ion.

197. (A): Benzyl carbanion is more stable than propyl carbanion.

(R): The carbon atom in carbanion is trivalent.

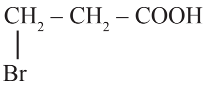
198. (A): Same number of electron pairs are present in resonance structures.

(R): Resonance structures differ in the location of electrons around the constituent atoms.

199. (A): In benzyne, two out of six carbon aoms are sp hybridized.

(R): Benzyne as one C ≡ C bond.

200. (A): When $CH_2 = CH – COOH$ is reacted with HBr, then



$$\underset{\displaystyle Br}{\underset{|}{CH_2}} – CH_2 – COOH$$

is obtained.

(R) : The carbocation formed has the stability order

$\overset{\oplus}{C}H_2 – CH_2COOH > CH_3–\overset{\oplus}{C}H– COOH$

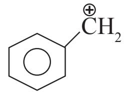
201. (A): The acetate ion is a weaker base than the ethoxide ion.

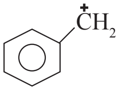
(R) : In carboxylic acids, the carbonyl group is polarized and so the carbon of the carbonyl group bears a +ve charge.

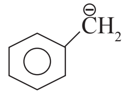
Matrix-Match Type Questions

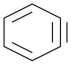
202. Match the following:

Column I

(a) 

(b) 

(c) 

(d) 

Column II

(p) sp^2- hybridisation
(q) Paramagnetic
(r) Diamagnetic
(s) sp^3 - hybridisation

203. Match the following:

Column I

(a) SN1 (b) SN2
(c) E1 (d) E2

Column II

(p) Carbocation formation
(q) Transition state
(r) Polar solvents
(s) Steric factors
(t) Electronic factors

204. Match the following:

List I

(a) Carbocation (b) Resonance
(c) NO_2 (d) Carbanion

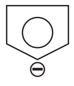
List II

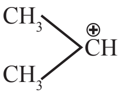
(p) delocalization of π e^- (q) coplanar
(r) pyramidal (s) –I , –R group

205. Match the following:

Column I

(a):CCl_2 (b) $CH_3 – O – \overset{\oplus}{C}H_2$

(c) 

(d) 

Column II
(p) Electron deficient
(q) Reimen- Tiemann reaction
(r) Resonance stabilized
(s) Aromatic in nature
(t) Stabilised by hyperconjugation

206. Match the following:

Column I
(a) Inductive effect
(b) Electromeric effect
(c) Resonance
(d) Hyperconjugation

Column II
(p) Delocalisation of π e^-
(q) Displacement of σ e^-
(r) α -H- atoms
(s) Influence stability of carbocation
(t) Complete transfer of π e^-

207. Match the following:

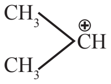
Column I (Type of reaction)
(a) SN^2
(b) SN^1
(c) E_2
(d) E_{1Cb}

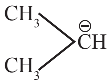
Column II (Phenomenon)
(p) Walden inversion
(q) carbanion intermediate
(r) Antiperiplanar configuration
(s) carbocation intermediate

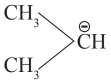
208. Match the following:

Column I

(a):CCl_2

(b) 

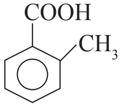
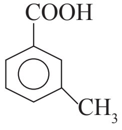
(c) 

(d) 

Column II
(p) sp^2- hybridized
(q) Electrophile by nature
(r) 6 α - H- atoms
(s) sp^3 -hybridised

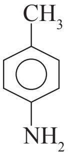
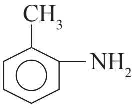
209. Match the following:

Column I

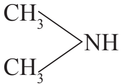
(a)  > 

Acidic Nature

(b) $CH_2X\ COOH > CH_3COOH$

(c)  > 

Basic Nature

(d)  > $(CH_3)_3N$

Basic nature

Column II
(p) + I, +R effect
(q) –I effect
(r) ortho effect
(s) Para effect
(t) Due to steric hinderance

210. Match the following:

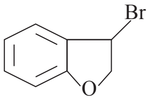
List I (Compounds/Ions)
(a) C_6H_5CHO
(b) $CH_3C \equiv CH$
(c) CN^-
(d) I^-

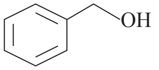
List II (Properties)
(p) gives precipitate with 2, 4- dinitro phenyl hydrazine
(q) gives precipitate with $AgNO_3$
(r) is a nucleophile
(s) is involved in cyanohydrin formation

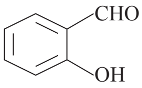
[IIT 2007]

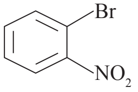
211. Match the following:

Column I

(a) 

(b) 

(c) 

(d) 

Column II.
(p) Nucleophilic substitution
(q) Elimination
(r) Neucleophilic addition
(s) Esterfication with acetic anhydride
(t) Dehydrogenation

The IIT-JEE Corner

212. In the following groups:
–OAc (I), –OMe (II)
$-OSO_2Me$ (III), $-OSO_2CF_3$ (IV)
the order of the leaving group ability is

[IIT 1997]

(a) I > II > III > IV (b) IV > III > I > II
(c) III > II > I > IV (d) II > III > IV > I.

213. The formation of cyanohydrin from a ketone is an example of

[IIT 1998]

(a) electrophilic addition
(b) nucleophillic addition
(c) nucleophilic substitution
(d) electrophilic substitution.

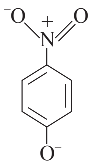
214. In the compound,
$CH_2 = CH - CH_2 - CH_2 - C \equiv CH$, the
$C_2 - C_3$ bond is of the type

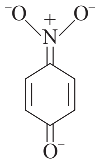
[IIT 1999]

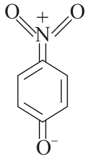
(a) $sp - sp^2$ (b) $sp^3 - sp^3$
(c) $sp - sp^3$ (d) $sp^2 - sp^3$

215. The most unlikely representation of resonance structures of p-nitrophenoxide ion is

[IIT 1999]

(a)


(b)


(c)


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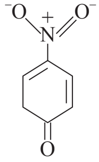


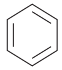
216. Which of the following has the highest nucleophilicity?

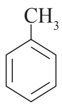
[IIT 2000]

(a) F^- (b) OH^-
(c) CH_3^- (d) NH_2^-

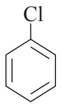
217. Identify the correct order of reactivity in electrophilic substitution reactions of the following compounds:

[IIT 2002]

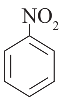

I



II



III

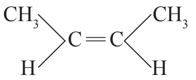


IV

(a) I > II > III > IV (b) IV > III > II > I
(c) II > I > III > IV (d) II > III > I > IV

218. Which of the following hydrocarbons has the lowest dipole moment?

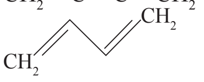
[IIT 2002]

(a)


(b) $CH_3 - C \equiv C - CH_3$
(c) $CH_3\ CH_2\ CH = CH_2$
(d) $CH_2 = CH - C \equiv CH$

219. Which of the following represents the given mode of hybridisation $sp^2 - sp^2 - sp - sp$ from left to right?

[IIT 2003]

(a) $CH_2 = CH - C \equiv CN$
(b) $CH \equiv C - C \equiv N$
(c) $CH_2 = C = C = CH_2$
(d)


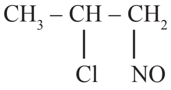
220. (I) 1,2-dihydroxy benzene
(II) 1,3-dihydroxy benzene
(III) 1,,4-dihydroxy benzene
(IV) Hydroxy benzene
The increasing order of boiling points of above mentioned alcohols is:

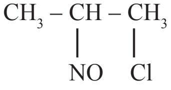
[IIT 2006]

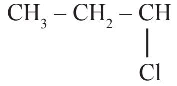
(a) I < II < III < IV (b) I < II < IV < III
(c) IV < I < II < III (d) IV < II < I < III

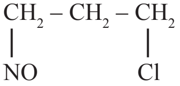
221. $CH_3 - CH = CH_2 + NOCl \rightarrow P$
Identify the adduct:

[IIT 2006]

(a)

$\begin{array}{ccccc} CH_3 & - & CH & - & CH_2 \\ & & | & & | \\ & & Cl & & NO \end{array}$

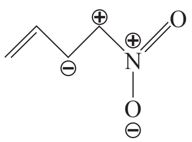
(b)

$\begin{array}{ccccc} CH_3 & - & CH & - & CH_3 \\ & & | & & | \\ & & NO & & Cl \end{array}$

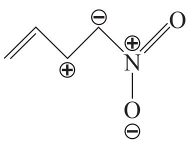
(c)

$\begin{array}{ccccc} CH_3 & - & CH_2 & - & CH \\ & & & & | \\ & & & & Cl \end{array}$

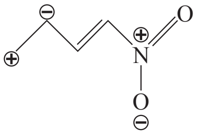
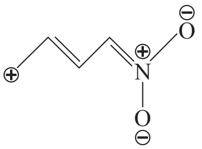
(d)

$\begin{array}{ccccc} CH_2 & - & CH_2 & - & CH_2 \\ | & & & & | \\ NO & & & & Cl \end{array}$

222. Among the following, the least stable resonance structure is

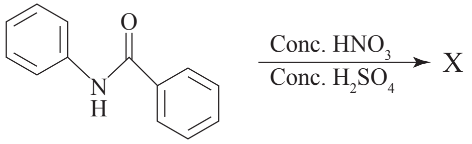
[IIT 2007]

(a)


(b)


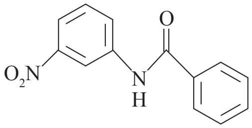
(c)  (d) 

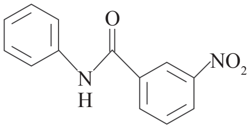
223. In the following reaction

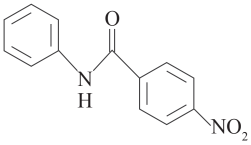


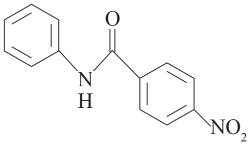
the structure of the major product 'X' is

[IIT 2007]

(a) 

(b) 

(c) 

(d) 

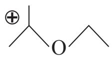
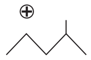
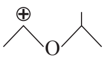
224. Hyperconjugation involves overlap of the following orbitals

(a) $\sigma - \sigma$ (b) $\sigma - p$

(c) $p - p$ (d) $\pi - \pi$

225. The correct stability order for the following species is

[IIT 2008]

(I) (II) (III) (IV)

(a) (II) > (IV) > (I) (III)

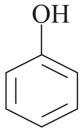
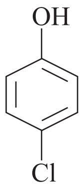
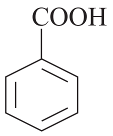
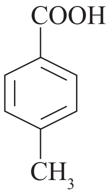
(b) (I) > (II) > (III) > (IV)

(c) (II) > (I) > (IV) > (III)

(d) (I) > (III) > (II) > (IV)

226. The correct acidity order of the following is

[2009]

(I) (II) (III) (IV)

(a) (III) > (IV) > (II) > (I)

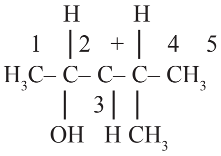
(b) (IV) > (III) >(I) > (II)

(c) (III) > (II) > (I) > (IV)

(d) (II) > (III) > (IV) > (I)

227. In the following carbocation, H / CH_3 that is most likely to migrate to the positively charged carbon is

[2009]



$$\underset{1}{H_3C}-\underset{OH}{\overset{H}{\underset{2}{C}}}-\underset{H}{\overset{+}{\underset{3}{C}}}-\underset{CH_3}{\overset{H}{\underset{4}{C}}}-\underset{5}{CH_3}$$

(a) CH_3 at C – 4

(b) H at C – 4

(c) CH_3 at C -2

(d) H at C – 2

228. The correct stability order of the following resonance structures is

[IIT 2009]

$H_2C = \overset{+}{N} = \overset{-}{N}$

(I)

$H_2C\text{-}\overset{+}{N} - \overset{-}{N}$

(II)

$H_2\overset{-}{C} - \overset{+}{N} \equiv N$

(III)

$H_2\overset{-}{C} - N = \overset{+}{N}$

(IV)

(a) (I) > (II) > (IV) > (III)

(b) (I) > (III) > (II) > (IV)

(c) (II) > (I) > (III) > (IV)

(d) (III) > (I) > (IV) > (II)

ANSWERS

Straight Objective Type Questions

1. (b) **2.** (a) **3.** (c) **4.** (d) **5.** (a) **6.** (c) **7.** (a) **8.** (b) **9.** (a) **10.** (a)
11. (c) **12.** (d) **13.** (a) **14.** (b) **15.** (c) **16.** (d) **17.** (b) **18.** (a) **19.** (a) **20.** (b)
21. (b) **22.** (b) **23.** (d) **24.** (b) **25.** (c) **26.** (d) **27.** (c) **28.** (b) **29.** (c) **30.** (a)
31. (b) **32.** (b) **33.** (a) **34.** (c) **35.** (d) **36.** (b) **37.** (b) **38.** (a) **39.** (b) **40.** (c)
41. (d) **42.** (b) **43.** (a) **44.** (c) **45.** (b) **46.** (d) **47.** (c) **48.** (c) **49.** (a) **50.** (b)
51. (c) **52.** (c) **53.** (d) **54.** (c) **55.** (b) **56.** (d) **57.** (c) **58.** (b) **59.** (a) **60.** (a)
61. (a) **62.** (c) **63.** (c) **64.** (a) **65.** (b) **66.** (a) **67.** (c) **68.** (b) **69.** (c) **70.** (b)
71. (d) **72.** (d) **73.** (b) **74.** (a) **75.** (a)

Brainteasers Objective Type Questions

76. (d) **77.** (a) **78.** (d) **79.** (b) **80.** (a) **81.** (a) **82.** (a) **83.** (c) **84.** (c) **85.** (d)
86. (d) **87.** (c) **88.** (b) **89.** (b) **90.** (a) **91.** (b) **92.** (a) **93.** (c) **94.** (c) **95.** (b)
96. (c) **97.** (b) **98.** (b) **99.** (b) **100.** (d) **101.** (b) **102.** (c) **103.** (a) **104.** (d) **105.** (a)
106. (c) **107.** (d) **108.** (a) **109.** (d) **110.** (d) **111.** (b) **112.** (c) **113.** (d) **114.** (b) **115.** (b)
116. (d) **117.** (c) **118.** (a) **119.** (c) **120.** (c) **121.** (a) **122.** (a) **123.** (c) **124.** (a) **125.** (d)
126. (c) **127.** (c) **128.** (a) **129.** (a) **130.** (a)

Decisive Thinking Objective Type Questions

131. (b), (d) **132.** (a), (b), (d) **133.** (a), (b), (c) **134.** (a), (b), (c) **135** (a), (b), (c)
136. (a), (b), (d) **137.** (b), (c), (d) **138.** (a), (b), (c) **139.** (a), (b), (c), (d) **140.** (b), (c), (d)
141. (a), (b), (c) **142.** (a), (b), (d) **143.** (a), (b), (c), (d) **144.** (a), (d) **145.** (a), (b), (c)
146. (b), (c), **147.** (b), (c), (d) **148.** (a), (b), (d) **149.** (a), (b), (d) **150.** (a), (b), (d)
151. (a), (b), (d) **152.** (b), (c) , (d) **153.** (a), (c), (d) **154.** (b), (c), (d) **155.** (a), (b), (d)
156. (a), (c) **157.** (a), (b) ,(d) **158.** (a), (b), (d) **159.** (a), (c), (d) **160.** (a), (b), (d)

Linked-Comprehension Type Questions

161. (b) **162.** (b) **163.** (a) **164.** (d) **165.** (d) **166.** (b) **167.** (d) **168.** (c) **169.** (d)
170. (b) **171.** (d) **172.** (b) **173.** (b) **174.** (c) **175.** (d)

Assertion-Reason Type Questions

176. (a) **177.** (c) **178.** (a) **179.** (a) **180.** (d) **181.** (a) **182.** (b) **183.** (c) **184.** (a) **185.** (b)
186. (d) **187.** (a) **188.** (a) **189.** (b) **190.** (a) **191.** (a) **192.** (b) **193.** (d) **194.** (a) **195.** (a)
196. (a) **197.** (b) **198.** (d) **199.** (a) **200.** (a) **201.** (b)

Matrix-Match Type Questions

202. (a) - (p, r), (b) - (p, q), (c) - (p, r, s), (d) - (p, r) **203.** (a) - (p, r, t), (b) - (q, s), (c) - (p, r, t), (d) - (q, s)
204. (a) - (q), (b) - (p), (c) - (s), (d) - (r) **205.** (a)- (p, q), (b) - (p), (c) - (r, s), (d) - (p, t)
206. (a) - (q, s), (b) - (t), (c) - (p, s), (d) - (p, r, s) **207.** (a) - (p), (b) - (s), (c) - (r), (d) - (q)
208. (a) - (p, q), (b) - (p, q, r), (c) - (r, s), (d) - (p, r) **209.** (a) - (p, r), (b) - (q), (c) - (p, s), (d) - (t)
210. (a)- (p, q, s), (b)- (q), (c)- (q, r, s), (d)- (q, r) **211.** (a) - (p, q, t), (b) - (p, s, t), (c) - (r, s), (d) - (p)

The IIT-JEE Corner

212. (b) **213.** (b) **214.** (d) **215.** (c) **216.** (c) **217.** (c) **218.** (b) **219.** (a) **220.** (c) **221.** (a)
222. (a) **223.** (c) **224.** (b) **225.** (d) **226.** (a) **227.** (d) **228.** (b)

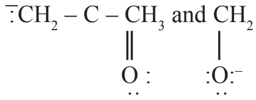
HINTS AND EXPLANATIONS

Straight Objective Type Questions

1. It is Hyperconjugation effect.

3. It will make the cabocation less stable because its high electronegativity withdraws electron density and makes the carbocation more positive. Increasing charge destabilizes ions. (Carbocation stability)

4.



$\overset{-}{:}CH_2 - \underset{\underset{O:}{\|}}{C} - CH_3$ and $CH_2 = \underset{\underset{:O:^-}{|}}{C} - CH_3$ are

These structures involve only movement of electrons but not of atoms and are resonating structures.

5. This is a case of hyperconjugation when there is benzylic or allylic group.
$(CH_3)_3C- > (CH_3)_2CH > CH_3CH_2 > CH_3$

8. $>C = O$ group is electron withdrawing hence $-CH_2$ group in between $-OH$ and $>C=O$ is acidic, so dehydration is maximum.

10. For 1°, 2°, 3° alkyl halides. The case of (i) SN_1 reaction increases as $1^o < 2^o < 3^o$.

11. $CH_3 - \overset{sp^3}{\underline{C}H_2} - OH$

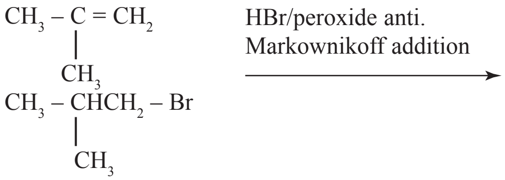
12. Being 3° carbocation, $(CH_3)_3C^+$ is the most stable.

14. C – H bond dissociation energy is the lowest where free radical produced is the most stable.

15. Carbanions have complete octet, that is, 8 electrons.

24. Strongest acid has the lowest pKa value.

25.

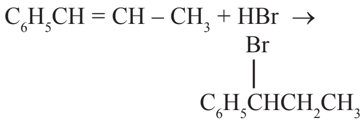


$$CH_3 - \underset{\underset{CH_3}{|}}{C} = CH_2 \xrightarrow{\text{HBr/peroxide anti. Markownikoff addition}} CH_3 - \underset{\underset{CH_3}{|}}{C}HCH_2 - Br$$

26. SN^1 reaction is favoured by heavy group on the carbon atom attached to halogens and nature of carbonium ion in substrate is
Benzyl > allyl > tertiary > secondary > primary > methylhalides

30. It has no effect on the reaction rate because HCl is not involved in the rate - determining step of this reaction (the formation of the carbocation) (Alcohol reaction.

31.



$$C_6H_5CH = CH - CH_3 + HBr \rightarrow C_6H_5\overset{\overset{Br}{|}}{C}HCH_2CH_3$$

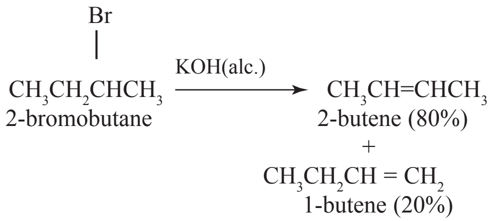
33. Due to resonance of electron pair in aniline, basic strength decreases. In benzylamine electron pair is not involved in resonance.

36.

$$(CH_3)_2CHCH_2CH_3 \xrightarrow{BR_2/\ HV\ 127^OC} (CH_3)_2C(Br)CH_2CH_3$$

38. Cl^- is the best leaving group among the given options.

42.



$$\underset{\text{2-bromobutane}}{CH_3CH_2\overset{\overset{Br}{|}}{C}HCH_3} \xrightarrow{KOH(alc.)} \underset{\text{2-butene (80\%)}}{CH_3CH{=}CHCH_3} + \underset{\text{1-butene (20\%)}}{CH_3CH_2CH = CH_2}$$

In elimination reaction of alkyl halide major product is obtained according to Saytzeff's rule, which states that when two alkenes may be formed, the alkene which is most substituted one predominates.

49. Reactivity of halides towards SN^1 mechanism is
Benzyl > allyl > 3° > 2° > 1°

53. This is the only tertiary carbocation; thus it is the most stable of the four ions.

56. It will follow Hoffmann elimination rule.

59. 2- bromo -2- methylpentane is the product that results when the Br atom bonds to the only tertiary C atom. Br is very selective and a significant percentage of the reaction mixture is this products.

61. The order of stability of free radicals is as follows:
Tertiary > secondary > primary

Brainteasers Objective Type Questions

77. The order of increasing stability is the following :
A < B < C < D
Carbocation (A) is least stable because it is primary.

80. Nitrogen -X is not involved in any resonance. Nitrogen -Y is sp^2 hybridized and is most electronegative among the given nitrogens, hence it could not be removed easily.

87. (c) strong bases are generally good nucleophiles.

91. $C_6H_5O^-$ possesses less nucleophilicity due to stabilized nature of phenoxide ion. CH_3OH is weaker acid than CH_3COOH:

92. $(CH_3)_2C^+CH_3$, a tertiary carbocation results when a hydride shift occurs in this reaction.

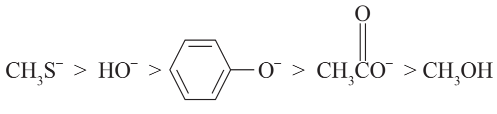
94. III < I < IV < II is the correct order from leas to most stable. The least stable corbocation is primary, I. Next in stability is the secondary carbocation, I, The remaining two cations are tertiary, but II is more stable because it is an allylic cation (Carbocations).

97. As the order of reactivity depends upon how easily the substrate can form carbocation and stability of carbocation.

114. In (3) the resonance of the electron pair on the nitrogen atom is hindered by the two ortho methyl groups. In (1) and (4) there is more electron density on the nitrogen atom. In (2), which is least basic, there is extensive resonance of the electron pair with the ring.

118. I is a saturated compound, there is no delocalization of nitrogen electron pair in the ring. in II, the oxygen atom is electronegative compound III is virtually non -basic.

120. Order of decreasing nucleophilcity in an aqueous solution is correct here



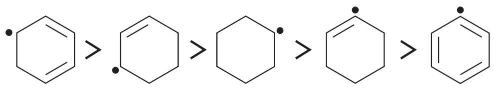
Decisive Thinking Objective Type Questions

133. Tert. Butyl carbanion (sp^3 hybridisation) is pyramidal.

141. None of A, B, C is correct because free radicals have an odd number of electrons and cannot obey Hückel's rule.

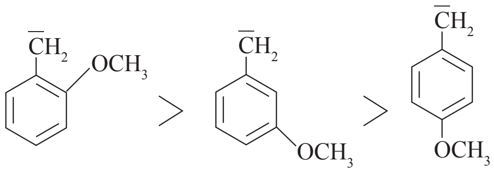
Linked-Comprehension Type Questions

161. As the correct order in 3rd case is



162. As in perkin's reaction carbanion is involved while in cannizaro's reaction C^+ is not formed.

163. As the correct order in 4th case is



171. As it is a S_N1 reaction so it is independent of the conc^n of the nucleophile:

172. As it is a S_N2 mechanism reaction so favoured by non-polar a protic solvent and more basic nucleophile.

Assertion-Reason Type Questions

181. In pyrrolidine lone pair of electron is not delocalized hence is more basic. In pyrrole lone of pair of electron is delocalized hence less basic.

187. $HC \equiv C^-$ has 50% s-character and $H_2C= C^-$ has 33% s-character. Stability of carbanions increases with an increase in the s-character at the carbanion. So $HC \equiv C^-$ is more stable than $H_2C = C^-$.

194. $N^+(CH_3)_3$ group acts as electron withdrawing group hence it is meta directing.

198. Resonance structures contain the same number of unpaired electrons.

The IIT-JEE Corner

212. Weaker bases are better leaving groups. The basic strength of the given groups is in the order :

–OMe (II) > –OAc (I) > $–OSO_2Me$ (III) > $–OSO_2CF_3$ (IV)

213. This is an example of nucleophilic addition to > C = O group.

214. If there is a choice, the numbering is done from the end nearer to the double bond that is,

$\overset{1}{C}H_2 = \overset{2}{C}H - \overset{3}{C}H_2 - \overset{4}{C}H_2 - \overset{5}{C} \equiv \overset{6}{C}H$. Thus,

$C_2 - C_3$ bond is of the type $sp^2 - sp^3$ hybridised

215. Among the given structures, the most unlikely structure is given in option (C) because in this structure N is shown to be pentavalent.

216. As the electronegativity of the atom decreases (F > O > N > C), its tendency to donate electron pair increases that is, nucleophilicity increases. Thus CH_3^- has the highest nucleophilicity.

217. CH_3^- group is activating while Cl^- and NO_2^- groups are deactivating. Therefore 2 should be most reactive, followed by 1.

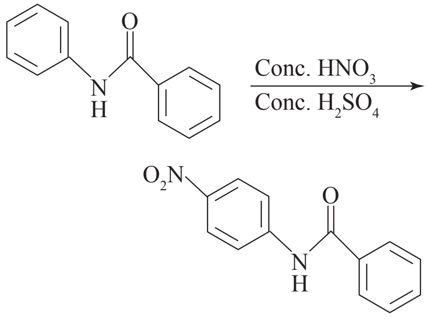
218. Linear symmetrical structures have zero dipole moment.

219. $\overset{sp^2}{H_2C} = \overset{sp^2}{CH} - \overset{sp}{C} \equiv \overset{sp}{C}N$

221. $\overset{+}{N}\overset{-}{O}Cl$ → MarkowniKoff's addition

222. As same charges are present at nearest position (less stable).

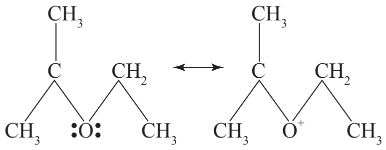
223.



Due to presence of lone pair of electron on nitrogen atom, it will activate the ring and it will stabilize intermediate cation at o- and p- positions.

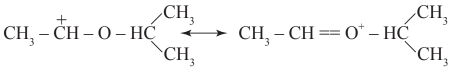
224. Hyperconjugation involves delocalization of σ and π bond orbitals that is, it undergoes $\sigma - \pi$ conjugation. The kind of declalization involving sigma bond orbital is known as hyperconjugation.

225.



Resonance stabilized having six hyperconjugating H-atom

III.

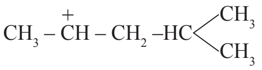


$CH_3-\overset{+}{C}H-O-HC(CH_3)_2 \longleftrightarrow CH_3-CH=O^+-HC(CH_3)_2$

Resonance stabilized

having three hyperconjugating H-atom

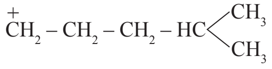
II.



$CH_3-\overset{+}{C}H-CH_2-HC(CH_3)_2$

five hyperconjungating H- Atom

IV.

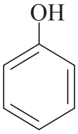


$\overset{+}{C}H_2-CH_2-CH_2-HC(CH_3)_2$

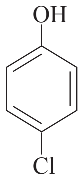
Two hyperconjugating H –atom

Stability of the following species depends upon the no. of α –hydrogen which can undergo hyperconjugation as well as resonance. Higher the no. of α-hydrogen, higher will be the stability of the compound.

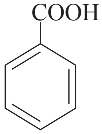
226.



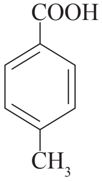
(I)



(II)



(III)

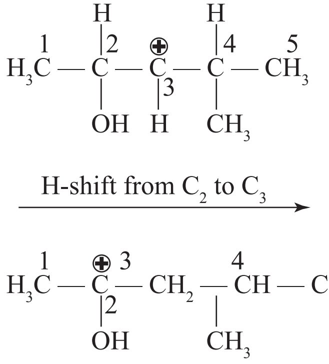


(IV)

pKa = 9.98 pKa = 9.38 pKa = 4.17 pKa = 4.37

Decreasing order of acidic strength III > IV > II > I

227.



$H_3C-CH(OH)-\overset{\oplus}{C}H-CH(CH_3)-CH_3 \xrightarrow{\text{H-shift from } C_2 \text{ to } C_3} H_3C-\overset{\oplus}{C}(OH)-CH_2-CH(CH_3)-CH_3$

(Driving force is conjungation fromoxygen)

228. It is on the basis of stability of resonating structures.

SUBJECTIVE SOLVED EXAMPLES

1. Which one is more soluble in diethyl ether - anhydrous $AlCl_3$ or hydrous $AlCl_3$? Explain in terms of bonding.

[IIT 2003]

Solution

Anhydrous $AlCl_3$ is more soluble in diethyl ether as the oxygen atom of ether donates its lone pair of electrons to vacant orbital of aluminium atom by forming coordinate bond. In hydrated $AlCl_3$ aluminium atom is not electron deficient as the oxygen atom of water molecule has already donated its lone pair of electrons to aluminium atom.

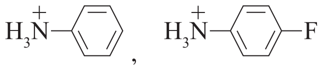
2. What effect should the following resonance of vinyl chloride have on its dipole moment?

$$CH_2 = CH - Cl \longleftrightarrow CH_2^- - CH_2 = Cl^+$$

Solution

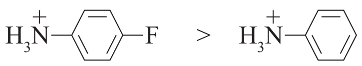
Here resonance decreases the dipole moment value for vinyl chloride. Here the positive charge on chlorine and negative charge on carbon atom apposes each other and diminish the electronegativity of chlorine atom which causes decrease of dipole moment.

3. Which of the following is more acidic and why?



[IIT 2004]

Solution



p-Fluoroanilinium ion is more acidic than anilinium ion due to the presence of strongly electronegative F. Recall that presence of an electron-attracting group increases acidity of the compound.

4. Arrange the following:

(i) Increasing reactivity towards HCN

CH_3CHO, CH_3COCH_3, HCHO,
$C_2H_5\ COCH_3$

Solution

As the number of carbon atoms increases the tendency to show nucleophillic addition decreases hence the order is given as:

$C_6H_5COCH_3 < CH_3COCH_3 < CH_3CHO <$ HCHO

(ii) n-butane, n-butanol, n-butyl chloride, isobutane in increasing order of boiling point.

Solution

Isobutane < n-butane < n-butyl chloride < n-butanol
Least More Dipole-dipole Due to
surface surface area attraction H-bonding
area & no attraction

As in alkanes boiling point are directly proportional to surface area and during branching surface area decreases.

(iii) Benzene, toluene, methoxybenzene, chlorobenzene in increasing order of reactivity towards sulphonation with fuming sulphuric acid.

Solution

Chlorobenzene < benzene < toluene < methoxy benzene

As in methoxy benzene OCH_3 group is highly ring activating due to +R effect, in toluene CH_3 group is ring activating due to +I effect while in chlorobenzene, chlorine atom is ring deactivating due to –I effect.

(iv) Increasing order of acid strength:

(I) $ClCH_2COOH$ (II) CH_3CH_2COOH
(III) $ClCH_2CH_2COOH$ (IV) $(CH_3)_2CHCOOH$
(V) CH_3COOH

[IIT 1991]

Solution

Acidic strength is favoured by electron attracting (–I) chlorine atom while decreased by electron releasing (+I) CH_3 groups so the correct order is $(CH_3)_2CHCOOH < CH_3CH_2COOH < ClCH_2CH_2COOH < CH_3COOH < ClCH_2COOH$

(v) Increasing reactivity in nucleophillic substitution reactions

$CH_3F, CH_3I, CH_3Br, CH_3Cl$

[IIT 1992]

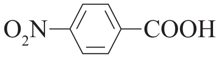
Solution

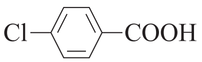
As leaving group tendency is inversely proportional to basicity in case of X^-. Hence the increasing order of basicities of X^- is $I^- < Br^- < Cl^- < F^-$.

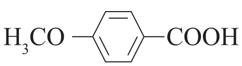
$CH_3F < CH_3Cl < CH_3Br < CH_3I$

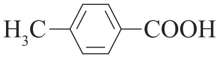
5. Match the Ka values

(a) Benzoic acid

(b) 

(c) 

(d) 

(e) 

Ka Values

(i) 3.3×10^{-5} (ii) 10.2×10^{-5}

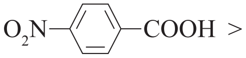
(iii) 30.6×10^{-5} (iv) 6.4×10^{-5}

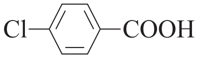
(v) 4.2×10^{-5}

[IIT 2003]

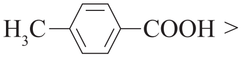
Solution

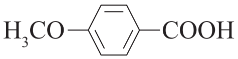
The correct order of acidic strength of the following acids is given as:

(b) 

(c) 

(a) Benzoic acid >

(e) 

(d) 

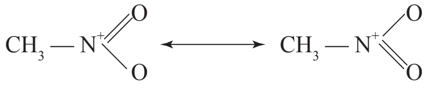
As higher the Ka value, more stronger is the acid, so Ka values

$$\underset{(iii)}{30.6 \times 10^{-5}} > \underset{(ii)}{10.2 \times 10^{-5}} > \underset{(iv)}{6.4 \times 10^{-5}} > \underset{(v)}{4.2 \times 10^{-5}} > \underset{(i)}{3.3 \times 10^{-5}}$$

6. For nitromethane molecule, write structure:

(i) Showing significant resonance stabilization

Solution



(ii) Indicating tautomerism.

Solution

$$\underset{\displaystyle O}{CH_3 - \overset{}{N} = O}\ \text{(with N} \downarrow \text{O)} \qquad CH_3 - N(\downarrow O) = OH$$

(nitro form) (aci-form)

7. Given reasons for the following:

(i) Carbon–oxygen bond lengths in formic acid are 1.23 Å and 1.36 Å and both the carbon-oxygen bonds in sodium formate have the same value i.e., 1.27 Å.

Solution

As in case of formic acid resonance does not exist so there are two types of C – O bonds while in sodium formate resonance exists as follows:

(ii) Phenyl group is known to exert negative inductive effect. But each phenyl ring in biphenyl ($C_6H_5 - C_6H_5$) is more reactive than benzene towards electrophillic substitution.

[IIT 1992]

Solution

Biphenyls are more reactive than benzene because in them one of the phenyl group acts as electron donor and the other one acts as electron acceptor.

(iii) Aryl halides are less reactive than alkyl halides towards nucleophillic reagents.

[IIT 1994]

Solution

Aryl halides fails to show nucleophillic substitution reactions under ordinary conditions as in them halogen atom acquires a double bond character with carbon atom and it is resonance stabilized as a result halogen atom becomes shorter and stronger so it can not be replaced easily by nucleophiles like –OH, NH_2 , CN.

(iv) $CH_2 = CH^-$ is more basic than $HC \equiv C^-$.

Solution

Ethyne is more acidic than ethene as in it carbon atom is sp-hybridised so it will have more s % (acidic nature ∝ s %)

(v) Normally, benzene gives electrophillic substitution reaction rather than electrophillic addition reaction although it has double bonds.

[IIT 1994]

Solution

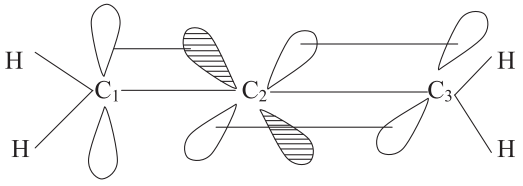
Benzene can easily give electrophilic substitution reaction but not electrophilic addition reaction as it resonance stabilized and have a stable benzene ring in the product.

8. Discuss the hybridisation of carbon atoms in allene (C_3H_4) and show the π-orbital overlaps.

[IIT 1999]

Solution

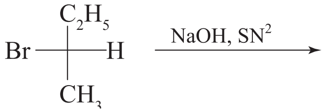
$\underset{sp^2}{CH_2} = \underset{sp}{C} = \underset{sp^2}{CH_2}$ (Allene) - hybrid state



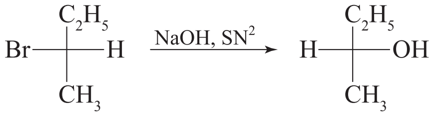
The π -bonds between C_1 and C_2 are perpendicular to that of C_2 and C_3 by πp - πp overlapping. Therefore, the hydrogen attached to C1 and those attached to C_2 are in different planes (i.e., perpendicular) σ - bonds between C_1 -C_2 and C_2 - C_3 are sp^2 - sp and sp- sp^2 overlapping on their axes.

9. Draw the stereochemical structures of the products in the following reactions:

(i)



Solution

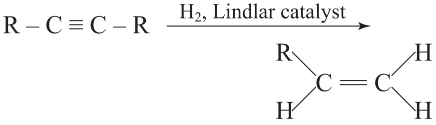


This example is according to Walden inversion.

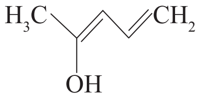
(ii) $R - C \equiv C - R \xrightarrow{H_2,\text{ Lindlar catalyst}}$

[IIT 1994]

Solution



10.

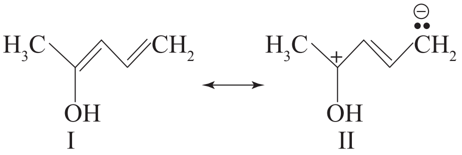


Write resonance structure of the given compound.

[IIT 2003]

Solution

Resonating structures are as follows:



CHAPTER 3

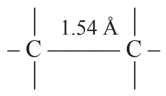
HYDROCARBONS

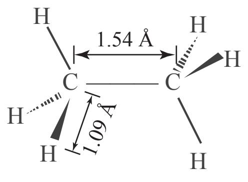
CHAPTER CONTENTS

Preparation, properties and reactions of alkanes: Homologous series, Physical properties of alkanes (melting points, boiling points and density); Combustion and halogenation of alkanes; Preparation of alkanes by Wurtz reaction and decarboxylation reactions.

Preparation, properties and reaction of alkenes and alkynes: Physical properties of alkenes and alkynes (boiling point, density and dipole moments); Acidity of alkynes; Acid catalysed hydration of alkenes and alkynes (excluding the stereochemistry of addition and elimination) ; Reactions of alkenes with KMnO$_4$ and ozone; Reduction of alkenes and alkynes; Reaction of alkenes with X$_2$, HX, HOX and H$_2$O (X = halogen); Addition reaction of alkynes Metal acetaldehye. Reaction of Benzene: Structure and aromaticity; Electrophilic substitution reactions; halogenation, nitration, sulphonation, Fiedel-Craft alkylation and acylation; Effect of o$^-$, m$^-$ and p- directing groups in monosubstituted benzenes and various level of multiple-choice questions.

ALKANES





ethane

- The general formula of alkanes is C_nH_{2n+2} and their main sources are petroleum, natural gas and coal.
- Alkanes are also known as parafins due to their less activity or almost inertness.
- In alkanes, C – C bond length is 1.54 Å and that of C – H bond is 1.11 Å. In them C – C bond energy is 80 kcal per mol and that of C – H bond is 97 kcal per mol.
- They are non-polar in nature.
- Alkanes show chain, position and conformational isomerism.

METHODS OF PREPARATION

By Wurtz Reaction

- Here alkyl halide is treated with sodium metal in presence of dry ether to give alkane. In place of sodium finely divided Ag, Cu, can also reuse here we take dry ether as wet ether gives rise to formation of alcohol.

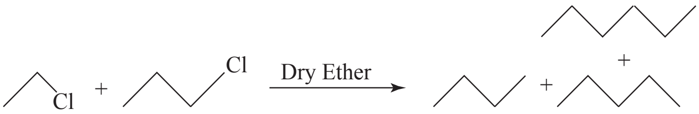
  $$R-X + 2Na + X-R \xrightarrow{\text{dry ether}} R-R + 2NaX$$

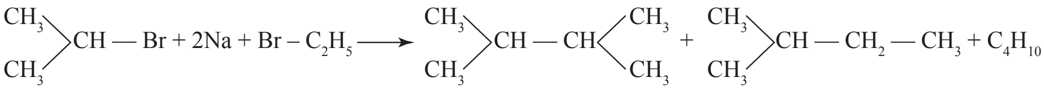
  If R is CH_3, product is C_2H_6 and if R is C_2H_5 product is C_4H_{10}

- If R is same only one alkane in formed but if 'R' is different, three alkanes are formed:

  $$R-X + 2Na + X-R' \xrightarrow[-2NaX]{\text{Dry ether}} R-R + R'-R' + R-R'$$

  For example,





$$(CH_3)_2CH-Br + 2Na + Br-C_2H_5 \longrightarrow (CH_3)_2CH-CH(CH_3)_2 + (CH_3)_2CH-CH_2-CH_3 + C_4H_{10}$$

Mechanism

Two mechanism have been proposed

(I) Free-Radical Mechanism which follows via generation of alkyl free-radical

Step-1 Generation of Free-Radical
Homolys is

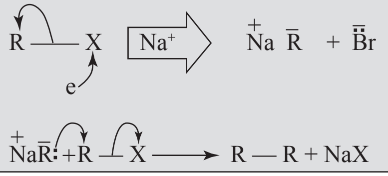
$$R \vdots\!- X + Na^{-} \longrightarrow R^{\cdot} + NaX$$

Step-2 Coupling between two Free-Radicals

$$R^{\cdot} + {}^{\cdot}R \longrightarrow R-R$$

(II) Ionic Mechanism

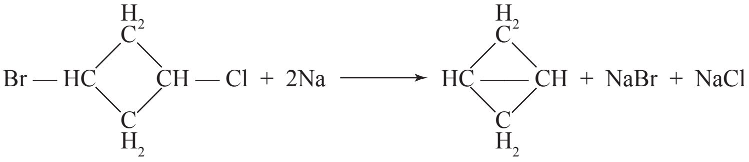
$$Na^{\cdot} \longrightarrow \overset{+}{Na} + e$$



$$R-X \xrightarrow{Na^+} \overset{+}{Na}\,\bar{R} + \bar{Br}$$

$$\overset{+}{Na}\bar{R}: + R-X \longrightarrow R-R + NaX$$

Example,



$$Br-HC(CH_2)_2CH-Cl + 2Na \longrightarrow HC(CH_2)_2CH + NaBr + NaCl$$

Yield : 93-96%

- **Limitation** This reaction can be used only when halides used are primary and secondary as incase of tertiary halide elimination occurs to give alkene. Here disproportion may also occur to give alkene due to which the amount of alkane is decreased.

  $C_2H_5\,I + Na \rightarrow \dot{C}_2H_5 + NaI$
  Ethyl Radical

  $2\dot{C}_2H_5 \rightarrow C_2H_4 + C_2H_6$

- **By Frankland Reaction** Here alkyl halide is treated with zinc dust in a close tube to prepare alkanes and rest is just like in Wurtz reaction.

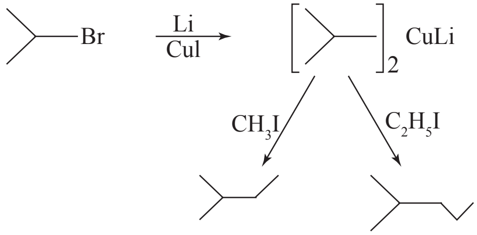
  $R - X + Zn + X - R \xrightarrow{\Delta} R - R + ZnX_2$

- **By Corey House Synthesis** It is suitable for the preparation of alkanes with odd number of carbon atoms.

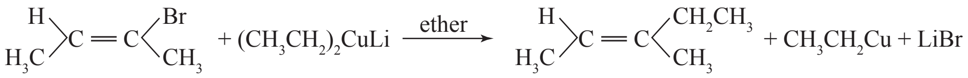
  $R - X \xrightarrow[\text{Ether}]{\text{Li}} R - Li \xrightarrow{\text{CuI}} R_2CuLi$
  Gillman's Reagent

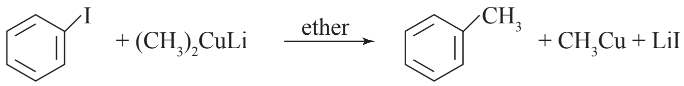
  $\xrightarrow{R' - X} R - R' + R - Cu + LiX$

  For example,

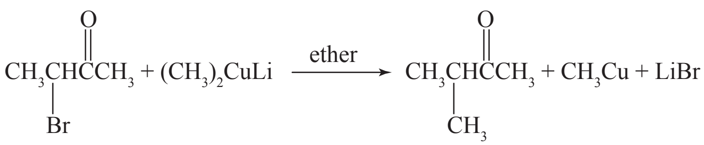


2-Methyl butane 2-Methyl pentane

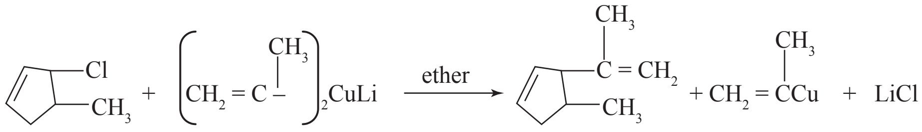




Gliman reagent can even replace halogens in compounds that contain other functional groups.



$$CH_3\underset{\underset{Br}{|}}{C}H\overset{\overset{O}{\|}}{C}CH_3 + (CH_3)_2CuLi \xrightarrow{\text{ether}} CH_3\underset{\underset{CH_3}{|}}{C}H\overset{\overset{O}{\|}}{C}CH_3 + CH_3Cu + LiBr$$



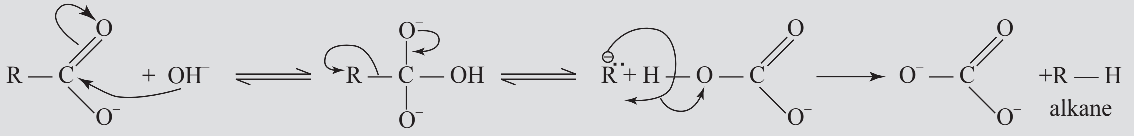
By Decraboxylation of Fatty Acids When anhydrous sodium salt of fatty acid is fused with soda lime (NaOH + CaO) a paraffin dry ether having one carbon atom less than the fatty acid is obtained.

$$RCCONa + NaOH(+CaO) \xrightarrow{Fuse} RH + Na_2CO_3$$

$$CH_3COONa + NaOH(+CaO) \xrightarrow{Fuse} CH_4 + Na_2CO_3$$

Sodium acetate

Mechanism



- **By Kolbe Synthesis** Sodium or potassium salts of carboxylic acid on electrolytic hydrolysis give alkanes at anode as follows:

$$2R - COONa \xrightarrow{\text{electrolytic hydrodlysis}} \underset{\text{at anode}}{R - R} + 2CO_2 + \underset{\text{at cathode}}{2NaOH + H_2} \downarrow$$

Mechanism

$2R.\ COOK \rightarrow 2R.COO^-$ + $2K^+$

Anode Cathode

$\downarrow$-2e $\downarrow$+2e

2R.COO 2K

$\downarrow$ $\downarrow+2H_2O$

$R—R + 2CO_2\uparrow$ $2KOH + H_2\uparrow$

For example, $2CH_3 - COONa \xrightarrow{\text{electrolytic hydrodlysis}} \underset{\text{at anode}}{H_3C - CH_3} + 2CO_2 + \underset{\text{at cathode}}{2NaOH + H_2} \uparrow$

$$\begin{matrix} CH_3COOK \\ + \\ C_2H_5COOK \end{matrix} \xrightarrow{\text{electrolytic hydrodlysis}} C_2H_6 + C_4H_{10} + C_3H_8 + 2KOH + H_2 \uparrow$$

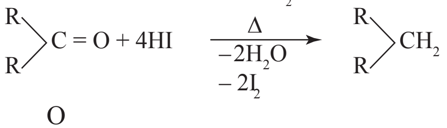
- Here pH increases during the reaction as strong bases are formed.
- If two different acid salts are used a mixture of three alkanes will be formed.
- It involves both ionic as well as free radical mechanism.
- CH_4 cannot be prepared by this method.

By the Reduction of R – OH, R – CHO, R – CO –R, R – COOH

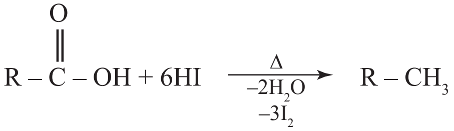
- **By Using HI and Red 'P' at 150 – 200°C**

(i) $R - OH + 2HI \xrightarrow{\Delta} R - H + H_2O + I_2$

(ii) $R - CH = O + 4HI \xrightarrow[\substack{-2H_2O \\ -2I_2}]{\Delta} R - CH_3$

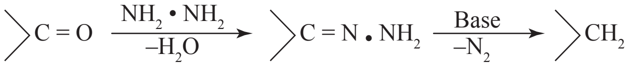
(iii)


$$R_2C = O + 4HI \xrightarrow[\substack{-2H_2O \\ -2I_2}]{\Delta} R_2CH_2$$

(iv)


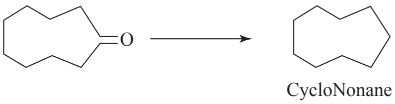
$$R - \overset{\overset{\displaystyle O}{\|}}{C} - OH + 6HI \xrightarrow[\substack{-2H_2O \\ -3I_2}]{\Delta} R - CH_3$$

By Wolf Kishner Reduction Here carbonyl compounds are reduced into alkanes by hydrazine and a base, here bases are sodamide, C_2H_5ONa etc., as follows:

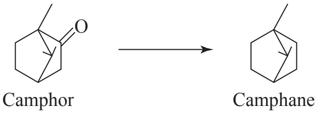


For example,

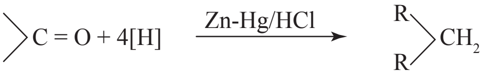
(1)



(2)

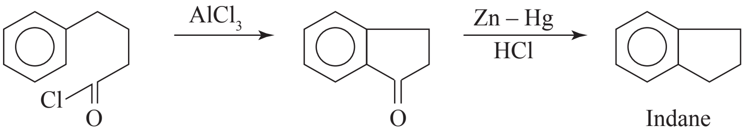


By Clemmenson Reduction Here carbonyl compounds are reduced into alkanes by Zn – Hg/HCl as follows:

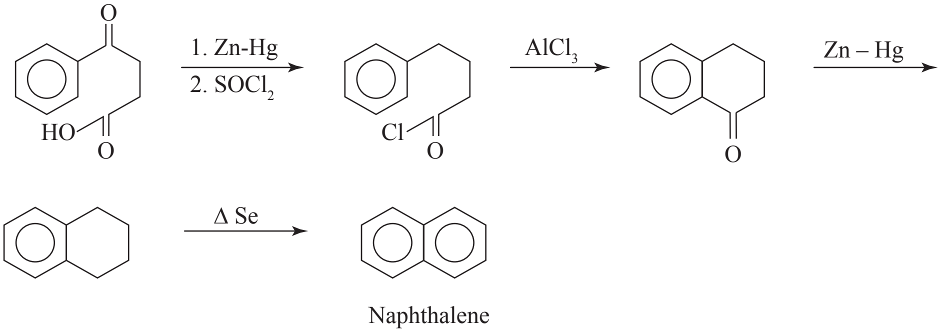


For example,

(1)

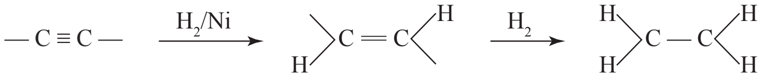


(2)

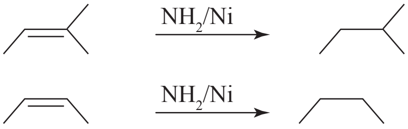


By Sabitier and Sendersen Reaction

- Here the catalysts used are Raney Ni [Alloy of Ni-Al] Pd – Pt (Adam's catalyst) and the temperature range is 200 – 300°C.



For example,



From the Reduction of R – X Here the reducing agent is mainly Zn + NaOH or HCl or Zn-Cu/Acid, Na/alcohol.

$$R-X+H-H \xrightarrow{H_2/Ni} R-H+HX.$$

$$R-I+HI \xrightarrow{\Delta,\ 150^{o}C} R-H+I_2\uparrow$$

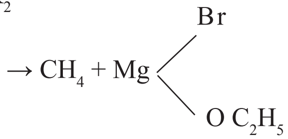
$$R-X \xrightarrow{(Ph)_3\ SnH} R-H+HX$$

By Decomposition of Grignard Reagent

- Any compound with an active hydrogen atom gives this reaction with Grignard reagent.

$R-MgX+H_2O \rightarrow R-H+Mg.X.OH$
or H_2NR
or HOR
or $HC \equiv CR$
or $H-NR_2$

For example,



$$CH_3MgBr+C_2H_5OH \rightarrow CH_4+Mg\begin{matrix}Br\\ OC_2H_5\end{matrix}$$

REMEMBER

Moles of alcohols × Number of active H atoms per mole (n) = Moles of alkane, that is,

OR

$$\frac{\text{Weight of alcohol (gm)}}{\text{Molecular weight of alcohol}}\times n=\frac{\text{Volume (ml) of alkane}}{22400}$$

PHYSICAL PROPERTIES

- Physical state

C_1-C_4: Colourless, odourless Gas (due to weak forces)
C_5-C_{17}: Colourless ,odourless Liquid
C_{18} … ..: Colourless, odourless waxy solid

- Density: They are lighter than water and there density increases with the increase of molar mass

Density α molecular weight

- Solubility: These are insoluble in polar solvents but soluble in non-polar solvents like CCl_4, ether etc.

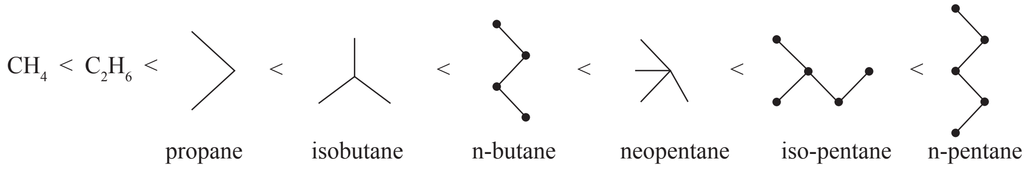
$$\text{Solubility}\ \alpha\ \frac{1}{\text{Mol.wt.}}$$

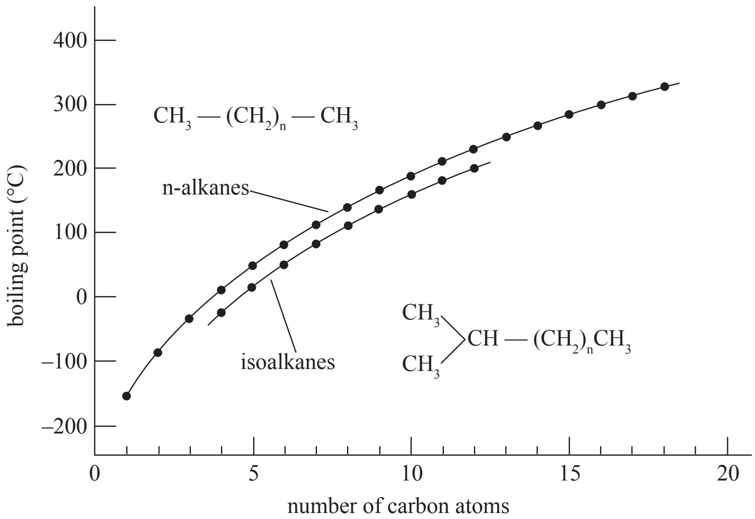
e.g., $CH_4 > C_2H_6 > C_3H_8 > C_4H_{10}$

Boiling point: The value of boiling point of alkanes increases with increase in molecular mass and for each successive member molecular formula differ by $(-CH_2-)$ and B.P. differ by 20 – 30°C. When molecular is same boiling point decreases with branching as due to decrease in surface area intermolecular forces also decreases

B.P. α Surface area
Normal > iso > Neo

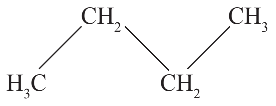
For example,



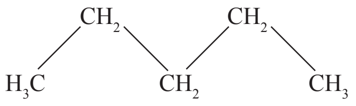


- Melting point: Melting point of alkane also increases with the increase of molar mass. However, the melting point of alkanes do not show regular variation with increase in molecular size. In general, M.P. of even number of carbon atom alkane is greater than M. P. of odd number of carbon atom alkane. It is due the fact that in case of alkanes of even number of carbon atom there is more symmetrical arrangement. This is called as alternation effect or oscillation effect. The compound with even number of carbon of atoms being more symmetrical fits well into the crystal lattice and more energy is required to break them. Therefore they have higher m.p. Branching of an alkane chain increases the m.p. because increased branching leads to a more compact molecule that can pack more closely into a solid lattice.

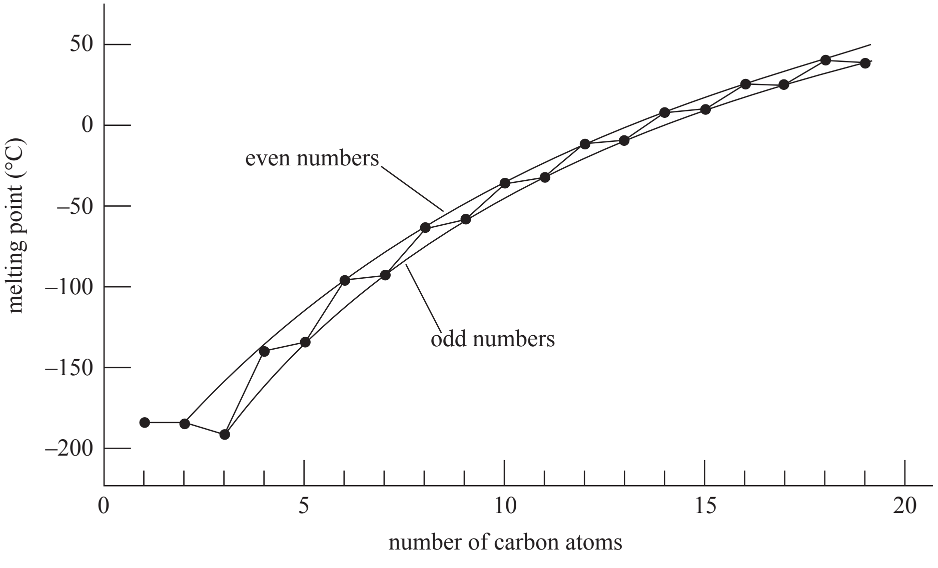
  That is, $C_{15} < C_{16} > C_{17}$



Even number of carbon atoms



Odd number of carbon atoms



CHEMICAL PROPERTIES

Alkanes are inert towards acids, bases, oxidising agents etc. due to non polar nature, non ability to donate or accept electron and because of stables C- C and C-H bonds.

(1) Halogenation It occurs in hv, dark at high temperature 1250–4000^{o}C and the presence of O_2 suppresses the reaction here. It is initiated by dibenzoyl peroxide, $Pb(Et)_4$.

Reactivity of X_2 is --- $F_2 > Cl_2 > Br_2 > I_2$

- Replacement of H-atom is easy if free Radicul formed is stable
  Benzyl > t > s > p > methyl
-

For example,

$$CH_4 + Cl \xrightarrow{hv} \underset{\text{Final product}}{CCl_4}$$

$$2R - X + HgF_2 \longrightarrow 2R - F + HgX_2$$
$$(X = Br, I)$$

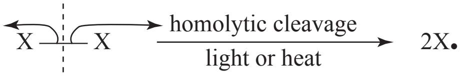
Mechanism Of Halogenation

Halogenation of alkanes through free-radical intermediates is termed as homolytic substitution reaction, and such type of reactions require light or heat for initiation. A general scheme may be shown as

$$R - H + X - X \xrightarrow{\text{light or heat}} R - X + H - X$$

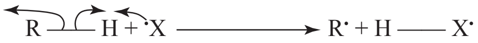
The mechanism involves a radical chain reaction that consists of the following major steps:

Initiation



$$X - X \xrightarrow[\text{light or heat}]{\text{homolytic cleavage}} 2X\bullet$$

Propagation



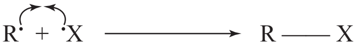
$$R - H + {}^{\bullet}X \longrightarrow R^{\bullet} + H - X^{\bullet}$$

$$R^{\bullet} + X - X \longrightarrow R - X + X^{\bullet}$$

Termination

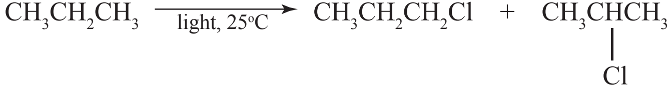
$$X^{\bullet} + {}^{\bullet}X \longrightarrow X - X$$

$$R^{\bullet} + {}^{\bullet}R \longrightarrow R - R$$



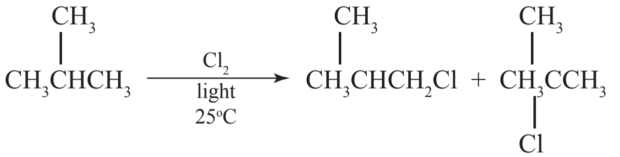
$$R^{\bullet} + {}^{\bullet}X \longrightarrow R - X$$

For example



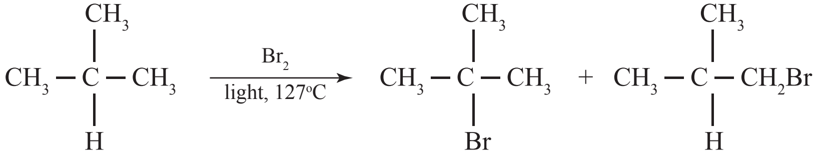
$$\underset{\text{Propane}}{CH_3CH_2CH_3} \xrightarrow[\text{light, 25}^oC]{Cl_2} \underset{\substack{\text{1 -Chloropropane} \\ (45\ \%)}}{CH_3CH_2CH_2Cl} + \underset{\substack{\text{2- Chloropropane} \\ (55\ \%)}}{CH_3\underset{Cl}{\underset{|}{C}}HCH_3}$$

Propane 1 -Chloropropane (45 %) 2- Chloropropane (55 %)



$$CH_3\overset{\overset{CH_3}{|}}{C}HCH_3 \xrightarrow[\text{light}\ 25^{o}C]{Cl_2} CH_3\overset{\overset{CH_3}{|}}{C}HCH_2Cl + CH_3\underset{\underset{Cl}{|}}{\overset{\overset{CH_3}{|}}{C}}CH_3$$

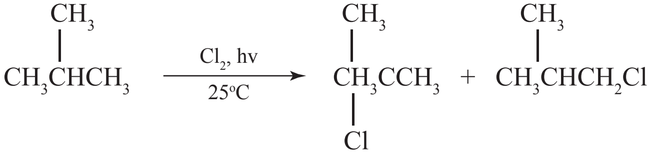
2- Methylpropane 1- Chloro -2- methyl-propane (63 %) 2- Chloro -2- methyl propane (37 %)



$$CH_3-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 \xrightarrow[\text{light, } 127^{o}C]{Br_2} CH_3-\underset{\underset{Br}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 + CH_3-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2Br$$

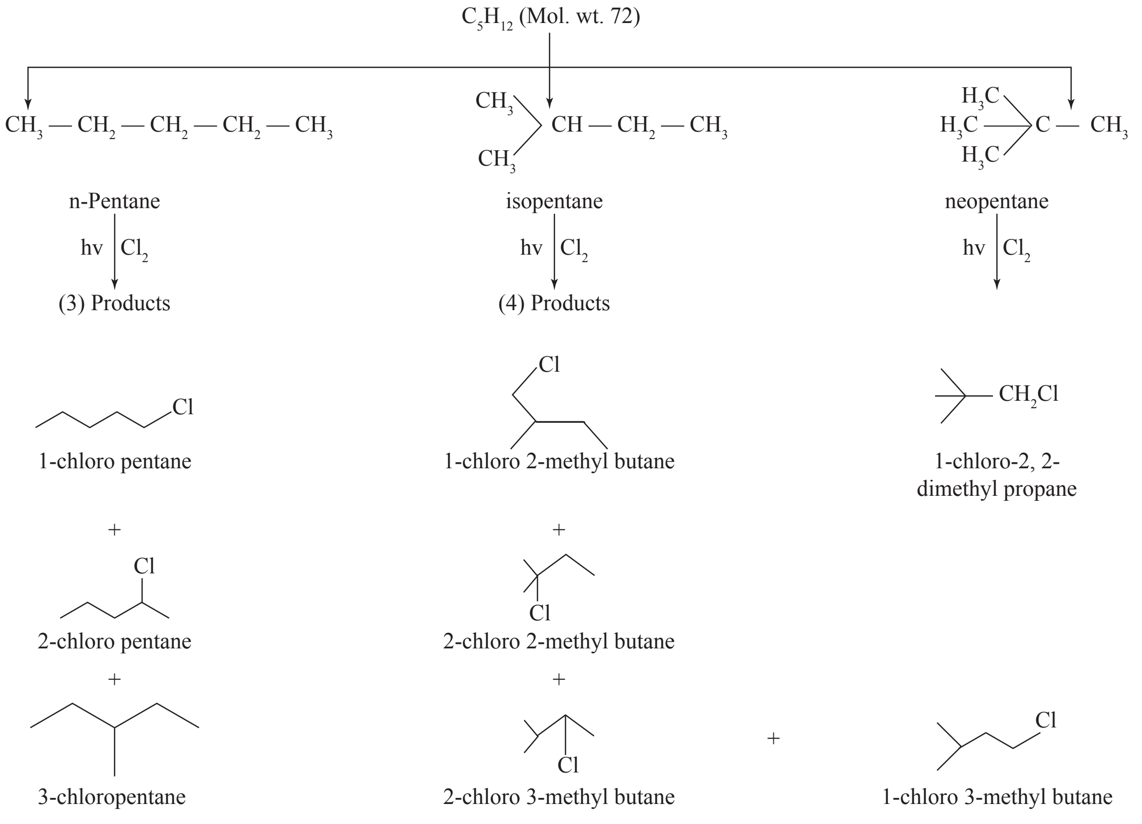
(> 99 %) (trace)

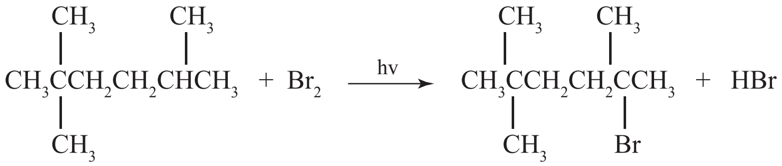
A very different result is obtained when 2- methylpropane reacts with chlorine.



$$CH_3\overset{\overset{CH_3}{|}}{C}HCH_3 \xrightarrow[25^{o}C]{Cl_2,\ hv} CH_3\underset{\underset{Cl}{|}}{\overset{\overset{CH_3}{|}}{C}}CH_3 + CH_3\overset{\overset{CH_3}{|}}{C}HCH_2Cl$$

(37 %) (63 %)

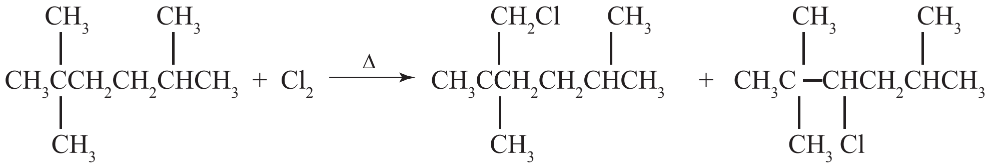




$$CH_3\overset{CH_3}{\underset{CH_3}{C}}CH_2CH_2\overset{CH_3}{CH}CH_3 + Br_2 \xrightarrow{hv} CH_3\overset{CH_3}{\underset{CH_3}{C}}CH_2CH_2\overset{CH_3}{\underset{Br}{C}}CH_3 + HBr$$

2,2,4- trimethylhexane

2- bromo -2, 5,5- trimethylhexane (82 %)



$$CH_3\overset{CH_3}{\underset{CH_3}{C}}CH_2CH_2\overset{CH_3}{CH}CH_3 + Cl_2 \xrightarrow{\Delta} CH_3\overset{CH_2Cl}{\underset{CH_3}{C}}CH_2CH_2\overset{CH_3}{CH}CH_3 + CH_3\overset{CH_3}{\underset{CH_3}{C}}-\underset{Cl}{CH}CH_2\overset{CH_3}{CH}CH_3$$

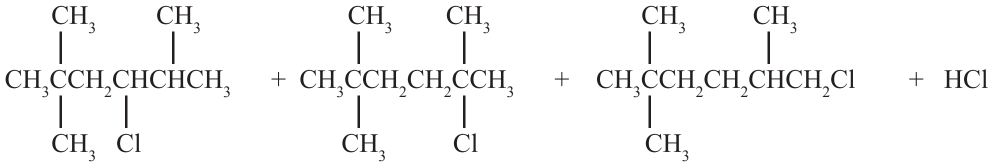
2,2, 5- trimethylhexane

9 × 1.0 = 9.0

$\frac{9.0}{35}$ = 26%

2 × 2.8 = 7.6

$\frac{7.6}{35}$ = 22 %



$$CH_3\overset{CH_3}{\underset{CH_3}{C}}CH_2\underset{Cl}{CH}\overset{CH_3}{CH}CH_3 + CH_3\overset{CH_3}{\underset{CH_3}{C}}CH_2CH_2\overset{CH_3}{\underset{Cl}{C}}CH_3 + CH_3\overset{CH_3}{\underset{CH_3}{C}}CH_2CH_2\overset{CH_3}{CH}CH_2Cl + HCl$$

2 × 3.8 = 7.6

$\frac{7.6}{35}$ = 22 %

1 × 5.0 = 5.0

$\frac{5.0}{35}$ = 14 %

6 × 1.0 = 6.0

$\frac{6.0}{35}$ = 17%

REMEMBER

The free radical chlorination of the methane occurs approximately twelve times faster than tetradeuteromethane, CD_4 although D and H are chemically identical, as C- D bonds are slightly stronger than C – H bonds. So $\Delta H^{\ddagger}$ for abstraction of D is slightly greater than for H. Since abstraction is the slow step, removal of H will be faster.

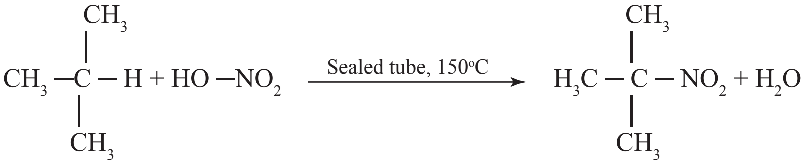
(2) Nitration

$$R-H + HNO_3 \xrightarrow[\text{High temp}\ 400^\circ C]{\Delta} R.NO_2 + H_2O$$

Nitroalkane

$$C_6H_{13}H + OH-NO_2 \xrightarrow{40^\circ C} C_6H_{13}.NO_2 + H_2O$$

Hexane foming- nitric acid Nitro -hexane (10 % yeild)

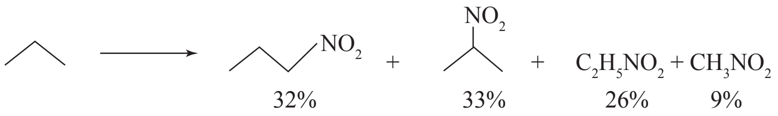


$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-H + HO-NO_2 \xrightarrow{\text{Sealed tube, }150^\circ C} H_3C-\overset{CH_3}{\underset{CH_3}{C}}-NO_2 + H_2O$$

Iso -butane

2- nitro -2- methyl propane (22 % yield)

- This reaction is for hexane, heptane etc while in case of lower alkanes only vapour phase nitration takes place. Which is possible when a gases mixture of hydrocarbon and nitric acid vapour is passed over a reactor tube at 1 atm pressure and 6 93 K as follows:
  For example,



(3) Sulphonation

$$R - OH + H_2SO_4 \xrightarrow[\text{Prolonged Heating}]{\Delta\ SO_3} R - SO_3H + H_2O$$

$$C_6H_{13}H + OH.SO_3H \xrightarrow{400^{o}C} C_6H_{13}SO_3H + H_2O$$

- It is given by alkanes having minimum 6 carbon atoms that is, hexane, heptane etc. While lower members react with SO_3 to form sulphonic acids.

  e.g., $C_3H_8 + SO_3 \rightarrow C_3H_7SO_3H$

REMEMBER

Chloro - Sulphonation: When alkanes are treated with sulphuryl chloride in presence of pyridine and light sulphonyl chlorides are obtained.

$$RH + SO_2Cl_2 \rightarrow R.SO_2Cl + HCl$$

(4) Oxidation Reactions

(a) Combustion or complete oxidation

$$(CnH_{2n+2}) + \frac{(3n+1)}{2} O_2 \xrightarrow{\Delta} nCO_2 + (n+1)H_2O$$

(b) Oxidation [Incomplete combustion]

For example,

$$CH_4 + O_2 \xrightarrow{\text{Burn}} \underset{\text{Carbon black}}{C} + 2H_2O$$

- Carbon black is used in printing ink.

$$2CH_4 + 3O_2 \xrightarrow{\text{Burn}} 2CO + 4H_2O$$

(c) Catalytic oxidation

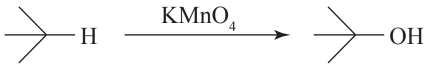
For example,

$$CH_4 + [O] \xrightarrow[\text{100 atm } 200^{o}C]{\text{Cu-Tube}} CH_3OH$$

For example,

$$CH_3 - (CH_2)n - CH_3 \xrightarrow[\substack{100 - 160^{o}C \\ \text{Mn-Stearate}}]{O_2} (CH_3) - (CH_2)n - COOH$$

(d) Chemical oxidation (only alkane with 3° carbon atom)



t^6 - butyle alcolol

(5) Pyrolysis or Cracking

- Here higher alkane splits into lower alkane, alkene, hydrogen when heated strongly at a high temperature in absence of air. During pyrolysis C – C bonds breaks rather than C – H bonds as bond energy of C – H > C – C.

$$R-H \xrightarrow[\text{Absence of } O_2]{\Delta} \underset{\text{lower alkane and alkene}}{R-H + R=R + H_2\uparrow}$$

For example,

$$CH_4 \xrightarrow{1000^\circ C} C + 2H_2$$

$$C_2H_6 \xrightarrow[Cr_2O_3 + Al_2O_3]{500^\circ C} CH_4 + CH_2 = CH_2 + H_2$$

$C_8H_{18} \longrightarrow$

$C_4H_{10} + C_4H_8$

$C_6H_{14} + C_2H_4$

$C_4H_{10} + CH_4 + C_2H_4 + C$

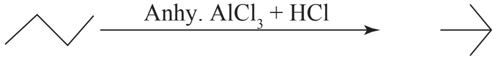
$C_3H_8 + C_2H_6 + C_2H_4 + C$

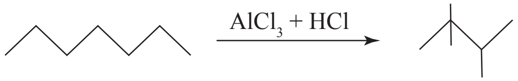
$C_8H_{16} + H_2$

(6) Isomerization

Here higher alkanes are heated with aluminium chloride at high temperature to convert them into their isomers. It is helpful in petroleum industry to increase the octane number of gasoline.

$$\text{Normal chain isomer} \xrightarrow[\substack{\text{or} \\ \text{anhy. AlCl}_3 + \text{HBr} \\ 200^\circ C}]{\text{anhy. AlCl}_3 + \text{HCl}} \text{Iso isomer}$$





n-heptane

2, 2, 3 Trimethyl butane

2-methyl pentane

2, 3 dimethyl butane

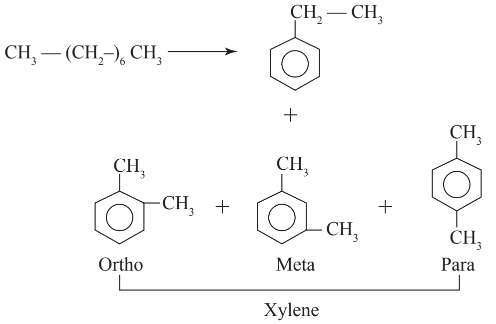
(7) Aromatization Here higher alkanes are changed into aromatic alkanes as follows:

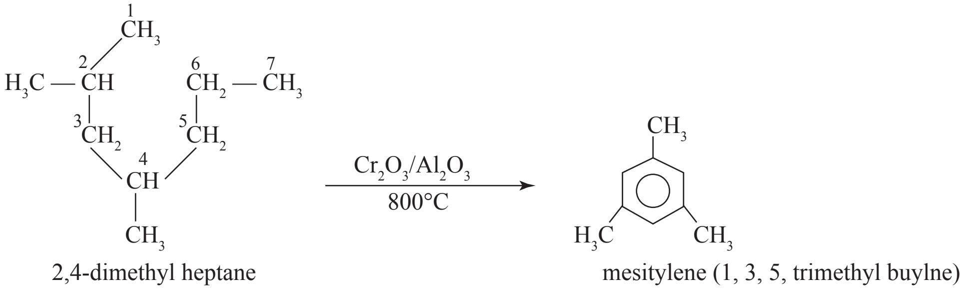
$$\text{Aliphatic Alkanes} \xrightarrow[\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3,\ 600^\circ\text{C}]{\Delta} \text{Aromatic Alkanes}$$

For example,

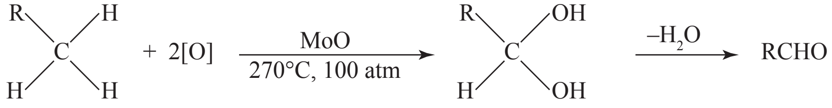
$$\underset{\text{Normal hexane}}{CH_3-(CH_2)_4-CH_3} \longrightarrow C_6H_6 + 4H_2\uparrow$$

$$\underset{\text{Normal heptane}}{CH_3-(CH_2)_5-CH_3} \longrightarrow C_6H_5CH_3 + 4H_2$$



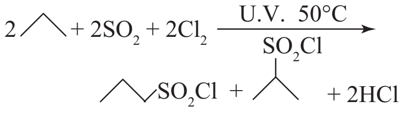


(8) Specific Reactions

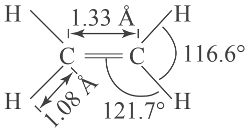


$$6CH_4 + 2O_2 \xrightarrow{1500^\circ C} 2CH \equiv CH + 2CO_2 + 10\ H_2\uparrow$$

- $\underset{\text{cellulose}}{(C_6H_{10}O_5)n} + nH_2O \rightarrow 3n\ CH_4 + 3n\ CO_2$
- Chlorosulphonation (Reed Reaction)



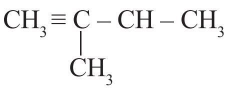
ALKENES OR OLEFINS



ethylene

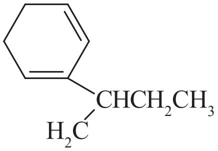
- These are unsaturated hydrocarbons having C = C with a general formula C_nH_{2n}.
- The word olefins means oil making. For example, Lower members give oily products on halogenation.
- Here unsaturated carbon atoms are sp^2 hybridized with a trigonal planar shape.
- Here C = C bond length is 1.34 Å and bond energy is 143.1 kcal per mol.
- Here C – H bond length is 1.1 Å and bond energy is 98.7 kcal per mol.

$CH_2 \equiv CH– CH_2 – CH_3$
but-1-ene

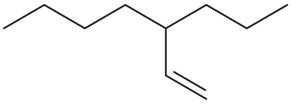


$CH_3 \equiv \underset{\displaystyle CH_3}{\underset{|}{C}} – CH – CH_3$

2-methylbut-2-ene



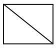
2-sec-butylcyclohexa-1,3-diene

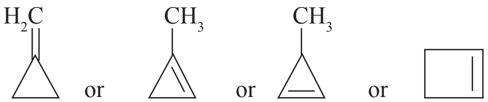


3-n-propylhept-1-ene
=>

- Alkenes may show chain position, ring chain, functional, geometrical and optical isomerisms.

  For example, C_4H_6.

  C_4H_6 has 2° of unsaturation as follows: two double bonds, $H_2C = CH^{-}CH = CH_2$ or $H_2C = C{=}CH^{-}CH_3$; one triple bond: $HC \equiv C–CH_2CH_3$ or $CH_3C \equiv CCH_3$; two rings ; one ring and one double bond.



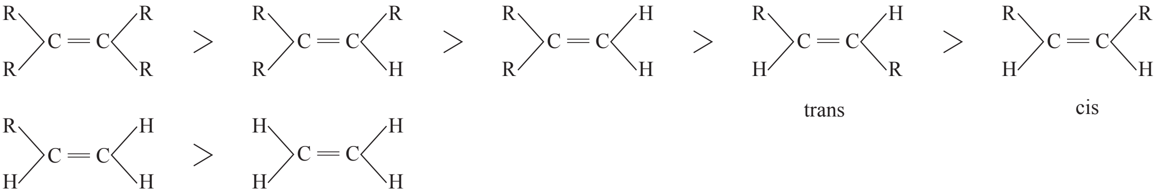
- Test of unsaturation: Alkenes show unsaturations as they
  - (i) Decolourize Br_2 in CCl_4
  - (ii) Decolourize 1per cent Alk. $KMnO_4$ or Baeyer’s Reagent
- Ozonolysis decides the number and location of (=) bonds in alkene.

Stability of alkene

$$\text{Stability } \alpha \ \frac{1}{\text{Heat of hydrogenation}}$$

Symm. Alkene > Un-symm. Alkene> trans alkene > cis alkene

Stability in Decreasing Order



trans

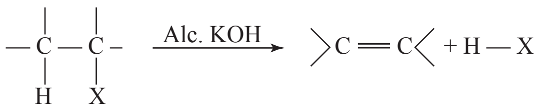
cis

METHODS OF PREPARATION OF ALKENE

(1) By α, β Elimination Reaction

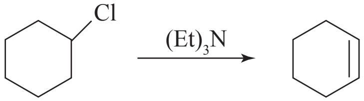
(A) By Dehydrohalogenation of Haloalkanes

- When alkyl halides are heated with reagents like $C_2H_5O^-$, alc. KOH, $NaNH_2$, KNH_2, $(Me)_3COK$ etc. alkene are formed as follows

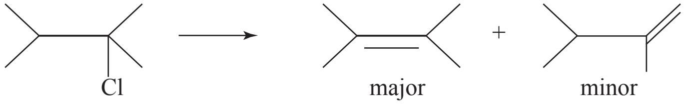


$$\underset{\displaystyle\ \ H\quad\ \ X}{-\overset{|}{C}-\overset{|}{C}-}\xrightarrow{\text{Alc. KOH}}\ >C=C<\ +H-X$$

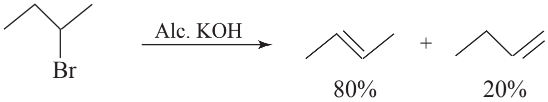
For example, (1)



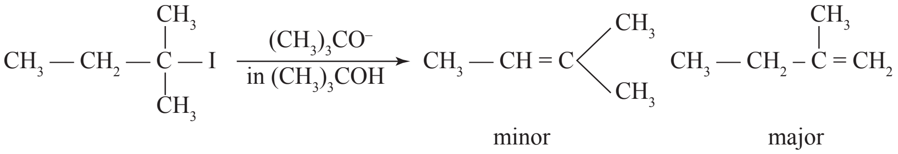
For example, (2)



(3)

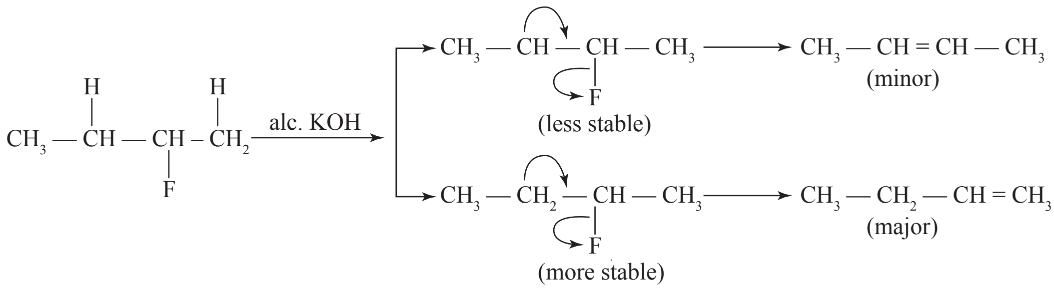


(4)



$$CH_3-CH_2-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-I\xrightarrow[\text{in }(CH_3)_3COH]{(CH_3)_3CO^-}\underset{\text{minor}}{CH_3-CH=C\begin{matrix}CH_3\\CH_3\end{matrix}}\quad\underset{\text{major}}{CH_3-CH_2-\overset{\displaystyle CH_3}{\overset{|}{C}}=CH_2}$$

(5)

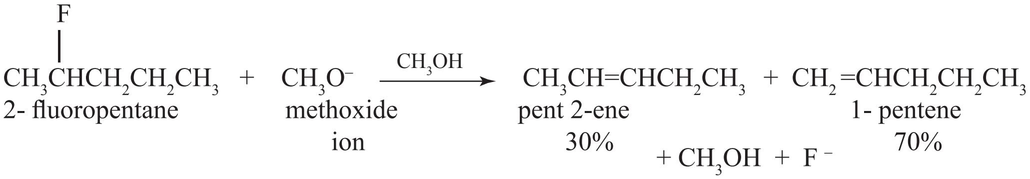


$$CH_3-\overset{\displaystyle H}{\overset{|}{C}H}-\underset{\displaystyle F}{\underset{|}{C}H}-\overset{\displaystyle H}{\overset{|}{C}H_2}\xrightarrow{\text{alc. KOH}}$$

$$\to \underset{\text{(less stable)}}{CH_3-CH-\underset{\displaystyle F}{\underset{|}{C}H}-CH_3}\longrightarrow \underset{\text{(minor)}}{CH_3-CH=CH-CH_3}$$

$$\to \underset{\text{(more stable)}}{CH_3-CH_2-\underset{\displaystyle F}{\underset{|}{C}H}-CH_3}\longrightarrow \underset{\text{(major)}}{CH_3-CH_2-CH=CH_3}$$

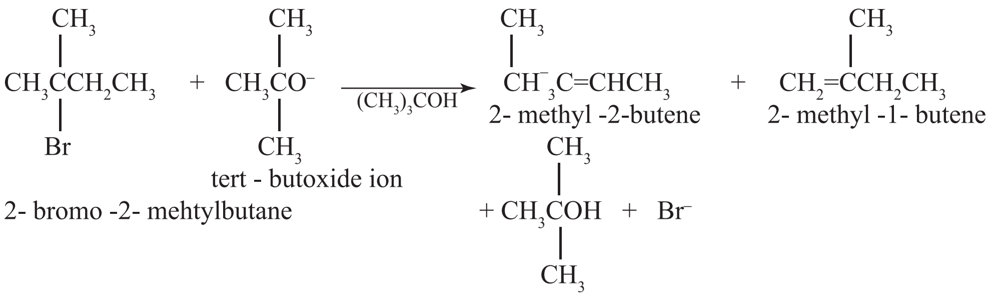
(6)



$$\underset{\text{2- fluoropentane}}{CH_3\overset{\displaystyle F}{\overset{|}{C}}HCH_2CH_2CH_3}+\underset{\text{methoxide ion}}{CH_3O^-}\xrightarrow{CH_3OH}\underset{\substack{\text{pent 2-ene}\\30\%}}{CH_3CH=CHCH_2CH_3}+\underset{\substack{\text{1- pentene}\\70\%}}{CH_2=CHCH_2CH_2CH_3}+CH_3OH+F^-$$

In examples 4, 5, 6 Hoffmann Rule is used to decide the product

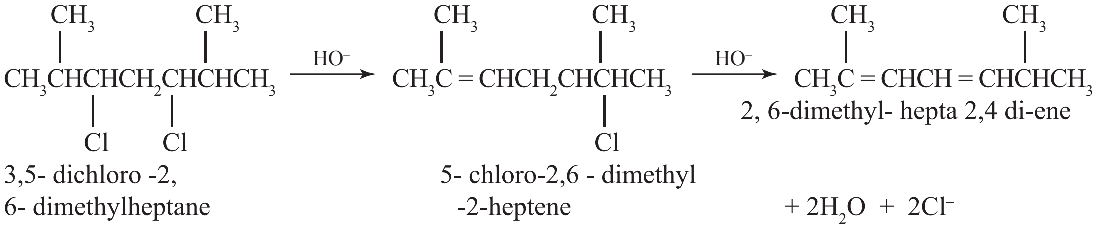
(7)



$$CH_3\overset{CH_3}{\underset{Br}{C}}CH_2CH_3 + CH_3\overset{CH_3}{\underset{CH_3}{C}}O^- \xrightarrow[(CH_3)_3COH]{} CH_3\overset{CH_3}{C}=CHCH_3 + CH_2=\overset{CH_3}{C}CH_2CH_3 + CH_3\overset{CH_3}{\underset{CH_3}{C}}OH + Br^-$$

2- bromo -2- mehtylbutane; tert - butoxide ion; 2- methyl -2-butene; 2- methyl -1- butene

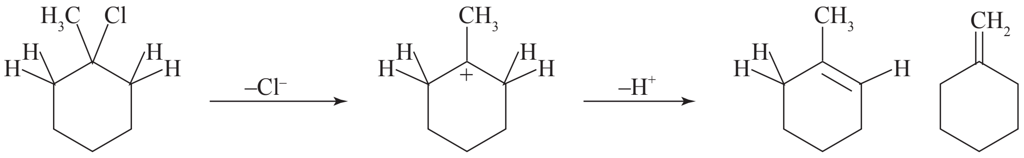
(8)



$$CH_3\overset{CH_3}{CH}\underset{Cl}{CH}CH_2\underset{Cl}{CH}\overset{CH_3}{CH}CH_3 \xrightarrow{HO^-} CH_3\overset{CH_3}{C}=CHCH_2\underset{Cl}{CH}\overset{CH_3}{CH}CH_3 \xrightarrow{HO^-} CH_3\overset{CH_3}{C}=CHCH=CH\overset{CH_3}{CH}CH_3 + 2H_2O + 2Cl^-$$

3,5- dichloro -2, 6- dimethylheptane; 5- chloro-2,6 - dimethyl -2-heptene; 2, 6-dimethyl- hepta 2,4 di-ene

(9)

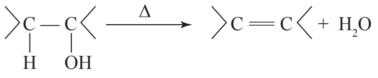


1-chloro-1-methylcyclohexane I II

Of these two products, the first one (which is trisubstituted) will be favoured over the second one (which is disubstitute.)

(B) By The Dehydration of Alcohol

- When alcohols are heated with dehydrating agents like H_2SO_4 170°C, H_3PO_4 200°C,. P_2O_5, $ZnCl_2$ 350°C, BF_3, dry HCl, $KHSO_4$ etc. alkenes are formed as follows:

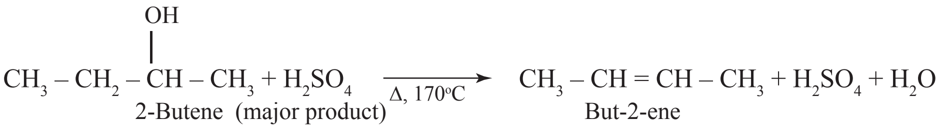


$$>\underset{H}{C}-\underset{OH}{C}< \xrightarrow{\Delta} >C=C< + H_2O$$

For example, (1)

$$CH_3CH_2OH \xrightarrow{\Delta,\ conc.\ H_2SO_4\ 170^oC} CH_2=CH_2 + H_2O$$

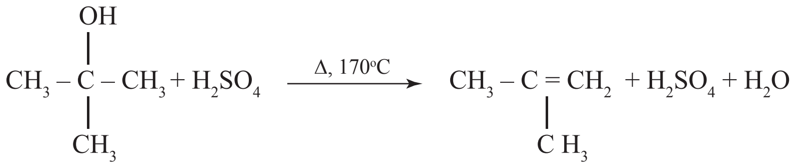
(2)



$$CH_3-CH_2-\overset{OH}{CH}-CH_3 + H_2SO_4 \xrightarrow[\Delta,\ 170^oC]{} CH_3-CH=CH-CH_3 + H_2SO_4 + H_2O$$

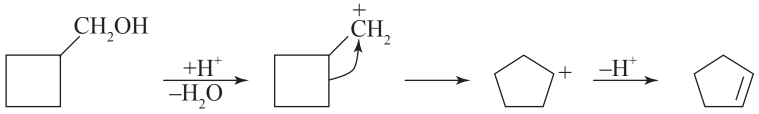
2-Butene (major product) But-2-ene

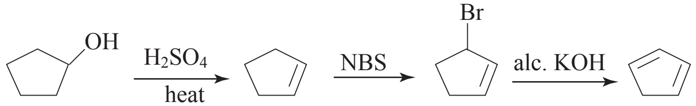
(3)



$$CH_3-\underset{CH_3}{\overset{OH}{C}}-CH_3+H_2SO_4 \xrightarrow{\Delta,\ 170^\circ C} CH_3-\underset{CH_3}{C}=CH_2+H_2SO_4+H_2O$$

Iso butyene (major product)





Cyclopentanol Cyclopentene

From De-Halogenation of Di-halogen Derivative

(a) From gem dihalides: When gem dihalides are heated with zinc then alkenes are formed as follows.

$$R-CHX_2+2Zn+X_2CH-R \xrightarrow[-2ZnX_3]{\Delta} R-CH=CH-R$$

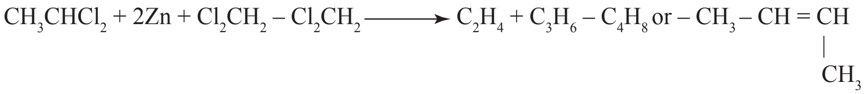
For example,

$$CH_3-CHCl_2+2Zn+Cl_2CH-CH_3 \xrightarrow[-2ZnCl_3]{\Delta} CH_3-CH=CH-CH_3$$

But - 2 - ene

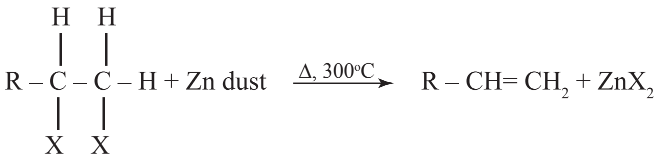
- If we take two different types of gem dihalides then we obtain three different types of alkenes in this reaction.

For example,



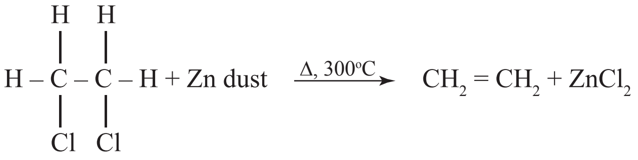
$$CH_3CHCl_2+2Zn+Cl_2CH_2-Cl_2CH_2 \longrightarrow C_2H_4+C_3H_6-C_4H_8\text{ or }-CH_3-CH=\underset{CH_3}{CH}$$

(b) From vicinal dihalides: When vicinal dihalides are heated with Zn dust, alkene having same number of carbon is obtained.



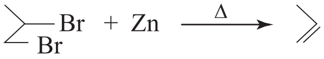
$$R-\underset{X}{\overset{H}{C}}-\underset{X}{\overset{H}{C}}-H+\text{Zn dust} \xrightarrow{\Delta,\ 300^\circ C} R-CH=CH_2+ZnX_2$$

For example, (1)



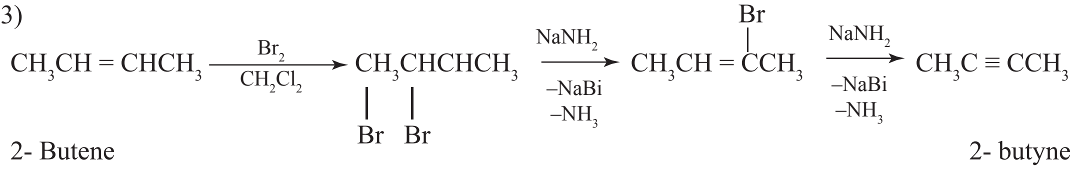
$$H-\underset{Cl}{\overset{H}{C}}-\underset{Cl}{\overset{H}{C}}-H+\text{Zn dust} \xrightarrow{\Delta,\ 300^\circ C} CH_2=CH_2+ZnCl_2$$

(2)



1,2-Dibromopropane Propene

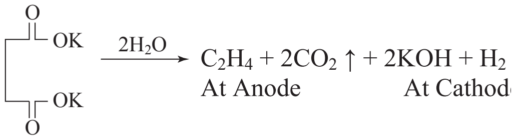
(3)



$$CH_3CH = CHCH_3 \xrightarrow[CH_2Cl_2]{Br_2} CH_3\underset{Br}{C}H\underset{Br}{C}HCH_3 \xrightarrow[\substack{-NaBi \\ -NH_3}]{NaNH_2} CH_3CH = \overset{Br}{C}CH_3 \xrightarrow[\substack{-NaBi \\ -NH_3}]{NaNH_2} CH_3C \equiv CCH_3$$

2- Butene 2- butyne

(4) By Kolbe's Electrolytic Reaction



$$\xrightarrow{2H_2O} C_2H_4 + 2CO_2\uparrow + 2KOH + H_2$$

At Anode At Cathod

Potassium succinate

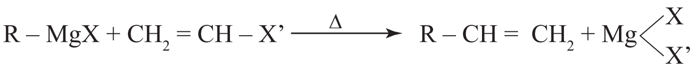
(5) By Partial Reduction of Alkyne

$$R - C \equiv CH + H_2 \xrightarrow[Catalyst]{lindlar} R - CH = CH_2$$

- Lindlar catalyst is Pd-$BaSO_4$ poisoned by sulphur or quinoline. It is used to avoid further reduction of alkene into alkane.

Some Other Methods (But Not For IIT-JEE)

(6) From Grignard Reagent



$$R - MgX + CH_2 = CH - X' \xrightarrow{\Delta} R - CH = CH_2 + Mg\begin{matrix} X \\ X' \end{matrix}$$

(7) From Other Organometallic Compound

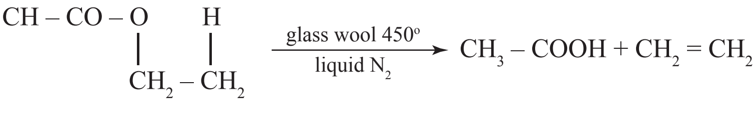
$$CH_2 = CH - Cl + CuR_2 \xrightarrow{alc.\ KOH} R - CH = CH_2 + R - Cu - Cl$$

Here R may be CH_3, C_6H_6 etc.

(8) By Heating Tetra-alkyl Ammonium Halide or Hydroxide

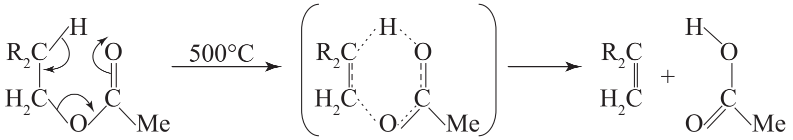
$$(C_2H_5)_4N.OH \xrightarrow{\Delta} C_2H_4 + H_2O + (C_2H_5)_3N$$

(9) From Esters by Pyrolysis When esters are heated in presence of liquid N_2 and glass wool, then alkyl part of ester converts into respective alkene while alkanoate part of ester converts into respective acid.



$$\underset{\hspace{4em}CH_2 - CH_2}{CH - CO - O \quad H} \xrightarrow[liquid\ N_2]{glass\ wool\ 450^o} CH_3 - COOH + CH_2 = CH_2$$

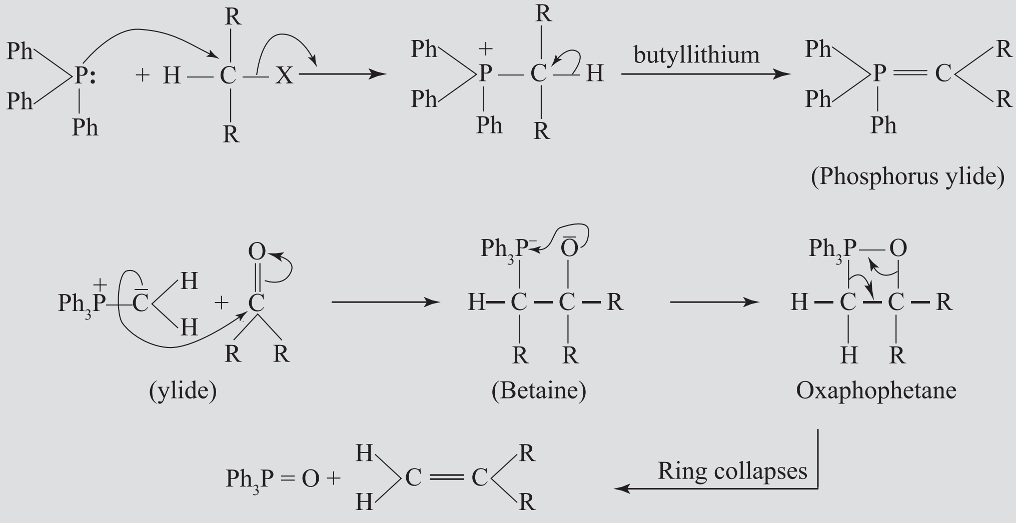
Thermal cleavage of an ester usually acetate involves the formations of a six membered ring as the transition state leading to the elimination of acid leaving behind alkene. As a direct consequence of cyclic transition state, both the leaving groups namely proton and carboxylic ion are in the cis position. This is an example of cis elimination.



(10) The Wittig Reaction Here methylene triphenyl phosphorane or phosphorous ylide is treated with a carbonyl compound to prepare an alkene.

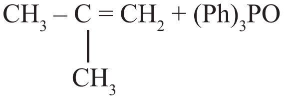
$$>C = O + (Ph)_3 P = C< \longrightarrow >C = C< + (Ph)_3PO$$

Mechanism



For example, (1) $CH_3 - CHO + (Ph)_3 P = \xrightarrow{CH_2} CH_3 - CH = CH_2 + (Ph)_3PO$
Acetaldehyde Propene

(2) $CH_3 - CO - CH_3 + (Ph)_3 P = CH_2 \longrightarrow$
Acetone



$$CH_3 - \underset{\displaystyle CH_3}{\underset{|}{C}} = CH_2 + (Ph)_3PO$$

Iso butene

Physical Properties

- Physical state:
  C_1 to C_4: Colourless gas
  C_5 to C_{16}: Colourless liquid
  C_{17} … ..: Colourless waxy solid

- These are colourless, odourless, lighter than water. Alkenes are insoluble in water but soluble in organic solvents.
- Alkenes have slightly higher values of B. P. M. P. than alkanes and the value of B. P. M . P. increase with the increase of molar mass.
- Cis alkene has more value of boiling point, dipole moment, reactivity, heat of hydrogenation, refractive index than trans alkene. Trans alkene has more melting point than a cis alkene. It is due to more tight packing in crystal lattice in trans.

CHEMICAL PROPERTIES OF ALKENES

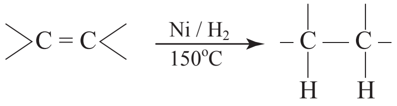
Addition Reactions of Alkenes

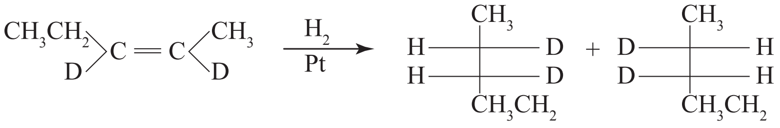
- Alkenes show electrophilic addition reaction mainly with HX, H_2, X_2, H-OH, H-OSO_3H etc as the pi- electrons in double bond are loosely held it means they are easily Polarizable and double bond is broken.

With H_2

This reaction occurs at the surface of catalysts like Raney Nickel(Ni + Al), Pd, Pt etc. in a cis addition manner. Reducing agents like Wilkinson catalyst $[RhCl(Ph)_3 P]$ and $NaBH_4 .PtCl_2$ can also be used here. Birch reagent Na/liquid NH_3 with alcohol can also be used in case of terminal alkenes. This reaction is exothermic and with the increase of steric hinderance the reactivity of alkenes decreases as follows.

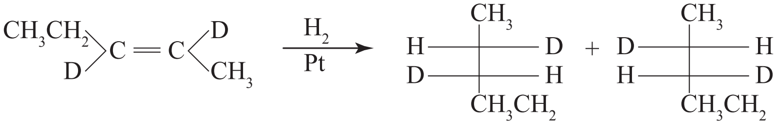
$$CH_2 = CH_2 > RCH= CH_2 > RCH = CHR > R_2C=CHR > R_2C = CR_2$$





cis -2, 3- dideuterio -2-pentene

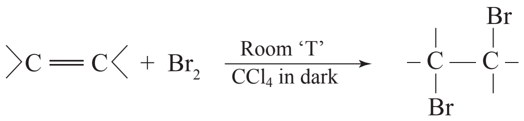
erythro enantiomers

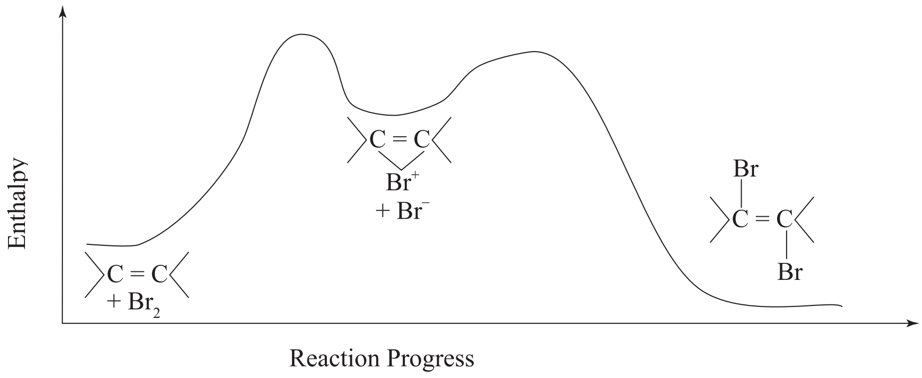


trans -2, 3-dideuterio-
2-pentene

threo enantiomers

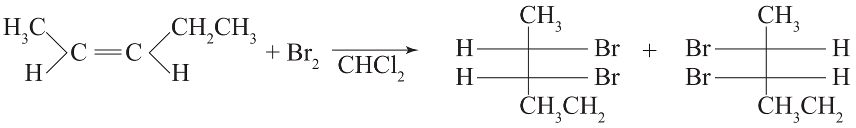
With X_2 Alkenes react with $X_{2/}CCl_4$ (inert solvent) to give di -halides and the addition is anti -addition. It is test of unsaturation as here colour of Br_2/H_2O disappears.





An enthalpy-reaction progress diagram for addition of Br_2 to an alkene.

For example (1)

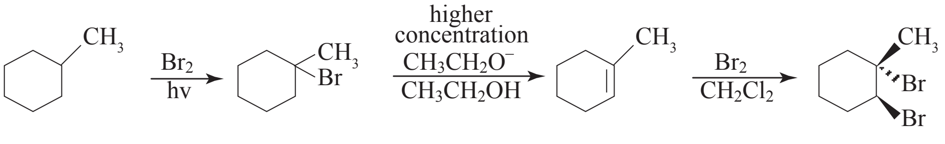


trans -2 pentene

erythro enantiomers
(Fischer projections)

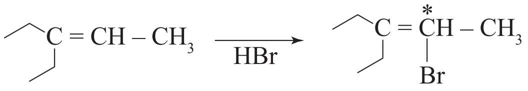
cis -2 pentene

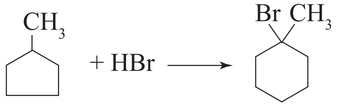
threo enantiomers
Fischer projections

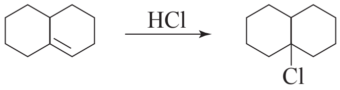


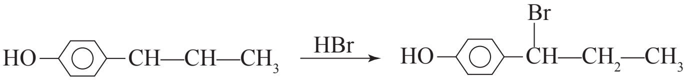
With HX Alkenes react with HX to give haloalkanes using Markownikoff and Anti-Markownikoff rules incase of unsymmetrical alkenes (Discussed in Chapter 2).

For example,



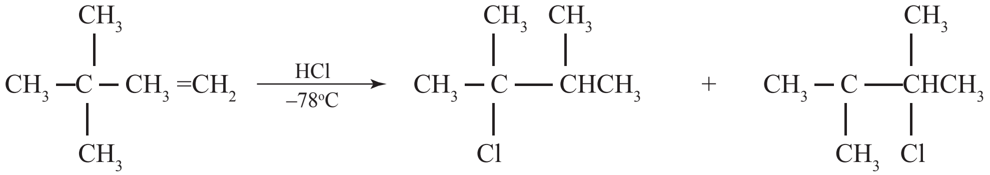






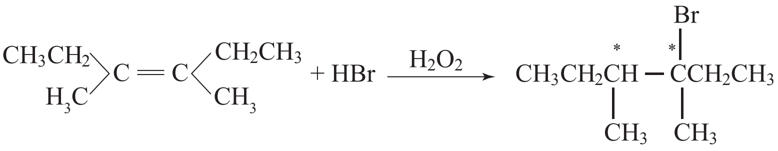
$$R-CH=CH_2 \xrightarrow[Cl.CCl_3]{CCl_4} R-CHCl-CH_2CCl_3$$

$$R-CH=CH_2 \xrightarrow[peroxide]{CHCl_3} R-CH_2-CH_2.CCl_3$$

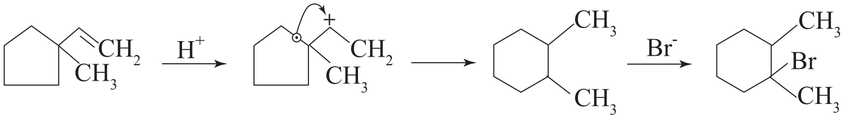


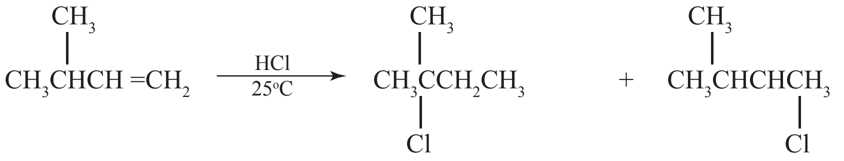
$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_3=CH_2 \xrightarrow[-78^{\circ}C]{HCl} CH_3-\overset{CH_3}{\underset{Cl}{C}}-\overset{CH_3}{C}HCH_3 + CH_3-\underset{CH_3}{C}-\overset{CH_3}{\underset{Cl}{C}}HCH_3$$

3, 3, -dimethyl butene — 2- chloro -2, 3- dimethylbutane (61 %) — 3- chloro -2, 2- dimethylbutane (37 %)



cis -3, 4- dimethyl -3- hexane — 3- bromo -3, 4- dimehtylhexane



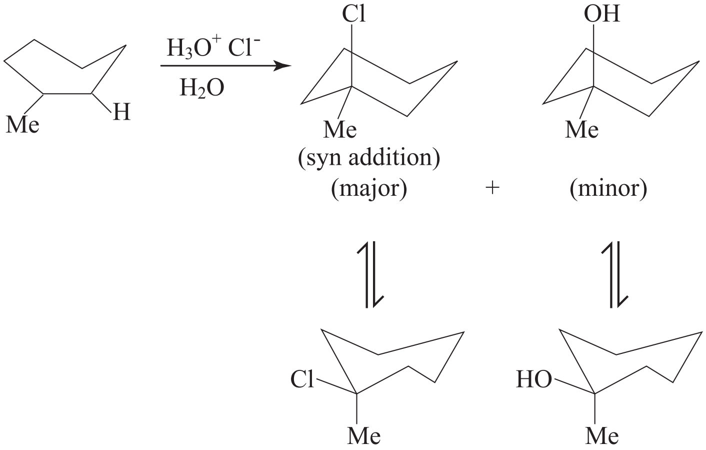


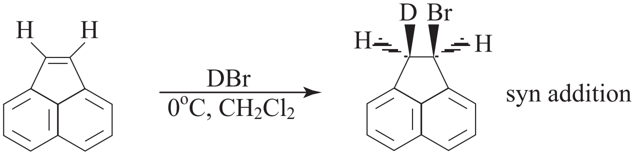
$$CH_3\overset{CH_3}{\overset{|}{C}}HCH{=}CH_2 \xrightarrow[25^{o}C]{HCl} CH_3\underset{Cl}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}CH_2CH_3 + CH_3\overset{CH_3}{\overset{|}{C}}H\underset{Cl}{\underset{|}{C}}HCH_3$$

3- methyl but -1- ene

2- chloro -2- methylbutane ~ 50 %

2- chloro -3- methylbutane ~ 50 %

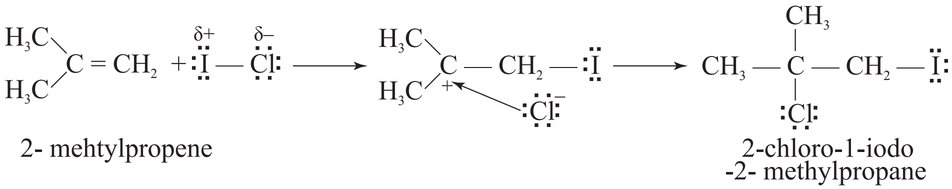




Modern Statement of Markovnikov's Rule

In the ionic addition of an unsymmetrical reagent to a double bond, the positive portion of the adding reagent attaches itself to a carbon atom of the double bond so as to yield the more stable carbocation as an intermediate. For e.g.,

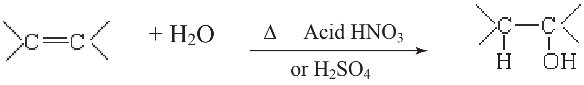
The addition of ICl to 2- metyhlpropene takes place in the following way produces 2- chloro -1- 2- methylpropane.



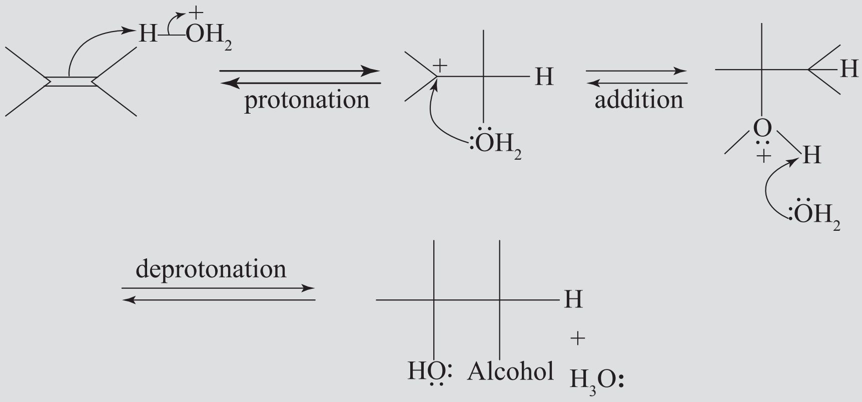
2- mehtylpropene

2-chloro-1-iodo -2- methylpropane

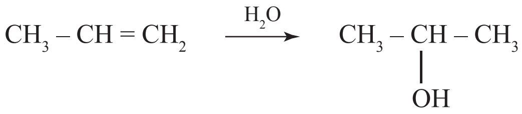
With H_2O Alkenes react with water in presence of dilute acid or BF_3 to give alcohols according to Markownikoff rule.



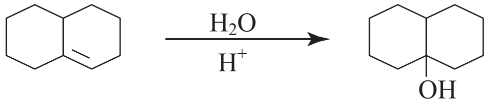
Mechanism

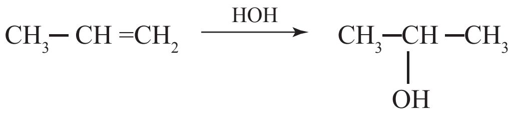


For example,

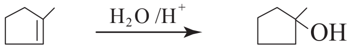


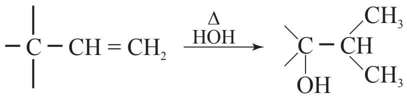
$$CH_3-CH=CH_2 \xrightarrow{H_2O} CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$$

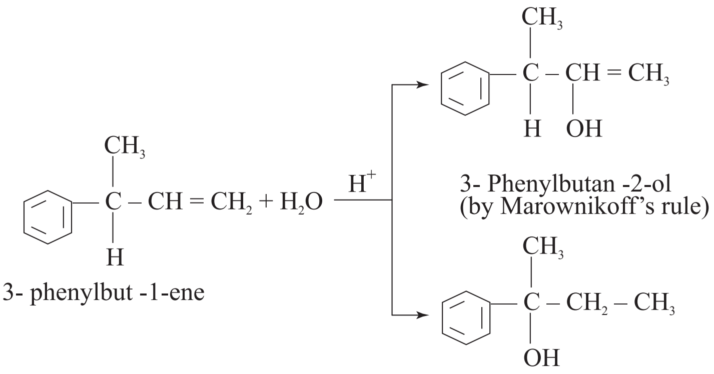




$$CH_3-CH=CH_2 \xrightarrow{HOH} CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$$







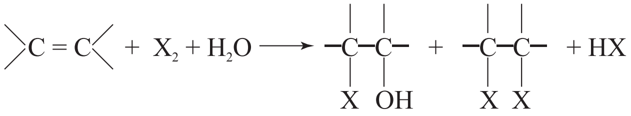
3- phenylbut -1-ene

3- Phenylbutan -2-ol
(by Marownikoff's rule)

2- Phenylbutan -2-ol
(by 1,2- hydride shift)

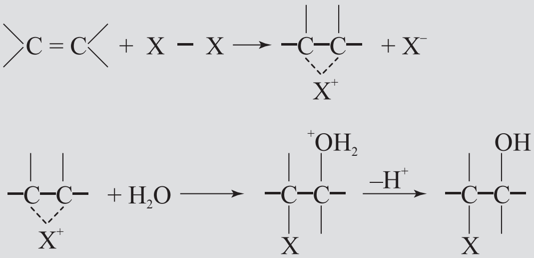
Halohydrin Formation or With HXO

If the halogenation of an alkene is carried out in aqueous solution (rather than in CCl_4), the major product of the overall reaction is a halo-alcohol known as haloydrin. In this case, the molecules of the solvent become reactant.

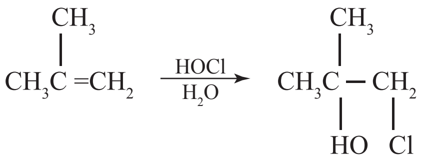


X_2 may be Cl_2 or Br_2

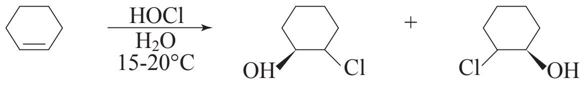
Mechanism



The addition of $\overset{+}{X}$ and $\overset{-}{OH}$ occurs in the trans manner, as the reaction proceed by the formation of halonium ion intermediate.(Order of reactivity is HOCl > HOBr > IOH)

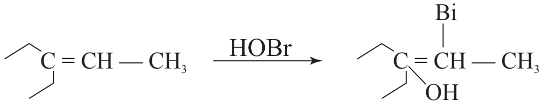


2- methylpropene 1- chloro-2- methyl- 2- propanol



cyclohexene

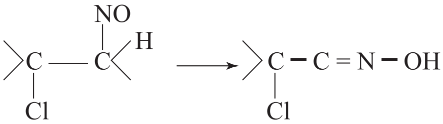
trans -2- chlorocyclohexanol;
chlorohydrin of cyclohexene
70%
racemic mixture



With NOCl Alkenes react with NOCl using Markownikoff's rule as follows:

RCH= CH_2 + NOCl → $RCHClCH_2NO$

Here attacking reagent is NO^+ and the Product formed is stable only when carbon atom bearing NO group does not have hydrogen since hydrogen atom present formed more stable oxime.

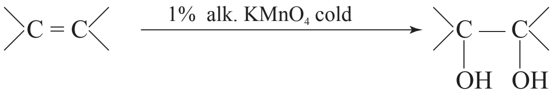


Oxime

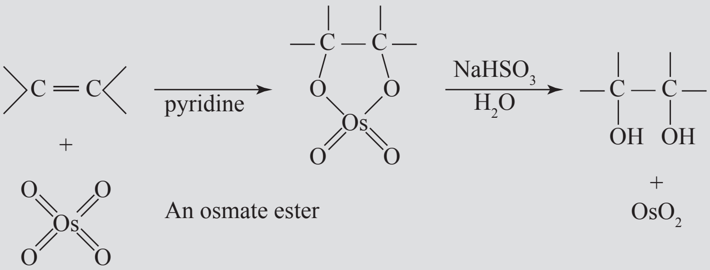
Hydroxylation

Hydroxylation occurs by using 1per cent alk. $KMnO_4$ (Baeyer's Reagent), OsO_4, Pyridine or $NaHSO_3/H_2O$ at low temperature to give dihydroxy compound. On hydroxylation all of these reagents give syn addition and the colour of $KMnO_4$ disappears. Hence it also a test of unsaturation.

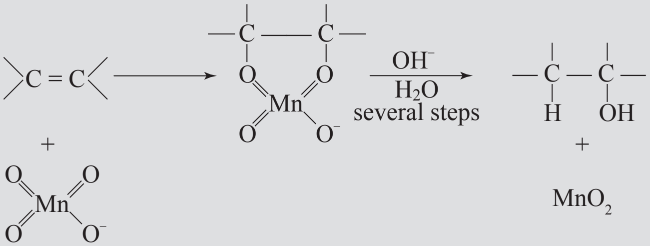
For example,



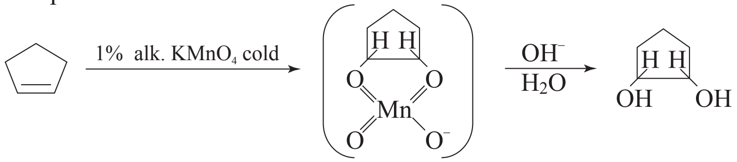
Mechanism



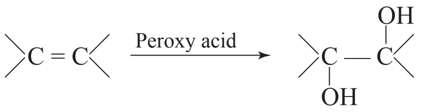
Mechanism



For example



- Anti Hydro-oxylation is not much common and is as follows:



trans 1,2-Diols

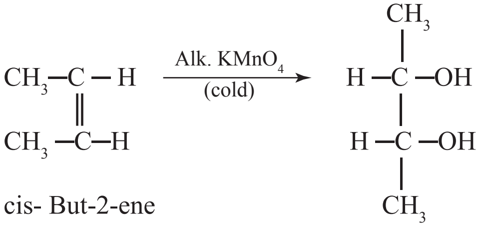
Stereochemistry of Hydroxylation

cis alkene + cis mode reagent → Meso
1% alk. $KMnO_4$ Product
or OsO_4

trans Alkene + cis mode → Racemic
reagent mixture
cis Alkene + trans mode → Racemic
reagent mixture

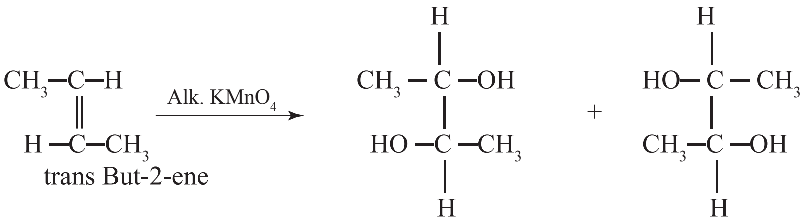
(Φ – C OO – OH)
trans + trans mode → Meso Product
Alkene reagent

For example,



cis- But-2-ene

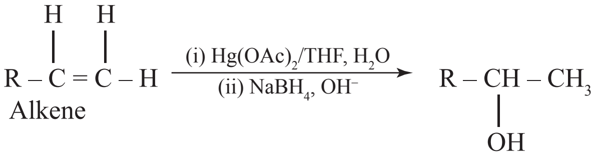
(Meso butan -2,3 -di-ol)



trans But-2-ene

Racemic Mixture of butan -2,3 -di-ol

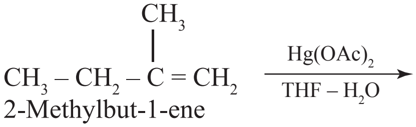
Oxymercuration-Demercuration It involves synthesis of alcohols or ethers from alkenes in accordance with Markownikoff's ruleand oxymercuration-demercuration is not prone to hydride or alkanide rearrangement.



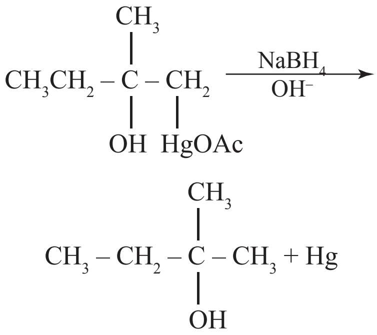
Alkene

Alcohol

For example,

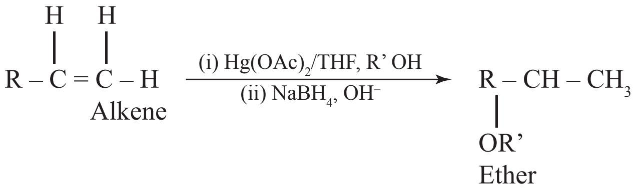


2-Methylbut-1-ene



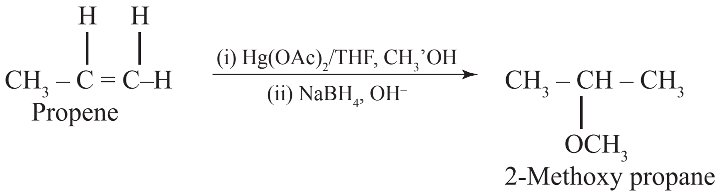
$$CH_3CH_2-\underset{OH}{\overset{CH_3}{C}}-\underset{HgOAc}{CH_2} \xrightarrow[OH^-]{NaBH_4} CH_3-CH_2-\underset{OH}{\overset{CH_3}{C}}-CH_3 + Hg$$

2-Methylbutan-2-ol

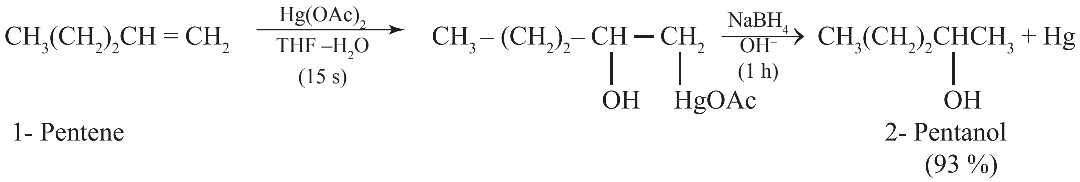


$$\underset{Alkene}{R-\overset{H}{C}=\overset{H}{C}-H} \xrightarrow[\text{(ii) NaBH}_4\text{, OH}^-]{\text{(i) Hg(OAc)}_2\text{/THF, R' OH}} \underset{Ether}{R-\underset{OR'}{CH}-CH_3}$$

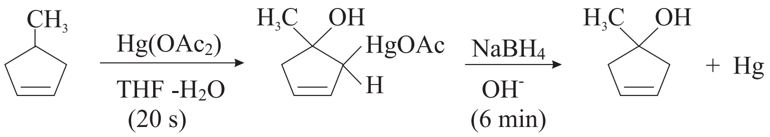
For example,



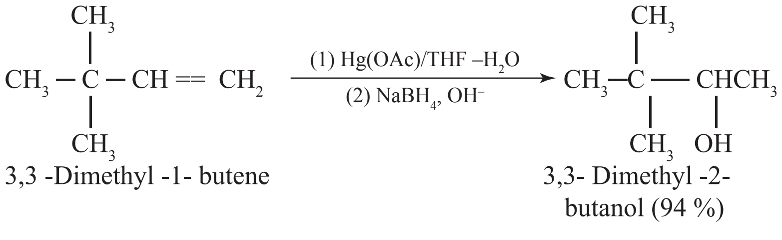
$$\underset{Propene}{CH_3-\overset{H}{C}=\overset{H}{C}-H} \xrightarrow[\text{(ii) NaBH}_4\text{, OH}^-]{\text{(i) Hg(OAc)}_2\text{/THF, CH}_3\text{'OH}} \underset{\text{2-Methoxy propane}}{CH_3-\underset{OCH_3}{CH}-CH_3}$$



$$\underset{\text{1- Pentene}}{CH_3(CH_2)_2CH=CH_2} \xrightarrow[\substack{\text{THF –H}_2\text{O} \\ \text{(15 s)}}]{Hg(OAc)_2} CH_3-(CH_2)_2-\underset{OH}{CH}-\underset{HgOAc}{CH_2} \xrightarrow[\substack{OH^- \\ \text{(1 h)}}]{NaBH_4} \underset{\substack{\text{2- Pentanol} \\ \text{(93 \%)}}}{CH_3(CH_2)_2\underset{OH}{CH}CH_3} + Hg$$

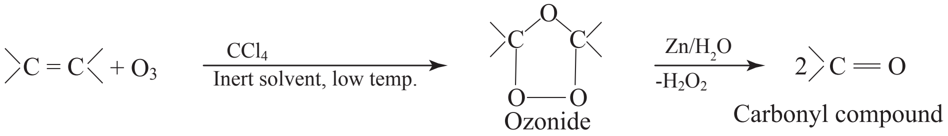


1- methylcyclopentene 1- methylcyclopentanol

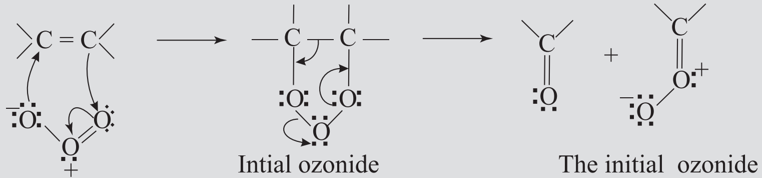


$$\underset{\text{3,3 -Dimethyl -1- butene}}{CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH=CH_2} \xrightarrow[\text{(2) NaBH}_4\text{, OH}^-]{\text{(1) Hg(OAc)/THF –H}_2\text{O}} \underset{\substack{\text{3,3- Dimethyl -2-} \\ \text{butanol (94 \%)}}}{CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{OH}{CH}CH_3}$$

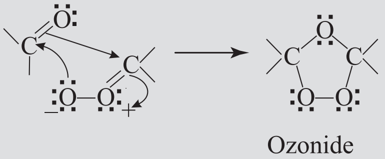
Ozonolysis It is an important reaction to find number of double bonds and their location. When a stream of ozone or ozonized oxygen is passed through alkene in a inert solvent like CCl_4 at low temperature an intermediate compound ozonide is formed which on reduction gives two moles of carbonyl compound.



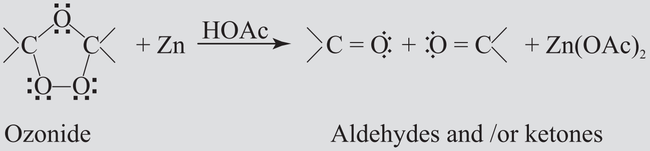
Mechanism



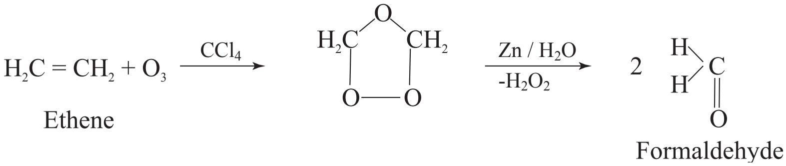
Ozone adds to the alkene to form an initial ozonide.

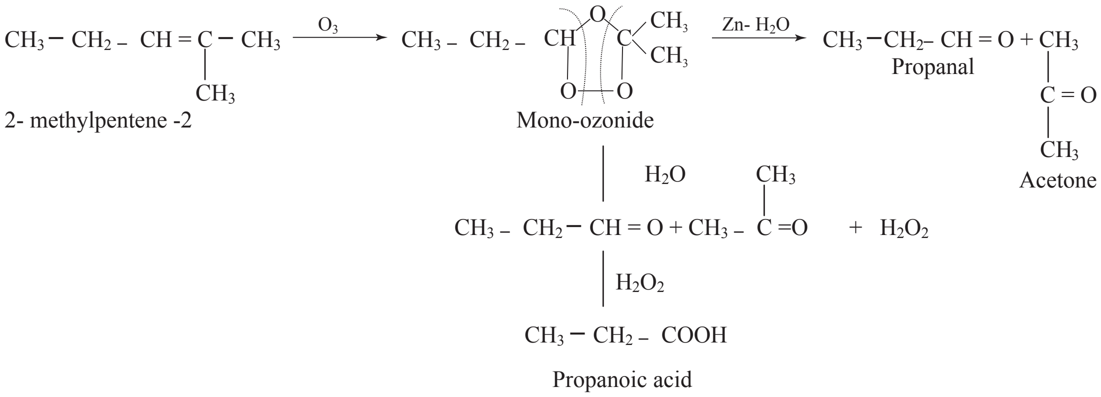


The fragments recombine to form the ozonide



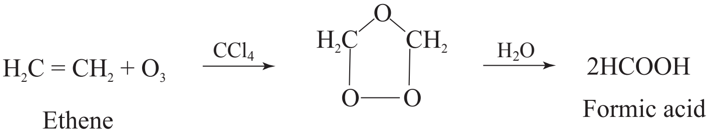
For example,

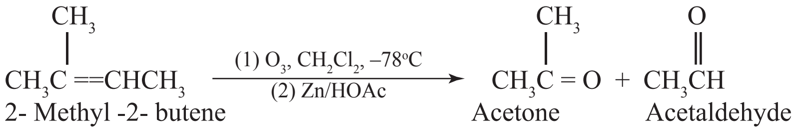




- If zinc is not used, aldehydes get oxidized into acids.

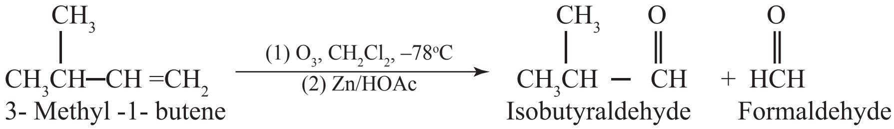
For example,





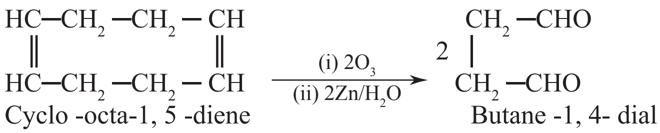
$$CH_3C(CH_3){=\!=}CHCH_3 \xrightarrow[\text{(2) Zn/HOAc}]{\text{(1) }O_3,\ CH_2Cl_2,\ -78^\circ C} CH_3C(CH_3)=O + CH_3CH{=}O$$

2- Methyl -2- butene — Acetone — Acetaldehyde



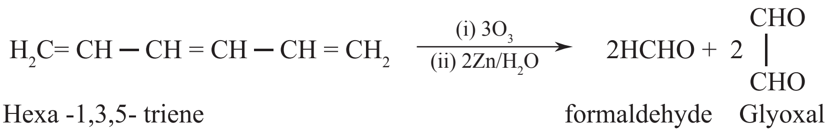
$$CH_3CH(CH_3)-CH=CH_2 \xrightarrow[\text{(2) Zn/HOAc}]{\text{(1) }O_3,\ CH_2Cl_2,\ -78^\circ C} CH_3CH(CH_3)-CH{=}O + HCH{=}O$$

3- Methyl -1- butene — Isobutyraldehyde — Formaldehyde



$$\text{Cyclo-}(HC=CH-CH_2-CH_2-CH=CH-CH_2-CH_2) \xrightarrow[\text{(ii) }2Zn/H_2O]{\text{(i) }2O_3} 2\ \begin{array}{l}CH_2-CHO\\ |\\ CH_2-CHO\end{array}$$

Cyclo -octa-1, 5 -diene — Butane -1, 4- dial



$$H_2C=CH-CH=CH-CH=CH_2 \xrightarrow[\text{(ii) }2Zn/H_2O]{\text{(i) }3O_3} 2HCHO + 2\ \begin{array}{l}CHO\\ |\\ CHO\end{array}$$

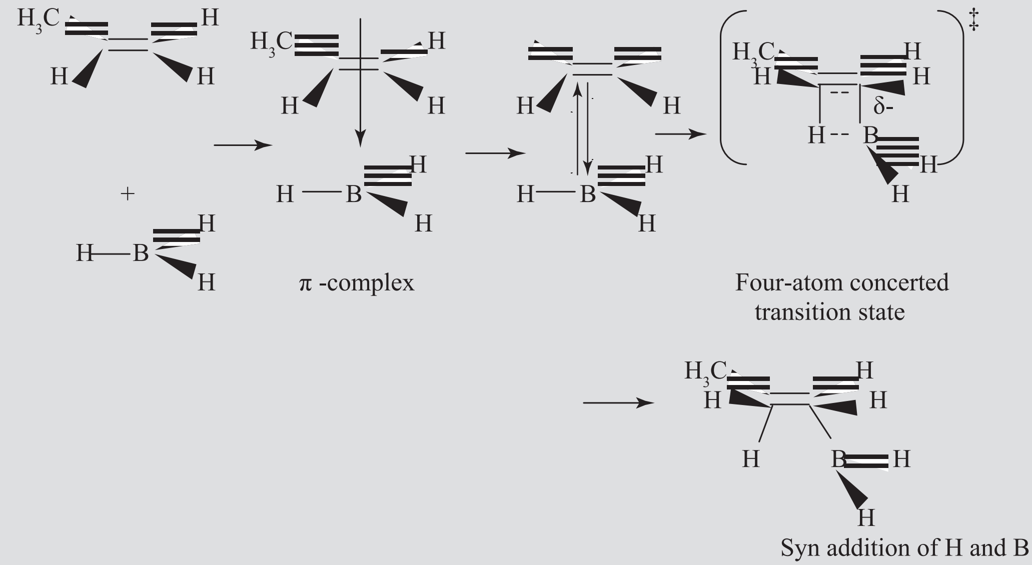
Hexa -1,3,5- triene — formaldehyde — Glyoxal

Hydroboration Oxidation It is used to prepare alcohols in accordance with Anti-MarkowniKoff's rule as follows.

$$R-CH=CH_2 \xrightarrow[H_2O_2-NaOH]{B_2H_6} R-CH_2-CH_2-OH$$

Alkene

Mechanism



For example,

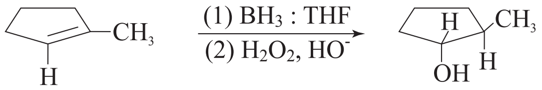
$$H_2C = CH_2 \xrightarrow[H_2O_2 - NaOH]{B_2H_6} H_3C - CH_2 - OH$$

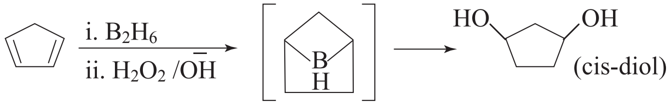
Ethene Ethanol

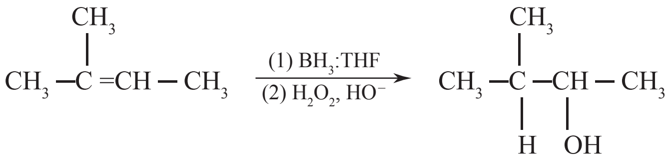
For example,

$$H_3C - CH = CH_2 \xrightarrow[H_2O_2 - NaOH]{B_2H_6} H_3C - CH_2 - CH_2 - OH$$

Propene Propan-1-ol

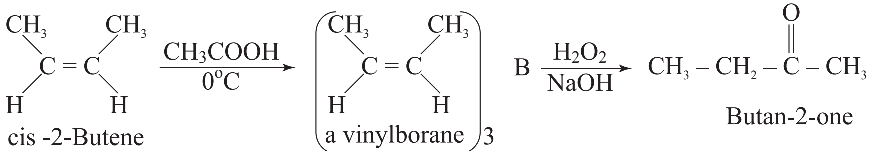






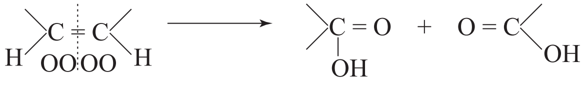
$$CH_3-\overset{\overset{\Large CH_3}{|}}{C}=CH-CH_3 \xrightarrow[(2)\ H_2O_2,\ HO^-]{(1)\ BH_3:THF} CH_3-\underset{\underset{\Large H}{|}}{\overset{\overset{\Large CH_3}{|}}{C}}-\underset{\underset{\Large OH}{|}}{CH}-CH_3$$

2 -Methyl -2- butene 3 -Methyl -2- butanol

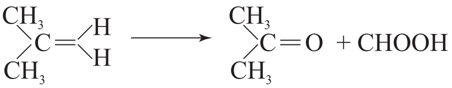


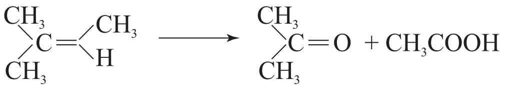
Oxidative Cleavage with Hot Potassium Permanganate

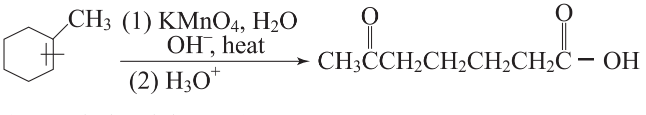
When alkenes are treated with hot alkaline or acidic $KMnO_4$ or $K_2Cr_2O_7$, they get oxidized into acids, Ketones (If un- saturated C has no H- atom a ketone is formed) as follows:



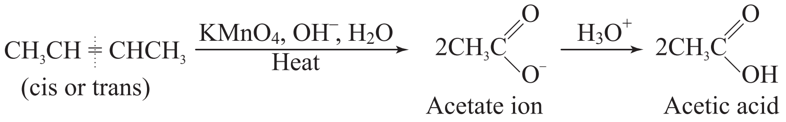
For example,

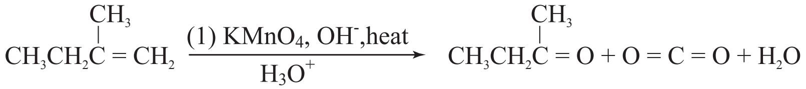




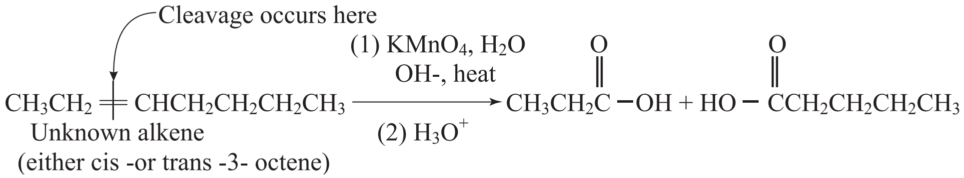


(1- Methylcyclohexene)



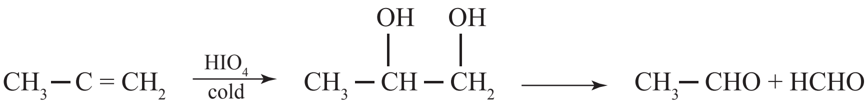


$$CH_3CH_2\overset{CH_3}{\overset{|}{C}}=CH_2 \xrightarrow[H_3O^+]{(1)\ KMnO_4,\ OH^-,heat} CH_3CH_2\overset{CH_3}{\overset{|}{C}}=O+O=C=O+H_2O$$

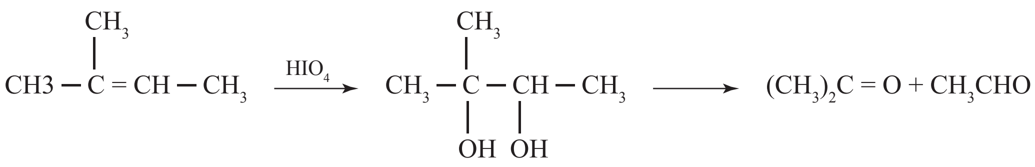


$$CH_3CH_2=CHCH_2CH_2CH_2CH_3 \xrightarrow[(2)\ H_3O^+]{(1)\ KMnO_4,\ H_2O,\ OH\text{-},\ heat} CH_3CH_2\overset{O}{\overset{\|}{C}}-OH+HO-\overset{O}{\overset{\|}{C}}CH_2CH_2CH_2CH_3$$

The moderate oxidation of alkenes using HIO_4 or lead tetra acetate, $Pb(OCOCH_3)_4$ gives rise to ketones or aldehydes.



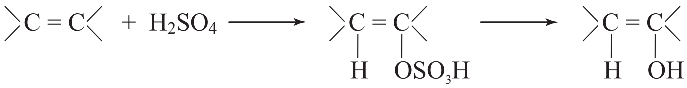
$$CH_3-C=CH_2 \xrightarrow[cold]{HIO_4} CH_3-\overset{OH}{\overset{|}{CH}}-\overset{OH}{\overset{|}{CH_2}} \longrightarrow CH_3-CHO+HCHO$$



$$\text{CH3}-\overset{CH_3}{\overset{|}{C}}=CH-CH_3 \xrightarrow{HIO_4} CH_3-\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-\underset{OH}{\underset{|}{CH}}-CH_3 \longrightarrow (CH_3)_2C=O+CH_3CHO$$

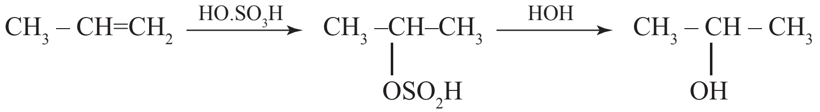
Some Other Reactions (Not For IIT-JEE)

With H_2SO_4 Alkenes react with H_2SO_4 (dil.) to give alcohols as follows:

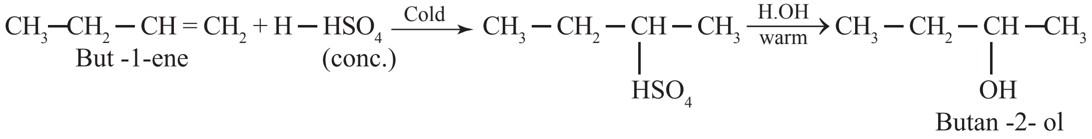


$$>C=C< + H_2SO_4 \longrightarrow >\underset{H}{C}=\underset{OSO_3H}{C}< \longrightarrow >\underset{H}{C}=\underset{OH}{C}<$$

For example,

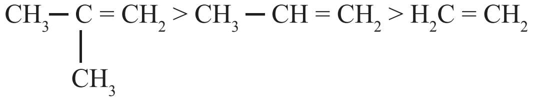


$$CH_3-CH=CH_2 \xrightarrow{HO.SO_3H} CH_3-\underset{OSO_2H}{CH}-CH_3 \xrightarrow{HOH} CH_3-\underset{OH}{CH}-CH_3$$



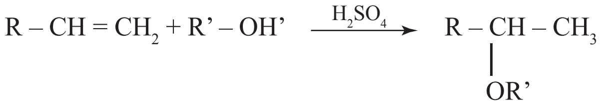
$$\underset{\text{But -1-ene}}{CH_3-CH_2-CH=CH_2} + \underset{\text{(conc.)}}{H-HSO_4} \xrightarrow{\text{Cold}} CH_3-CH_2-\underset{HSO_4}{CH}-CH_3 \xrightarrow[\text{warm}]{H.OH} \underset{\text{Butan -2- ol}}{CH_3-CH_2-\underset{OH}{CH}-CH_3}$$

Acid catalysed hydration of alkenes with Markownikoff's rule are regioselective reactions. The order of hydration is



$$CH_3-\underset{CH_3}{C}=CH_2 > CH_3-CH=CH_2 > H_2C=CH_2$$

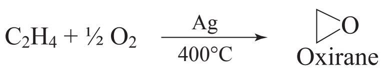
With R – OH Alkenes react with alcohol to give Esters using Markownikoff rule as follows:



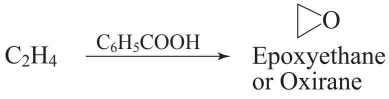
$$R-CH=CH_2 + R'-OH' \xrightarrow{H_2SO_4} R-\underset{OR'}{CH}-CH_3$$

Addition of O_2 Alkenes on reaction with O_2 or with peroxy acid in presence of catalyst Ag gives epoxy ethers (epoxides). It is syn addition

For example,



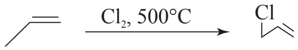
Oxirane

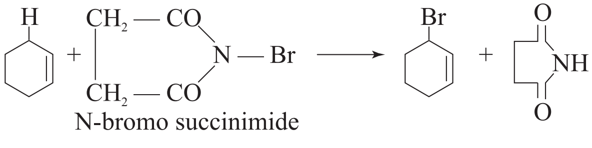


Epoxyethane or Oxirane

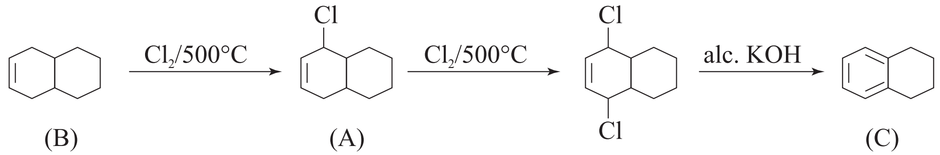
Substitution Reaction

Alkenes can undergo substitution only at allylic position and at a high temperature of 450 – 500°C.

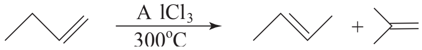




N-bromo succinimide



Isomerization



Mechanism

$$CH_3-CH_2-CH_2-CH=CH_2+AlCl_3 \rightleftharpoons CH_3-CH_2-CH_2-CH-CH_2-\overset{+}{AlCl_3}$$

$$-H^+ \;\Updownarrow\; +H^+$$

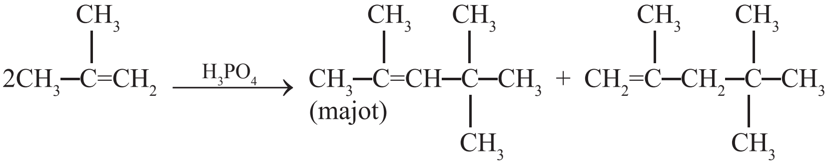
$$H_3C-CH_2-CH=CH-CH_2-AlCl_3$$

$$-H^+ \;\Updownarrow\; +H^+$$

$$AlCl_3+CH_3-CH_2-CH=CH-CH_3$$

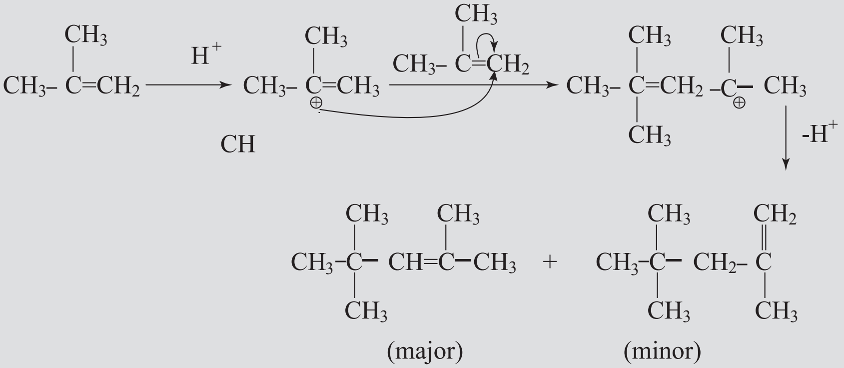
Acid Catalyzed Dimerization of Alkenes

(I) In case of monoalkene, two alkenes dimerize to form a larger alkene.

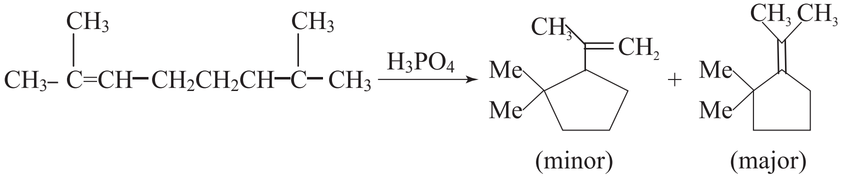


$$2CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2 \xrightarrow{H_3PO_4} \underset{\text{(majot)}}{CH_3-\overset{\overset{CH_3}{|}}{C}=CH-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3} + CH_2=\overset{\overset{CH_3}{|}}{C}-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

Mechanism



(II) In case of diene, ring formation takes place depending upon the structure of diene.



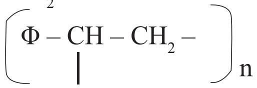
- **Polymerization**

The most common catalyst used for polymerization of olefins is Zeigler Natta catalyst [$TiCl_4 + (Et)_3Al$].

$$nH_2C = CH_2 \xrightarrow[\text{high 'T'} \\ \text{high 'P'}]{\Delta} [–CH_2 – CH_2 –]n$$

Polythene

$$n\Phi – CH = CH_2 \longrightarrow$$



$$\left(\Phi – CH – CH_2 – \right)_n$$

Poly Styrene [rubber]

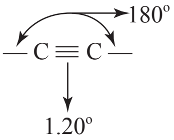
$$n\ CF_2 = CF_2 \longleftrightarrow [– CF_2 – CF_2 –]_n$$

Teflon (Poly Tetra fluoroethylene)

Combustion

$$C_nH_{2n} + 3n/2\ O_2 \xrightarrow{\Delta} n\ CO_2 + nH_2O\ (n = –ve)$$

ALKYNES

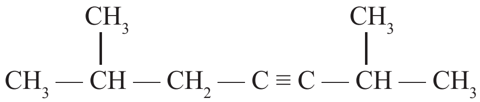


- These have a general formula [C_nH_{2n-2}] and known as alkynes.

  For example,

  $CH \equiv CH$ Ethyne
  $CH_3 – C \equiv CH$ Propyne
  $CH_3 – C \equiv C – CH_3$ Butyne – 2.

  $(CH_3)_3CC \equiv CC(CH_3)_3$
  2,2,5,5 -tetra- methyl- hex 3-yne



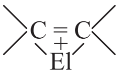
$$CH_3 — \underset{}{\overset{CH_3}{\overset{|}{CH}}} — CH_2 — C \equiv C — \overset{CH_3}{\overset{|}{CH}} — CH_3$$

  2, 6 -di -methyl - hept -3- yne

- Alkynes show chain, position, functional isomerism (with alka dienes)
- All terminal alkynes are acidic in nature and acidic nature with the increase in c-atom number decrease as follows

  $CH \equiv CH > CH_3 – C \equiv CH > CH_3 – CH_2 – C \equiv CH > …..$

  [$R – C \equiv H > R – CH = CH_2 > R – CH_3$]
- C_2H_2 is linear, poisonous with garlic smell due to impurities of AsH_3, PH_3, H_2S.
- C_2H_2 is dibasic acids with very strong bases like NH_2^-, CH_3^-.
- Alkynes are less reactive towards electrophilic addition as greater activation energy is needed due to formation of a less stable cyclic reaction intermediate species.

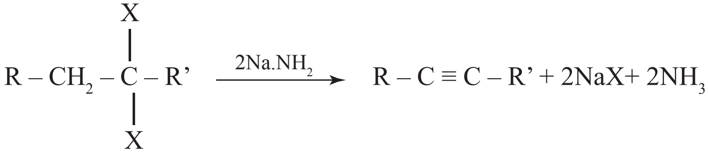


Test of Terminal Alkynes

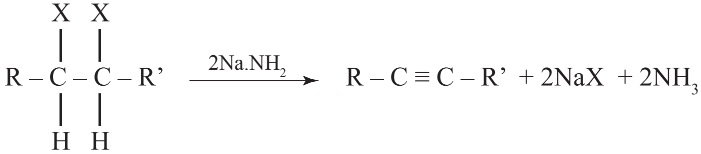
- They give white precipitate of $R-C\equiv CAg$ with ammonical silver nitrate $AgNO_3$.
- They give red precipitate of $R-C\equiv C.Cu$ with ammonical Cu_2Cl_2.

METHODS OF PREPARATION

(1) By Elimination Reaction Here dihalides undergo α, β-elimination reaction with $NaNH_2$ or alcoholic KOH to give alkynes.

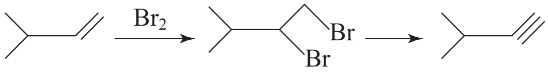


$$R-CH_2-\underset{\underset{X}{|}}{\overset{\overset{X}{|}}{C}}-R' \xrightarrow{2Na.NH_2} R-C\equiv C-R' + 2NaX + 2NH_3$$



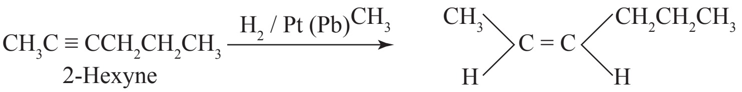
$$R-\underset{\underset{H}{|}}{\overset{\overset{X}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{X}{|}}{C}}-R' \xrightarrow{2Na.NH_2} R-C\equiv C-R' + 2NaX + 2NH_3$$

For example,



$$CH_3CH=CHCH_2CH_2CH_3 \xrightarrow{Br_2} CH_3CH-CHCH_2CH_2CH_3 \xrightarrow{NaNH_2}$$

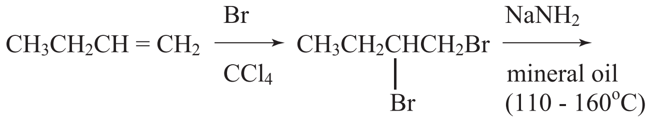
cis-and *trans*-2-Hexene



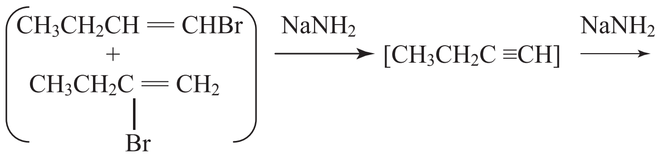
$$CH_3C\equiv CCH_2CH_2CH_3 \xrightarrow{H_2\,/\,Pt\,(Pb)}$$

2-Hexyne
or
Hex-2-yne

(Z)-or *cis*-2-Hexene



$$CH_3CH_2CH=CH_2 \xrightarrow[CCl_4]{Br} CH_3CH_2\underset{\underset{Br}{|}}{C}HCH_2Br \xrightarrow[\substack{\text{mineral oil}\\(110-160^{\circ}C)}]{NaNH_2}$$



$$\left(\begin{array}{c} CH_3CH_2CH=CHBr \\ + \\ CH_3CH_2\underset{\underset{Br}{|}}{C}=CH_2 \end{array}\right) \xrightarrow{NaNH_2} [CH_3CH_2C\equiv CH] \xrightarrow{NaNH_2}$$

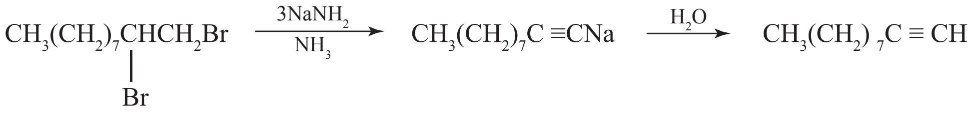
$$CH_3CH_2C\equiv C{:}^{-}\,Na^{+} \longrightarrow CH_3CH_2C\equiv CH + NH_3 + NaCl$$

$$(CH_3)_3CCH_2CHCl_2 \xrightarrow[NH_3]{3NaNH_2} (CH_3)_3CC\equiv CNa \xrightarrow{H_2O} (CH_3)_3CC\equiv CH$$

1,1 -Dichloro -3, 3-dimethylbutane

Sodium salt of alkyne product (not isolated)

3,3- Dimethyl - 1 -butyne (56 -60 %)

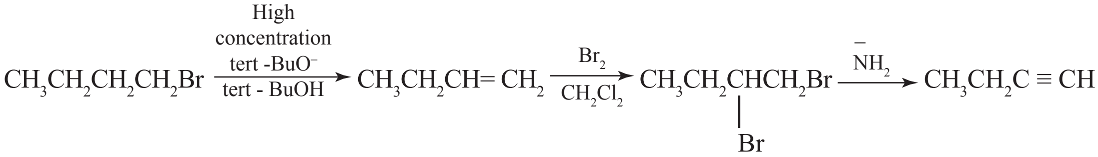


$$CH_3(CH_2)_7\underset{\underset{\displaystyle Br}{|}}{C}HCH_2Br \xrightarrow[NH_3]{3NaNH_2} CH_3(CH_2)_7C\equiv CNa \xrightarrow{H_2O} CH_3(CH_2)_7C\equiv CH$$

1, 2- Dibromodecane

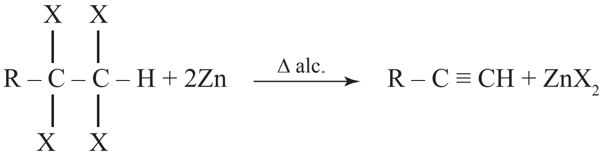
Sodium salt of alkyne product (not isolated)

1- Decyne (54 %)



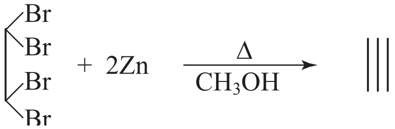
$$CH_3CH_2CH_2CH_2Br \xrightarrow[\text{tert - BuOH}]{\text{High concentration tert -BuO}^-} CH_3CH_2CH{=}\,CH_2 \xrightarrow[CH_2Cl_2]{Br_2} CH_3CH_2\underset{\underset{\displaystyle Br}{|}}{C}HCH_2Br \xrightarrow{\overset{-}{N}H_2} CH_3CH_2C\equiv CH$$

(2) From Tetra Halogen Compounds



$$R-\underset{\underset{\displaystyle X}{|}}{\overset{\overset{\displaystyle X}{|}}{C}}-\underset{\underset{\displaystyle X}{|}}{\overset{\overset{\displaystyle X}{|}}{C}}-H + 2Zn \xrightarrow{\Delta\ \text{alc.}} R-C\equiv CH + ZnX_2$$

For example,



Some Other Methods

(3) From Carbides

$$CaO + 3C \xrightarrow{1800\text{-}2100^{\circ}C} CaC_2 \xrightarrow{2H_2O} C_2H_2 + Ca(OH)_2$$

$$Mg_2C_3 \xrightarrow{4H_2O} CH_3-C\equiv CH + 2Mg(OH)_2$$

(4) From CH_4

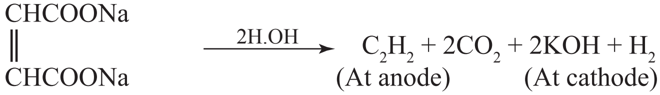
$$2CH_4 \xrightarrow[1200^{\circ}C]{\text{elec arc}} C_2H_2 + 3H_2$$

$$6CH_4 + O_2 \xrightarrow{1500^{\circ}C} 2\,C_2H_2 + 2CO + 10H_2$$

(5) By Heating CHX_3 With Ag Powder

$$CHX_3 + 6Ag + X_3CH \xrightarrow{\Delta} HC\equiv CH + 6AgX$$

(6) Kolbe's Method Sodium or potassium maleate or fumerate on electrolysis of its aqueous solution gives acetylene at anode.



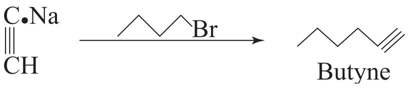
$$\begin{array}{l}CHCOONa\\ \|\\ CHCOONa\end{array} \xrightarrow{2H.OH} \underset{\text{(At anode)}}{C_2H_2 + 2CO_2} + 2KOH + \underset{\text{(At cathode)}}{H_2}$$

Sodium maleate
or fumerate

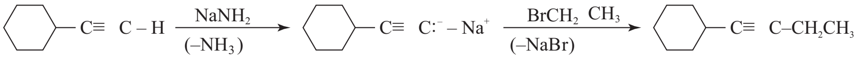
(7) Preparation of Alkynes by Alkylation of Acetylene or Terminal Alkynes

$$R-C\equiv CH \xrightarrow{NaNH_2} R-C\equiv C.Na \xrightarrow{R'X} R-C\equiv C-R' + NaX$$

For example,

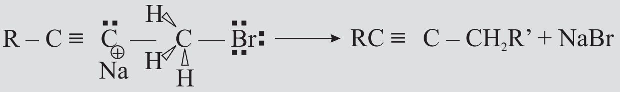


For example,2

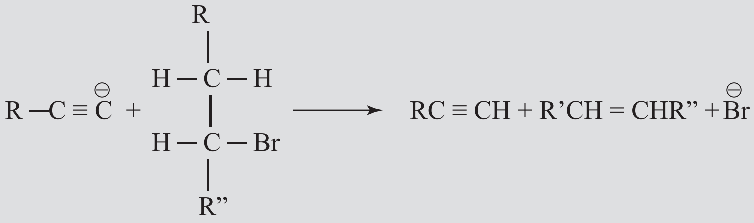


REMEMBER

It is to be noted that alkynide ion acts as a nucleophile and displaces a halide ion from the primary alkyl halide. The result is an S_N2 reaction.



However, if secondary of tertiary alkyl halides are used because the alkynide ion acts as a base rather than a nucleophile and the major result is an E_2 reaction. The products are an alkene and the alkyne from which the sodium alkynide was originally formed.



$$R-C\equiv \overset{\ominus}{C} + R-CH_2-CHBr-R'' \longrightarrow RC\equiv CH + R'CH=CHR'' + \overset{\ominus}{Br}$$

PHYSICAL PROPERTIES

- Alkyne with >3-carbon atoms are liquids and with $>C_{14}$ carbon atoms are solids.
- Acetylene is a colourless gas with garlic like smell and with a boiling point of –84°C and it is poisonous and lighter than air.
- Boiling and melting points are higher in alkynes than for alkenes and alkanes, due to greater polarity of bond in alkynes.

CHEMICAL PROPERTIES

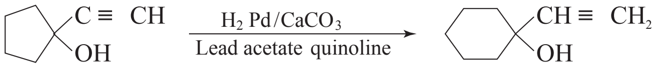
The chemical properties of alkynes can be given as:

(A) Addition Reactions

Hydrogenation: Alkynes are more reactive than alkene towards hydrogenation. It is because the alkynes can be easily adsorbes on the surface of catalyst due to cylindrical nature of π -bond.

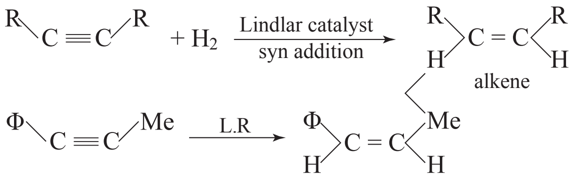
$$R-C\equiv C-R \xrightarrow[H_2]{\text{Pt, Pd, Ni, etc.}} R-CH{=}CH-R \xrightarrow{H_2} R-CH_2-CH_2-R$$

- Lindlar catalyst [$PdCO_3/BaCO_3$ poisoned by quinoline or lead acetate] is used for selective hydrogenation to prepare alkene only.

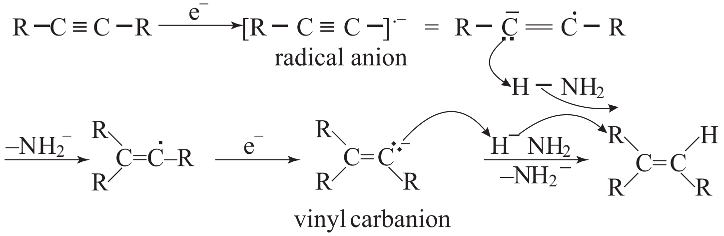


1-vinyl cyclo hexanol

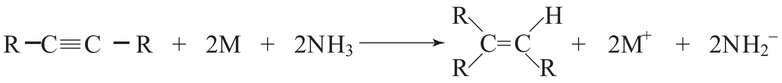
Stereochemistry of the Reaction



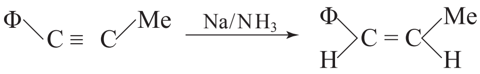
- Nickel boride (P-2) also gives syn addition while in case of Na/NH_3 hydrogenation is anti-addition.

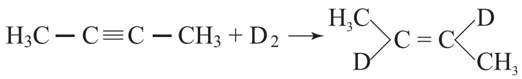


The net reaction for this dissolving metal reduction is

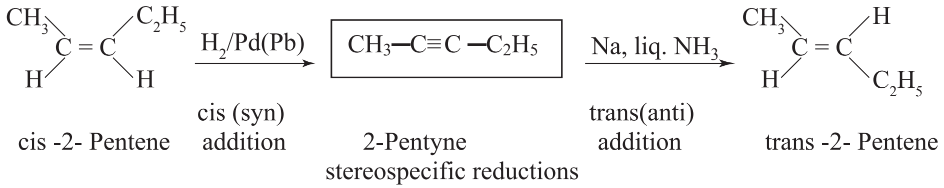


For example,

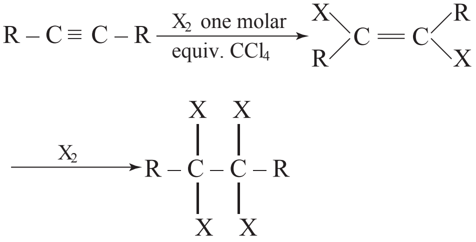




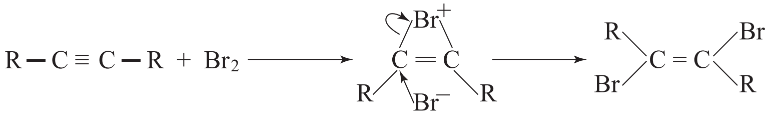
But -2- ene(trans)



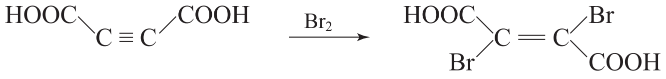
With Halogen



- Here addition is Anti and it shouldn't surprise you to find that addition to alkynes involving such electrophiles as Br^+, RS^+, and HgX^+ leads to predominant anti addition via cyclic 'onium ion intermediates.

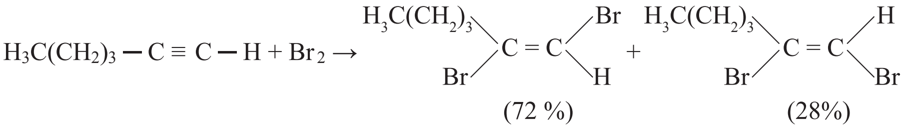


For example,



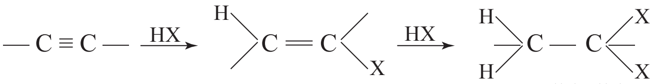
$$CH\equiv CH \xrightarrow{Cl_2} CHCl = CHCl \xrightarrow{Cl_2} \underset{\text{Westrone}}{CHCl_2 - CHCl_2} \xrightarrow{BaCl_2} \underset{\text{Westrosol}}{CCl_2 = CHCl}$$

- Both Westrone and Westrosol are good industrial solvents for oil, fat, waxes etc.



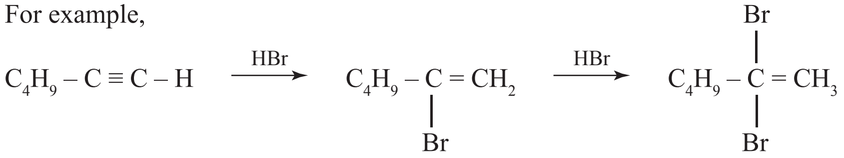
Addition of HX

Addition occurs according to Markoni koff's rule and Anti-Markownikoff's rule



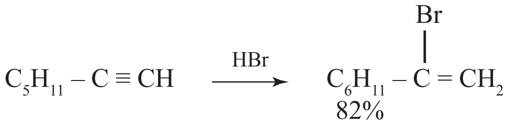
Gem di halide

For example,



$$C_4H_9-C\equiv C-H \xrightarrow{HBr} C_4H_9-\underset{\underset{Br}{|}}{C}=CH_2 \xrightarrow{HBr} C_4H_9-\overset{\overset{Br}{|}}{\underset{\underset{Br}{|}}{C}}=CH_3$$

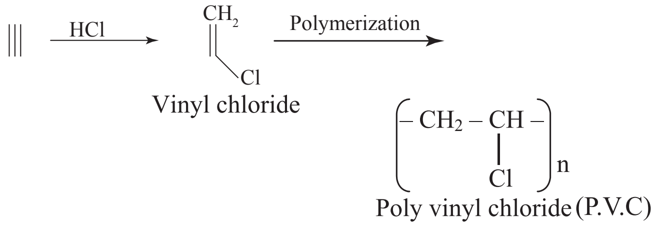
- If we use CH_3COBr/Alumina rate of reaction increases here

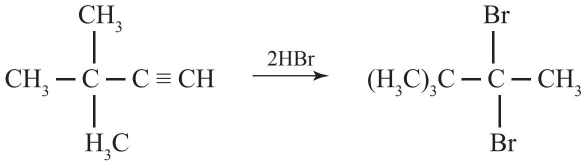


$$C_5H_{11}-C\equiv CH \xrightarrow{HBr} C_6H_{11}-\overset{\overset{\displaystyle Br}{|}}{C}=CH_2$$

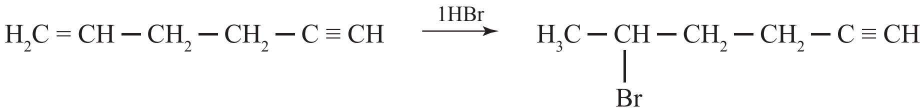
82%

-

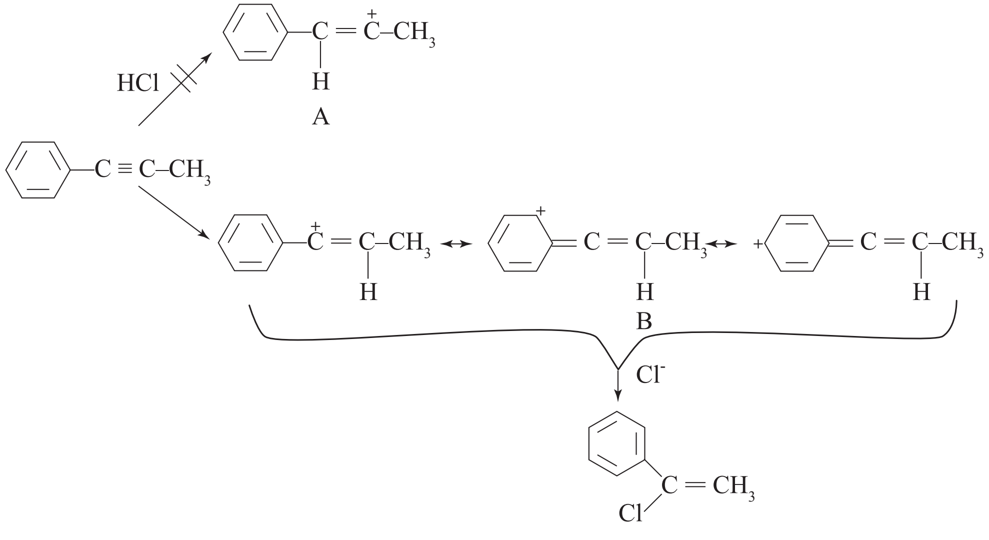




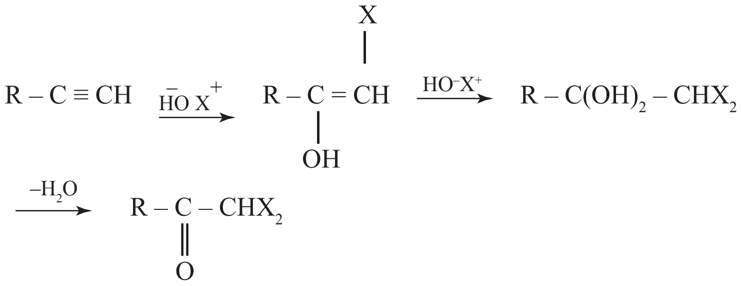
$$CH_3-\underset{\underset{\displaystyle H_3C}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-C\equiv CH \xrightarrow{2HBr} (H_3C)_3C-\underset{\underset{\displaystyle Br}{|}}{\overset{\overset{\displaystyle Br}{|}}{C}}-CH_3$$



$$H_2C=CH-CH_2-CH_2-C\equiv CH \xrightarrow{1HBr} H_3C-\underset{\underset{\displaystyle Br}{|}}{CH}-CH_2-CH_2-C\equiv CH$$



With $\overset{-}{HO}\overset{+}{X}$: Here addition occurs according to Markoni koff's Rule and X^+ is attacking reagent.



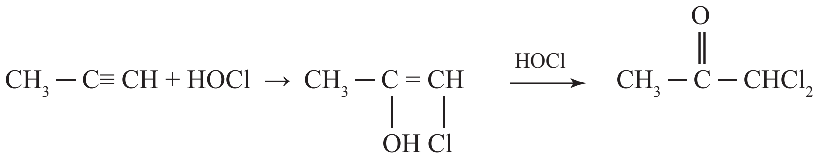
$$R-C\equiv CH \xrightarrow{\overset{-}{HO}\,X^{+}} R-\underset{\displaystyle OH}{\underset{|}{C}}=\overset{\displaystyle X}{\overset{|}{CH}} \xrightarrow{HO^-X^+} R-C(OH)_2-CHX_2$$

$$\xrightarrow{-H_2O} R-\underset{\displaystyle O}{\underset{\|}{C}}-CHX_2$$

For example,

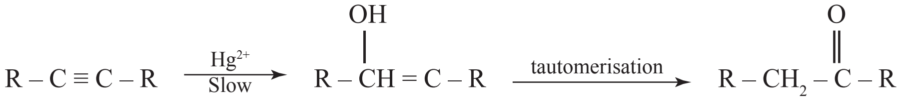
$$CH\equiv CH \xrightarrow{HOCl} CHOH=CHCl \xrightarrow{HOCl} CH(OH)_2-CHCl_2 \xrightarrow{-H_2O} CHO-CHCl_2$$

Dichloro acetaldehyde



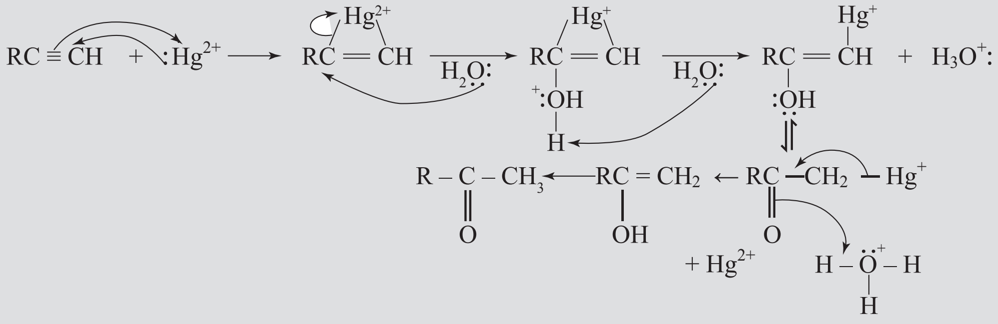
$$CH_3-C\equiv CH+HOCl \rightarrow CH_3-\underset{\displaystyle OH}{\underset{|}{C}}=\underset{\displaystyle Cl}{\underset{|}{CH}} \xrightarrow{HOCl} CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-CHCl_2$$

Hydration of Alkynes

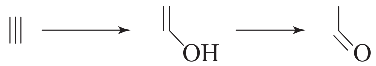


$$R-C\equiv C-R \xrightarrow[\text{Slow}]{Hg^{2+}} R-\overset{\displaystyle OH}{\overset{|}{CH}}=C-R \xrightarrow{\text{tautomerisation}} R-CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-R$$

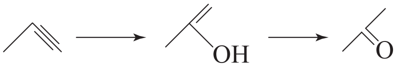
Mechanism

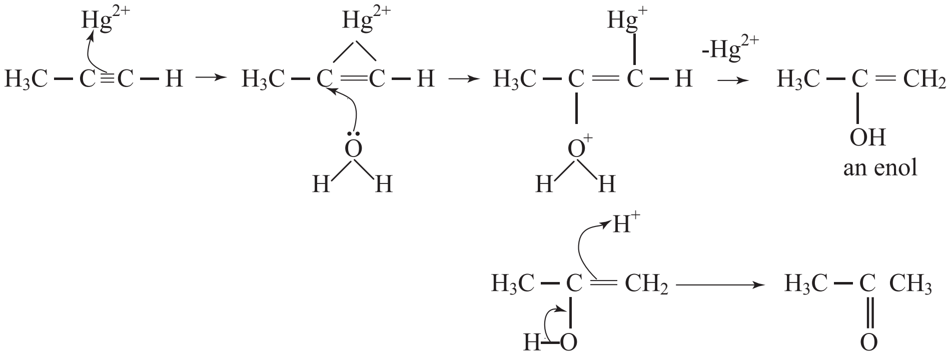


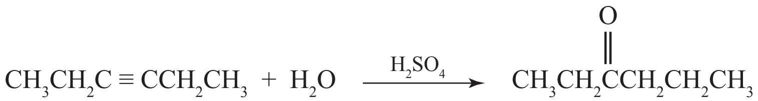
For example, 1



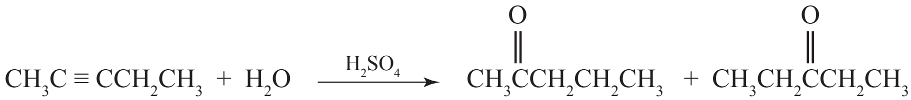
For example, 2







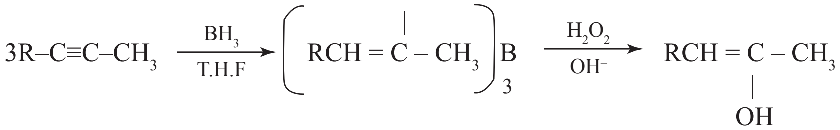
$$CH_3CH_2C\equiv CCH_2CH_3 + H_2O \xrightarrow{H_2SO_4} CH_3CH_2\overset{\overset{\displaystyle O}{\|}}{C}CH_2CH_2CH_3$$



$$CH_3C\equiv CCH_2CH_3 + H_2O \xrightarrow{H_2SO_4} CH_3\overset{\overset{\displaystyle O}{\|}}{C}CH_2CH_2CH_3 + CH_3CH_2\overset{\overset{\displaystyle O}{\|}}{C}CH_2CH_3$$

Hydroboration

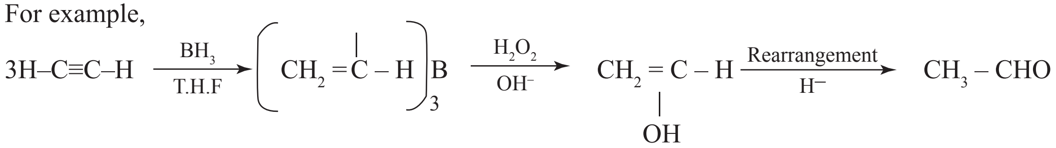
- It is used to prepare ketones from alkynes except ethyne which gives acetaldehyde.



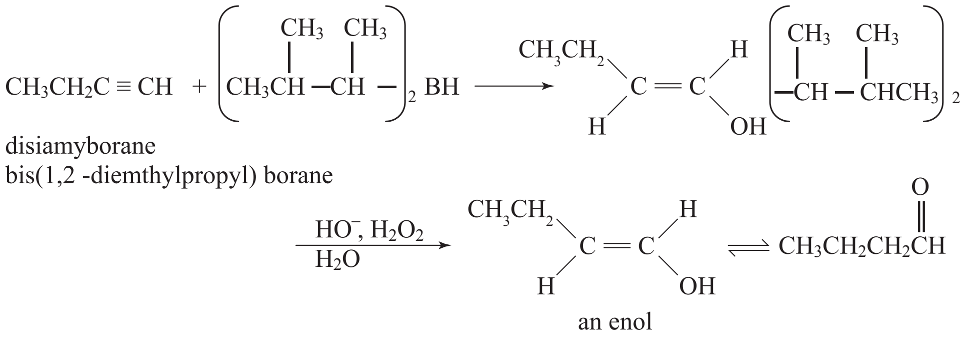
$$3R–C\equiv C–CH_3 \xrightarrow[T.H.F]{BH_3} \left(RCH=\overset{|}{C}-CH_3\right)_3 B \xrightarrow[OH^-]{H_2O_2} RCH=\underset{\underset{\displaystyle OH}{|}}{C}-CH_3$$

$$\xrightarrow{\text{Rearrangement}} RCH_2-CO-CH_3$$

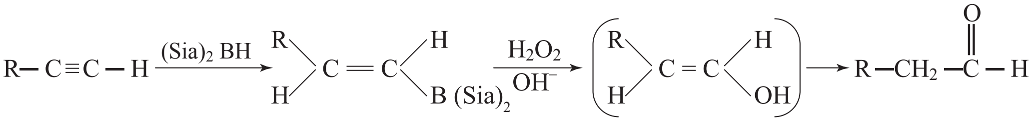
For example,



$$3H–C\equiv C–H \xrightarrow[T.H.F]{BH_3} \left(CH_2=\overset{|}{C}-H\right)_3 B \xrightarrow[OH^-]{H_2O_2} CH_2=\underset{\underset{\displaystyle OH}{|}}{C}-H \xrightarrow[H^-]{\text{Rearrangement}} CH_3-CHO$$



disiamyborane
bis(1,2 -diemthylpropyl) borane

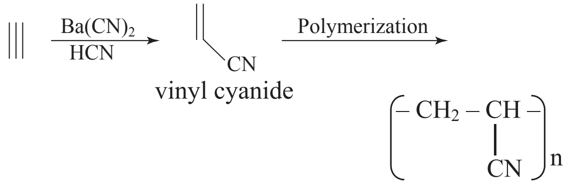


$$CH_3CH_2C\equiv CH \xrightarrow{Sia_2BH} CH_3CH_2\,CH=CHBSia_2 \xrightarrow{H_2O_2} CH_3CH_2CH=CHOH \rightleftharpoons CH_3CH_2CH_2CHO$$

$$\boxed{Sia_2BH \Rightarrow [Me_2CHCH(Me)_2]BH}$$

Some Other Addition Reactions (Not For IIT-JEE)

With HCN

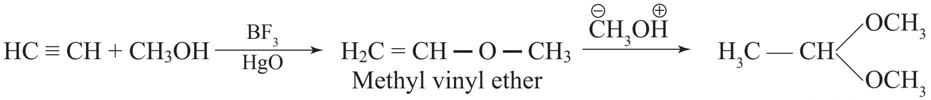


vinyl cyanide

Orlon or Acrylo nitrile (synthetic fibre)
or Poly vinyl cyanide

With Alcohol

$$CH\equiv CH \xrightarrow[HgSO_4]{C_2H_5OH} CH_2=CH-OC_2H_5 \xrightarrow{H_2O} CH_3-CHO + C_2H_5OH$$



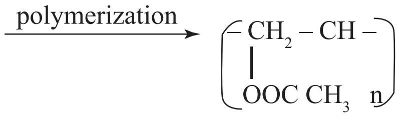
$$HC\equiv CH + CH_3OH \xrightarrow[HgO]{BF_3} H_2C=CH-O-CH_3 \xrightarrow{\overset{\ominus}{C}H_3O\overset{\oplus}{H}} H_3C-CH\begin{matrix}OCH_3\\OCH_3\end{matrix}$$

Methyl vinyl ether

Methylal

With Acetic Acid

$$CH\equiv CH \xrightarrow[HgSO_4]{CH_3COOH} CH_2=CH-OOCCH_3$$



$$\xrightarrow{\text{polymerization}} \left(\begin{matrix}-CH_2-CH-\\ \quad\quad | \\ \quad\quad OOC\,CH_3\end{matrix}\right)_n$$

Poly vinyl acetate
(adhesive)

Vinyl acetate on polymerization forms polyvinyl acetate (PVA), used in plastic industry and ethylidene acetate on heating at 300 – 400°C yields acetaldehyde and acetic anhydride.

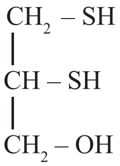
$$CH_3CH\begin{matrix}OOCCH_3\\OOCCH_3\end{matrix} \xrightarrow[300\text{ - }400^\circ C]{\text{heat}} \underset{\text{Acetaldehyde}}{CH_3CHO} + \underset{\text{Acetic anhydride}}{(CH_3CO)_2O}$$

With $AsCl_3$

$$CH\equiv CH \xrightarrow{AsCl_3} CH_2Cl=CHAsCl_2$$

Lewisite or Lewis gas
(war gas)

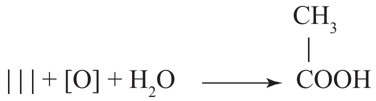
- Lewisite (β-chloro vinyl dichloro arsine) is a powerful poisonous gas which causes death at once.
- Its antidote is British Anti Lewisite (B.A.L.)



$$\begin{array}{l} CH_2-SH \\ | \\ CH-SH \\ | \\ CH_2-OH \end{array}$$

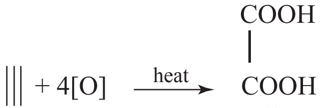
(b) Oxidation Reactions

(a) By $K_2Cr_2O_7/H_2SO_4$



$$||| + [O] + H_2O \longrightarrow \begin{array}{c} CH_3 \\ | \\ COOH \end{array}$$

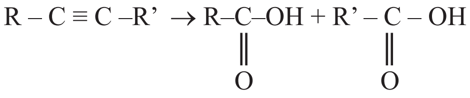
(b) By alkaline $KMnO_4$:



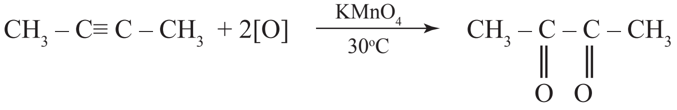
$$||| + 4[O] \xrightarrow{heat} \begin{array}{c} COOH \\ | \\ COOH \end{array}$$

Oxalic acid

(c) With hot acidic or alkaline $KMnO_4$ Here oxidative cleavage occurs to give acids.

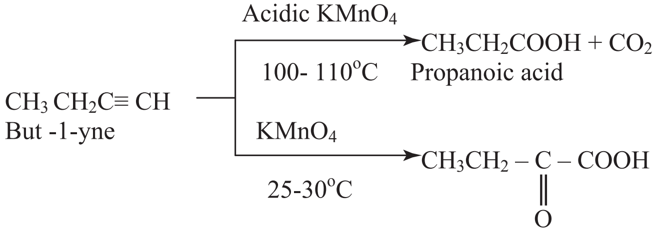


$$R-C\equiv C-R' \rightarrow R-\underset{\underset{O}{\|}}{C}-OH + R'-\underset{\underset{O}{\|}}{C}-OH$$



$$CH_3-C\equiv C-CH_3 + 2[O] \xrightarrow[30^\circ C]{KMnO_4} CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-CH_3$$

Butane -2,3- dione



$$\begin{array}{l} \underset{\text{But -1-yne}}{CH_3CH_2C\equiv CH} \end{array} \begin{cases} \xrightarrow[100-110^\circ C]{\text{Acidic } KMnO_4} \underset{\text{Propanoic acid}}{CH_3CH_2COOH + CO_2} \\ \xrightarrow[25-30^\circ C]{KMnO_4} CH_3CH_2-\underset{\underset{O}{\|}}{C}-COOH \end{cases}$$

2- Ketobutanoic acid

- If triple bond is at corner formic acid is formed which oxidizes into CO_2 and water.

For example,

$$\begin{tikzcd}
CH_3 - C \equiv CH \arrow[r, "\text{hot alk } KMnO_4"] & CH_3COOH + HCOOH \arrow[d] \\
& H_2O + CO_2
\end{tikzcd}$$

(d) With Seleniun Dioxide

$$R - C \equiv CH + 2[O] \xrightarrow{SeO_2} R - CO - CHO$$

For example,

$$CH \equiv CH \xrightarrow{SeO_2} \underset{\text{Glyoxal}}{CHO - CHO}$$

$$\underset{\text{Propyne}}{CH_3 - C \equiv CH} + 2[O] \xrightarrow{SeO_2} \underset{\text{2- Ketopropanal}}{CH_3COCHO}$$

(e) Combustion

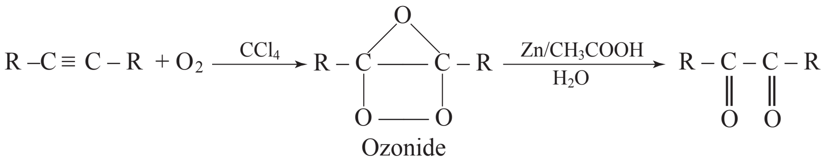
$$C_n\,H_{2n-2} + 3_{n-1}O_2 \xrightarrow{\Delta} nCO_2 + n - 1\;H_2O$$

For example,

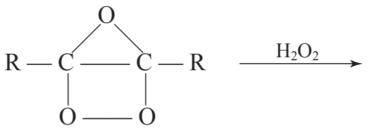
$$C_2H_2 + 5/2\;O_2 \xrightarrow{\Delta} 2CO_2 + H_2O$$

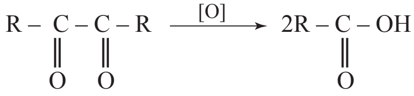
$$C_3H_4 + 4O_2 \xrightarrow{\Delta} 3CO_2 + 2H_2O$$

Ozonolysis



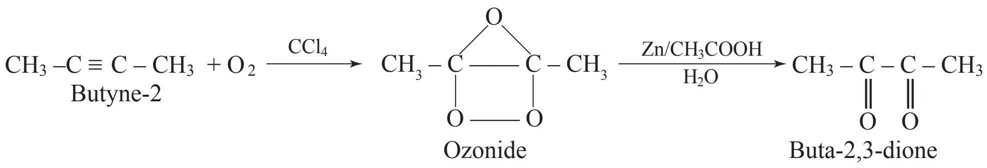
- If the decomposition is carried out by H_2O_2 or Zn/CH_3COOH is not used dicarbonyl compounds formed undergo further oxidation to give acids.

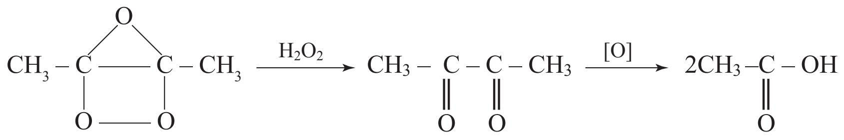




$$R - \underset{\underset{O}{\|}}{C} - \underset{\underset{O}{\|}}{C} - R \xrightarrow{[O]} 2R - \underset{\underset{O}{\|}}{C} - OH$$

For example,

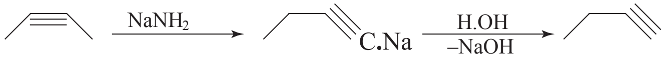


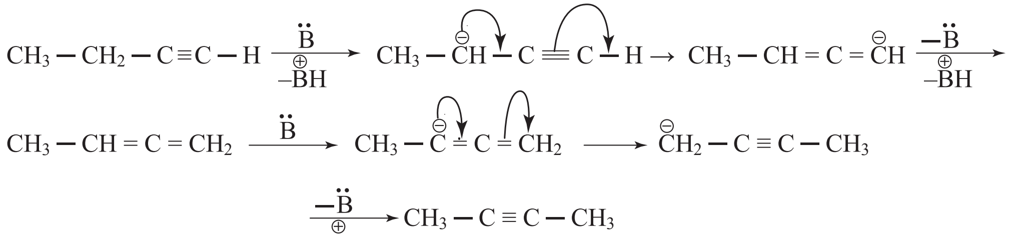


(C) Other Reactions

Isomerization

Butyne-1 Butyne-2

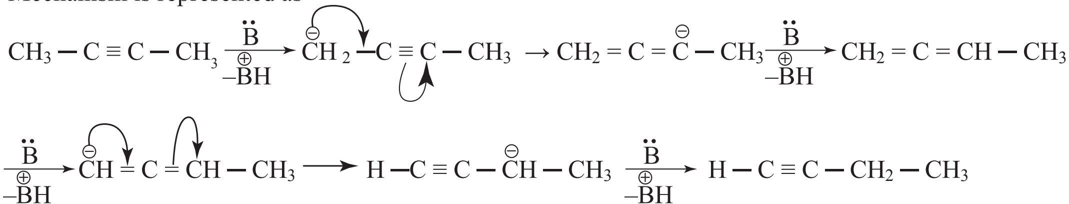




2- Butyne

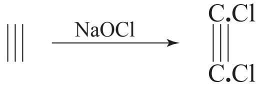
On heating alkyne with sodamide ($NaNH_2$ in liquid NH_3) the triple bond shift towards end.

Mechanism is represented as



1- Butyne

Substitution

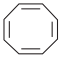


$$R-C\equiv CH \xrightarrow{NaOCl} R-C\equiv C-Cl$$

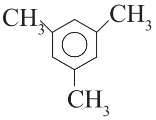
Polymerization

(A) Cyclic Polymerization Here alkynes polymerize to give aromatic compounds as follows:

- $3\,C_2H_2 \xrightarrow{\text{red hot tube}} C_6H_6$
  Ethyne Benzene

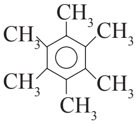
- $4\ C_2H_2 \xrightarrow{Ni\ (CN)_2}$ 

  Cyclo octa-1,3,5,7-tetra-ene

- $3\ CH_3 - C \equiv CH \xrightarrow{\text{red hot tube}}$ 

  Propyne

  Mesitylene

- $3\ CH_3 - C \equiv C - CH_3 \xrightarrow{\text{red hot tube}}$ 

  But-2-yne

  Hexa methyl benzene

(B) Linear Polymerization

$$\underset{}{2CH \equiv CH} \xrightarrow{Cu_2Cl_2\ NH_4Cl} \underset{\text{Vinyl Acetylene}}{CH_2 = CH - C \equiv CH} \xrightarrow{C_2H_2} \underset{\text{Di vinyl acetylene}}{CH_2 = CH - C \equiv C - CH = CH_2}$$

$$CH_2 = CH - C \equiv CH \xrightarrow{HCl} CH_2 = CH - CHCl = CH_2$$

Chloro prene or 2-Chloro-buta-1, 3-diene

- Here addition of HCl occurs at triple bonded carbon atom in place of double bonded carbon atom due to the formation of more stable conjugated di-ene product.

Acidity of Terminal Alkynes

Terminal alkynes are slightly acidic in nature. It is conformed by following reactions:

(a) With Ammonical Silver Nitrate

Here terminal alkynes react with it as follows

$$R - C \equiv CH + \underset{\text{Solution in nitric acid}}{Ag(NH_3)_2^+ + OH^-} \rightarrow R - C \equiv C.Ag \downarrow + H_2O + 2NH_3$$

For example,

$$CH \equiv CH + 2AgNO_3 + 2NH_4OH \rightarrow Ag.\ C \equiv C.Ag + 2NH_4NO_3 + 2H_2O$$

White ppt.
Acetilide Silver

(b) With Ammonical Cuprous Chloride

$$R - C \equiv CH + Cu(NH_3)_2^+ + OH^- \rightarrow R - C \equiv C.Cu \downarrow + H_2O + 2NH_3$$

Red ppt.

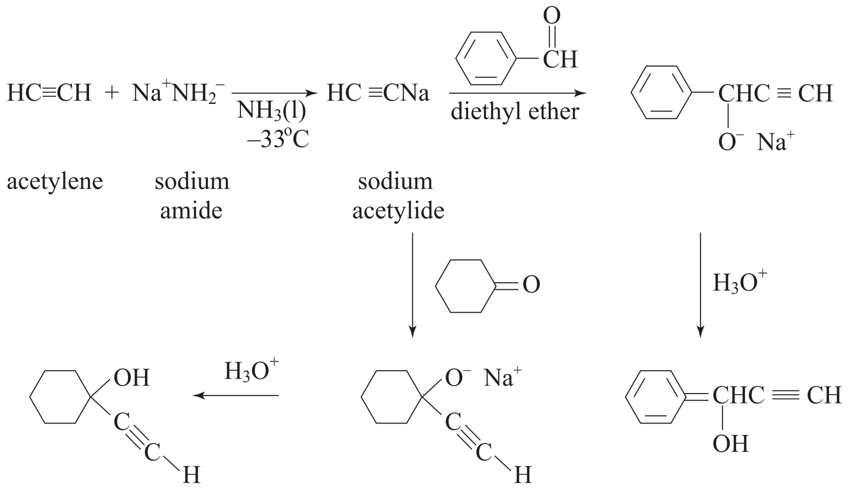
For example,

$$CH \equiv CH + Cu_2Cl_2 + 2NH_4OH \rightarrow Cu.C \equiv C.Cu + 2NH_4Cl + 2H_2O$$

Red ppt.
cuprousacetilide

(c) Replacement of Terminal H-atom From Terminal Alkynes

$$R - C \equiv CH \xrightarrow[Liq\ NH_3]{NaNH_2} R - C \equiv C.Na \xrightarrow{R'-CH_2X} R - C \equiv C - CH_2R'$$

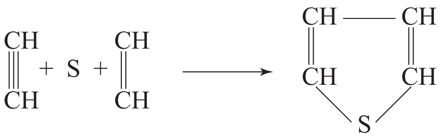


1- ethynylcyclohexanol
70 %
(a tertiary alcohol)

1- phenyl -2-propyn -1-ol
65 %
(a secondary alcohol
racemic mixture)

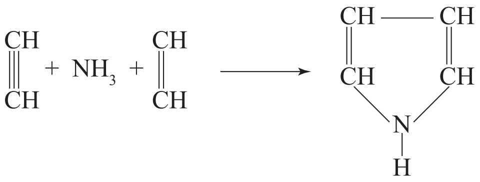
Formation of Hetero Cyclic Compounds

- When ethyne is passed over iron pyrite at 300°C it reacts with sulphur atom of iron pyrite to give thiophene.



Thiophene

- Ethyne on reaction with ammonia gives pyrrole.



Pyrrole

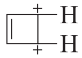
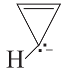
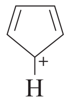
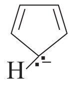
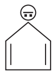
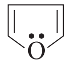
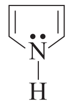
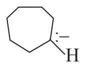
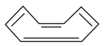
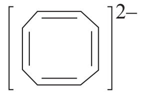
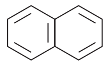
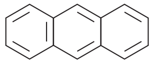
With Nitrogen

$$CH \equiv CH + N_2 \xrightarrow{\text{electric arc}} 2HCN$$

Aromaticity and Huckel's Rule

- Aromaticity is defined as "An aromatic compound having a cyclic planar structure with $(4n + 2)\pi$ electrons and have high resonance energy and stability due to delocalization of π-electrons "
  Any compound is aromatic when:
- It has a cyclic planar structure (for complete delocalization of π electrons).
- Has a high resonance energy.

- Has a conjugate system.
- Has number of π electrons according to 4n + 2 or Huckel's rule that is, 2, 6, 10, 14, 18. Here n = number of cyclic planar rings.
- If number of π electrons 4 'n' or 0, 4, 8, 12, 16, it will be anti-aromatic.
- If any of these conditions is not obeyed it will be non-aromatic.

Structure	*Number of π Electrons*	*Aromaticity*
	2	Aromatic
	2	Aromatic
	4	Anti-aromtic
	4	Anti-aromtic
	4	Anti-aromtic
 , or 	6	Aromatic
 ,  , 	6	Aromatic
	8	Antiaromatic
	8	Non-aromatic $^+$ (nonpolar)
	10	Aromatic
	10	Aromatic
	14	Aromatic

BENZENE

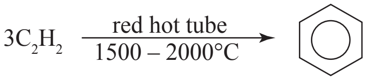
- Benzene was discovered by Faraday in 1825 and the structure of benzene was given by Kekule in 1865.

METHODS OF PREPARATION

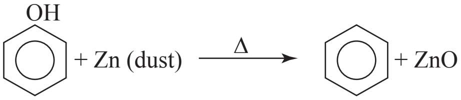
- **From Light Oil Fraction** The light oil fraction of coal tar contains benzene, toluene, xylene. This mixture on fractional distillation gives benzene as one of the product.
- **From Petroleum**

$$\text{n –Hexane} \xrightarrow[\text{High pressure } -4H_2]{Cr_2O_3,\ Al_2O_3,\ 600°C} \text{Benzene}$$

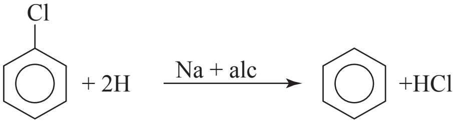
- **From Acetylene** Acetylene on passing through red hot tube polymerizes into benzene.



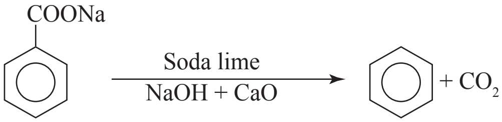
- **From Phenol** Phenol on distillation with zinc dust gives benzene.



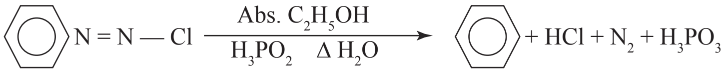
- **From Chlorobenzene** Chlorobenzene or halobenzene on reduction with Na/Alcohol or Ni – Al alloy gives benzene.



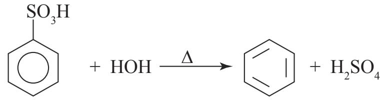
- **From Benzoic Acid** Benzoic acid or sodium benzoate on heating with soda lime gives benzene.



- **From Benzene Diazonium Chloride** Benzene diazonium chloride on reaction with hypo phosphorous acid gives benzene.



- **From Benzene Sulphonic Acid** Benzene sulphonic acid on treatment with steam gives benzene.



PHYSICAL PROPERTIES

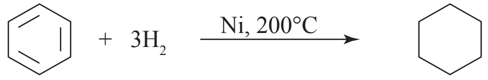
- It is a colourless volatile, mobile liquid.
- It is immiscible in water.
- It is highly inflammable (Burns with sooty flame).
- Its freezing point is 5.5°C and boiling point is 80°C.
- It is lighter than water and insoluble in it.
- It is a good solvent of fat, rubber, resin etc.

CHEMICAL PROPERTIES

Benzene has three alternative double bonds however it fails to show usual addition reaction or test of unsaturation with bromine water, Baeyer's reagent etc., moreover it also shows electrophilic substitution reaction it is due to resonance or complete delocalization of six pi electrons.

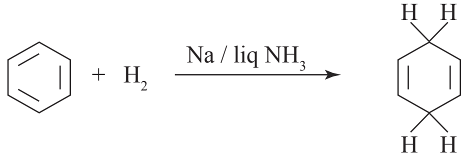
Addition Reactions

- ***Hydrogenation***



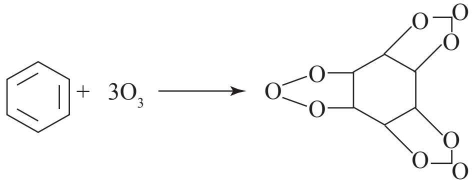
Cyclohexane

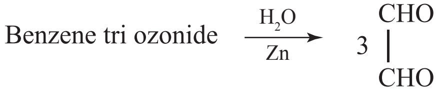
- ***Birch Reduction or Selective Hydrogenation***



1,4-dihydro benzene

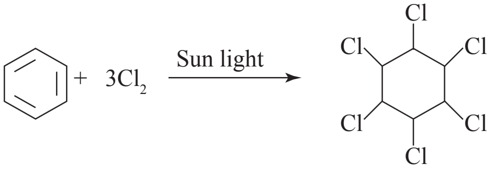
- ***Ozonolysis*** Benzene on ozonolysis gives glyoxal as follows





Glyoxal

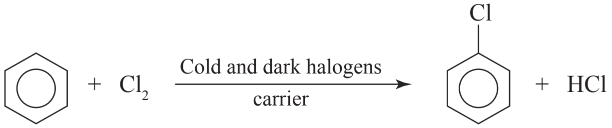
- ***With Chlorine*** Benzene on chlorination in presence of sunlight gives Gammexane or 666 or γ-Lindane a famous insecticide.

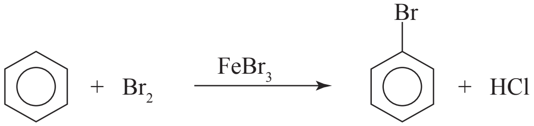


or $C_6H_6Cl_6$
Benzene hexa chloride (BHC)
gammexene

Electrophilic Substitution Reaction

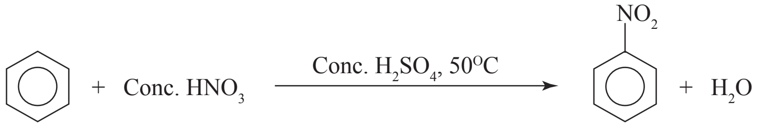
- ***Halogenation***

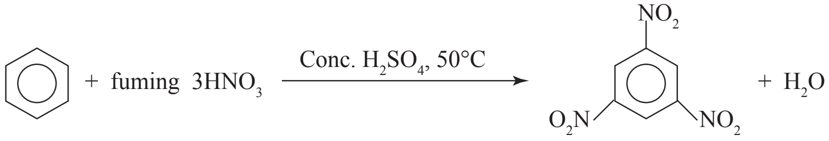




- Iodination of benzene is a slow and a reversible process so it is carried out in presence of oxidants like HIO_3 or HgO to check HI formation.

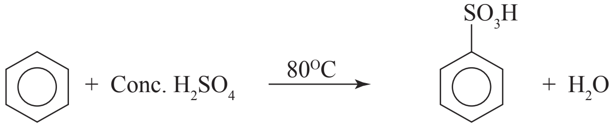
- ***Nitration***

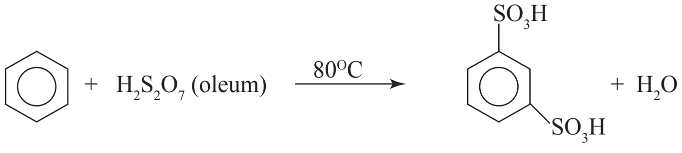


- 

Trinitrobenzene (explosive)

- ***Sulphonation***

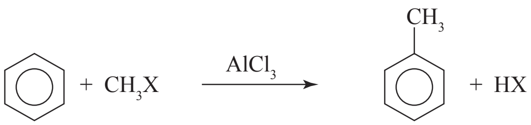


- 

Benzene disulphonic acid

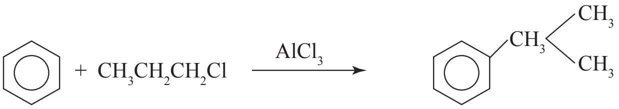
Friedal Craft Reaction Here alkylation or acylation takes place in presence of catalysts like anhydrous $AlCl_3$, $FeCl_3$, BF_3, $ZnCl_2$, $SnCl_4$ etc.

- ***Alkylation*** For alkylation alkyl halide in presence of anhydrous aluminium chloride, alcohol or alkene in presence of conc. H_2SO_4 can be used.



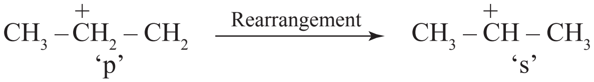
Toluene

Here one time rearrangement of carbocation is possible. For example,



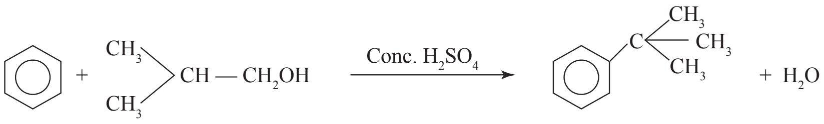
Cumine or isopropyl benzene

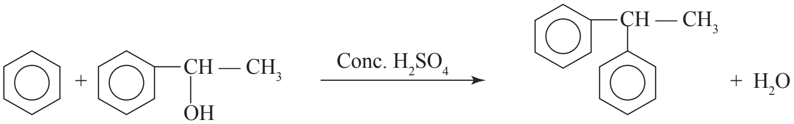
Cumine or isopropyl benzene

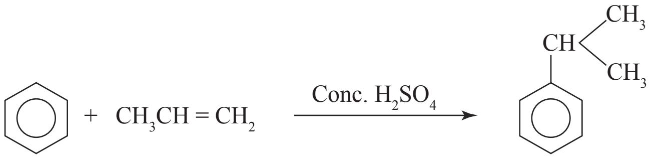


$$CH_3-\underset{\text{‘p’}}{\overset{+}{C}H_2}-CH_2 \xrightarrow{\text{Rearrangement}} CH_3-\underset{\text{‘s’}}{\overset{+}{C}H}-CH_3$$

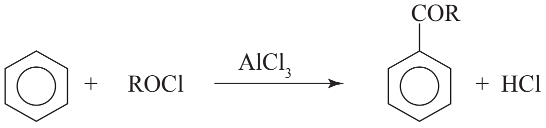
More stable carbocation

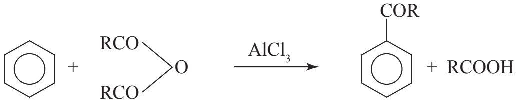
- 

- 

- 

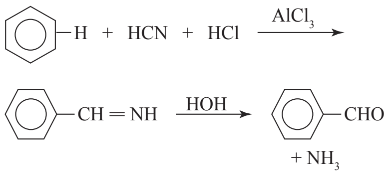
- ***Acylation*** For acylation acid halides or acid anhydrides can be used with anhydrous $AlCl_3$.



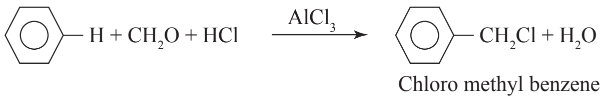
- 

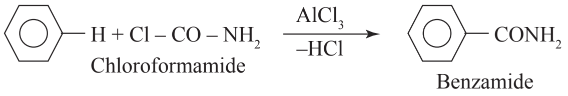
- Here R may be CH_3COCl, C_6H_5COCl.

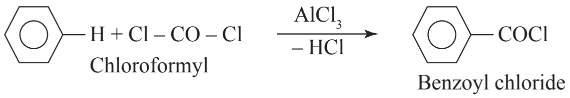
- **Gatterman Aldehyde Reaction**



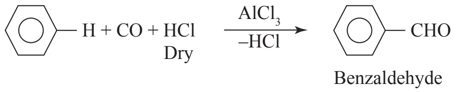
- **Chloro Methylation**



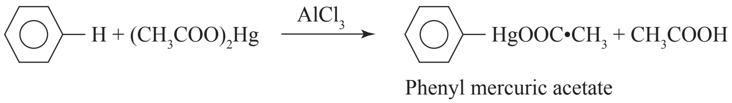
- 

- 

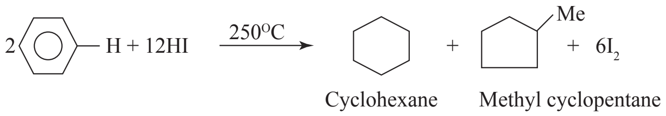
- **Gattermann Koch or Formylation**



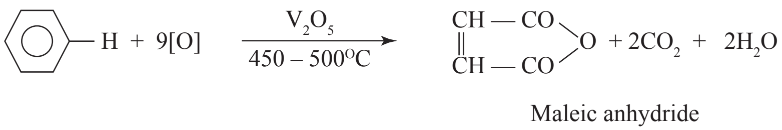
- In Friedal craft reaction the electrophiles are R^+, RC^+O, $C^+H = NH$, C^+OCl, C^+ONH_2, HC^+O,
- **Mercuration**



- **Reduction**



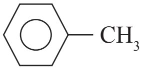
- **Oxidation**



- **Combustion**

$$2C_6H_6 + 15O_2 \xrightarrow{\Delta} 12CO_2 + 6H_2O$$

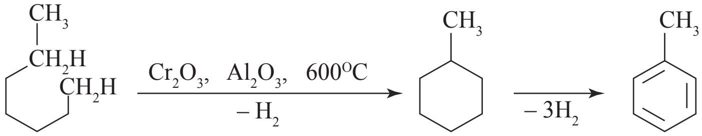
TOLUENE OR METHYL BENZENE



- It was first obtained by the dry distillation of tolubalsam. It is also known as Toluol.

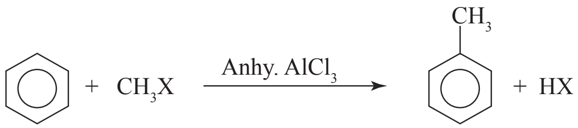
METHODS OF PREPARATION

- **From Light Oil Fraction of Coal Tar** The light oil fraction contains mainly Benzene, Toluene and Xylene. All the three can be separated by fractional distillation, at 110°C toluene is collected.
- **From Petroleum**

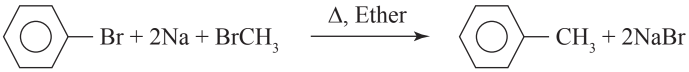


N-Heptane

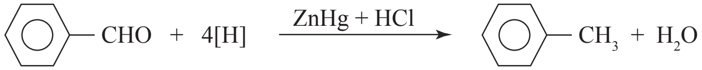
- **Friedal Craft Reaction**



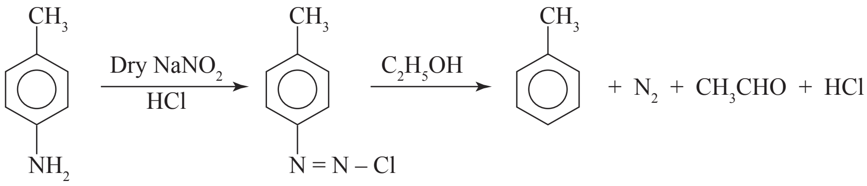
- **By Wurtz fittig Reaction**



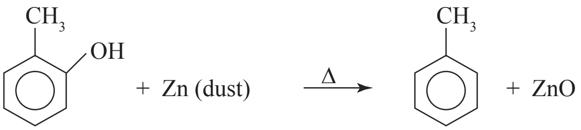
- **By the Reduction of Benzaldehyde**



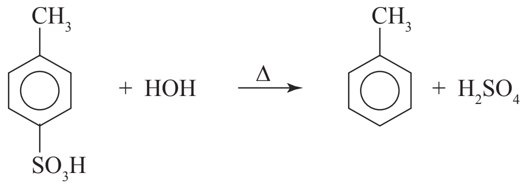
- **From Toluidine**



- **From Cresol**



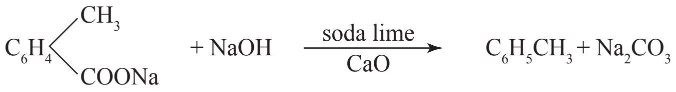
- **From Toluene Sulphonic Acid**



- **From Grignard Reagent**

$$C_6H_5MgX + CH_3X \longrightarrow C_6H_5CH_3 + MgX_2$$

- **From Decarboxylation of Sodium Toluate**



$$C_6H_4\begin{cases} CH_3 \\ COONa \end{cases} + NaOH \xrightarrow[CaO]{\text{soda lime}} C_6H_5CH_3 + Na_2CO_3$$

PHYSICAL PROPERTIES

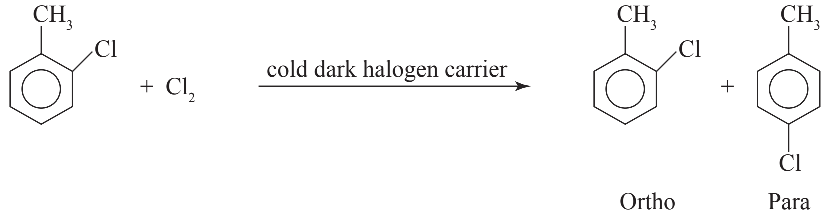
- It is a colourless liquid.
- Its boiling point is 111°C.
- It is immiscible in water.
- It is used as a solvent and also in the synthesis of compounds.

CHEMICAL PROPERTIES

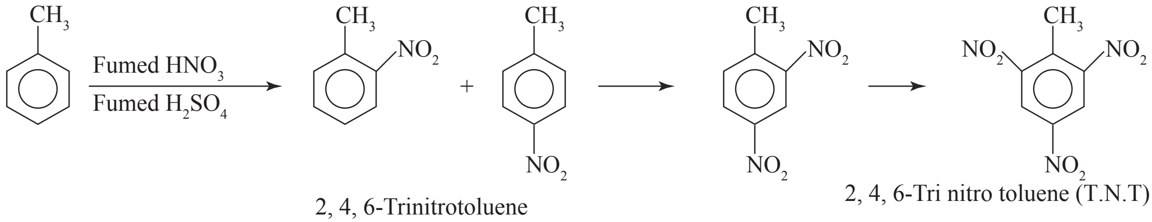
Reactions Due to Benzene Ring

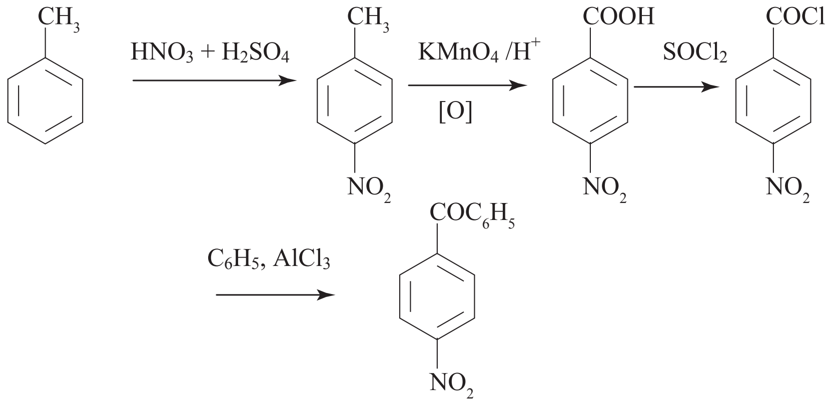
- Here Methyl group activates the benzene ring therefore further substitution takes place at o- and p- positions and the rate of substitution will be more fast than benzene.

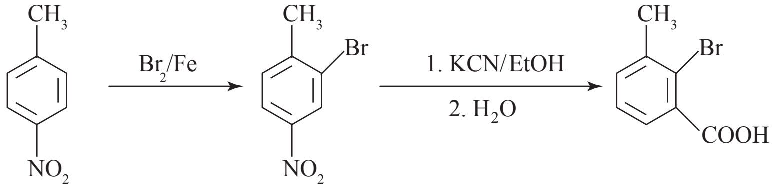
- ***Halogenation***



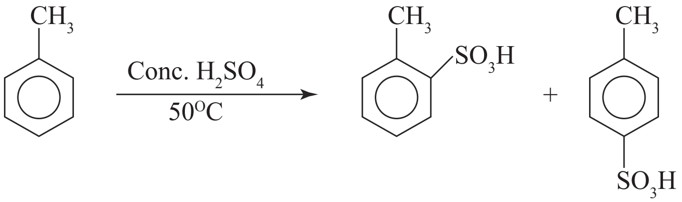
- ***Nitration***





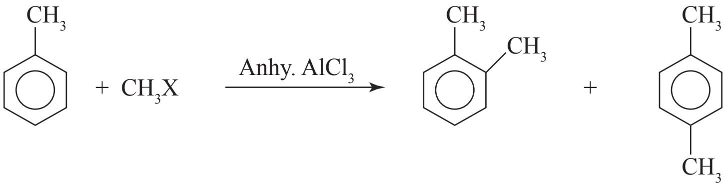


- ***Sulphonation***

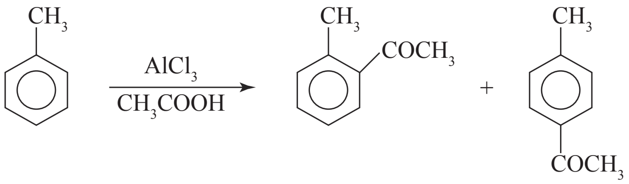


ortho, para toluene sulphonic acid

- ***Friedal Craft Reaction***



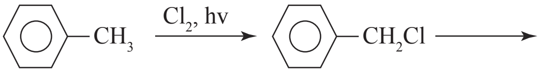
'o' and 'p' xylene



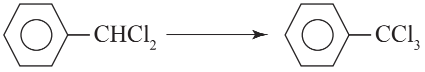
ortho, para methyl acetophenone

Reactions Due to Methyl Group or Side Chain Reactions

- ***Halogenation***

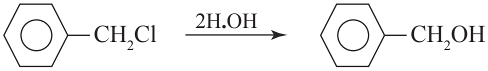


Benzyl chloride

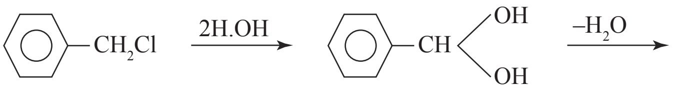


Benzoyl chloride

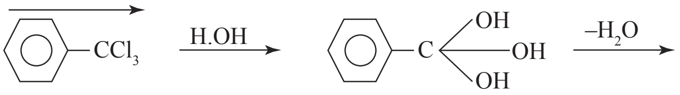
Benzo tri chloride

- 

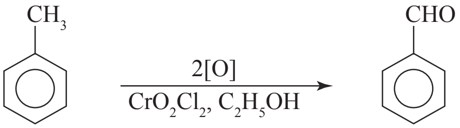
  Benzyl alcohol

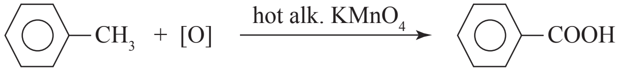
- 

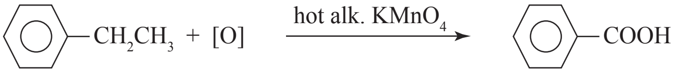
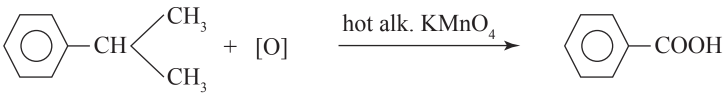
  Benzaldehyde

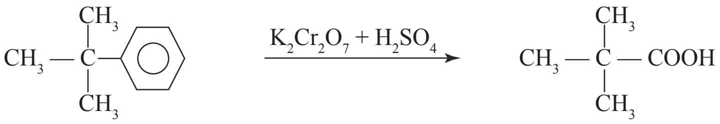
- 

  Benzoic acid

- **Oxidation Reactions**
- **By Chromyl Chloride or Etard Reaction** 
- **By Hot Alkaline $KMnO_4$ or $Na_2Cr_2O_7$** Here alkyl group having α-hydrogen atom get oxidized into COOH group.

- 
- 
- If alkyl group has no α-hydrogen atom or benzylic hydrogen atom the benzene ring gets oxidized into –COOH group.

  No Benzylic H-atom

ENHANCE YOUR KNOWLEDGE

- Alkanes are inert at room temperature as (C – C), (C – H) bonds are non-polar.
- The fire of burning liquid paraffins can not be extinguished by water as it is lighter than water so flots over water.
- On heating ethyne in presence of spongy copper or Cu_2O a cork like substance cuprene is formed which is used in the manufacture of linoleum.
- The light oil fraction of coal tar mainly contains the hydrocarbons Benzene (72%), Toluene (13%) and Xylenes (4per cent). This is known as BTX.
- When toluene is treated with Cl_2 in presence of Lewis acid catalyst ($FeCl_3$), substitution takes place at ortho and para positions. These products do not give white precipitate with alcoholic $AgNO_3$.
- Benzene hexa chloride (BHC) can exist in nine stereoisomeric forms.
- Chloramine-T is the sodium salt of N-chloro-p-toluene sulphonamide.

MULTIPLE-CHOICE QUESTIONS

Straight Objective Type Questions (Single Choice only)

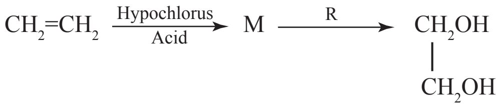
1. The compound with the highest boiling point is

(a) n-pentane (b) 2-methylbutane
(c) 2,2-dimethylpropane (d) n-hexane

2. A hydrocarbon with molecular formula C_8H_{18} gives only one monochloro derivative. The hydrocarbon is

(a) n- Octane
(b) 2,2,4- Trimethylpentane
(c) 2- Methylpentane
(d) 2,2,4,3 -Tetramethylbutane

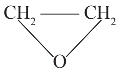
3. In the reactions:



$$CH_2{=}CH_2 \xrightarrow[\text{Acid}]{\text{Hypochlorus}} M \xrightarrow{R} \begin{array}{c} CH_2OH \\ | \\ CH_2OH \end{array}$$

M and R are respectively

(a) CH_3CH_2Cl and NaOH

(b)  and heat

(c) CH_3CH_2OH and HCl

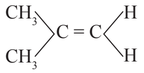
(d) CH_2ClCH_2OH and aq. $NaHCO_3$

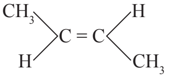
4. Which of the following compounds does not dissolve in conc. H_2SO_4 even on warming?

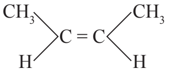
(a) aniline (b) benzene
(c) ethylene (d) hexane

5. Which of the following compounds reacts with HBr obeying Markownikoff's rule?

(a) $CH_2 = CH_2$

(b) 

(c) 

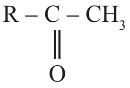
(d) 

6. When propyne is treated with aqueous H_2SO_4 in presence of $HgSO_4$ the major product is

(a) acetone
(b) propanol
(c) propanal
(d) propyl hydrogensulphate

7. Alkene $R - CH = CH_2$ reacts readily with B_2H_6 and the product on oxidation with alkaline hydrogen peroxide produces

(a) $R - CH_2 - CH_2OH$ (b) $R - CH_2 - CHO$

(c) 

$$R - \underset{\underset{O}{\|}}{C} - CH_3$$

(d) 

$$R - \underset{\underset{OH}{|}}{CH} - CH_2OH$$

8. 1-butyne reacts with cold alkaline $KMnO_4$ to yield
(a) $CH_3CH_2COOH + CO_2$
(b) CH_3CH_2COOH
(c) $CH_3CH_2CH_2COOH$
(d) $CH_3CH_2COOH + HCOOH$

9. Baeyer's reagent is
(a) acidified permanganate solution
(b) alkaline permanganate solution
(c) neutral permanganate solution
(d) aqueous bromine solution

10. When 3, 3-dimethyl-2-butanol is heated with H_2SO_4, the major product obtained is
(a) 3, 3-Dimethyl-1-butene
(b) 2, 3-Dimethyl-1-butene
(c) 2, 3-Dimethyl-2-butene
(d) cis and trans isomer of product named under (B)

11. Acidic hydrogen is present in
(a) Ethyne (b) Ethene
(c) Benzene (d) Ethane.

12. Which of the following reactions is expected to readily give a hydrocarbon product in good yield?
(a) $RCOOK \xrightarrow{\text{electrolytic reduction}}$
(b) $RCOOAg \xrightarrow{I_2}$
(c) $CH_3 - CH_3 \xrightarrow{Cl_2,\ hv}$
(d) $(CH_3)_3CCl \xrightarrow{C_2H_5OH}$

13. The reaction conditions leading to the best yield of C_2H_5Cl are
(a) C_2H_6 (excess) + $Cl_2 \xrightarrow{\text{UV light}}$
(b) $C_2H_6 + Cl_2 \xrightarrow{\text{dark, room temperature}}$
(c) $C_2H_6 + Cl_2$ (excess) $\xrightarrow{\text{UV light}}$
(d) $C_2H_6 + Cl_2 \xrightarrow{\text{UV light}}$

14. Formation of polyethene from calcium carbide takes place as follows:

$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2\ ;$$
$$C_2H_2 + H_2 \rightarrow C_2H_4\ ;$$
$$nC_2H_4 \rightarrow (-CH_2 - CH_2 -)n$$

the amount of polyethene obtained from 64 kg of CaC_2 is
(a) 7 kg (b) 14 kg
(c) 28 kg (d) 20 kg

15. The highest boiling point is expected for
(a) iso-octane
(b) n-octane
(c) 2,2,3,3-Tetramethylbutane
(d) n-Butane

16. Benzene reacts with CH_3COCl in the presence of anhydrous $AlCl_3$ to give:
(a) $C_6H_5CH_3$ (b) C_6H_5Cl
(c) $C_6H_5O_2Cl$ (d) $C_6H_5COCH_3$

17. Which of the following will have least hindered rotation about carbon-carbon bond?
(a) ethane
(b) ethylene
(c) acetylene
(d) hexachloroethane

18. In the reaction of phenol with $CHCl_3$ and aqueous NaOH at 70°C (343 K), the electrophile attacking the ring is
(a) $CHCl_3$ (b) $\dot{C}HCl_2$
(c) $:CCl_2$ (d) $COCl_2$

19. 0.037 g of an alcohol, R – OH was added to CH_3MgI and the gas evolved measured 11.2 cm^3 at STP. What is the molecular mass of R – OH?
(a) 46 (b) 60
(c) 74 (d) 88

20. Ozonolysis of 2, 3-dimethyl-1-butene followed by reduction with zinc and water gives:
(a) Methanoic acid and 3-Methyl-2-butanone
(b) Methanal and 3-Methyl-2-butanone
(c) Methanal and 2-methyl-3-butanone
(d) Methanoic acid and 2-Methyl-3-butanone.

21. Which is the decreasing order of strength of bases: OH^-, NH_2^-, $HC \equiv C^-$ and $CH_3CH_2^-$?
(a) $CH_3CH_2^- > NH_2^- > HC \equiv C^- > OH^-$
(b) $HC \equiv C^- > CH_3CH_2^- > NH_2^- > OH^-$
(c) $OH^- > NH_2^- > HC \equiv C^- > CH_3CH_2^-$
(d) $NH_2^- > HC \equiv C^- > OH^- > CH_3CH_2^-$

22. Among the following compounds which have more than one type of hybridisation for carbon atom?
I. $CH_3^- CH_2^- CH_2^- CH_3$
II. $CH_3^- CH = CH - CH_3$
III. $CH_2 = CH - C \equiv CH$
IV. $CH_2 = CH_2$
(a) II (b) II and III
(c) III (d) III and IV

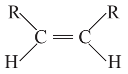
23. Addition of water to acetylene compounds is catalysed by ………. and ……….
(a) Ba^{+2} salt and $HgSO_4$
(b) Hg^{+2} salt and conc. acid
(c) Hg^{+2} salt and dil. acid
(d) H_2O/H^+

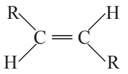
24. The most reactive compound for electrophilic nitration is
(a) benzene (b) nitrobenzene
(c) toluene (d) benzoic acid

25. In the addition of HBr to propene in the absence of peroxides, the first step involves the addition of

(a) H^+ (b) Br^-
(c) $H^\bullet$ (d) $Br^\bullet$

26. $R-C\equiv C-R \xrightarrow[\text{Lindlar catalyst}]{H_2} ?$

(a) 

(b) 

(c) both (A) and (B) (d) $R-CH_2-CH_2-R$

27. The intermediate during the addition of HCl to propene in presence of peroxide is

(a) $CH_3\dot{C}HCH_2Cl$ (b) $CH_3\overset{+}{C}HCH_3$
(c) $CH_3CH_2\dot{C}H_2$ (d) $CH_3CH_2\overset{+}{C}H_2$

28. The number of pi bonds in the product formed by passing acetylene through dil. H_2SO_4 containing mercuric sulphate is

(a) 3 (b) 2
(c) 1 (d) 0

29. When cyclohexane is poured on water, it floats because

(a) Cyclohexane is in 'boat' form
(b) Cyclohexane is in 'chair' form
(c) Cyclohexane is in 'crown' form
(d) Cyclohexane is less dense than water.

30. Chloroethane reacts with magnesium in dry ether to form X. when X is hydrolysed, a carbon compound Y and Z are formed. Which of the following is Y?

(a) C_2H_4 (b) C_2H_2
(c) C_2H_6 (d) C_6H_6

31. The intermediate during the addition of HCl to propene in the presence of peroxide is

(a) $CH_3\overset{o}{C}HCH_2Cl$ (b) $CH_3\overset{+}{C}HCH_3$
(c) $CH_2CH_2\overset{o}{C}H_2$ (d) $CH_3CH_2\overset{+}{C}H_2$

32. Reaction of one molecule of HBr with one molecule of 1,3-butadiene at 40°C gives predominantly

(a) 3-bromobutene under kinetically controlled conditions
(b) 1-bromo-2-butene under thermodynami-cally controlled conditions
(c) 3-bromobutene under thermodynamically controlled conditions
(d) 1-bromo-2-butene under kinetically controlled conditions.

33. 18 C – H and 7C – C sigma bonds are present in

(a) n-heptane
(b) cyclohexane
(c) 3, 3-dimethyl pentane
(d) 2, 2, 3-trimethyl pentane

34. $(CH_3)_3CMgCl$ on reaction with D_2O produces

(a) $(CH_3)_3CD$ (b) $(CH_3)_3OD$
(c) $(CD_3)_3CD$ (d) $(CD_3)_3OD$.

35. Both methane and ethane can be prepared in one step by the reaction of:

(a) C_2H_4 (b) CH_3Br
(c) CH_3OH (d) CH_3CH_2OH

36. $CaC_2 + H_2O \longrightarrow (A)$
$\xrightarrow{H_2SO_4,\ HgSO_4} (B)$

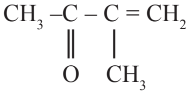
Then A and B are

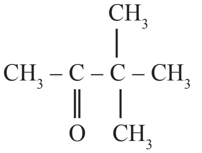
(a) CH_4 and HCOOH
(b) C_2H_4 and CH_3COOH
(c) C_2H_2 and CH_3CHO
(d) C_2H_2 and CH_3COOH

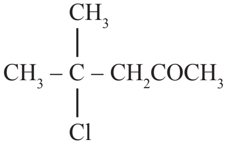
37. When 2-butyne is treated with dil. $H_2SO_4/HgSO_4$, the product formed is

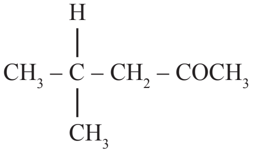
(a) 2-Butanone (b) Butanol-1
(c) Butanal (d) Butanol-2

38. Indicate the organic structure for product expected when 2-methylpropene is heated with acetyl chloride in the presence of anhydrous $ZnCl_2$

(a) 
$CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{C}=CH_2$

(b) 
$CH_3-\underset{\underset{O}{\|}}{C}-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$

(c) 
$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{Cl}{|}}{C}}-CH_2COCH_3$

(d) 
$CH_3-\overset{\overset{H}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-COCH_3$

39. When $CH_3CH_2CHCl_2$ is treated with $NaNH_2$, the product formed is

(a) $CH_3-CH=CH_2$ (b) $CH_3CH_2CH.(Cl)_2$
(c) $CH_3CH_2CH.(NH_2)_2$ (d) $CH_3-C\equiv CH$

40. In the following reaction, A and B respectively are

$C_2H_6 \xrightarrow{A} C_2H_5Cl \xrightarrow{Zn/HCL} B$

(a) PCl_3 and C_2H_4

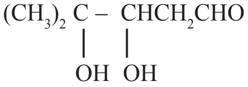
(b) Cl_2/uv light and C_2H_6

(c) HCl and C_2H_6

(d) Cl_2 and C_2H_2

41. On vigorous oxidation by permanganate solution $(CH_3)_2C = CHCH_2CHO$ gives

(a) $(CH_3)_2CO$ and $OHCCH_2CHO$

(b) 

$(CH_3)_2\underset{OH}{\underset{|}{C}} - \underset{OH}{\underset{|}{C}}HCH_2CHO$

(c) $(CH_3)_2CO$ and $OHCCH_2COOH$

(d) $(CH_3)_2CO$ and $CH_2(COOH)_2$

42. The treatment of benzene with isobutene in the presence of sulphuric acid gives

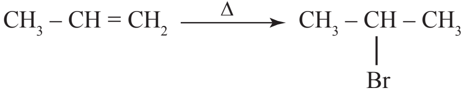
(a) isobutyl benzene

(b) n-butyl benzene

(c) tert-butyl benzene

(d) no reaction

43. Which one of the following reactions proceeds via a secondary free radical?

(a) 

$CH_3 - CH = CH_2 \xrightarrow{\Delta} CH_3 - \underset{Br}{\underset{|}{C}H} - CH_3$

(b) $C_6H_6 \xrightarrow{Br_2/FeBr_2} C_6H_5Br$

(c) $CH_3 - CH = CH_2 \xrightarrow{HBr, UV light}$

$CH_3 - CH_2 - CH - Br$

(d) $C_6H_6 \xrightarrow{Br_2, UV Light} C_6H_6Br_6$

44. Wurtz reaction of methyl iodide yields an organic compound X. which one of he following reactions also yields X?

(a) $CHCl_3 \xrightarrow{Ag powder, \Delta}$

(b) $C_2H_5Cl + C_2H_5ONa \longrightarrow$

(c) $C_2H_5Cl + LiAlH_4 \longrightarrow$

(d) $C_2H_5Cl + Mg \xrightarrow{dry ether}$

45. The compound

$CH_3 - \overset{CH_3}{\overset{|}{C}} = CH - CH_3$ on reaction with $NaIO_4$ in the presence of $KMnO_4$ gives:

(a) $CH_3COCH_3 + CH_3COOH$

(b) CH_3COCH_3

(c) $CH_3COCH_3 + CH_3CHO$

(d) $CH_3CHO + CO_2$

46. What are X and Y in the reaction

$C_2H_4 + H_2SO_4 \xrightarrow{80^\circ C} X \xrightarrow{H_2O, \Delta} Y?$

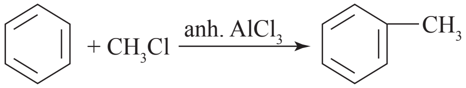
(a) C_2H_4, C_2H_5SH

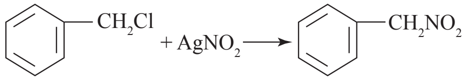
(b) $C_2H_5OSO_3H$, C_2H_5OH

(c) C_2H_2, CH_3CHO

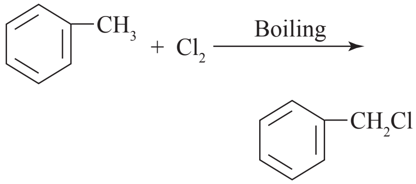
(d) C_2H_6, C_2H_5OH

47. Which of the following is a free radical substitution reaction?

(a) 

(b) 

(c) $CH_3CHO + HCN \longrightarrow CH_3CH(OH)CN$

(d) 

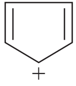
[CBSE 2003]

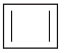
48. Which one of the following has the minimum boiling point?

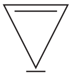
(a) n-butane (b) 1-butyne

(c) 1-butene (d) isobutene

49. Among the following, the aromatic compound is

(a) 

(b) 

(c) 

(d) 

50. Elimination of bromine from 2-bromobutane results in the formation of

(a) equimolar mixture of 1 and 2-butene

(b) predominantly 2-butene

(c) predominantly 1-butene

(d) predominantly 2-butyne

51. Products of the following reaction,

$CH_3C \equiv CCH_2 - CH_3 \xrightarrow[\text{(ii) hydrolysis}]{\text{(i) } O_3}$?

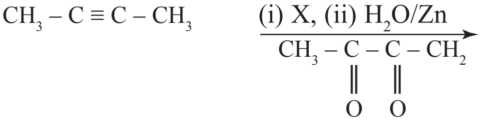
(a) $CH_3COOH + CO_2$

(b) $CH_3COOH + HOOC.CH_2CH_3$

(c) $CH_3CHO + CH_3CH_2CHO$

(d) $CH_3COOH + CH_3COCH_3$

52. Identify (X) in the following reaction:



$$CH_3-C\equiv C-CH_3 \xrightarrow{\text{(i) X, (ii) } H_2O/Zn} \underset{\underset{O}{\|}}{CH_3-C}-\underset{\underset{O}{\|}}{C}-CH_2$$

(a) O_2 (b) HNO_3
(c) $KMnO_4$ (d) O_3

53. The major product obtained on treatment of $CH_3CH_2CH(F)CH_3$ with CH_3O^-/CH_3OH is
(a) $CH_3CH_2CH(OCH_3)CH_3$
(b) $CH_3CH = CHCH_3$
(c) $CH_3CH_2CH = CH_2$
(d) $CH_3CH_2CH_2CH_2OCH_3$

54. 3-phenylpropene on reaction with HBr gives (as a major product)
(a) $C_6H_5CH_2CH(Br)CH_3$
(b) $C_6H_5CH(Br)CH_2CH_3$
(c) $C_6H_5CH_2CH_2CH_2Br$
(d) $C_6H_5CH(Br)CH = CH_2$

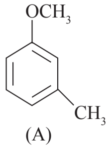
55. An alkene on reductive ozonolysis gives 2 molecules of $CH_2(CHO)_2$. The alkene is
(a) 2,4-hexadiene
(b) 1,3-cyclohexadiene
(c) 1,4-cyclohexadiene
(d) 1,2-dimethyl cyclopropene

56. Which of the following sequence of reactions (reagents) can be used for the conservation of $C_6H_5CH_2CH_3$ into C_6H_5 $CH =CH_2$?
(a) $SOCl_2$; H_2O (b) SO_2Cl_2 ; alc. KOH
(c) Cl_2/hv ; H_2O (d) $SOCl_2$; alc KOH

57. Ethene and ethyne can be distinguished by
(a) Br_2 water
(b) $KMnO_4$ solution
(c) cuprous chloride solution
(d) any of the above

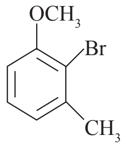
58. Which among the following will give a precipitate with ammonical silver nitrate?
(a) 2-butene (b) 2-butyne
(c) chlorobenzene (d) 3-methyl-1-butyne

59. The major product obtained on the monobromination (with $Br_2/FeBr_3$) of the following compound A is

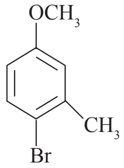


(A)

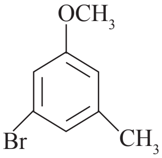
(a)



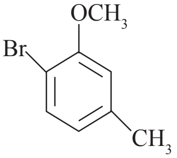
(b)



(c)



(d)



60. Reaction of trans-2-phenyl-1-bromocyclopentane on reaction with alcoholic KOH produces:
(a) 4-phenylcyclopentene
(b) 2-phenylcyclopentene
(c) 1-phenylcyclopentene
(d) 3-phenylcyclopentene

61. Markownikoff's rule is best applicable to the reaction between
(a) $C_3H_6 + Br_2$ (b) $C_2H_4 + HCl$
(c) $C_3H_8 + Cl_2$ (d) $C_3H_6 + HBr$

62. An organic compound decolourises Br_2 water and also gives red ppt. with Cu_2Cl_2 solution. The compound is
(a) $CH_2 = CH_2$ (b) $CH_3 - CH = CH_2$
(c) $CH_3 - C \equiv CH$ (d) $CH_3 - C \equiv C - CH_3$

63. How many sigma and pi bonds are present in the linear chain compound which has formula C_5H_4 and contains both double and triple bonds?
(a) 6 sigma and 4 pi
(b) 8 sigma and 4 pi
(c) 6 sigma and 6 pi
(d) 8 sigma and 2 pi

64. What is the %p character of the hybrid orbitals of C in methane, ethene and ethyne respectively?
(a) 50, 33, 25 (b) 75, 66, 50
(c) 25, 33, 50 (d) 50, 66, 75

65. The shape of π bond between two ethylenic carbon atoms is in which form?
(a) Two flat ellipsoids above and below the plane of the two carbon atoms.
(b) A sphere around the two carbon atoms
(c) A cylinder around the carbon atoms.
(d) An ellipsoid enveloping the carbon atoms.

66. An ozonide of an unsaturated compound gave acetone and acetaldehyde in equimolar quantity. Which is this organic compound?
(a) 1-pentene (b) 1-pentene
(c) 2-methyl-2-butene (d) 2-methyl-1-butene

67. 2-Methylbutane on reacting with bromine in the presence of sunlight gives mainly
(a) 1-bromo-3-methylbutane
(b) 2-bromo-3-methylbutane
(c) 2-bromo-2-methylbutane
(d) 1-bromo-2-methylbutane

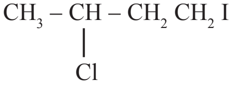
68. When 1-butene is mixed with excess bromine. What is the reaction product?
(a) Butylene gas
(b) 1, 2-dibromobutane
(c) 1-bromobutane
(d) Perbromobutane

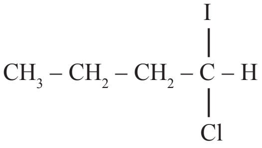
69. Naphthalene on treatment with concentrated sulphuric acid above 160°C temperature gives mainly which one of the following
(a) Phthalic anhydride
(b) Naphthalene-1,2-disulphonic acid
(c) β-naphthalene sulphonic acid
(d) α-naphthalene sulphonic acid

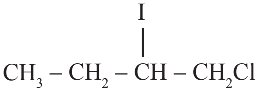
70. The order of decreasing reactivity towards an electrophillic reagent, for the following
(1) Benzene
(2) Toluene
(3) Chlorobenzene
(4) Phenol
would be:
(a) 1 > 2 > 3 > 4
(b) 2 > 4 > 1 > 3
(c) 4 > 3 > 2 > 1
(d) 4 > 2 > 1 > 3

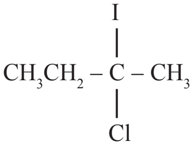
71. Predict the product C obtained in the following reaction butyne-1.

$$CH_3CH_2 - C \equiv CH + HCl \longrightarrow B \xrightarrow{HI} C$$

(a) 
$CH_3 - CH(Cl) - CH_2\,CH_2\,I$

(b) 
$CH_3 - CH_2 - CH_2 - C(I)(Cl) - H$

(c) 
$CH_3 - CH_2 - CH(I) - CH_2Cl$

(d) 
$CH_3CH_2 - C(I)(Cl) - CH_3$

72. Which of the compounds with molecular formula C_5H_{10} yields acetone on ozonolysis?
(a) 2-Methyl-2-butene
(b) 3-Methyl-1-butene
(c) Cyclopentane
(d) 2-Methyl-1-butene

73. Under which one of the following conditions, does the reaction:

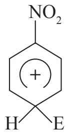
$$HC \equiv CH + CH_3OH \xrightarrow{?} CH_3O - C \equiv CH + H_2O$$

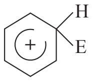
take place?
(a) Dilute HCl/THF, 80°C
(b) CH_3OK/160-200°C
(c) NH_4OH/80°C
(d) Conc. H_2SO_4/160°C
(E) Anhydrous $ZnCl_2$/150°C

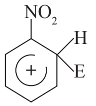
74. Which of the following reactions will yield 2, 2-dibromopropane?
(a) $CH_3CH = CHBr + HBr \rightarrow$
(b) $CH \equiv CH + 2HBr \rightarrow$
(c) $CH_3 - CH = CH_2 + HBr \rightarrow$
(d) $CH_3 - C \equiv CH + 2HBr \rightarrow$

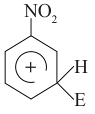
75. The hydrocarbon which can react with sodium in liquid ammonia is
(a) $CH_3CH_2CH_2C \equiv CCH_2CH_2CH_3$
(b) $CH_3CH_2C \equiv CH$
(c) $CH_3CH = CHCH_3$
(d) $CH_3CH_2C \equiv CCH_2CH_3$

76. In electrophile, $E^{\oplus}$ attacks the benzene ring to generate the intermediate σ-complex. Of the following, which σ-complex is of lowest energy?

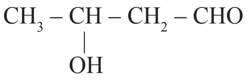
(a) 

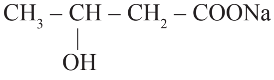
(b) 

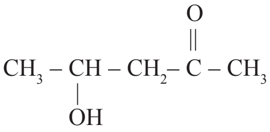
(c) 

(d) 

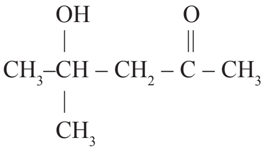
77. $CH \equiv CH \xrightarrow[H_2SO_4]{HgSO_4} A \xrightarrow[NaOH]{dilute} B$

The compound B is
(a) 
$CH_3 - CH(OH) - CH_2 - CHO$

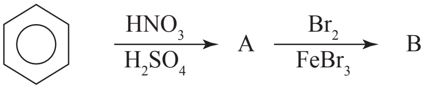
(b) 
$CH_3 - CH(OH) - CH_2 - COONa$

(c) 

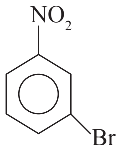
$CH_3-\underset{OH}{\underset{|}{CH}}-CH_2-\overset{O}{\overset{||}{C}}-CH_3$

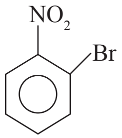
(d) 

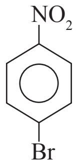
$CH_3-\overset{OH}{\overset{|}{\underset{CH_3}{\underset{|}{CH}}}}-CH_2-\overset{O}{\overset{||}{C}}-CH_3$

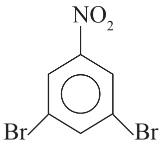
78. 

The compound B is

(a) 

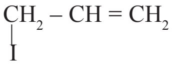
(b) 

(c) 

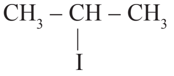
(d) 

79. The major product P in the following reaction is

$CH_3-CH=CH_2 \xrightarrow[\text{Peroxide}]{HI}$

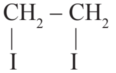
(a) 

$\underset{I}{\underset{|}{CH_2}}-CH=CH_2$

(b) 

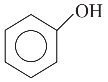
$CH_3-\underset{I}{\underset{|}{CH}}-CH_3$

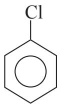
(c) $CH_3CH_2CH_2I$

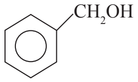
(d) 

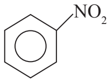
$\underset{I}{\underset{|}{CH_2}}-\underset{I}{\underset{|}{CH_2}}$

80. Which one of the following is most reactive towards electrophilic attack?

(a) 

(b) 

(c) 

(d) 

Brainteasers Objective Type Questions (Single choice only)

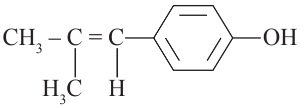
81. An alkane, C_6H_{14} gives two monochloroalklanes when chlorinated. What is the structure of the original alkane?

(a) 2,2- dimethylbutane
(b) 2, 3 -dimethylbutane
(c) 2- methylpentane
(d) 3 methylpentane

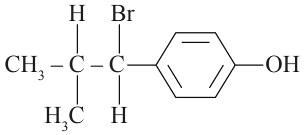
82. An unknown compound has a molecular mass of 84 and has only C and H atoms. When it undergoes chlorination in the presence of light, three monochlorinated products are isolated. Identify this compound.

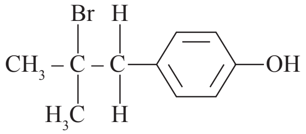
(a) Cyclohexane
(b) Methylcyclopentane
(c) 1, 3 - dimethylcyclobutane
(d) Hexane

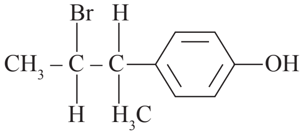
83. The reaction of

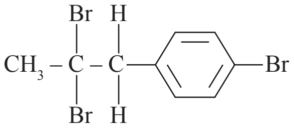


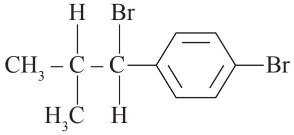
with HBr gives predominantly:

(a) 

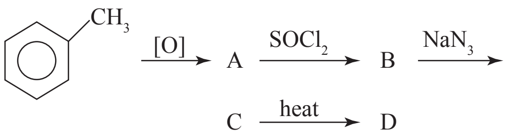
(b) 

(c) 

(d) 

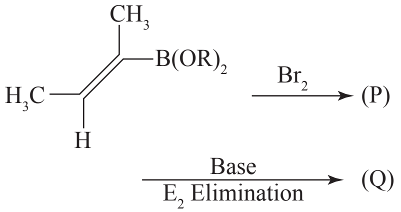
(e) 

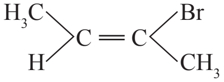
84. In the following sequence of reactions, what is D?

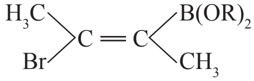


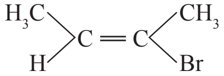
(a) primary amine
(b) an amide
(c) phenyl isocyante
(d) a chain lengthened hydrocarbon

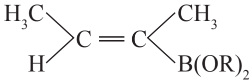
85. Identify (Q) in the following reactions



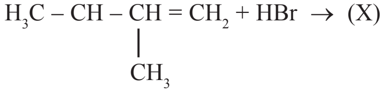
(a)


(b)


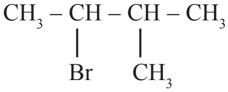
(c)


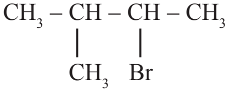
(d)


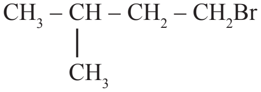
86. What products result when one mole of 1- pentyne is first treated with one mole of HCl and then with one mole o HBr?
(a) 2- chloro-1- bromopentane
(b) 1- chloro-2- bromopentane
(c) 1- chloro-1- bromopentane
(d) 2-chloro -2- bromopentane

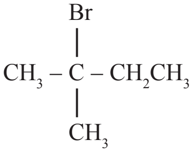
87.

$H_3C-\underset{CH_3}{\underset{|}{CH}}-CH=CH_2+HBr\rightarrow(X)$

Here (X) (predominantly) is:

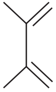
(a)

$CH_3-\underset{Br}{\underset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-CH_3$

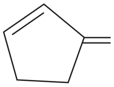
(b)

$CH_3-\underset{CH_3}{\underset{|}{CH}}-\underset{Br}{\underset{|}{CH}}-CH_3$

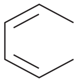
(c)

$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-CH_2Br$

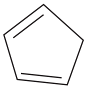
(d)

$CH_3-\overset{Br}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_2CH_3$

88. Which of the following is the order of decreasing reactivity in a Diels - Alder reaction?

(I)


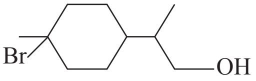
(II)


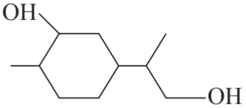
(III)


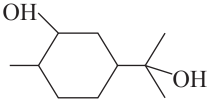
(IV)


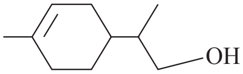
(a) IV > II > III> I
(b) IV > I > III > II
(c) IV > I > II > III
(d) I > IV > III > II

89. What product results from the complete hydroboration-oxidation of limonene?

(a)


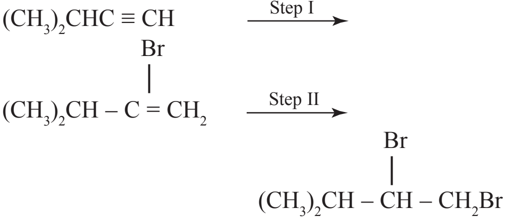
(b)


(c)


(d)


90. An organic compound with molecular formula C_6H_{12} upon ozonnolysis gave only acetone as the product. The compound is
(a) 2-hexene
(b) 2,-dimethyl-1-butene
(c) 3-hexene
(d) 2,3-dimethyl-2-butene
(e) 3-methyl-1-pentene

91. In the following reaction:


$(CH_3)_2CHC\equiv CH\xrightarrow{\text{Step I}}(CH_3)_2CH-\overset{Br}{\overset{|}{C}}=CH_2\xrightarrow{\text{Step II}}(CH_3)_2CH-\overset{Br}{\overset{|}{CH}}-CH_2Br$

Which of the following sets of reagents can be used for step I and step II?

	Step I	Step II
(1)	HBr	HBr & peroxide
(2)	HBr & peroxide	HBr
(3)	Br_2	HBr
(4)	Br_2	HBr & peroxide

select the correct answer using the codes given below.

(a) 1 alone (b) 1 and 2
(c) 1, 2 and 3 (d) 1, 2 and 4

92. The heat of hydrogenation of benzene is 50 kcal/mol. The resonance energy of benzene is 36 kcal/mol . The heat of hydrogenation of cyclohexene is approximately:

(a) 9 kcal/mol (b) 19 kcal/mol
(c) 29 kcal/mol (d) 27 kcal/mol

93. Consider the following reactions:

$$C_2H_2 \xrightarrow[\text{Iron tube, 500°C}]{\text{red hot}} A$$

$$A \xrightarrow[\text{70° C}]{\text{conc. HNO}_3\text{/conc. H}_2\text{SO}_4} B$$

$$B \xrightarrow{\text{LiAlH}_4} C_6H_5-N=N-C_6H_5$$

A and B are

(a) $A = C_6H_6$; $B = C_6H_5NO_2$
(b) $A = C_2H_4$; $B = C_6H_5NH_2$
(c) $A = C_2H_6$; $B = C_6H_5NH_2$
(d) $A = C_2H_4$; $B = C_6H_6$

94. Which of the following alkenes is most stable?

(a) 2- heptene
(b) 1, 2- dimethylcyclohexene
(c) 1- heptane
(d) 1- methylcyclohexene

95. Which of the following most readily undergoes E2 elimination with a strong base?

(a) 2- bromo - 3 - methylbutane
(b) 2 - bromopentane
(c) 2- bromo-2- methylbutane
(d) 1- bromo-2, 2- dimethylpropane

96. Identify (Y) in the following reaction:

$$CH \equiv CH \xrightarrow{O_3} (X) \xrightarrow{Zn/CH_3OH} (Y)$$

(a) $CH_3 - CH_3$ (b) $CH_2OH - CH_2OH$
(c) CH_3COOH (d) C_2H_5OH

97. When 2- methylbutane is chlorinated, the per centage of $(CH_3)_2-CH-CH_2-CH_2Cl$ is nearly assuming reactivity ration of $3^oH : 2^oH : 1^oH = 5:3 . 8:2$.

(a) 28 % (b) 35 %
(c) 23 % (d) 14 %

98. Which of the following is the principal product of the reaction of 3- methyl -1- butene with HCl?

(a) 2- chloro- 3- methylbutane
(b) 2- chloro -2- methylbutane
(c) 1- chloro-3- methylbutane
(d) both B and C

99. A hydrocarbon of molecular formula C_6H_{10} reacts with sodamide and the same on ozonolysis followed by hydrogen peroxide oxidation gives two molecules of carboxylic acids, one being optically active. Then the hydrocarbon may be

(a) 3-methyl-1-pentyne
(b) 1-hexyne
(c) 2-hexyne
(d) 3-hexyne
(E) 3, 3-dimethyl-1-butyne

100. The heat of hydrogenation of benzene is 51 kcal/mol and its resonance energy is 36 kcal/mol. Then the heats of hydrogenation of cyclohexadiene and cyclohexene are respectively

(a) 58 kcal, 29 kcal
(b) 28 kcal, 59 kcal
(c) 58 kcal, 49 kcal
(d) 29 kcal, 48 kcal

101. $(CH_3)_2C = CH_2$ + Isobutane $\xrightarrow{H_2SO_4}$ (X)

The product (X) will be

(a) n-heptane
(b) 2,2,4-trimethyl pentane
(c) 2,2,3-trimethyl butane
(d) 2,2,3,3-tetramethyl butane

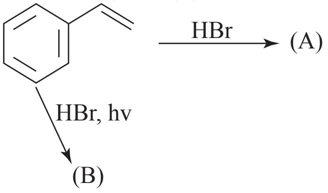
102. Consider the following alkenes:

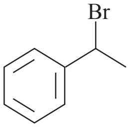
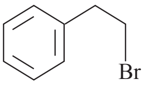
1. $H_2C = C(CH_2CH_3)CH(CH_3)_2$
2. $(CH_3)_2C = C(CH_3)CH_2CH_3$
3. $CH_3CH = C(CH_3)CH(CH_3)_2$

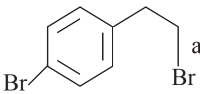
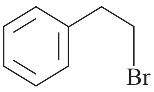
The correct sequence of increasing order of stability of these alkenes is

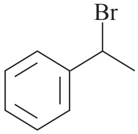
(a) 3, 1, 2 (b) 1, 3, 2
(c) 1, 2, 3 (d) 2, 1, 3

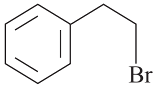
103. Observe the following reactions and predict the nature of (a) and (B)



(a) A =  and B = 

(b) A =  and B = 

(c) Both A and B are 

(d) Both A and B are 

104. Which of the following has the highest enthalpy of hydrogenation?

(a) 1, 2 - dimethylcyclopentene

(b) (Z) -4- methyl -2- pentene

(c) 2, 4- dimethyl -2- hexene

(d) (Z) - 2, 2,5, 5 - tetramethyl -3- hexane

105. Consider the following compounds:

1. $CH_3 – CH_2 – CHCl – CH_3$
2. $CH_2 = CH – CH_2 – CH_2Cl$
3. $CH_3 – CH_2 – CH_2 – CH_2Cl$

These compounds are dehydrohalogenated by treatment with a strong base under identical conditions. The correct sequence of the increasing order of reactivity of these compounds in the given reaction is

(a) 3, 1, 2 (b) 3, 2, 1

(c) 1, 2, 3 (d) 2, 1, 3

106. Consider the following compounds:

1. $CH_3CH_2CH_2CH_2OH$
2. $CH_3CH_2CH(OH)CH_3$
3. $(CH_3)_3COH$

These compounds are dehydrated by treatment with sulphuric acid. The correct sequence of increasing order of the reactivity of three compounds towards dehydration is

(a) 1, 3, 2 (b) 1, 2, 3

(c) 2, 1, 3 (d) 3, 1, 2

107. Oxidation of an alkene X gives a diol; further oxidation gives a diketone. Which one of the following could be X?

(a) $CH_3CH = C(CH_3)_2$

(b) $C_6H_5CH = CHC_6H_5$

(c) $(CH_3)_2C = C(CH_3)_2$

(d) $(CH_3)_2CHCH = CH_2$

(e) $(C_6H_5)_2C = CHCH_3$

108. Which of the following does not exist as geometric isomers?

(a) 3- bromo -2- methyl - 2- butene

(b) 3- methyl -2- pentene

(c) 3- bromo -1 - chloro -1- pentene

(d) cyclodecene

109. An alkyne that undergoes ozonolysis followed by hydrolysis and yields only 2- methylpropanoic acid, $CH_3CH(CH_3)COOH$ is?

(a) 2,5- dimethyl-3-hexyne

(b) 2,4- dimethyl-2-hexyne

(c) 2,4- dimethyl-3-hexyne

(d) none of these

110. The major product formed when a 3, 3-dimethylbutan-2-ol is heated with concentrated sulphuric acid is

(a) cis and trans isomers of 2, 3-dimethyl-1-butene

(b) 2, 3-dimethyl-1-butene

(c) 2, 3-dimethyl-2-butene

(d) cis and trans isomers of 3, 3-dimethyl-2-butene

(e) 3, 3-dimethyl-1-butene

111. The reaction between HI and C_2H_4 in C_2H_5OH gives 'predominantly' C_2H_5I, whereas the reaction with HCl under the same conditions gives predominantly $(C_2H_5)_2O$. Identify the correct order of nucleophilicity of the nucleophiles involved in the above reactions.

(a) $I^- > EtO^- > Cl^-$

(b) $I^- > Cl^- > EtOH$

(c) $EtOH > Cl^- > I^-$

(d) $I^- > EtOH > Cl^-$

112. Which of the following has the highest reaction rate when treated with bromine in a nonpolar solvent?

(a) 2- methylpropane

(b) ethene

(c) propane

(d) 2, 3- dimethyl 2, 2- butene

113. The addition of Br_2 to Z-2 butene gives:

(a) (R, R)-2,3-dibromobutane only

(b) (S, S)-2,3-dibromobutane only

(c) (R, S)-2,3-dibromobutane only

(d) a mixture of (R, R) and (S, S)-2,3-dibromobutanes (50% : 50%)

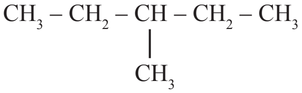
(e) (R, S)-1,2-dibromobutane

114. Viscosity coefficients of some liquids are given below:

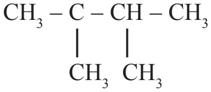
Liquid	η in millipoise at 30°C
$CH_3(CH_2)_3CH_3$	2.11
$CH_3(CH_2)_4CH_3$	2.89
$CH_3(CH_2)_5CH_3$	3.68

The order of viscosity coefficient of the liquids

(1) $CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$

(2) 

$CH_3-CH_2-CH(CH_3)-CH_2-CH_3$

(3) 

$CH_3-C(CH_3)-CH(CH_3)-CH_3$

(a) $1 > 2 > 3$ (b) $1 < 2 < 3$

(c) $1 > 2 = 3$ (d) remains same

115. 2- methyl pent -2- ene on ozonolysis gives

(a) propanal only

(b) propanal and methanal

(c) propan -2 - one and propanal

(d) propan -2- one and ethanal

116. One mole of an unsaturated hydrocarbon on ozonolysis gives one mole each of CH_3CHO, HCHO and OHC.CHO. the hydrocarbon is

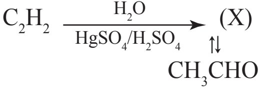
(a) $CH_3.CH_2C\equiv C.CH_3$

(b) $CH\equiv C.CH_2.CH_2.CH_3$

(c) $CH_3.CH=CH.CH=CH_2$

(d) $CH_2=CH.CH_2.CH=CH_2$

117. In the following reaction:



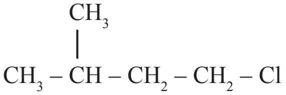
$$C_2H_2 \xrightarrow[HgSO_4/H_2SO_4]{H_2O} (X) \rightleftharpoons CH_3CHO$$

What is X?

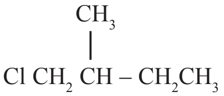
(a) CH_3CH_2OH (b) $CH_3\text{-}O\text{-}CH_3$

(c) CH_3CH_2CHO (d) $CH_2=CHOH$.

118. An alkylhalide (RCl) reacts with Li in ether medium to form RLi, which in turn reacts with H_2O to form 2-methylbutane. The halide also reacts with Na in ether to form 2,7-dimethyloctane. The structure of the alkylhalide is

(a) 

$CH_3-CH(CH_3)-CH_2-CH_2-Cl$

(b) 

$Cl\,CH_2\,CH(CH_3)-CH_2CH_3$

(c) $(H_3C)_2\,CH\,CH_2CH_2Br$

(d) $(CH_3)_2CH-CH_2-(CHCl)_2-CH_2\,CH(CH_3)_2$

119. Which of the following reagent converts 1- butene to 2- butanol in greatest yields?

(a) 1. O_3, 2. Zn, H_2O

(b) H^+, H_2O

(c) 1. $Hg(O_2CCH_3)_2$, H_2O, 2. $NaBH_4$, OH^-

(d) 1. BH_3, THF- H_2O, 2. H_2O_2, OH

120. Reaction of acetylene and propylene with $HgSO_4$ in presence of H_2SO_4 produces respectively:

(a) acetone and acetaldehyde

(b) acetaldehyde and acetone

(c) propanaldehyde and acetone

(d) acetone and propanaldehyde

121. Toluene in nitrated and the resulting product is reduced with tin and hydrochloric acid. The product so obtained is diazotized and then heated with cuprous bromide. The reaction mixture so formed contains

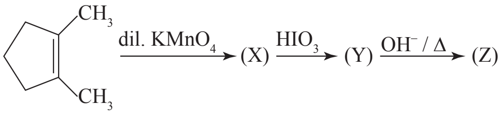
(a) Mixture of o- and p-bromotoluenes

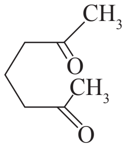
(b) Mixture of o- and p-dibromobenzenes

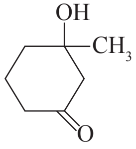
(c) Mixture of o- and p-bromoanilines

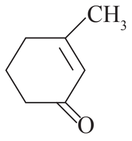
(d) Mixture of o- and m-bromotoluenes

122. Identify the product (Z) in the following reaction:



(a) 

(b) 

(c) 

(d) None of these

123. In the following sequence of reactions, the alkene affords the compound 'B'

$$CH_3CH=CHCH_3 \xrightarrow{O_3} (A) \xrightarrow[Zn]{H_2O} (B)$$

The compound (B) is

(a) CH_3CH_2CHO

(b) CH_3COCH_3

(c) $CH_3CH_2COCH_3$

(d) CH_3CHO

124. Which of the following sets of reagents can be used to convert 1- pentene to 1- pentyne?

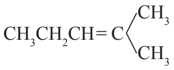
(a) 1. Br_2 in CCl_4, 2. $NaNH_2$ in THF

(b) 1. HBr in CCl_4 2. NaOH in ethanol

(c) 1. Br_2 in CCl_4, 2. H_2SO_4/Hg^{2+}

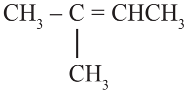
(d) 1. Br_2 in CCl_4, 2. KO in ethanol

125. Which alkene on ozonolysis gives CH_3CH_2CHO and $CH_3-CO-CH_3$

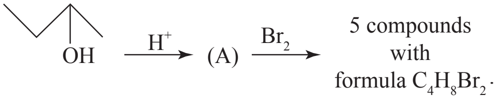
(a) 
$CH_3CH_2CH{=}C(CH_3)_2$

(b) $CH_3CH_2CH = CHCH_3$

(c) $CH_3CH_2CH = CHCH_2CH_3$

(d) 
$CH_3-C(CH_3)=CHCH_3$

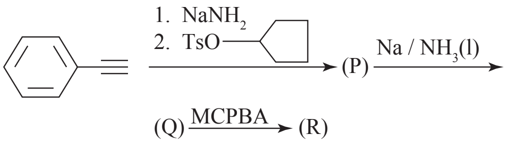
126. How many structures of (a) is possible



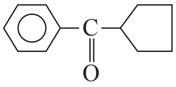
(a) Five (b) Four

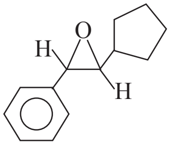
(c) Three (d) Two

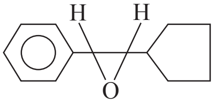
127.

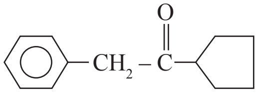


The compound (R) in this sequence of reaction is

(a) 

(b) 

(c) 

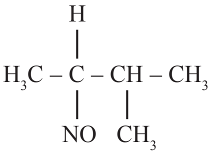
(d) 

128. $(H_3C)_2C = CHCH_3$ + NOBr → Product. The structure of the product is

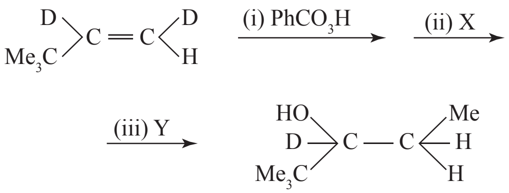
(a) $(CH_3)_2C(Br) - CH(NO)CH_3$

(b) $(CH_3)_2C(NO) - CH(Br)CH_3$

(c) $(CH_3)_2CH - C(NO)(Br)CH_3$

(d) 
$H_3C-C(H)(NO)-CH(CH_3)-CH_3$

129. In the reaction,



The reagents (X) and (Y) required for steps (ii) and (iii) are respectively:

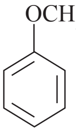
(a) CH_3OH and H_3O^+

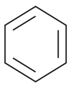
(b) CH_3I and NaOH

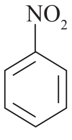
(c) CH_3MgBr and H_3O^+

(d) NaOH and CH_3Cl

130. Among the following compounds (I – III), the correct order in reaction with electrophile is


I

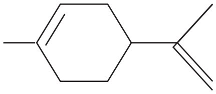

II

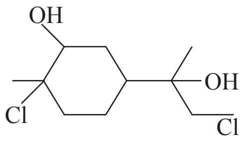

III

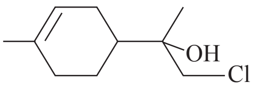
(a) I > II > III (b) III < I < II

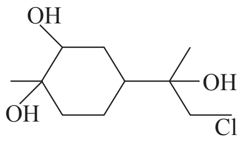
(c) II > III > I (d) I = II > III

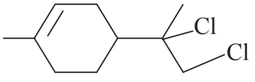
131. What product results from the reaction of limonene and chlorine water?

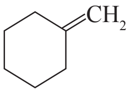

Limonene

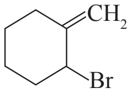
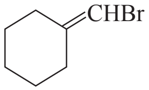
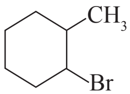
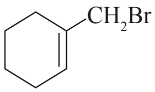
(a) 

(b) 

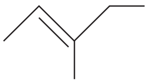
(c) 

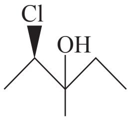
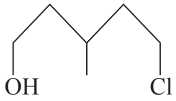
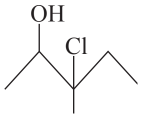
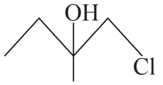
(d) 

132.  on reaction with NBS in CCl_4 solvent gives the major product

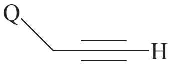
(a) 
(b) 
(c) 
(d) 

133. In this reaction A is

 $\xrightarrow{Cl_2,\ H_2O}$ A

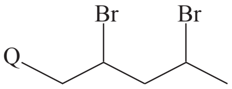
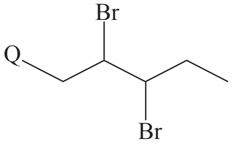
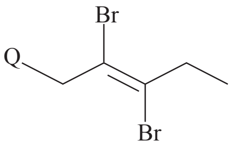
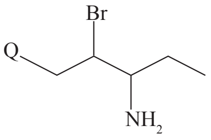
(a) 
(b) 
(c) 
(d) 

134. Identify is the final product, R in the following reaction sequences?

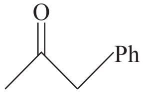
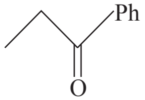
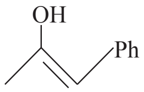
 $\xrightarrow[\text{2. } CH_3CH_2Br]{\text{1. } NaNH_3}$ P

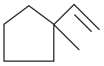
P $\xrightarrow{Na,\ NH_3\ (liq.)}$ Q

Q $\xrightarrow[CH_2Cl]{Br_2}$ R

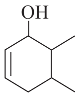
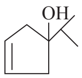
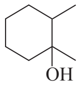
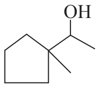
(a) 
(b) 
(c) 
(d) 

135. Ph – C ≡ C – CH_3 + H_2O $\xrightarrow[H_2SO_4]{HgSO_4}$

(a) 
(b) 
(c) 
(d) 

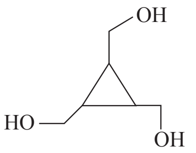
136.  $\xrightarrow{H_2O}$ Product (major)

Product is:

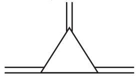
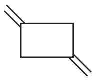
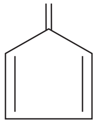
(a) 
(b) 
(c) 
(d) 

137. An alkane C_7H_{16} is produced by the reaction of lithium di(3-pentyl)cuprate with ethyl bromide. The structural formula of the product is
(a) 2-Methylpentnae
(b) 3-Ethylpentane
(c) 2-Methylhexane
(d) 3-Methylhexane

138.

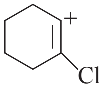
 $\xrightarrow[\Delta]{H^+\text{ (excess)}}$ (P).

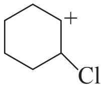
Product (P) is:

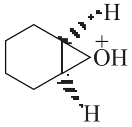
(a) 
(b) 
(c) 
(d) 

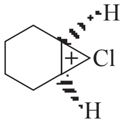
139. The number of structural and configurational isomers of a bromo compound, C_5H_9Br formed by the addition of HBr to 2-pentyne respectively are
(a) 1 and 2 (b) 2 and 4
(c) 4 and 2 (d) 2 and 1

140. Which of the species shown below is the most stable form of the intermediate in the electrophilic addition of Cl_2 in water to cyclohexene to form a halohydrin?

(a) 

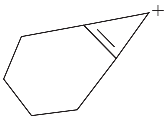
(b) 

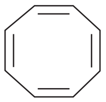
(c) 

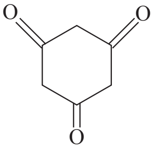
(d) 

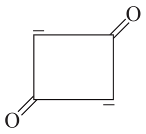
Decisive Thinking Objective Type Questions (One or more than one choice)

141. Which of these are aromatic here?

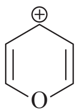
(a) 

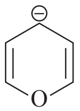
(b) 

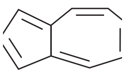
(c) 

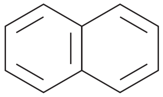
(d) 

142. Which of the following species is/are aromatic?

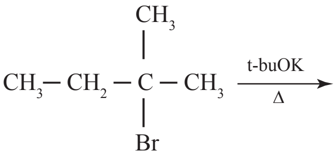
(a) 

(b) 

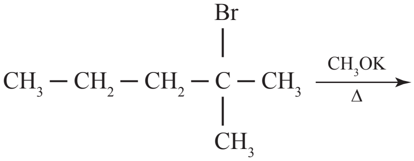
(c) 

(d) 

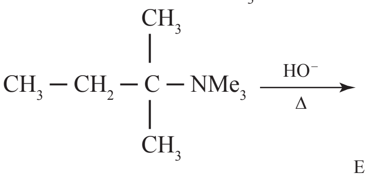
143. In which of the following reactions Hoffmann alkene is major product?

(a) 

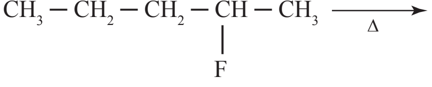
$$CH_3-CH_2-\underset{\underset{Br}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 \xrightarrow[\Delta]{\text{t-buOK}}$$

(b) 

$$CH_3-CH_2-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{Br}{|}}{C}}-CH_3 \xrightarrow[\Delta]{CH_3OK}$$

(c) 

$$CH_3-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-NMe_3 \xrightarrow[\Delta]{HO^-}$$

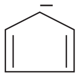
(d) 

$$CH_3-CH_2-CH_2-\underset{\underset{F}{|}}{CH}-CH_3 \xrightarrow[\Delta]{EtO^-}$$

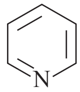
144. Which of the following carbides can give hydrocarbon on reaction with water?

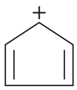
(a) SiC (b) CaC_2
(c) Be_2C (d) Al_4C_3

145. Which of the following compounds is/are aromatic?

(a) 

(b) 

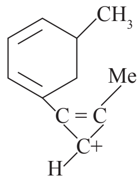
(c) 

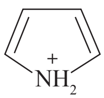
(d) 

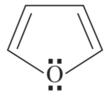
146. What product results when two moles of hydrogen chloride react with -4- methyl -2- pentyne?

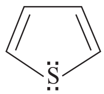
(a) 3,3- dichloro -4- methylpentane
(b) 2,2- dichloro -4- methylpentane
(c) 3 -chloro 4- methyl pentene
(d) 2- chloro 4- methyl pentene

147. Which of the following is/are aromatic compounds?

(a) 

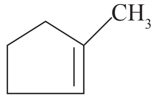
(b) 

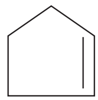
(c) 

(d) 

148. Molecular weight of unknown compound [A] is 82. compound [A] will be:

(a) $CH_3-CH_2-C\equiv C-CH_2-CH_3$
(b) $CH_2=CH_2-CH_2-CH_2-CH=CH_2$

(c) 

(d) 

149. Which is/are correct statements about oxymercuration-demercuration?

(a) Here rearrangement takes place.
(b) In the IInd step demercuration occurs that is $NaBH_4$ reduces – $HgOAc_2$ group to hydrogen
(c) The net reaction is addition of water according to Markonikoff rule.
(d) In the Ist step oxymercuration occurs that is water & $Hg(OAc)_2$ add to double bond.

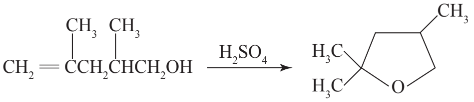
150. What products can be isolated when 2- hexyne reacts with aqueous sulfuric acid and Hg^{2+}?

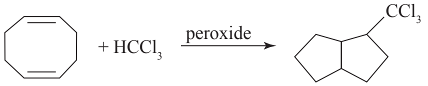
(a) 2- hexen -2-ol (b) 2 - hexanone
(c) 3- hexanone (d) 2- hexen -3- ol

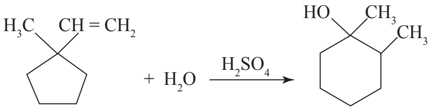
151. In the solvolysis of 3-methyl-3-bromohexane, which of the following statements is/are correct?

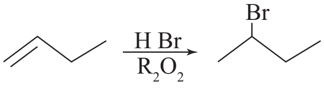
(a) it involves carbocation intermediate.
(b) it involves inversion of configuration.
(c) polar solvents accelerates the reaction.
(d) the rate of the reaction depends upon 3-methyl-3-bromohexane concentration.

152. In which of the following reaction the correct product is given?

(a)


(b)


(c)


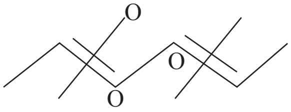
(d)


153. Which of the following is/are correct statements concerning the mechanism for hydroboration-oxidation?

(a) A three-centered two electron bond joins two C atoms and one B atom as borane bonds to the alkene.
(b) Three alkene molecules react with one borane.
(c) Borane forms a π complex with the alkene.
(d) Addition takes place according to Markownikoff's rule.

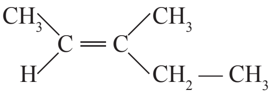
154. Which of the following is/are products that can be obtained from the oxidation of alkenes with potassium permanganate followed by acid hydrolysis?

(a) CO_2
(b) Ketones
(c) Corboxylic acid
(d) Aldehydes

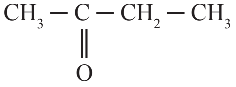
155.


Hexa 2, 4 di-one on ozonolysis by using O_3/CCl_4 following by H_2O/Zn gives

(a) Acetaldehyde	(b) Glyoxal
(c) Formaldehyde	(d) Propanaldehyde

156.


On oxidative cleavage gives

(a) CH_3COOH
(b) $CH_3-CH_2-CH_2-COOH$
(c)

$CH_3-\underset{\underset{O}{\|}}{C}-CH_2-CH_3$
(d) H_2O and CO_2

157. Butane on vapour phase nitration can give

(a) 2- nitrobutane	(b) nitro methane
(c) nitro propane	(c) nitro ethane

158. Anti-Markownikov's addition of HBr is/are observed in

(a) Propene	(b) But-1-ene
(c) But-2-ene	(d) Pent-3-ene.

159. Consider the given statements about the molecule and select the correct ones

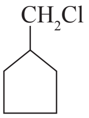
$(H_3C)_2CH–CH = CH – C \equiv C – CH = CH_2$

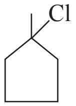
(a) Three carbons are sp^3 – hybridised
(b) Three carbons are sp^2 – hybridized
(c) Two carbons are sp – hybridized
(d) Here four carbon atoms are linearly arranged

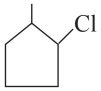
160.


products

Here products formed may be

(a)


(b)


(c)


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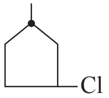
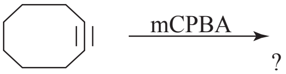
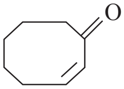
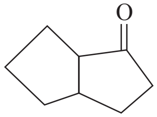
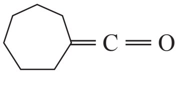


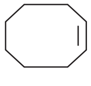
161.


Here the product are mCPBa stands for m- chloro perbenzoic acid

(a)


(b)


(c)


(d)


162. Which of these reaction can be used for

(a) $CH_3CH{=}\ CH_2 + HBr \xrightarrow{CCl_4}$

(b) $CH_3CH{=}CH_2 + HBr \xrightarrow{\text{peroxide}}$

(c) $CH_3CH{=}\ CH_2 + Br_2 \xrightarrow{CCl_4}$

(d) $CH_3CH_2CH_3 + Br_2 \xrightarrow{hv}$

163. Which one of the following is/are possible?

(a) $CH_3{-}\ SO_3H + H{-}C{\equiv}\ CNa \rightarrow CH_2SO_3Na +$ $H - C{\equiv}\ C - H$

(b) $CH_3COONa + HCl \rightarrow CH_3COOH + NaCl$

(c) $H - C \equiv C - H + NaNH_2 \rightarrow H{-}\ C \equiv C - Na$ $+ NH_3$

(d) $R - C{\equiv}\ C - H + PhONa \rightarrow PhOH +$ $R{-}\ C \equiv C - Na$

164. Which of the following is/are correct about the Diels-Alder reaction?

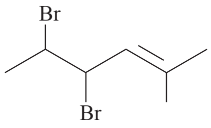
(a) It is a concerted [4 +2] cycloaddition reaction.

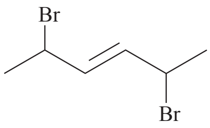
(b) It is stereospecific reaction

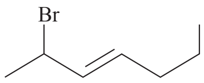
(c) The products are either cyclohexane or 1, 4 cyclohexadiene derivatives.

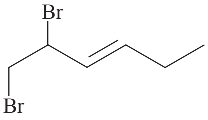
(d) It requires an s- cis diene and dienophile.

165. 2, 4- hexadiyne (C_6H_6) is allowed to react with Li in NH_3(liq). The product obtained is treated with 1 equivalent of Br_2 in CCl_4. Which of the following constitutional isomers are possible products?

(a)


(b)


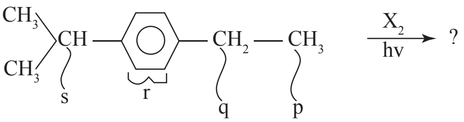
(c)


(d)


Linked-Comprehension Type Questions

Comprehension 1

Free radical substitution (halogenation) is shown by the compounds having at least one H-atom on sp^3 hybridised carbon-atom that is, by saturated compounds. Here substitution is due to a free radical this means a weak free radical substituent is substituted by a stronger one. It takes place in presence of sun light or heat ($\geq 500^oC$) or peroxide . The abstraction of hydrogen atom is on the basis of stability of free radical formed.

166.


Which of the following hydrogens can be most easily substitution from here by a X^o?

(a) p (b) q

(c) r (d) s

167. In the above reaction on single mono chlorination how many products are possible?

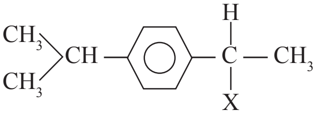
(a) 3 (b) 4

(c) 5 (d) 7

168. Which of these H-atoms can be substituted to get an optically active halide?

(a) p (b) q

(c) r (d) s

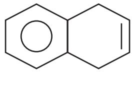


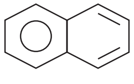
Comprehension 2

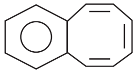
Aromatic hydrocarbon can show electrophilic substitution reaction, oxidation, and acidic nature. They are weakly acidic and they can be oxidized by acidic $K_2Cr_2O_7$ or $KMnO_4$ into carboxylic acids.

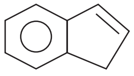
If alkyl group attached to benzene ring has α -H-atom, it is oxidized in to -COOH group.

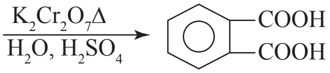
169. Which of the following aromatic hydrocarbons is the stronger acid?

(a)


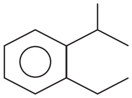
(b)


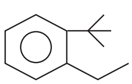
(c)


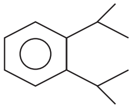
(d)


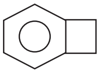
170. A


Out of the given compounds, which can give this product on oxidation?

(I)


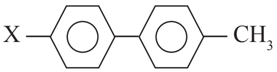
(II)


(III)


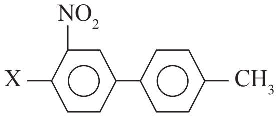
(IV)


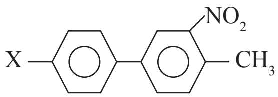
(a) I, II, III (b) I, III, IV

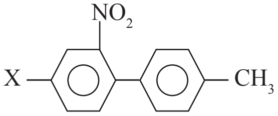
(c) I, III (d) II, III

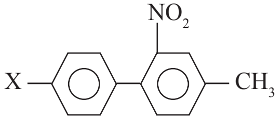
171.  $\xrightarrow[H_2SO_4]{\Delta\ HNO_3}$?

Here the product formed is?

(a) 

(b) 

(c) 

(d) 

Comprehension 3

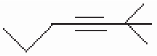
Terminal alkynes or 1 - alkynes are weakly acidic as terminal hydrogen atom can be easily substituted by a strong base like $NaNH_2$ etc.

This hydrogen atom can also be substituted by some metals like Na, Cu, Ag to give alkynides. Sodium alkynides can be used to prepare higher alkynes by treating it with halides or haloalkanes.

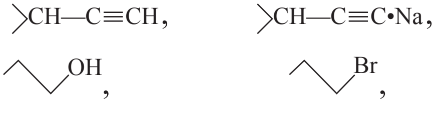
172. In this sequence of reactions:

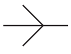
$P \xrightarrow{NaNH_2/NH_3} Q$

$R \xrightarrow[\Delta]{HBr} S$

$Q + S \longrightarrow$ 

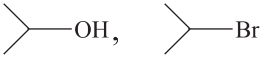
Which of the following set represents P, Q, R, S correctly and respectively.

(a) 

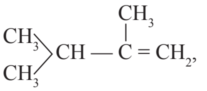
(b)  C≡CH $(CH_3)_3C{\cdot}C\equiv\overset{-}{C}\overset{+}{N}a$,

$CH_3 — CH_2— CH_2OH$, $CH_3 — CH_2— CH_2Br$

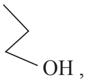
(c)  C≡CH, $(CH_3)_3C{\cdot}C\equiv\overset{-}{C}\overset{+}{N}a$,

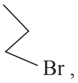


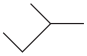
(d)

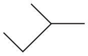


$(CH_3)_2CH—C(CH_3)=CH_2$, $(CH_3)_3CH — C\equiv C{\cdot}Na$





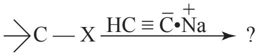
173. (I)  $X + CH_3 — C\equiv C^{-}{\cdot}Na^{+} \longrightarrow$

(II)  $C\equiv\overset{-}{C}{\cdot}\overset{+}{N}a + CH_3I \longrightarrow$

Which of the following two reactions is here effective to get 4- methyl hex 2- yne?

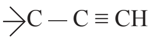
(a) II
(b) I
(c) Both are equally effective.
(d) Can not be said.

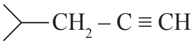
174. Which of the following is the major product for the reaction given below?

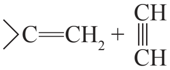


$\xrightarrow{HC\equiv\overset{-}{C}{\cdot}\overset{+}{N}a}$?

(a) 

(b) 

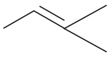
(c) 

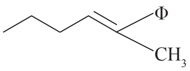
(d) 

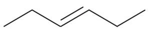
Comprehension 4

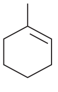
Unsymmetrical alkenes follow Markownikoff's rule or Anti-Markownikoff's rules for addition reactions. In such alkenes Markownikoff's rule is used during addition with HX, H_2O, oximercuration, demercuration , NOCl, $HXO(X_2+ H_2O)$. Anti-Markownikoff's rule is obeyed during addition reaction with HBr/ peroxide, hydroboration etc.

175. In which of the following alkenes during addition reactions Markownikoff's rule or Anti-Markownikoff's rule may be used:

(I) 

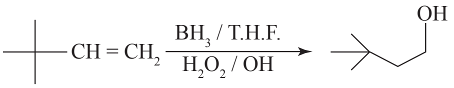
(II) 

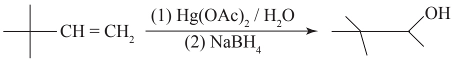
(III) 

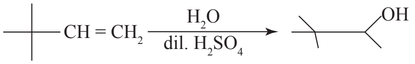
(IV) 

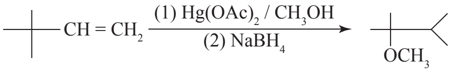
(a) I, II , IV
(b) II , III , IV
(c) II , IV
(d) I , II , III

176. Consider the given reactions:

(I) 

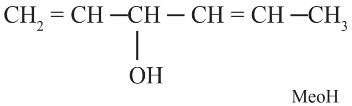
(II) 

(III) 

(IV) 

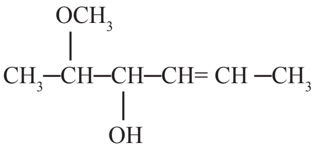
Here in which reactions, the product formed is correctly given?

(a) I , II, III (b) I, II only
(c) I, III, IV (d) I, II, IV

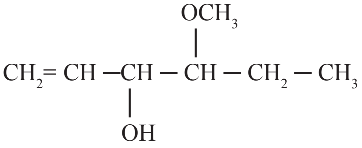
177. 

$CH_2=CH-\underset{\substack{|\\ OH}}{CH}-CH=CH-CH_3 \xrightarrow[H_2SO_4]{MeoH}$

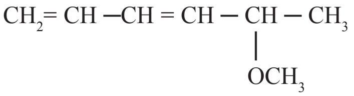
Here the product formed is?

(a) 

$CH_3-\overset{\substack{OCH_3\\ |}}{CH}-\underset{\substack{|\\ OH}}{CH}-CH=CH-CH_3$

(b) 

$CH_2=CH-\underset{\substack{|\\ OH}}{CH}-\overset{\substack{OCH_3\\ |}}{CH}-CH_2-CH_3$

(c) 

$CH_2=CH-CH=CH-\underset{\substack{|\\ OCH_3}}{CH}-CH_3$

(d) None of these

Comprehension 5

Consider the sequence of reaction given below

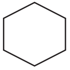
$\underset{C_6H_{12}}{(P)} \xrightarrow{HCI} \underset{C_6H_{13}Cl}{Q} + \underset{C_6H_{13}Cl}{R}$

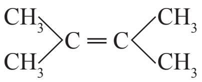
$Q \xrightarrow[\text{Alc. KOH}]{} S$ (Isomer of P)

$S \xrightarrow[\text{(ii) } H_2O/Zn]{\text{(i) } O_3/CCI_4} T$

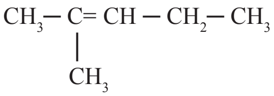
'T' cannot reduce Tollen's reagent but can show Haloform reaction.

178. If ozonolysis of (P) gives two molecules of carbonyl compounds which can show cannizaro reaction than the compound (P) is?

(a) 

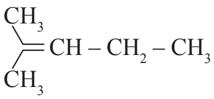
(b) 

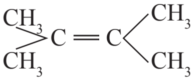
(c) 

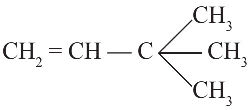
(d) 

$CH_3-\underset{\substack{|\\ CH_3}}{C}=CH-CH_2-CH_3$

179. Here compound (S) can be given as if it gives two molecules of same carbonyl compound can be?

(a) 

(b) 

(c) 

(d) Any of these

180. Which of the following statement is not correct about (P) here?

(I) On reaction with Cl it gives a compound which is optically active
(II) This reaction involves carbanion formation
(III) This reaction involves $-CH_3-$ shift
(IV) It follows Markownikoff's rule for addition

(a) I, II, III (b) I, II, IV
(b) I, III, IV (d) I, IV only

Assertion-Reason Type Questions

In the following question two statements (Assertion) A and Reason (R) are given Mark

(a) if A and R both are correct and R is the correct explanation of A;
(b) if A and R both are correct but R is not the correct explanation of A;
(c) A is true but R is false;
(d) A is false but R is true,
(e) A and R both are false.

181. (A): Alkanes undergo free radical substitution reactions.
(R): Alkanes undergo homolytic fission.

182. (A): Treatment of 1,3-dichloro propane on reaction with alc. KOH gives
$CH_2 = C = CH_2$
(R): It is nucleophilic elimination reaction.

183. (A): $CH \equiv CH$ reacts with HCl in the presence of $HgCl_2$ while $CH_2 = CH_2$ does not.
(R): There is more unsaturation in $CH\equiv CH$ than in $CH_2 = CH_2$.

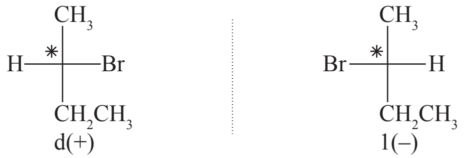
184. (A): The melting point of neopentane is higher than n-pentane but boiling point of neopentane is lower than n-pentane.
(R): Melting point depends upon packing of molecules whereas boiling point depends upon surface area. Neopentane fits into crystal lattice readily but has minimum surface area.

185. (A): Benzene does not decolourise alkaline $KMnO_4$.
(R): benzene is stabilized by resonance and π-electrons are delocalized.

186. (A): Benzene reacts with Cl_2 in presence of sunlight to form benzene hexachloride (BHC).
(R): BHC or Gammaxane or 666 is used as insecticide.

187. (A): Parafix wax is mixture of hydrocarbons.
(R): All hydrocarbons are combustible.

188. (A): Addition of HBr to 1-butene gives two optical isomers.
(R): The product contains one chiral carbon atom.
$CH_2 = CH - CH_2 - CH_3 + HBr \rightarrow$

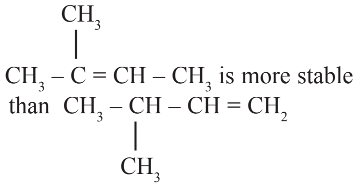


189. (A): Benzene on heating with conc. H_2SO_4 gives benzene sulphonic acid (used in forming detergents) which when heated with super heated steam under pressure gives benzene.
(R): Sulphonation is a reversible process.

190. (A): In α, β unsaturated compounds with C =1, and C = O conjugated, attack of nucleophile takes place on C = C.
(R): The C = O bond is stronger than C= C.

191. (A): Toluene undergoes nitration much more readily than benzene.
(R): it is due to electron releasing nature of $-CH_3$ group which increases electron density on benzene and electrophillic substitution reaction like nitration becomes faster.

192.



(A): $CH_3 - \overset{CH_3}{\overset{|}{C}} = CH - CH_3$ is more stable than $CH_3 - \underset{CH_3}{\underset{|}{CH}} - CH = CH_2$
(R): More alkyl substituted alkenes are more stable due to hyperconjugation.

193. (A): Treatment of 1,3-dichloropropane on treatment with Zn dust gives cyclopropane.
(R): The reaction of alkyl halide with Zn dust is dehydrogenation and called Frankland reaction.

194. (A): $CH_3 - C \equiv C - CH_3$ is more reactive than $CH \equiv CH$ towards HCl.
(R): The carbocation formed is more stable in the case of $CH_3 - C \equiv C - CH_3$ than $CH \equiv CH$.

195. (A): Addition of HCl to acetylene in presence of $HgCl_2$ give vinyl chloride.
(R): $HgCl_2$ acts as positive catalyst.

196. (A): Friedal Crafts Acylation of benzene with acetic anhydride in presence of anhydrous $AlCl_3$ yields acetophenone and not poly substituted products.
(R): It is due to stearic hindrance of bulky acyl group ($CH_3 - \overset{O}{\overset{\|}{C}} -$) and also, it is a deactivating group.

197. (A): When $CH_2 = CH - COOH$ is reacted with HBr, then $\underset{Br}{\underset{|}{CH_2}} - CH_2 - COOH$ is obtained.
(R): The carbocation formed has the stability order

$$\overset{\oplus}{C}H_2 - CH_2COOH > CH_3–\overset{\oplus}{C}H– COOH$$

198. (A): n-butane on heating in presence of $AlCl_3$ gives isobutane.
(R): n-butane and isobutane are isomers.

199. (A): Alkyl iodides are more reactive than alkyl chlorides for elimination reactions.
(R): I is better leaving group than Cl^-.

200. (A): Additionof Br_2 to 1- butene gives two optical isomers.
(R): The product contains one asymmetric carbon.

201. (A): Dimethyl sulphide is commonly for the reduction of an ozonide of an alkene to get the carbonyl compound.

(R): IT reduces the ozonide giving water soluble dimethyl sulphoxide and excess of it evaporates.

202. (A): Addition of bromine to trans -2-butene yields meso -2, 3- dibromo butane.

(R): Bromine addition to an alkene is an electrophilic addition

203. (A): Benzene reacts with CO and HCl in presence of $AlCl_3$ to give benzaldehyde.

(R): The electrophillic reagent formed is

$\mathrm{H-\underset{\underset{\displaystyle O}{\|}}{C}-Cl}$ and it is an electrophillic substitution reaction.

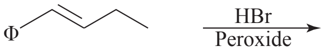
204. (A): Cycloheptatrienyl is aromatic.

(R): Aromatic molecules have high degree of thermodynamic stability.

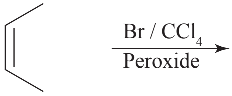
Matrix-Match Type Questions

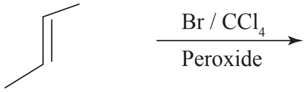
205. Match the following:

Column I

(a) 

(b) 

(c) 

(d) 

Column II

(p) Follows anti Markownikoff's rule
(q) Follows Markownikoff's rule
(r) Meso product
(s) Racemic product
(t) Anti mode of addition

206. Match the following:

Column I

(compound/ion)
(a) Cyclo-octatetraene
(b) Cyclo-heptatrienyl cation
(c) Cyclo-pentadienyl cation
(d) Cyclo-pentadiene

Column II

(nature)
(p) Aromatic (q) Non-aromatic
(r) Antiaromatic (s) Aliphatic

207. Match the following:

List I

(a) Ethane (b) Ethylene
(c) Acetylene (d) Benzene

List II

(p) 2sp carbons (q) $6sp^2$ carbons
(r) $2sp^3$ carbons (s) $2sp^2$ carbons

208. Match the following:

List I

(a) Propyne
(b) Cyclohexane (chair form)
(c) planar cyclopentane
(d) propene

List II

(p) 108° (q) 180°
(r) 120° (s) 109.5°

209. Match the following:

List I (compound)

(a) Ethane (b) Ethylene
(c) Acetylene (d) Benzene

List II

(C-C bond length in Å)
(p) 1.20 (q) 1.40
(r) 1.54 (s) 1.33

210. Match the following:

Column I

(a) oxidation of naphthalene
(b) acylation of benzene
(c) oxidation of toluene by $KMnO_4$
(d) ozonolysis of styrene

Column II

(p) benzaldehyde (q) acetophenone
(r) benzoic acid (s) phthalic acid
(t) Formaldehyde

211. Match the following:

Column I

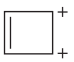
(a) Benzene (b) Ethylene
(c) Acetaldehyde (d) Chloroform

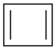
Column II

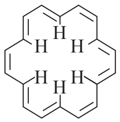
(p) Phosgene (q) Silver mirror
(r) Mustard gas (s) (4n + 2) π electrons
(t) carbylamine

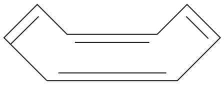
212. Match the following:

Column I

(a) 

(b) 

(c) 

(d) 

Column II

(p) Aromatic (q) Antiaromatic
(r) Non-aromatic (s) Non-planaromatic

213. Match the following:

Column I (Compounds)

(a) 2-methyl butane (b) 2,3-dimethyl butane
(c) 2-methyl propane (d) Toluene

Column II (total no. of possible halogenated product on single halogenation)

(p) 1 (q) 2
(r) 3 (s) 4
(t) Optically active product

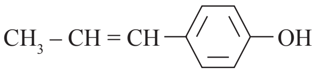
The IIT-JEE Corner

214. Benzyl chloride ($C_6H_5CH_2Cl$) can be prepared from toluene by chlorination with

[IIT 1998]

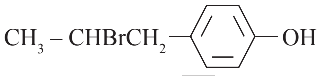
(1) SO_2Cl_2 (2) $SOCl_2$
(3) Cl_2 (4) NaOCl
(a) 1 and 2 (b) 1 and 4
(c) 2 and 3 (d) 4

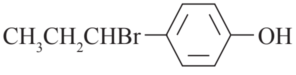
215. The reaction of

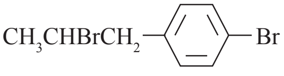


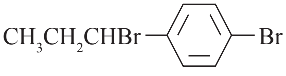
with HBr gives

[IIT 1998]

(a) 

(b) 

(c) 

(d) 

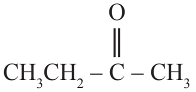
216. Among the following compounds, the strongest acid is

[IIT 1998]

(a) HC ≡ CH (b) C_6H_6
(c) C_2H_6 (d) CH_3OH

217. The product (s) obtained via oxymercuration ($HgSO_4$ + H_2SO_4) of But-1-yne would give

[IIT 1999]

(a) 

$CH_3CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$

(b) $CH_3CH_2CH_2-CHO$
(c) $CH_3CH_2CHO + HCHO$
(d) $CH_3CH_2COOH + HCOOH$.

218. In the compound $CH_2{=}CH{-}CH_2{-}CH_2{-}C{\equiv}CH$, the C_2 —C_3 bond is of the type: **[IIT 1999]**

(a) sp —sp^2 (b) sp^3 —sp^3
(c) sp— sp^2 (d) sp^2 —sp^3

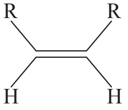
219. Propyne and propene can be distinguished by

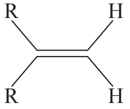
[IIT 2000]

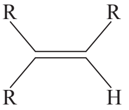
(a) Conc. H_2SO_4 (b) Br_2 in CCl_4
(c) Dil. H_2SO_4 (d) $AgNO_3$ in ammonia.

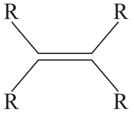
220. Which of the following alkenes will react fastest with H_2 under catalytic condition?

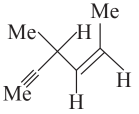
[IIT 2000]

(a) 

(b) 

(c) 

(d) 

221. 

Hydrogenation of the above compound in the presence of poisoned palladium catalyst gives

[IIT 2001]

(a) optically active compound
(b) an optically inactive compound
(c) a racemic mixture
(d) a diastereomeric mixture.

222. The reaction of propene with HOCl proceeds via the addition of:

[IIT 2001]

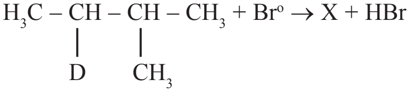
(a) H^+ in the first step
(b) Cl^+ in the first step
(c) OH^- in the first step
(d) Cl^+ and OH^- in a single step

223. In the presence of peroxide, and hydrogen chloride and hydrogen iodide do not anti-Markownikov's addition to alkenes because

[IIT 2001]

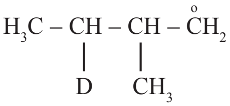
(a) Both are highly ionic
(b) one is oxidizing and other is reducing
(c) one of the steps is endothermic in both the cases
(d) all the steps are exothermic in both the cases.

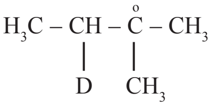
224. Consider the following reaction

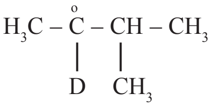


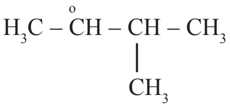
$H_3C-\underset{\underset{\displaystyle D}{|}}{CH}-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_3 + Br^o \rightarrow X + HBr$

Identify the structure of the major product X

(a) 
$H_3C - \underset{D}{CH} - \underset{CH_3}{CH} - \overset{o}{C}H_2$

(b) 
$H_3C - \underset{D}{CH} - \underset{CH_3}{\overset{o}{C}} - CH_3$

(c) 
$H_3C - \underset{D}{\overset{o}{C}} - \underset{CH_3}{CH} - CH_3$

(d) 
$H_3C - \overset{o}{C}H - \underset{CH_3}{CH} - CH_3$

[IIT 2002]

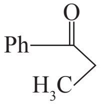
225. Identify the reagent from the following list which can easily distinguish between 1-butyne and 2-butyne.

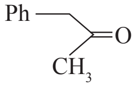
[IIT 2002]

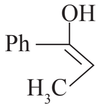
(a) Bromine, CCl_4
(b) H_2, Lindlar catalyst
(c) Dilute H_2SO_4, $HgSO_4$
(d) Ammonical Cu_2Cl_2

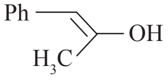
226. $Ph - C \equiv C - CH_3 \xrightarrow{Hg^{+2}/H^{+}}$ A, A is

[IIT 2003]

(a) 

(b) 

(c) 

(d) 

227. Which of the following used for the conversion of 2-hexyne into trans-2-hexane?

[IIT 2004]

(a) $H_2/Pd/BaSO_4$
(b) H_2, PtO_2
(c) $NaBH_4$
(d) $Li\text{-}NH_3/C_2H_5OH$

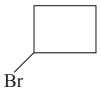
228. The product of acid catalysed hydration of 2-phenyl propene is

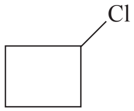
[IIT 2004]

(a) 3-phenyl-2-propanol
(b) 1-phenyl-2-propanol
(c) 2-phenyl-2-propanol
(d) 2-phenyl-1-propanol

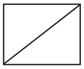
229. What would be the product formed when 1- bromo -3- chloro cyclobutane reacts with two equivalents of metallic sodium in either?

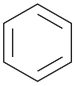
[IIT 2005]

(a) 

(b) 

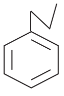
(c) 

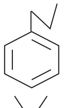
(d) 

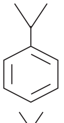
230.  $+ Cl - CH_2CH_2 - CH_3 \xrightarrow{AlCl_3} P$

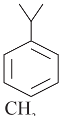
$\xrightarrow[(ii)\ H_3O^+]{(i)\ O_2/\Delta} Q + \text{Phenol}$

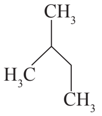
[IIT 2006]

(a)  and CH_3CH_2CHO

(b)  and CH_3COCH_3

(c)  and CH_3COCH_3

(d)  and CH_3CH_2CHO

231. 

$\xrightarrow{Cl_2,\ hv}$ N (isomeric products)

$C_5H_{11}Cl \xrightarrow[\text{distillation}]{\text{fractional}}$ M (isomeric products)

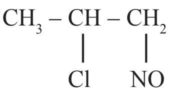
[IIT 2006]

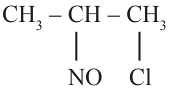
(a) 6, 6
(b) 6, 4
(c) 4, 4
(d) 3, 3

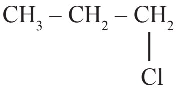
232. $CH_3 - CH = CH_2 + NOCl \rightarrow P$

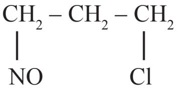
Identify the adduct:

[IIT 2006]

(a) 
$CH_3 - \underset{Cl}{CH} - \underset{NO}{CH_2}$

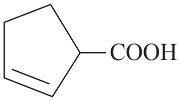
(b) 
$CH_3 - \underset{NO}{CH} - \underset{Cl}{CH_3}$

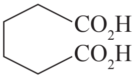
(c) 
$CH_3 - CH_2 - \underset{Cl}{CH_2}$

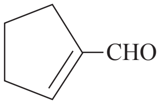
(d) 
$\underset{NO}{CH_2} - CH_2 - \underset{Cl}{CH_2}$

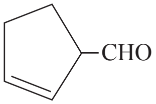
233. Cyclohexene on ozonolysis followed by reaction with zinc dust and water gives compound E. Compound E on further treatment with aqueous KOH yields compound F. Compound F is

[IIT 2007]

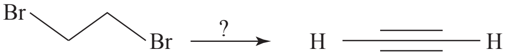
(a) 

(b) 

(c) 

(d) 

234. The reagent (s) for the following conversion,



is/are

[IIT 2007]

(a) Zn/CH_3OH
(b) alcoholic KOH
(c) alcoholic KOH followed by $NaNH_2$
(d) aqueous KOH followed by $NaNH_2$

ANSWERS

Straight Objective Type Questions

1. (d) **2.** (d) **3.** (d) **4.** (d) **5.** (b) **6.** (a) **7.** (a) **8.** (a) **9.** (b) **10.** (c)
11. (a) **12.** (a) **13.** (a) **14.** (c) **15.** (b) **16.** (d) **17.** (a) **18.** (c) **19.** (c) **20.** (b)
21. (a) **22.** (b) **23.** (c) **24.** (c) **25.** (a) **26.** (a) **27.** (b) **28.** (c) **29.** (d) **30.** (c)
31. (b) **32.** (b) **33.** (d) **34.** (a) **35.** (b) **36.** (c) **37.** (a) **38.** (c) **39.** (d) **40.** (b)
41. (d) **42.** (c) **43.** (c) **44.** (c) **45.** (a) **46.** (b) **47.** (d) **48.** (d) **49.** (d) **50.** (b)
51. (b) **52.** (d) **53.** (b) **54.** (b) **55.** (c) **56.** (b) **57.** (c) **58.** (d) **59.** (b) **60.** (d)
61. (d) **62.** (c) **63.** (b) **64.** (b) **65.** (a) **66.** (c) **67.** (c) **68.** (b) **69.** (c) **70.** (d)
71. (d) **72.** (a) **73.** (b) **74.** (d) **75.** (b) **76.** (b) **77.** (a) **78.** (a) **79.** (b) **80.** (a)

Brainteasers Objective Type Questions

81. (b) **82.** (c) **83.** (a) **84.** (c) **85.** (a) **86.** (d) **87.** (d) **88.** (b) **89.** (b) **90.** (d)
91. (a) **92.** (c) **93.** (a) **94.** (b) **95.** (c) **96.** (b) **97.** (d) **98.** (b) **99.** (a) **100.** (a)
101. (b) **102.** (b) **103.** (a) **104.** (a) **105.** (a) **106.** (b) **107.** (b) **108.** (a) **109.** (a) **110.** (c)
111. (d) **112.** (d) **113.** (d) **114.** (d) **115.** (c) **116.** (c) **117.** (d) **118.** (a) **119.** (c) **120.** (b)
121. (a) **122.** (c) **123.** (d) **124.** (a) **125.** (a) **126.** (c) **127** (b) **128.** (a) **129.** (c) **130.** (a)
131. (c) **132.** (d) **133.** (a) **134.** (b) **135.** (b) **136.** (c) **137.** (b) **138.** (d) **139.** (b) **140.** (d)

Decisive Thinking Objective Type Questions

141. (a), (c) **142.** (a), (c), (d) **143.** (a), (c), (d) **144.** (b), (c), (d) **145.** (a), (b) (c)
146. (a), (b) **147.** (a), (c) , (d) **148.** (a), (b), (c) **149.** (b), (c), (d) **150.** (b), (c)
151. (a), (c), (d) **152.** (a), (b), (c) **153.** (a), (b), (c) **154.** (a), (b), (c) **155.** (a), (b)
156. (a), (c) **157.** (a), (b), (c), (d) **158.** (a), (b), (d) **159.** (a), (c), (d) **160.** (a), (b), (c), (d)
161. (a), (b), (c) **162.** (a), (c) **163.** (a) , (b), (c) **164.** (a), (b), (d) **165.** (a), (b)

Linked-Comprehension Type Questions

166. (d) **167.** (b) **168.** (b) **169.** (d) **170.** (b) **171.** (b) **172.** (b) **173.** (a) **174.** (d) **175.** (a)
176. (b) **177.** (c) **178.** (c) **179.** (b) **180.** (c)

Assertion-Reason Type Questions

181. (a) **182.** (a) **183.** (b) **184.** (a) **185.** (a) **186.** (b) **187.** (b) **188.** (a) **189.** (a) **190.** (c)
191. (a) **192.** (a) **193.** (b) **194.** (a) **195.** (c) **196.** (a) **197.** (a) **198.** (b) **199.** (a) **200.** (a)
201. (a) **202.** (c) **203.** (a) **204.** (b)

Matrix-Match Type Questions

205. (a) - (p), (b) - (q), (c) - (s), (t), (d) - (r), (t)
206. (a) - (q), (b) - (p), (c) - (r), (d) - (q)
207. (a) - (r), (b) - (s), (c) - (p), (d) - (q)
208. (a) - (q), (b) - (s), (c) - (p), (d) - (r)
209. (a) - (r), (b) - (s), (c) - (p), (d) - (q)
210. (a) - (s) - (b) - (q), (c) - (r), (d) - (p), (t)
211. (a) - (s), (b) - (r), (c) - (q), (d) - (p), (t)
212. (a) - (p), (b) - (q) - (c) - (p), (d) - (r), (s)
213. (a)-(s), (t), (b)-(r), (t), (c)-(q), (d)-(p)

The IIT-JEE Corner

214. (a) **215.** (b) **216.** (d) **217.** (a) **218.** (d) **219.** (d) **220.** (a) **221.** (b) **222.** (b) **223.** (c)
224. (b) **225.** (d) **226.** (a) **227.** (d) **228.** (c) **229.** (d) **230.** (c) **231.** (b) **232.** (a) **233.** (c)
234. (c)

HINTS AND EXPLANATION

Straight Objective Type Questions

1. Higher the number of C-atoms, higher is the boiling point i.e, n-hexane.

4. $CH_2 = CH_2 + H_2SO_4 \rightarrow CH_3CH_2OSO_3H$
$C_6H_6 + H_2SO_4 \rightarrow C_6H_5SO_3H + H_2O$
$C_6H_{14} + H_2SO_4 \rightarrow$ No reaction

$C_6H_5NH_2 + H_2SO_4 \rightarrow C_6H_5\overset{+}{N}H_3\ HSO_4^-$
Only hexane does not dissolve in conc. H_2SO_4 even on warming.

5. This alkene has unsymmetrical double bond.

6. $CH_3C \equiv CH + H_2O \xrightarrow[Hg_2SO_4]{H_2SO_4}$
$[CH_3CH(OH) = CH_2] \rightarrow \underset{\text{(acetone)}}{CH_3COCH_3}$

7. This is hydrocarbon oxidation reaction. Here water molecule adds to double bond in anti MarkowniKoff's fashion.

8. $CH_3CH_2C \equiv CH + 4[O] \xrightarrow{\text{alk. KMnO}_4}$
$CH_3CH_2COOH + CO_2$

9. Baeyer's reagent is alkaline permanganate solution.

10. 2, 3-Dimethyl-2-butene

11. Acidic hydrogen is the hydrogen attached to ≡ C (triple bonded carbon).

13. C_2H_6 must be in excess for the best yield of C_2H_5Cl.

14. $CaC_2 \equiv C_2H_4$
64 kg 28 kg

15. n-octane and 2, 2, 3, 3-Tetramethylbutane both contain eight carbons but n-octane has a straight chain while 2, 2, 3, 3-tetramethylbutane has a branched chain.

16. $C_6H_6 + Cl - CO - CH_3 \xrightarrow{\text{anhyd. AICl}_3}$
$C_6H_5COCH_3 + HCl$
Acetophenone

17. In case of ethane and hexachloroethane, there is less hindered rotation because of the presence of C – C single bond. Out of these, ethane has least hindered rotation because Cl is bigger than H.

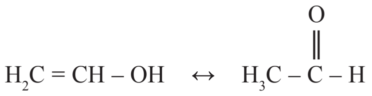
18. In Reimer-Tiemann reaction, CCl_2 is attacking species.

24. CH_3 group activates the benzene ring towards electrophillic substitution.

25. In the absence of peroxides, electrophillic addition is observed. The first step is the addition of H^+ to alkene.

27. Peroxide effect is not applicable to addition of HCl. The reactions takes place via more stable intermediate carbocation.

28. $H - C \equiv C - H + H_2O\ H_2SO_4/HgSO_4$



$H_2C = CH - OH \leftrightarrow H_3C - \overset{\overset{\displaystyle O}{\|}}{C} - H$

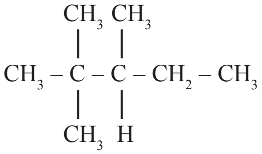
Acetaldehyde is having one π bond.

30. $C_2H_5Cl + Mg \xrightarrow{\text{dryether}} \underset{(X)}{C_2H_5MgCl}$
$\xrightarrow{H_2O} \underset{(Y)}{C_2H_6} + \underset{(Z)}{Mg.(Cl).OH}$

32. 1,2-addition product is kinetically controlled product while 1,4-addition product is thermodynamically controlled product and formed at comparatively higher temperature.

$CH_2{=}CH-CH{=}CH_2 \xrightarrow{HBr,\ 40^\circ}$
$CH_2(Br)CH{=}CHCH_3$
1,4-addition
$+ CH_3CH(Br){-}CH{=}CH_2$
1,2-addition
Therefore, 1-bromo-2-butene will be the main product under thermodynamically controlled conditions.

33.



$$\begin{array}{c} \quad CH_3\ CH_3 \\ CH_3-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-CH_2-CH_3 \\ \quad CH_3\ \ H \end{array}$$

[number of C – C sigma bonds = (number of carbons – 1)] and
[number of C – H sigma bonds = number of hydrogens]

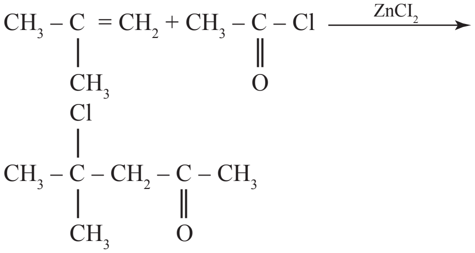
35. $2CH_3Br + 2Na \longrightarrow CH_3-CH_3 + 2NaBr$

$CH_3Br + 2[H] \xrightarrow{Zn/HCl} CH_4 + HBr$

36. $CaC_2 + H_2O \longrightarrow C_2H_2$
$\xrightarrow{H_2SO_4,HgSO_4} CH_3CHO$

37. $CH_3-C\equiv C-CH_3 + H_2O \xrightarrow{H_2SO_4,HgSO_4}$
2-Butyne
$CH_3COCH_2CH_3$
2-Butanone

38.



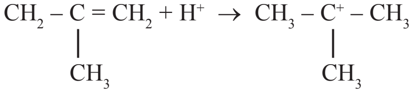
$$CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2 + CH_3-\underset{\underset{O}{\|}}{C}-Cl \xrightarrow{ZnCl_2}$$

$$CH_3-\overset{\overset{Cl}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-\underset{\underset{O}{\|}}{C}-CH_3$$

This is an example of electrophillic addition. The electrophile that initiates the addition is CH_3-CO^+. Addition obeys MarkownoKoff's rule.

39. Propyne is formed through removal of two molecules of HBr.

42.



$$CH_2-\underset{\underset{CH_3}{|}}{C}=CH_2 + H^+ \rightarrow CH_3-\underset{\underset{CH_3}{|}}{C^+}-CH_3$$

45. $(CH_3)_2C=CH-CH_3 + 3[O] \xrightarrow[\text{in presence of } KMnO_4]{NaIO_4}$

$(CH_3)_2C=O + CH_3COOH$

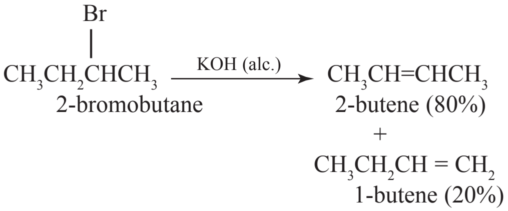
48. Isobutene $C.(CH_3)_2=CH_2$ has minimum force of attraction (due to stearic hindrance). So minimum boiling point.

49. According to Huckel's rule, the cyclic, planar, conjugated system which have $(4n + 2)\pi$ electrons, show aromatic character.

$+ 2\pi e^-$ $(4 \times 0 + 2 = 2)$

It obeys Huckel's rule so it is aromatic in nature. All other species here are anti aromatic as they have 4 electrons.

50.

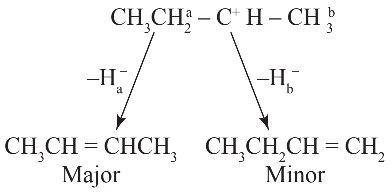


$$\underset{\text{2-bromobutane}}{CH_3CH_2\overset{\overset{Br}{|}}{C}HCH_3} \xrightarrow{KOH\ (alc.)} \underset{\text{2-butene (80\%)}}{CH_3CH{=}CHCH_3} + \underset{\text{1-butene (20\%)}}{CH_3CH_2CH=CH_2}$$

In elimination reaction of alkyl halide major product is obtained according to Saytzeff's rule, which states that when two alkenes may be formed, the alkene which is most substituted one predominates.

51. $CH_3C\equiv CCH_2\,CH_3 \xrightarrow[(ii)\ H_2O]{(i)\ O_3/CCl_4}$
$CH_3COOH + CH_3CH_2COOH$

53. According to Saytzeff's rule,
$CH_3CH_2CH(F)CH_3$ CH_3O^-/CH_3OH



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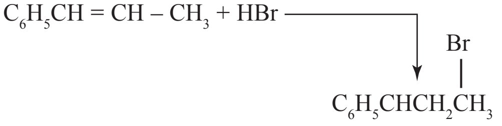

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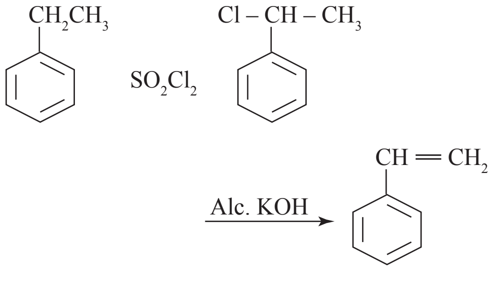


57. Terminal alkynes (having acidic H) react with ammonical cuprous chloride solution to form red precipitate.

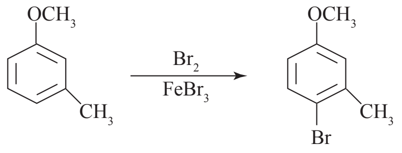
$2H-C\equiv C-H + Cu_2Cl_2 + 2NH_4OH \rightarrow$

Acetylene

$2HC\equiv CCu + 2NH_4Cl + 2H_2O$

copper acetylide
(red ppt.)

59.



(A)

As methyl group is ortho- or para-directing.

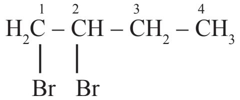
64. % of p character of hybrid orbital of C in

methane	ethene	ethyne
sp^3	sp^2	sp
$\frac{3}{4}\times 100\ \%$	$\frac{2}{3}\times 100\ \%$	$\frac{1}{2}\times 100\ \%$
75 %	66.67 %	50 %

65. The shape of π-bond between two ethylenic carbon atoms is in the form of two flat ellipsoids above and below the plane of the two carbon atoms

68. $H_2C=CH-CH_2-CH_3 + Br_2 \rightarrow$

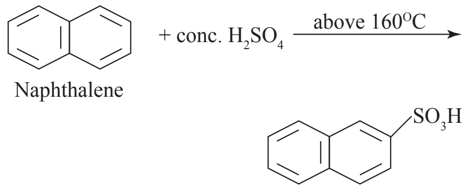
1-butene (excess)



$\overset{1}{H_2C}(Br)-\overset{2}{CH}(Br)-\overset{3}{CH_2}-\overset{4}{CH_3}$

1,2-dibromobutane

69.



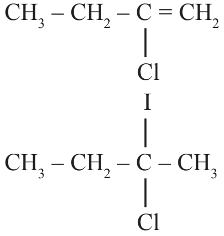
Naphthalene

β-naphthalene sulphonic acid
(85%)

70. As the attack of the electrophile is favoured by electron releasing groups (+I) that is,

$OH > CH_3 > H > Cl$

71. $CH_3-CH_2-C\equiv CH + HCl \xrightarrow{HI}$

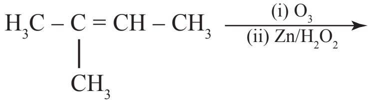


$CH_3-CH_2-C(Cl)=CH_2$

I

$CH_3-CH_2-C(I)(Cl)-CH_3$

72.

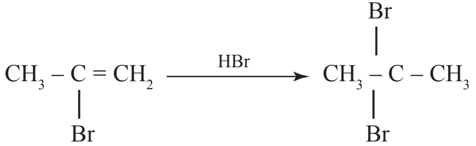


$H_3C-\underset{CH_3}{C}=CH-CH_3 \xrightarrow[(ii)\ Zn/H_2O_2]{(i)\ O_3}$

2-methyl-2-butene

$CH_3COCH_3 + CH_3CHO$

74. $CH_3-C\equiv CH + 2HBr \xrightarrow[H^+\ (from\ HBr)]{electrophillic\ addition\ of}$



$CH_3-\underset{Br}{C}=CH_2 \xrightarrow{HBr} CH_3-\overset{Br}{\underset{Br}{C}}-CH_3$

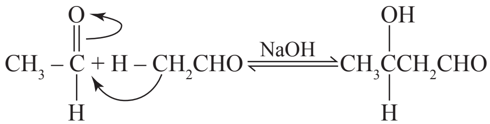
75. $CH_3CH_2-C\equiv H \xrightarrow[\Delta]{Na/liq.\ NH_3}$

$CH_3CH_2C\equiv C^{\ominus}\ Na^{\oplus}$

As it is a terminal alkyne, having acidic hydrogen so it reacts with Na in liquid ammonia.

76. As $-NO_2$ is electron withdrawing so it will destabilize σ-complex.

77. A = CH_3-CHO, which then undergo aldol condensation to give compound B.



$CH_3-\overset{O}{\underset{H}{C}} + H-CH_2CHO \overset{NaOH}{\rightleftharpoons} CH_3\overset{OH}{\underset{H}{C}}CH_2CHO$

78. $-NO_2$ is a meta-directing group. As it is also a deactivating group so no chance of introduction of second-Br atom.

79. The product formation will be accordingly to Markownikoff's rule, because peroxide effect is effective only in the case of HBr and not effective in case of HI. Because iodine-free radical formed as H-I bond is weaker but iodine-free radicals combine with each other to form iodine molecules rather than to attack the double bond.

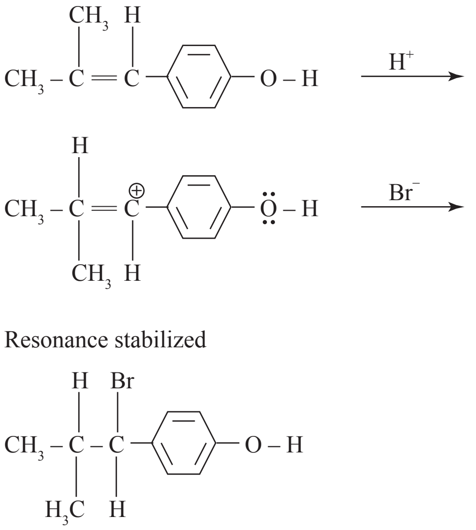
80. –OH group shows both –I effect and +M effect which predominates the –I character and electron density is increase in the benzene ring which facilitates electrophillic attack.

Brainteasers Objective Type Questions

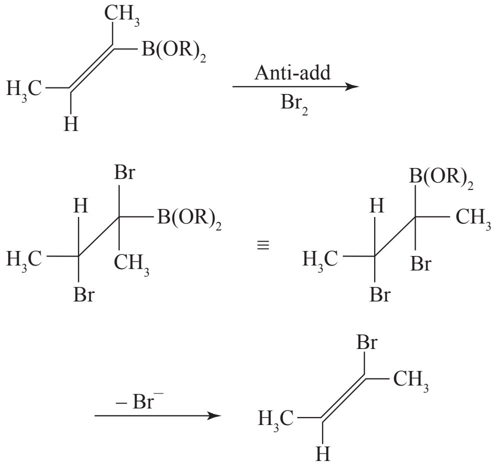
81. There are five isomers hexane . Only one,
2, 3 -dimethylbutane can give two different monochlorinated compounds: 1- chloro -2, 3- dimethylbutane, and 2- chloro, 3 –dimethylbutane.

82. 1, 3- Dimethylcyclobutane has the molecular formula of C_6H_{12}, which has a molecular mass of **84.** When chlorinated the Cl atom can bond at the 1 and 2 positions on the ring and the methyl group; thus three monochlorinated products could form. Cyclohexane only forms one monochlorinated product, and mehtycyclopentane can form four products (Alkane reactions).

83. The reaction sequence is as follows:

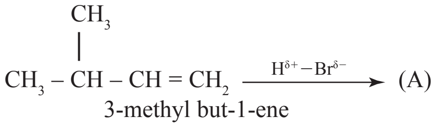


85.



86. 2- Bromo -2- chloropentaen is the product because both hydrohalogenation follow Markovnikov's rule.

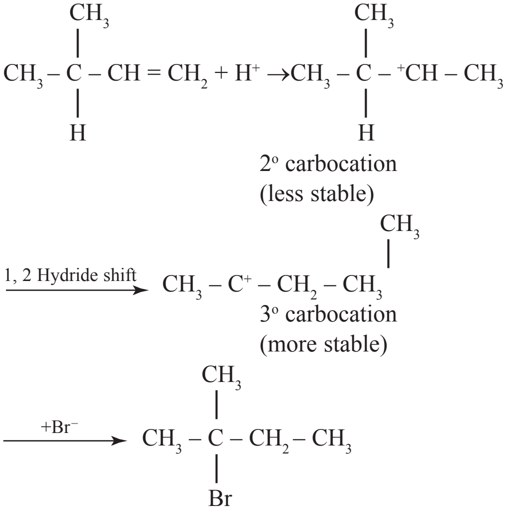
87. The reaction occurs as follows:



$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}H-CH=CH_2\xrightarrow{H^{\delta+}-Br^{\delta-}}(A)$$

3-methyl but-1-ene

Mechanism



$$CH_3-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH=CH_2+H^+\rightarrow CH_3-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-{}^{+}CH-CH_3$$

2° carbocation
(less stable)

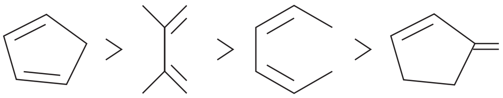
$$\xrightarrow{\text{1, 2 Hydride shift}}CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C^+}-CH_2-CH_3$$

3° carbocation
(more stable)

$$\xrightarrow{+Br^-}CH_3-\underset{\underset{\displaystyle Br}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_2-CH_3$$

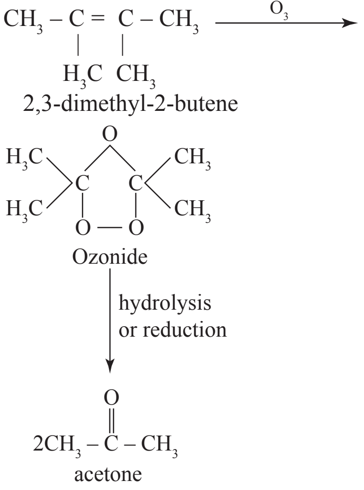
(Major product) 2-Bromo-2-methylbutane

88. The most reactivity diene has the double bonds locked in the s -cis conformation, whereas the least reactive diene cannot achieve the required s- cis conformation because it is locked in the s -trans conformation.



89. Hydroboration-oxidation places the OH group in the anti-Markovnikov position

90. The reaction sequence is as follows:



91. In the step (I), addition of HBr occurs in accordance with Markownikoff's rule and in step (II), addition of HBr occurs in presence of peroxide in accordance with peroxide effect (or anti-Markowni koff's rule).

92. Since the resonance energy of benzene is 36 kcal/mol, therefore benzene contains 36 kcal less energy than predicted. In other words, benzene is more stable by 36 kcal than cyclohexatriene.

So expected heat of hydrogenation of cyclohexatriene = 51 + 36 kcal/mol

= 87 kcal/mol

Hence, heat of hydrogenation per double bond = 87/3 = 29 kcal/mol

So heat of hydrogenation of cyclohexene

= 29 kcal/mol.

94. 1, 2- dimethylcyclohexene is the most stable alkene because it is only tetrasubstituted alkene.

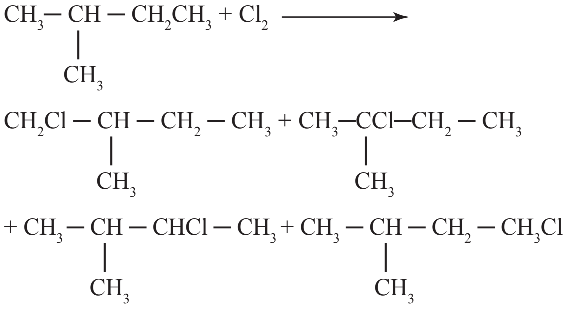
95. -bromo -2- methylbutane is the only listed tertiary alkyl bromide. Tertiary alkyl bromides are usually most reactive in E2 mechanisms.

96. $HC \equiv CH \xrightarrow{O_3} OCH - CHO$ (X)

$\xrightarrow[\text{Reduction}]{Zn/CH_3OH} H_2OCH_2 - CH_2OH$

Ethane-1,2-diol

97. Chlorination of 2- methylbutane gives four mono - chlorinated products.



$$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2CH_3 + Cl_2 \longrightarrow$$

$$CH_2Cl-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_3 + CH_3-\underset{\underset{CH_3}{|}}{CCl}-CH_2-CH_3$$

$$+ CH_3-\underset{\underset{CH_3}{|}}{CH}-CHCl-CH_3 + CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_2Cl$$

The reactivity ratio of 3°H : 2°H : 1°H towards chlorination is 5 : 3 : 8 : 1

$$\text{Per centage of D} = \frac{3}{31.6} \times 100 = 14\ \%$$

98. 2- chloro -2- methylbutane is the major product of this reactionbecause a 1,2- hydride shift occurs, producing a more stable tertiary carbocation.

100. Expected heat of hydrogenation of cyclohexatriene = 51 + 36 = 87 kcal

Hence heat of hydrogenation per double bond = 87 kcal/3 = 29 kcal

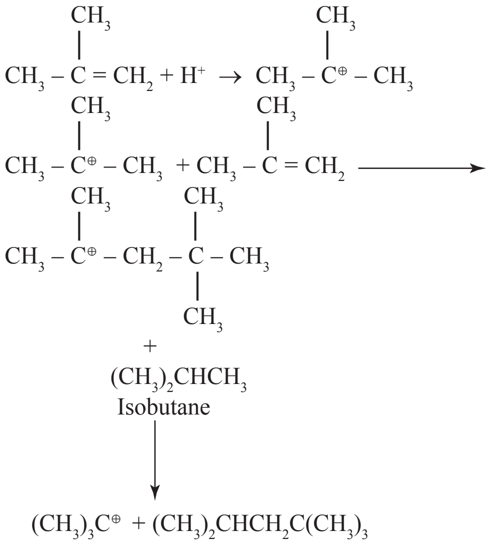
So heat of hydrogenation of cyclohexene

= 29 kcal/mol

Heat of hydrogenation of cyclohexadiene

= 2 × 29 = 58 kcal/mol

101.



$$CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2 + H^+ \rightarrow CH_3-\overset{\overset{CH_3}{|}}{C^{\oplus}}-CH_3$$

$$CH_3-\overset{\overset{CH_3}{|}}{C^{\oplus}}-CH_3 + CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2 \longrightarrow$$

$$CH_3-\overset{\overset{CH_3}{|}}{C^{\oplus}}-CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$$

$$+$$

$$(CH_3)_2CHCH_3$$

Isobutane

$$\downarrow$$

$$(CH_3)_3C^{\oplus} + (CH_3)_2CHCH_2C(CH_3)_3$$

102. Alkene stability increases with the increasing number of electron-releasing substituents attached to doubly bonded carbons.

Alkene 1 is disubstituted

Alkene 2 is tetrasubstituted

Alkene 3 is trisubstituted.

104. (Z) - 2, 2,5, 5 - tetramethyl -3- hexane has the highest enthalpy of hydrogenation because it is disubstituted with two t- butyl groups on the same side of the molecule. These groups repel each other, increasing the energy of the molecule .

107. The increasing order of stabilities of carbonium ions is 1° < 2° < 3°. Since carbonium ion is formed as an intermediate in the dehydration of alcohol, so ease of dehydration in the increasing order is

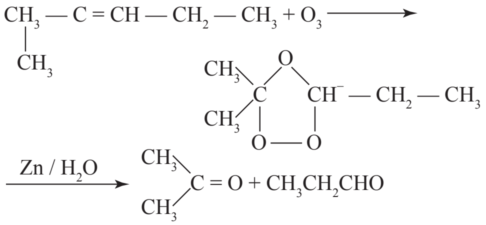
1° alcohol < 2° alcohol < 3° alcohol.

108. 3- bromo -2- methyl- 2- butene cannot exist as cis -trans isomers.

109. 2,5- Dimethyl - 3- hexyne undergoes oxidative cleavage to produce 2- methylpropanoic acid.

112. 2, 3- dimethyl 2, 2- butene reacts significantly faster than the others because it has four R groups bonded to the double bond. these electron releasing R groups help stabilize the cyclic bromonium ion that forms in the mechanism.

115.

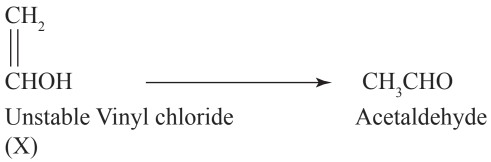


$$CH_3-\underset{\underset{CH_3}{|}}{C}=CH-CH_2-CH_3 + O_3 \longrightarrow$$

$$\xrightarrow{Zn\,/\,H_2O} \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=O + CH_3CH_2CHO$$

Hence the product are propan -2- one and propanal

117. $HC \equiv CH \xrightarrow[HgSO_4 / H_2SO_4]{H_2O}$
Acetylene


$$\begin{array}{l} CH_2 \\ \| \\ CHOH \end{array} \longrightarrow CH_3CHO$$
Unstable Vinyl chloride (X) Acetaldehyde

118. $(CH_3)_2\ CH.CH_2CH_2Cl + Li \longrightarrow$
$(CH_3)_2\ CH.CH_2CH_2\ Li \xrightarrow{H_2O}$
$(CH_3)_2\ CH\ CH_2CH_3$

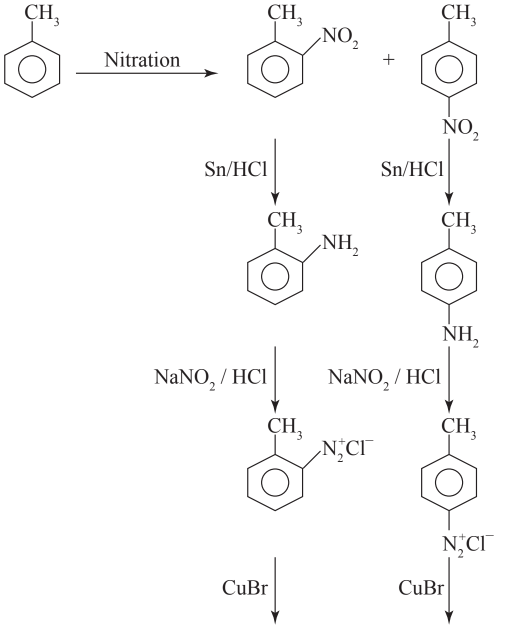
$2(CH_3)_2 CH.CH_2CH_2Cl \xrightarrow{Na/ether}$
$(CH_3)_2\ CH.CH_2CH_2\ - CH_2\,CH_2.CH(CH_3)_2$
2, 7-Dimethyloctane

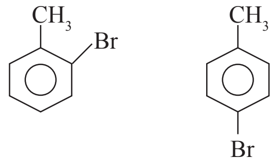
119. 1. $Hg(O_2CCH_3)_2$, H_2O, 2. $NaBH_4$, OH^-. The best yields for converting alkenes to alcohots are obtained by using oxymercuration-demercuration if the Markovnikov product is needed.

120. $CH \equiv CH + H_2O \xrightarrow{H_2SO_4,\ HgSO_4}$
Acetylene
$[CH_2 = CHOH] \rightarrow CH\ CHO$
Acetaldehyde

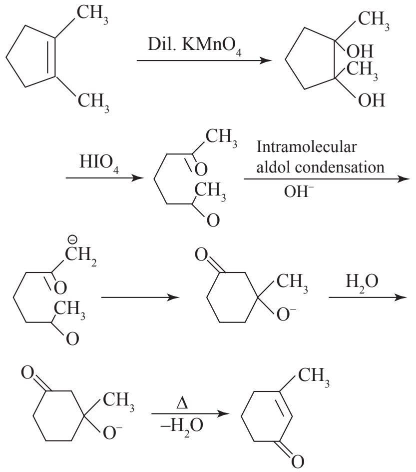
$CH_3C \equiv CH + H_2O \xrightarrow{H_2SO_4,\ HgSO_4}$
Propylene
$[CH_3C(OH) = CH_2] + CH_3COCH_3$
Acetone

121.

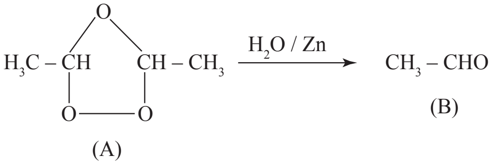




122.

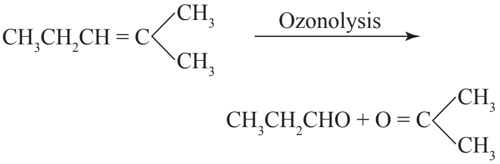


123. Here compound (B) is ethanal (CH_3CHO)
$H_3C - CH = CH - CH_3 \xrightarrow{O_3}$

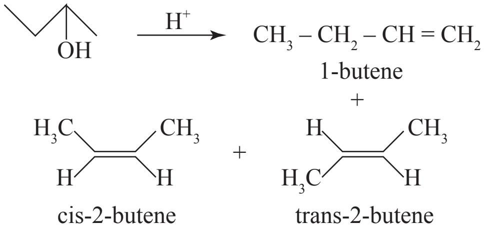


124. First add Br_2 in CCl_4 to brominate the double bond. Then add $NaNH_2$ in THF to double dehydrohalogenate the dihalide to 1- pentyne.

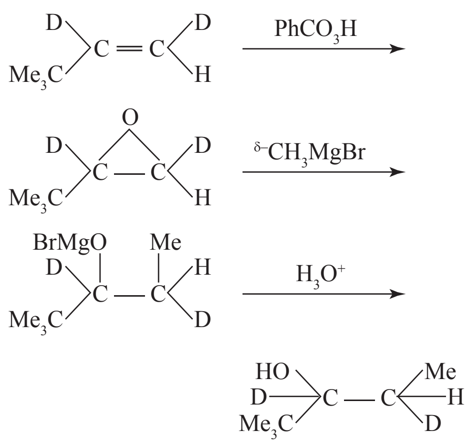
125.


$$CH_3CH_2CH = C\begin{matrix} CH_3 \\ CH_3 \end{matrix} \xrightarrow{\text{Ozonolysis}} CH_3CH_2CHO + O = C\begin{matrix} CH_3 \\ CH_3 \end{matrix}$$

126.



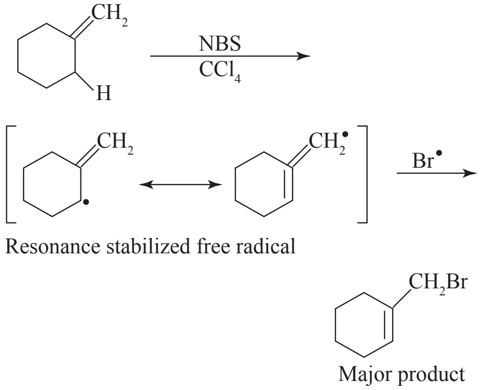
129.



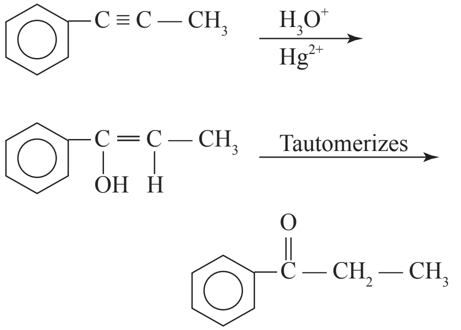
130. –OCH_3 activates while –NO_2 deactivates the ring towards electrophillic reactions.

131. This reaction forms a chlorohydrin at both double bonds. In the formation of the chlorohydrin, the OH group bonds to the tertiary position.

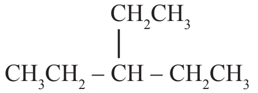
132.



135.



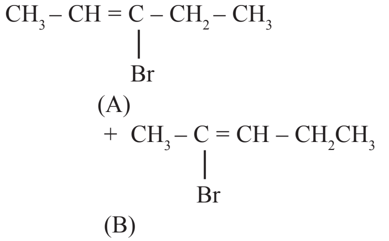
136. $[\{(CH_3CH_2)_2CH\}_2 Cu]^- Li^+ + CH_3CH_2Br \rightarrow$
Lithium di(3-pentyl)cuprate



$$CH_3CH_2-\underset{}{\overset{CH_2CH_3}{\overset{|}{CH}}}-CH_2CH_3$$

3-Ethylpentane (C_7H_{16})
+ $(CH_3CH_2)_2CHCu$ + LiBr

139. $CH_3-C\equiv C-CH_2-CH_3 \xrightarrow{HBr}$



$$\underset{\text{(A)}}{CH_3-CH=\underset{\underset{Br}{|}}{C}-CH_2-CH_3} + \underset{\text{(B)}}{CH_3-\underset{\underset{Br}{|}}{C}=CH-CH_2CH_3}$$

Pent-2-yne on addition of HBr gives two structural isomers (A and B). Each of these two isomers can exist as a pair of cis, trans isomers and therefore, there are four configurational isomers.

Decisive Thinking Objective Type Questions

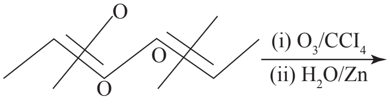
144. As all ionic carbides on hydrolysis can yield hydrocarbons while covalent carbides can not do.

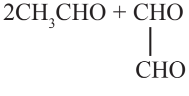
146. Both A and B are correct because 2,2- dichloro-4-methylpentane and 3,3- dichlor-2- methylpentane are formed in this reaction.

152. Both (b) and (c) are correct because the product of the hydration of an alkyne is a ketone. The carbonyl group can from on the second or third C atom.

154. As aldehydes oxidize to acids in this reaction because $KMnO_4$ is a strong oxidizing agent.

155.

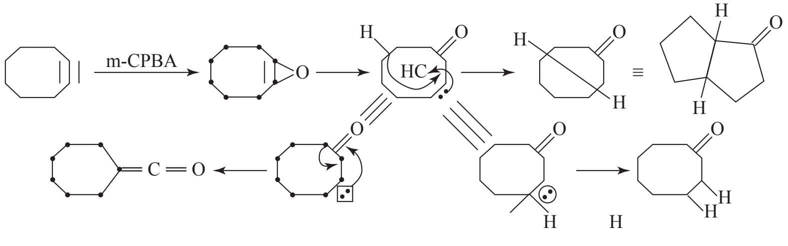




$$2CH_3CHO + \underset{\underset{CHO}{|}}{CHO}$$

158. As Markowni Koff's and anti-Markowni Koff's addition, both are not observed in symmetrical alkenes. and here but-2-ene is symmetrical alkene.

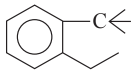
160.

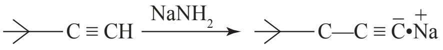


Linked-Comprehension Type Questions

166. As this C- atom will be most stable free radicle here.

168. It has one chiral C- atom so it can show optical isomerism.

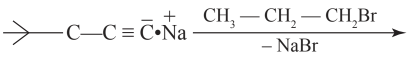
170.  has no α- H- atom so it can not give this product.

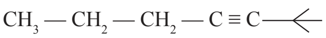
172. 

(P) (Q)

$CH_3-CH_2-CH_2OH \xrightarrow{HBr}$
(R)

$CH_3-CH_2-CH_2Br$
(S)

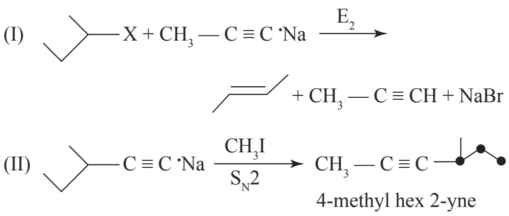




$CH_3-CH_2-CH_2-C\equiv C-$

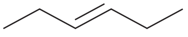
2, 2, di - methyl hex 3-yne

173. As the formation of 4- methyl hex 2- yne is based on S_N2 mechanism so here IInd reaction is better as in Ist reaction E_2 elimination occurs.

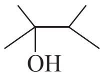


174. As halide is tertiary so elimination product is favourable here as E_1 dominates over S_N2 here.

175. As is a symmetrical alkene so need of these rules.

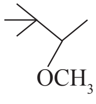


176. As acid catalysed hydration C$^+$ can undergo rearrangement so the product must be.

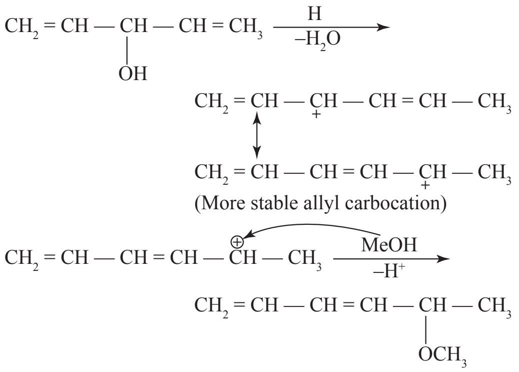


(2, 3 di- methyl butan 2- ol)

As rearrangement of C$^+$ does not occur in case of alkoxy mercuration reaction hence the product is



177. In this acid catalysed reaction due to- OH group first a C$^+$ is formed which further undergoes rearrangement to give a more stable C$^+$ as follows:



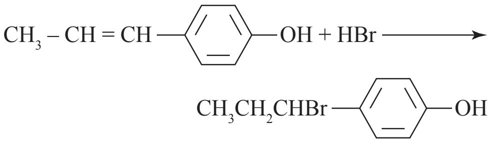
$$CH_2=CH-\underset{\displaystyle OH}{\underset{|}{CH}}-CH=CH_3 \xrightarrow[-H_2O]{H}$$

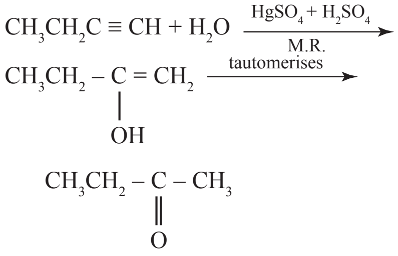
$$CH_2=CH-\overset{+}{C}H-CH=CH-CH_3 \updownarrow CH_2=CH-CH=CH-\overset{+}{C}H-CH_3$$

(More stable allyl carbocation)

$$CH_2=CH-CH=CH-\overset{\oplus}{C}H-CH_3 \xrightarrow[-H^+]{MeOH} CH_2=CH-CH=CH-\underset{\displaystyle OCH_3}{\underset{|}{CH}}-CH_3$$

The IIT-JEE Corner

215. 

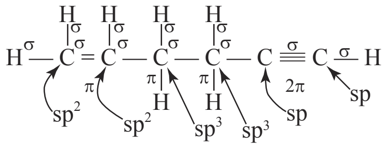
217. 

$$CH_3CH_2C\equiv CH + H_2O \xrightarrow[M.R.]{HgSO_4 + H_2SO_4}$$

$$CH_3CH_2-\underset{\displaystyle OH}{\underset{|}{C}}=CH_2 \xrightarrow{tautomerises}$$

$$CH_3CH_2-\underset{\displaystyle O}{\underset{\|}{C}}-CH_3$$

Butan-2-one

218. 

Hence, C_2 and C_3 are sp$_2$ and sp$_3$ - hybrid.

219. Propyne reacts with AgNO$_3$ to give white precipitate.

$CH_3-C\equiv CH \xrightarrow{AgNO_3 \text{ in ammonia}}$

$CH_3-C\equiv C-Ag$

(white ppt) on the other hand, propene does not react with AgNO$_3$ in ammonia.

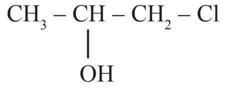
220. During catalytic hydrogenation, the hydrogens are transferred from the catalyst to the same side of the double bond thereby giving cis-alkenes. Evidently, smaller the number of R substituents, lesser is the steric hindrance and hence faster is the rate of hydrogenation.

221. Due to cis-addition of H_2 to the triple bond, the reduced product has a plane of symmetry and hence is optically inactive.

222. HOCl has $Cl^+ + OH^-$.

$$CH_3-CH=CH_2+Cl^+ \xrightarrow{\text{electrophilic addition}}$$

$$CH_3-CH^+-CH_2-Cl \xrightarrow{OH^-}$$



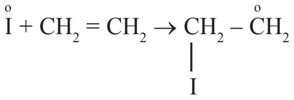
$$\underset{\displaystyle OH}{CH_3-\underset{|}{CH}}-CH_2-Cl$$

223. In both the cases, one of the steps is endothermic, that is, the reaction of HCl with carbon radical in case of HCl and addition of iodine radical to double bond in case of HI.

$$H-Cl+Cl-CH_2-\overset{\circ}{C}H_2 \rightarrow$$

$$Cl-CH_2-CH_2-H+\overset{\circ}{Cl}$$

$$\Delta H = +\ 12.6\ kJ/mole$$



$$\overset{\circ}{I}+CH_2=CH_2 \rightarrow \underset{\displaystyle I}{\underset{|}{CH_2}}-\overset{\circ}{C}H_2$$

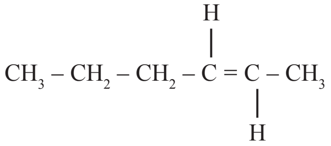
$$\Delta H = +\ 46.0\ kJ/mole$$

224. As a 3° carbon free radical (b) is more stable and is the major product.

225. Ammonical Cu_2Cl_2 will give red ppt. with 1-butyne (a terminal alkyne) and not with 2-butyne.

227. 2-hexyne gives trans-2-hexene on treatment Li/NH_3.

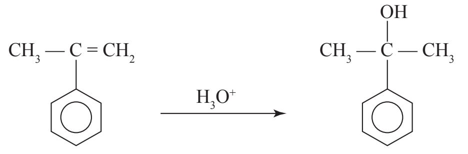
$$CH_3-CH_2-CH_2-C\equiv C-CH_3+H_2 \xrightarrow{Li/NH_3}$$



$$CH_3-CH_2-CH_2-\overset{\displaystyle H}{\overset{|}{C}}=\underset{\displaystyle H}{\underset{|}{C}}-CH_3$$

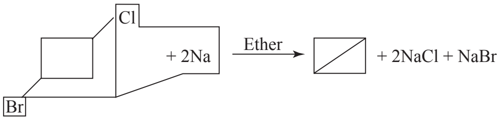
trans-2-hexene

228.

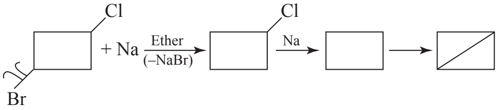


2-phenyl propene 2-phenyl-2-propanol

229.



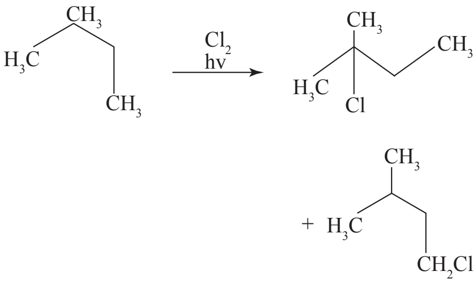
In this reaction following mechanism is possible,



(order of removal of halogen I > Br > Cl)

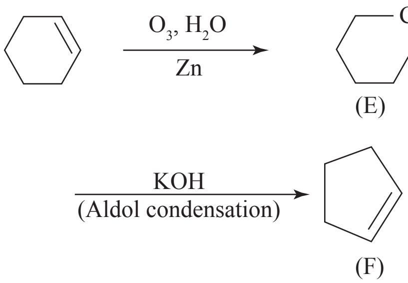
230. It is cumene hydroperoxide rearrangement reaction.

231.

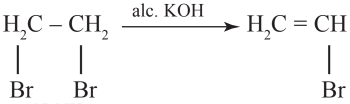


232. $\overset{+}{N}\overset{-}{O}Cl$ → MarkowniKoff's addition

233.



234.



$$\underset{\displaystyle Br}{\underset{|}{H_2C}}-\underset{\displaystyle Br}{\underset{|}{CH_2}} \xrightarrow{\text{alc. KOH}} H_2C=\underset{\displaystyle Br}{\underset{|}{CH}}$$

$$\xrightarrow{NaNH_2} HC\equiv CH$$

As $CH_2 = CH - Br$ has partial C – Br double bond character, it requires more stronger base to remove HBr.

SUBJECTIVE SOLVED EXAMPLES

1. Write down the heterogeneous catalyst involved in the polymerization of ethylene.

[IIT 2003]

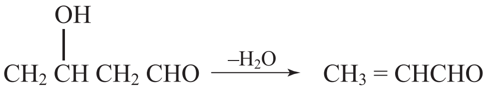
Solution Zeigler-Natta catalyst ($R_3Al + TiCl_4$)

2. Write the structural formula of the major product in each of the following cases:

(i) The compound obtained by the hydration of ethyne is treated with dilute alkali.

Solution

$$CH \equiv CH \xrightarrow{\text{Hydration}} CH_3CHO \xrightarrow{OH^-}$$



$$\overset{OH}{CH_2\ CH}\ CH_2\ CHO \xrightarrow{-H_2O} CH_3 = CHCHO$$

3-hydroxybutanal

(ii) Chloroform reacts with aniline in the presence of excess alkali.

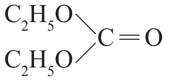
Solution

$$C_6H_5NH_2 + CHCl_3 \xrightarrow[\text{KOH}]{\text{alkali}} C_6H_5 - \overset{\rightarrow}{N = C}$$

Phenyl isocyanide

(iii) Bromoethane reacts with one-half of the molar quantity of silver carbonate.

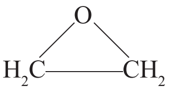
Solution



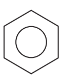
Diethyl carbonate

(iv) Ethene mixed with air is passed under pressure over a silver catalyst at 250°C.

Solution

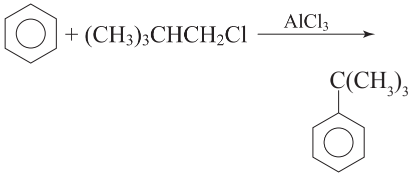


Ethylene oxide

(v)  $+ (CH_3)_3CHCH_2Cl \xrightarrow{AlCl_3}$

[IIT 1992]

Solution



$+ (CH_3)_3CHCH_2Cl \xrightarrow{AlCl_3}$ $C(CH_3)_3$

As the carbocation $(CH_3)_2\ CHC^+H_2$ formed during reaction rearranges to the more stable $(CH_3)_3C^+$ carbocation so the above product is formed.

(vi) $CH_3CH_2CHCl_2 \xrightarrow{\text{boil, alkali}}$

[IIT 1992]

Solution

$$CH_3CH_2CHCl_2 \xrightarrow[\text{Alkali}]{\text{boil}} CH_3CH_2CH(OH)_2$$

$$\xrightarrow{-H_2O} CH_3CH_2CHO$$

(vii) $C_6H_6 + (CH_3)_2CHCH_2OH \xrightarrow{H_2SO_4}$

[IIT 1994]

Solution

$$C_6H_6 + (CH_3)_2CHCH_2OH \xrightarrow{H_2SO_4} C_6H_5(CH_3)_3$$

Tert-Butylbenzene

Explanation:

$$(CH_3)_2CHCH_2OH \xrightarrow{H^+} (CH_3)_2CHC^+\ H_2$$

1° carbocation

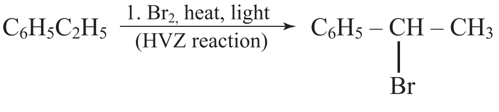
$$\xrightarrow{\text{rearranges to}} (CH_3)_3C^+ \xrightarrow{C_6H_6} C_6H_5C(CH_3)_3$$

3° carbocation

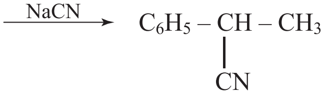
(viii) $C_6H_5C_2H_5 \xrightarrow[\text{2. NaCN}]{\text{1. } Br_2\text{, heat, light}}$

[IIT 1994]

Solution



$$C_6H_5C_2H_5 \xrightarrow[\text{(HVZ reaction)}]{\text{1. } Br_2\text{, heat, light}} C_6H_5 - \underset{Br}{CH} - CH_3$$



$$\xrightarrow{NaCN} C_6H_5 - \underset{CN}{CH} - CH_3$$

2-Phenylpropanenitrile

(ix) $CH_3CH_2Br \xrightarrow{AgCN}$

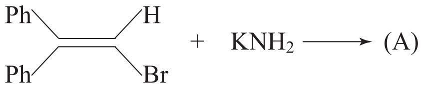
[IIT 1997]

Solution

$$CH_3CH_2Br \xrightarrow{AgCN} CH_3CH_2 - N \equiv C$$

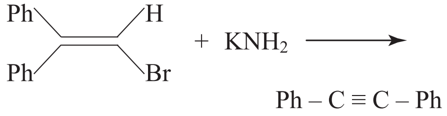
(Isocyanide)

(x)

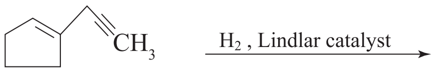


[IIT 1997]

Solution

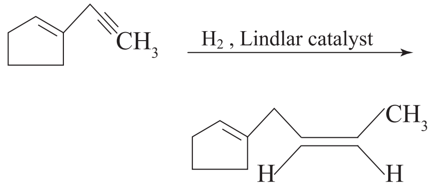


(xi)



[IIT 2000]

Solution

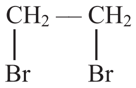


(Partial reduction and triple bond in syn-manner)

3. Online the reaction sequence for the conversion of ethene to ethyne (the number of steps should not be more than two).

Solution

$$\underset{\text{Ethene}}{CH_2 = CH_2} \xrightarrow{Br_2}$$



$$\underset{Br}{CH_2} — \underset{Br}{CH_2}$$

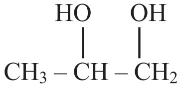
$$\xrightarrow[-2HBr]{2KOH,\ alc.} \underset{\text{Ethyne}}{CH \equiv CH}$$

4. State with balanced equations, what happens when:
(i) Propene is bubbled through a hot aqueous solution of potassium permanganate.
(ii) Chloral is heated with aqueous sodium hydroxide.

Solution

$$\underset{\text{Propene}}{CH_3 – CH = CH_2} + H_2O + [O] \xrightarrow{KMnO_4}$$

(i)



$$CH_3 – \overset{HO}{CH} – \overset{OH}{CH_2}$$

Propene glycol

(ii) $CCl_3CHO \xrightarrow{NaOH} CHCl_3 + HCOONa$

5. How can you prepare benzene from lime?

[IIT 1987]

Solution

$$\underset{\text{Lime}}{CaO} \xrightarrow[\text{Electric furnace}]{\text{Coke, 2000°C}} \underset{\text{Calcium carbide}}{CaC_2} \xrightarrow{H_2O}$$

$$\underset{\text{Acetylene}}{C_2H_2} \xrightarrow[\text{Red hot tube}]{\text{Polymerisation}} \underset{\text{Benzene}}{C_6H_6}$$

6. What happens when excess chlorine is passed through boiling toluene in the presence of sunlight?

Solution

$$C_6H_5CH_3 \xrightarrow[\text{UV light}]{Cl_2} C_6H_5CH_2Cl \xrightarrow{Cl_2}$$

$$C_6H_5CHCl_2 \xrightarrow{Cl_2} \underset{\text{Benzotrichloride}}{C_6H_5CCl_3}$$

It follows free radical mechanism.

7. Give reasons for the following:
(i) Methane does not react with chlorine in the dark.

Solution

Chlorination of methane is an example of free radical substitution reaction which occurs in sunlight. In dark, chlorine is unable to be converted into free radicals, so the reaction does not take place here.

(ii) Propene react with HBr to give isopropyl bromide but does not give n-propyl bromide.

Solution

Addition of unsymmetrical addendum to unsymmetrical olefin is according to Markowni Koff's rule

$$\underset{\text{Propene}}{CH_3\ CH = CH_2} + HBr \rightarrow \underset{\text{iso-propyl bromide}}{CH_3.CHBr.CH_3}$$

(iii) Although benzene is highly unsaturated, normally it does not undergo addition reaction.

Solution

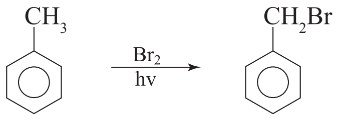
Unlike olefins, π-electrons of benzene are delocalized so benzene is unreactive towards addition reactions.

(iv) Toluene reacts with bromine in the presence of light to give benzyl bromide while in presence of $FeBr_3$ it gives p-bromotoluene. Give explanation for the above observations.

[IIT 1996]

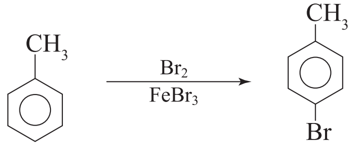
Solution

In presence of light, toluene undergoes side chain bromination through free radical mechanism as follows:



Benzyl bromide

In presence of $FeBr_3$, toluene undergoes electrophillic substitution as follows:



p-bromotoluene

(v) The central carbon-carbon bond in 1,3-butadiene is shorter than that of n-butane.

[IIT 1998]

Solution

Buta-1,3-diene is a conjugated diene which is resonance stabilized as follows:

Here the charged structures acquire some double bond character in the central C – C bond which leads to shortening of bond length or in it all the carbon atoms are sp^2-hybridised while in n-butane they are sp^3-hybridised so it has lower bond length than n-butane.

(vi) tert-Butylbenzene does not give benzoic acid on treatment with acidic $KMnO_4$.

[IIT 2000]

Solution

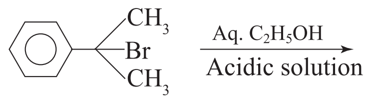
tert-Butylbenzene does not give benzoic acid on reaction with acidic $KMnO_4$ as t-butyl group does not have any hydrogen atom on carbon atom.

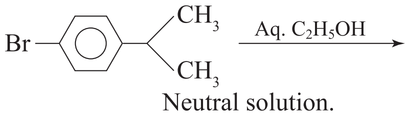
(vii) 7-Bromo-1, 3, 5-cycloheptatriene exists as ionic compound, while 5-bromo-1,3-cyclopentadiene does no ionize even in presence of Ag^+ ion. Explain.

[IIT 2004]

Solution

(viii)



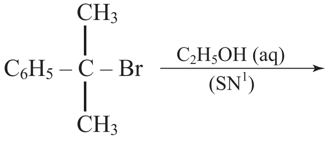


[IIT 2005]

Explain.

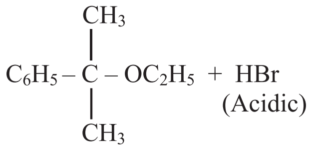
Solution

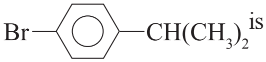
As this halide is a t-halide, so it undergoes SN^1 reaction giving HBr, which make solution acidic.



$$C_6H_5-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-Br \xrightarrow[(SN^1)]{C_2H_5OH\ (aq)} C_6H_5-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-OC_2H_5 + \underset{(Acidic)}{HBr}$$

3° bromide





is an aryl halide so it does not undergo nucleophillic substitution reactions. Thus the solution will remain neutral.

8. (i) "2-Metyhl propene can be converted into isobutyl bromide by hydrogen bromide" is true under what conditions.

Solution

Under normal conditions, tert-butyl is formed, isobutyl bromide is formed in presence of peroxide.

(ii) "Ethyne and its derivatives will give white precipitate with ammonical silver nitrate solution", is true under what conditions.

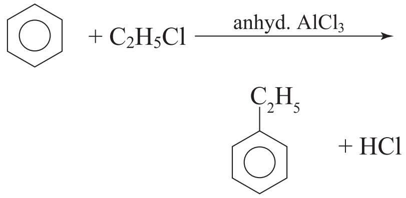
Solution

Ethyne (HC ≡ CH) and only those derivatives which have at least one acetylenic hydrogen atom (≡ C – H) will give white precipitate with ammonical silver nitrate solution.

9. Write down the reactions involved in the preparation of the following using the reagents indicated against it in parenthesis.

Ethyl benzene from benzene [C_2H_5OH, PCl_5, anhydrous $AlCl_3$].

Solution

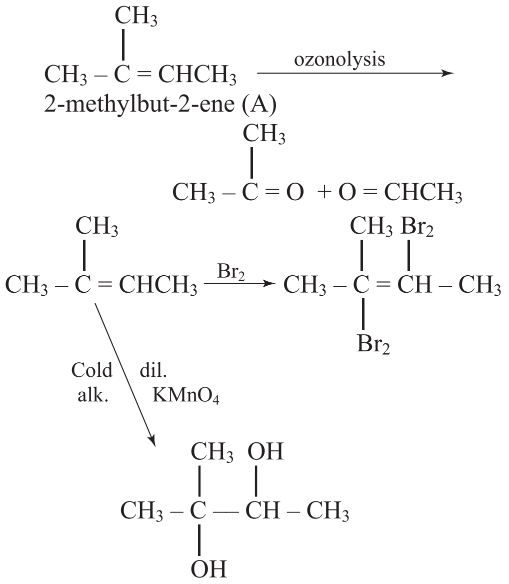


$[C_2H_5OH + PCl_5 \rightarrow C_2H_5Cl]$

10. One mole of hydrocarbons, (A) reacts with one mole of bromine giving a dibromo compound $C_5H_{10}Br_2$. Substance (A) on treatment with cold dilute alkaline potassium permanganate solution forms a compound $C_5H_{12}O_2$. On ozonolysis (A) gives equimolar quantities of propane and ethanal. Deduce the structural formula of (A).

Solution

As the ozonolysis of (A) yields an equimolar quantities of propanone and ethanal, so the compound (A) must be 2-methylbut-2-ene.



$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=CHCH_3 \xrightarrow{\text{ozonolysis}} CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=O + O=CHCH_3$$

2-methylbut-2-ene (A)

$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=CHCH_3 \xrightarrow{Br_2} CH_3-\underset{\underset{\displaystyle Br_2}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}=\overset{\overset{\displaystyle Br_2}{|}}{C}H-CH_3$$

$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=CHCH_3 \xrightarrow{\text{Cold alk. dil. } KMnO_4} CH_3-\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-\overset{\overset{\displaystyle OH}{|}}{C}H-CH_3$$

11. A certain hydrocarbon A was found to contain 85.7 % carbon and 14.3% hydrogen. This compound consumes one molar equivalent of hydrogen to give a saturated hydrocarbon B. 1.00 g of hydrocarbon A just decolourised 38.05 g of a 5 % solution (by weight) of Br_2 in CCl_4. Compound A, on oxidation with concentrated $KMnO_4$, gave compound C (molecular formula $C_4H_8O_3$) and acetic acid. Compound C could easily be prepared by the action of acidic aqueous mercuric sulphate on 2-butyne. Determine the molecular formula of A and deduce the structure of A, B and C.

Solution

Calculation of molecular formula of A:

Element	%	Relative No. of atoms		Simplest whole ratio
C	85.7	85.7/12 7.14	=	7.14/ 7.14 = 1
H	14.3	14.3/1 14.3	=	14.3/7.14 = 2

So empirical formula of A = CH_2

Calculation of molecular weight of A:

1 g of A consumes = 38.05 g of 5 % Br_2

$$=\frac{38.05\times 5}{100}\text{g of 100 \% } Br_2$$

= 1.90 g of 100 % Br_2

As 1.90 g of Br_2 is consumed by 1 g of compound A

$$\text{So 160 g (1 mole) of } Br_2 = \frac{1}{1.90}\times 160$$

$$= 84.2 \text{ g} \approx 84.0$$

As molecular weight of A = 84

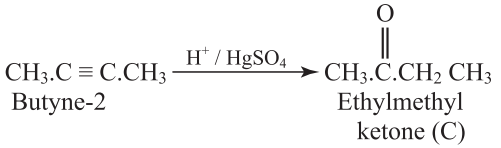
$$n=\frac{84}{12+2}=6$$

So molecular formula of A = $(CH_2)_6 = C_6H_{12}$

As the hydrocarbon A consumes 1 molar equivalent of hydrogen, so it must have one double bond. Oxidation of compound A with $KMnO_4$ to form compound C (C_4H_8O) and acetic acid indicates $=CH.CH_3$ fragment in A, that is,

$$\underset{A}{C_4H_8=CHCH_3} \xrightarrow{KMnO_4} \underset{C}{C_4H_8} + \underset{\text{Acetic acid}}{CH_3COOH}$$

Now the fragment C_4H_8 of (A) on oxidation gives the compound (C) (C_4H_8O) which can be obtained from butyne-2 by hydrolysis reaction as follows:



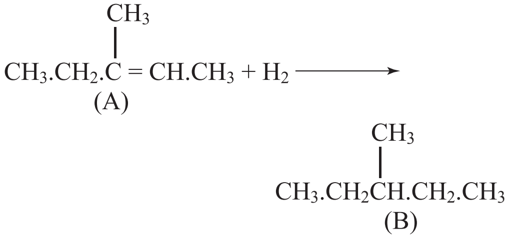
$$\underset{\text{Butyne-2}}{CH_3.C\equiv C.CH_3} \xrightarrow{H^+/HgSO_4} \underset{\text{Ethylmethyl ketone (C)}}{CH_3.\overset{\overset{\displaystyle O}{\|}}{C}.CH_2\,CH_3}$$

The formation of ethylmethyl ketone (C) from C_4H_8 fragment of (A) can be explained by the structure of (A) given below:

$$\underset{(A)}{CH_3CH_2C=CHCH_3} \xrightarrow{KMnO_4}$$

$$\underset{\text{Ethylmethyl ketone (C)}}{CH_3CH_2C=O} + \underset{\text{Acetic acid}}{CH_3COOH}$$

Now the formation of (B) by the hydrogenation of (A) can be given asL



$$\underset{(A)}{CH_3.CH_2.\overset{\overset{\displaystyle CH_3}{|}}{C}=CH.CH_3} + H_2 \longrightarrow \underset{(B)}{CH_3.CH_2\overset{\overset{\displaystyle CH_3}{|}}{C}H.CH_2.CH_3}$$

12. How would you distinguish between

(i) 2-butyne and 1-butyne

Solution

Terminal alkynes give white precipitate with ammonical $AgNO_3$ or red precipitate with amm. Cu_2Cl_2. (H atom attached on sp hybridized carbon is acidic).

$$2CH_3CH_2C\equiv CH + Ag_2O \longrightarrow 2CH_3CH_2C\equiv CAg + H_2O$$

$$CH_3-C\equiv C-CH_3 + Ag_2O \rightarrow \text{No reaction}$$

(ii) Cyclohexane and cyclohexene

Solution

Cyclohexene gives positive response to bromine water test and Baeyer's test while cyclohexane does not respond to these reagents.

13. Write down the structures of A and B.

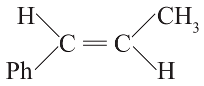
$$PhC \equiv CH \xrightarrow{NaNH_2.MeI} (A) \xrightarrow{Na / NH_3 (l)} (B)$$

[IIT1997]

Solution

$$PhC \equiv C - H \xrightarrow[\text{Me.I}]{NaNH_2} Ph - C \equiv C - Me$$
(Methylation)

$$\xrightarrow[\text{Birch reduction}]{Na / NH_3 (l)}$$



(trans-product)

14. An organic compound X, on analysis gives 24.24 % carbon and 4.04 % hydrogen. Further, sodium extract of 1.0 g of X gives 2.90 g of silver chloride with acidified silver nitrate solution. The compound X may be represented by two isomeric structures, Y and Z. Y on treatment with aqueous potassium hydroxide solution gives a dihydroxy compound while Z on similar treatment gives ethanal. Find out the molecular formula of X and give the structures of Y and Z.

Solution

Let the compound (X) has two isomers Y and Z. The compound (X) has C, H and Cl atoms.

$$\% \text{ of Cl in X} = \frac{35.5 \times 2.9}{143.5} \times 100 = 71.72\%$$

For empirical formula of (X)

Element	%	Relative No. of atoms	Simplest ratio
C	24.24	2.02	1
H	4.04	4.04	2
Cl	71.72	2.02	1

So empirical formula of (X) is CH_2Cl.
As X has two isomers Y and Z; both react with KOH (aq).

$$Y \xrightarrow{KOH (aq)} \text{Dihydroxy compound}$$

that is, 2Cl atoms on adjacent carbon

$$Z \xrightarrow{KOH (aq)} CH_3CHO$$

that is, Z should have 2Cl atoms on one C atom. Therefore Z should be CH_3CHCl_2 (1,1-dichloroethane) and Y should CH_2ClCH_2Cl (1,2-dichloroethane)

$$CH_3CHCl_2 \text{ (Z)} \xrightarrow{KOH (aq)} CH_3CH(OH)_2 \longrightarrow \underset{\text{Ethanal}}{CH_3CHO}$$

$$\underset{\text{(Y)}}{CH_2ClCH_2Cl} \xrightarrow{KOH (aq)} \underset{\text{Ethane-1,2-diol}}{CH_2OHCH_2OH}$$

15. n-Butane is produced by the monobromination of ethane followed by the Wurtz reaction. Calculate the volume of ethane at NTP required to produce 55 g n-butane, if the bromination takes place with 90 % yield and the wurtz reaction with 85 % yield.

Solution

$$2C_2H_6 \xrightarrow{\text{monobromination}} 2C_2H_5Br$$
(yield 90%)

$$2C_2H_5Br \xrightarrow[\text{reaction}]{\text{Wurtz}} C_4H_{10} + 2HBr$$
(yield 85%)

Amount of n-butane to be produced

$$= \frac{55 \text{ g}}{58 \text{ g mol}^{-1}} = 0.948 \text{ mol}$$

(As mol. mass of C_4H_{10} = 58)

As amount of C_2H_5Br needed to obtain 0.948 mol of C_4H_{10} would be 2 × 0.948 mol.
So amount of C_2H_5Br needed

$$= \frac{2 \times 0.948 \times 100}{85} \text{mol} \qquad \text{...... (i)}$$

Similarly 1 mole of C_2H_6 gives one mole of C_2H_5Br.

So amount of C_2H_6 needed for C_2H_5Br in equation (i)

$$= \frac{2 \times 0.948 \times 100 \times 100}{85 \times 90} \text{mol}$$

= 2.48 mol

Thus required volume of ethane at NTP

= 22400 × 2.48 = 55552 ml

= 55.55 litres

16. Identify, B (C_4H_8) which adds on HBr in the presence and in the absence of peroxide to give the same product, C_4H_9Br.

[IIT1993]

Solution

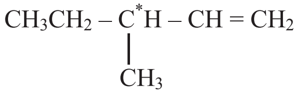
Here B must be a symmetric alkene (But-2-ene) $CH_3CH = CHCH_3$ as it will give the same product $CH_3 - CH(Br) - CH_2 - CH_3$ in presence or absence of peroxide on addition with HBr.

17. Identify, D (C_6H_{12}), an optically active hydrocarbon which on catalytic hydrogenation gives an optically inactive compound, C_6H_{14}.

[IIT1993]

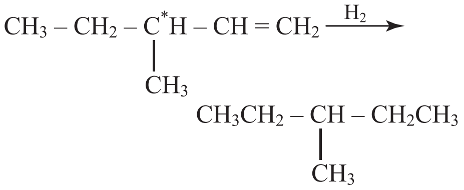
Solution

An optically active hydrocarbon must have an asymmetric C-atom that is, D (C_6H_{12}) will has an asymmetric C-atom and C_6H_{14} does not have any asymmetric C-atom so D will be 3-methylpentene,



$$CH_3CH_2 - \underset{\displaystyle CH_3}{\underset{|}{C^*H}} - CH = CH_2$$

Here C^* is the asymmetric C-atom.



$$CH_3 - CH_2 - \underset{\displaystyle CH_3}{\underset{|}{C^*H}} - CH = CH_2 \xrightarrow{H_2} CH_3CH_2 - \underset{\displaystyle CH_3}{\underset{|}{CH}} - CH_2CH_3$$

18. When gas 'A' is passed through dry KOH at low temperature, a deep red coloured compound 'B' and a gas 'C' are obtained. The gas 'A', on reaction with but-2-ene, followed by treatment with Zn / H_2O yields acetaldehyde. Identify A, B and C.

[IIT1994]

Solution

$$\underset{\text{Butene-2}}{CH_3 - CH = CH - CH_3} \xrightarrow[\text{(ii) Zn / }H_2O]{\text{(i) Gas A}} 2CH_3CHO$$

Here gas A is ozone because in this reaction, ozonolysis of butene-2 takes place.

$$\text{Gas A} + \text{KOH (dry)} \xrightarrow{\text{low temp.}} \underset{\text{(Deep red coloured)}}{B} + \underset{\text{(Gas)}}{C}$$

$$4O_3 + 4KOH \rightarrow \underset{(B)}{4KO_3} + 2H_2O + \underset{(C)}{O_2}$$

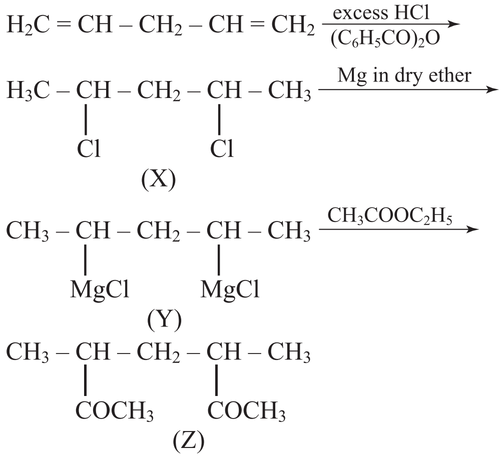
19. 1,4-Pentadiene reacts with excess of HCl in the presence of benzoyl peroxide to give compound X which upon reaction with excess of Mg in dry ether forms Y. Compound Y on treatment with ethyl acetate followed by dilute acid yields Z. Identify the structures of compounds X, Y and Z.

[IIT1995]

Solution

(i) Penta-1,4-diene reacts with HCl in presence of benzoyl peroxide according to Markownikoff's rule.

(ii) Grignard reagent reacts with ethyl acetate to give ketones or tertiary alcohol if Grignard reagent is taken in excess. So the given reactions can be shown as:



$$H_2C = CH - CH_2 - CH = CH_2 \xrightarrow[(C_6H_5CO)_2O]{\text{excess HCl}}$$

$$\underset{(X)}{H_3C - \underset{\displaystyle Cl}{\underset{|}{CH}} - CH_2 - \underset{\displaystyle Cl}{\underset{|}{CH}} - CH_3} \xrightarrow{\text{Mg in dry ether}}$$

$$\underset{(Y)}{CH_3 - \underset{\displaystyle MgCl}{\underset{|}{CH}} - CH_2 - \underset{\displaystyle MgCl}{\underset{|}{CH}} - CH_3} \xrightarrow{CH_3COOC_2H_5}$$

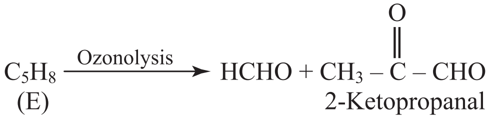
$$\underset{(Z)}{CH_3 - \underset{\displaystyle COCH_3}{\underset{|}{CH}} - CH_2 - \underset{\displaystyle COCH_3}{\underset{|}{CH}} - CH_3}$$

20. An organic compound E (C_5H_8) on hydrogenation gives compound F (C_5H_{12}). Compound E on ozonolysis gives formaldehyde and 2-ketopropanal. Deduce the structure of compound E.

[IIT1995]

Solution

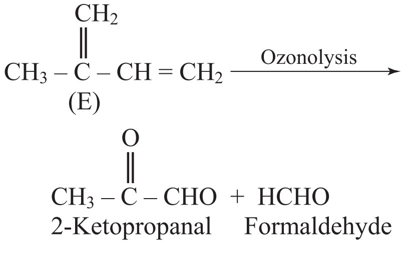
Summary of the given reactions is as follows:



$$\underset{(E)}{C_5H_8} \xrightarrow{\text{Ozonolysis}} HCHO + \underset{\text{2-Ketopropanal}}{CH_3 - \overset{\displaystyle O}{\overset{\|}{C}} - CHO}$$

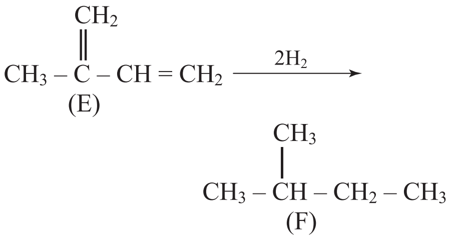
$$\underset{(E)}{C_5H_8} \xrightarrow{H_2} \underset{(F)}{C_5H_{12}}$$

As hydrogenation of (E) into (F) uses two molecules of H_2 so E must have two double bonds. It is also proved by the ozonolysis of (E) which gives two products having 3-carbonyl groups as follows:



$$\underset{(E)}{CH_3 - \overset{\displaystyle CH_2}{\overset{\|}{C}} - CH = CH_2} \xrightarrow{\text{Ozonolysis}}$$

$$\underset{\text{2-Ketopropanal}}{CH_3 - \overset{\displaystyle O}{\overset{\|}{C}} - CHO} + \underset{\text{Formaldehyde}}{HCHO}$$



$$\underset{(E)}{CH_3-\overset{\overset{\displaystyle CH_2}{\|}}{C}-CH=CH_2} \xrightarrow{2H_2} \underset{(F)}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_2-CH_3}$$

21. Give the structures of the major organic products from 3-ethyl-2-pentene under each of the following reaction conditions.

(a) HBr in the presence of peroxide

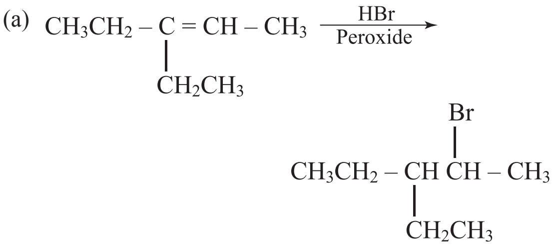
(b) Br_2 / H_2O

(c) $Hg(OAc)_2$ / H_2O; $NaBH_4$

[IIT1996]

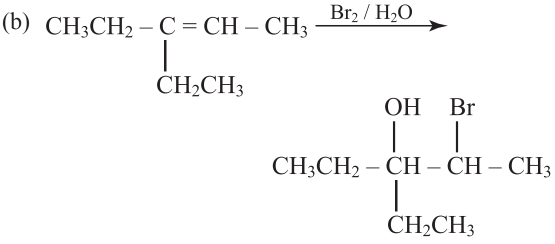
Solution

(a)



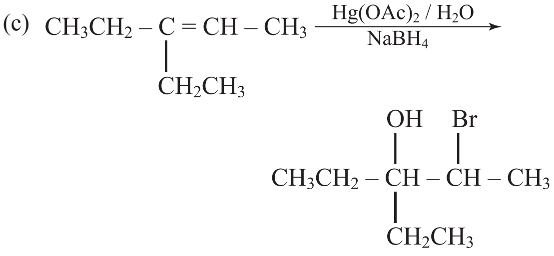
$$CH_3CH_2-\underset{\underset{\displaystyle CH_2CH_3}{|}}{C}=CH-CH_3 \xrightarrow[\text{Peroxide}]{HBr} CH_3CH_2-\underset{\underset{\displaystyle CH_2CH_3}{|}}{CH}\ \overset{\overset{\displaystyle Br}{|}}{CH}-CH_3$$

(b)



$$CH_3CH_2-\underset{\underset{\displaystyle CH_2CH_3}{|}}{C}=CH-CH_3 \xrightarrow{Br_2\,/\,H_2O} CH_3CH_2-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle CH_2CH_3}{|}}{CH}}-\overset{\overset{\displaystyle Br}{|}}{CH}-CH_3$$

(c)



$$CH_3CH_2-\underset{\underset{\displaystyle CH_2CH_3}{|}}{C}=CH-CH_3 \xrightarrow[NaBH_4]{Hg(OAc)_2\,/\,H_2O} CH_3CH_2-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle CH_2CH_3}{|}}{CH}}-\overset{\overset{\displaystyle Br}{|}}{CH}-CH_3$$

22. The hydrocarbon A, adds one mole of hydrogen in the presence of a platinum catalyst to form n-hexane. When A is oxidized vigorously with $KMnO_4$, a single carboxylic acid, containing three carbon atoms, is isolated. Give the structure of A and explain.

[IIT1997]

Solution

It should be an alkene as it adds one mole of H_2.

The C_6 alkene should be symmetrical because on oxidation it gives a single carboxylic acid having three carbon atoms.

$$\underset{(A)}{CH_3CH_2CH=CHCH_2CH_3} \xrightarrow[KMnO_4]{[O]} 2CH_3CH_2COOH$$

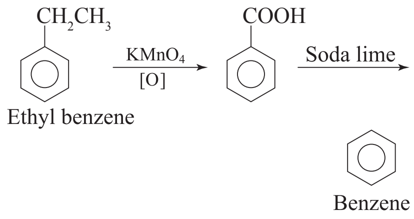
$$\underset{(A)}{CH_3CH_2CH=CHCH_2CH_3} \xrightarrow{H_2} \underset{\text{m-Hexane}}{CH_3(CH_2)_4CH_3}$$

23. Show the steps to carry out the following transformations.

(i) Ethylbenzene → Benzene

[IIT1998]

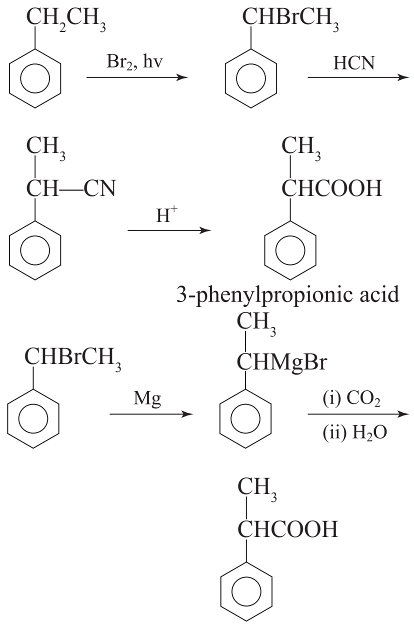
Solution



(ii) Ethylbenzene → 2-phenylpropionic acid.

[IIT1998]

Solution



2-Phenyl propionic acid

24. An alkene (A) $C_{16}H_{16}$ on ozonolysis gives only one product (B) C_8H_8O. Compound (B) on reaction with NaOH / I_2 yields sodium benzoate. Compound (B) reacts with KOH / NH_2NH_2 yielding a hydrocarbon (C) C_8H_{10}. Write the structures of compounds (B) and (C). Based on this information, two isomeric structures can be proposed for alkene (A). Write their structures and identify the isomer which on catalytic hydrogenation (H_2 / Pd-C) gives a racemic mixture.

[IIT2001]

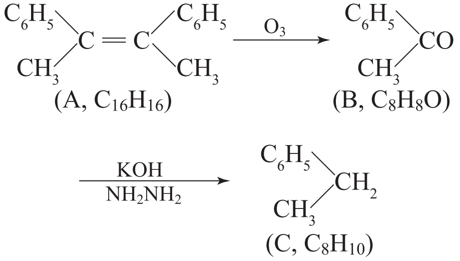
Solution

$$\underset{(A)}{C_{16}H_{16}} \xrightarrow{O_3} \text{only } \underset{(B)}{C_8H_8O} \xrightarrow{NaOH/\,I_2} C_6H_5COONa$$

$$\underset{(B)}{C_8H_8O} \xrightarrow{KOH/\,NH_2NH_2} \underset{(C)}{C_8H_{10}}$$

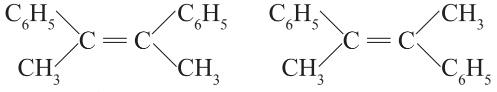
(i) Conversion of (B) to (C) involves iodoform reaction, hence (B) must contain –$COCH_3$ group leading to $C_6H_5COCH_3$ (C_8H_8O) as its molecular formula.

(ii) As only compound (B) is obtained from the alkene (A), so the latter must be



(A, $C_{16}H_{16}$) (B, C_8H_8O) (C, C_8H_{10})

The isomeric structures of A are as follows as:



cis trans

As catalytic hydrogenation of alkenes takes place in cis-(syn-) manner so racemic mixture will be formed by the trans-isomer.

25. An organic compound $C_XH_{2Y}O_Y$ was burnt with twice the amount of oxygen needed for complete combustion to CO_2 and H_2O. The hot gases when cooled to 0°C and 1 atm. pressure, measured 2.24 L. The water collected during cooling weighed 0.9 g. The vapour-pressure of pure water at 20°C is 17.5 mm Hg and is lowered by 0.104 mm when 50 g of the organic compound are dissolved in 1000 g of water. Give the molecular formula of the organic compound.

Solution

Complete combustion of organic compound is as follows:

$$C_XH_{2Y}O_Y + {}_XO_2 \rightarrow {}_XCO_2 + {}_YH_2O$$

As oxygen taken is 2X litre and thus X litre O_2 is left at STP after reaction. Also X litre of CO_2 is formed by 1 mole of organic compound.

So

$$2X = 2.24\text{ L}$$

$$X = 1.12\text{ L }CO_2$$

Or $X = \dfrac{1.12}{22.4}$ mole CO_2

$= 0.05$ mole CO_2

Moles of H_2O formed (Y) $= \dfrac{0.9}{18} = 0.05$

X : Y = 0.05

0.05 = 1 : 1

X = 1 and Y = 1

So empirical formula of organic compound $= CH_2O$

Empirical formula wt. of organic compound $= 30$

According to Raoult's law:

$$\frac{P° - P_S}{P_S} = \frac{w}{m} \times \frac{M}{W}\ .$$

$P° - P_S$ = lowering of V.P. = 0.104 mm

$P°$ = V.P. of pure solvent = 17.5 mm

$$\frac{0.104}{17.396} = \frac{50}{m} \times \frac{18}{1000}\ .$$

On solving, we get

m = 150.5

$$n = \frac{\text{Molecular wt.}}{\text{Empirical formula wt.}} = \frac{150.5}{30} = 5$$

Molecular formula = (Empirical formula)$_n$

$= (CH_2O)_5 = C_5H_{10}O_5$

26. When 20.02 g of a white solid (X) is heated, 4.4 g of an acid gas (A) and 1.8 g of a neutral gas (B) are evolved leaving behind a solid residue (Y) of weight 13.8 g. (A) turns lime water milky and (B) condenses into a liquid which changes anhydrous copper sulphate blue. The aqueous solution of (Y) is alkaline to litmus and gives 19.7 g of white precipitate (Z) with barium chloride solution. (Z) gives carbon dioxide with an acid. Identify A, B, X, Y and Z.

Solution

(i) As the acid gas (A) turns lime water milky so it is CO_2.

(ii) As the neutral gas (B) on condensing gives a liquid which changes anhydrous copper sulphate blue so it is H_2O.

(iii) As aqueous solution of (Y) gives white precipitate with $BaCl_2$, and it is also alkaline to litmus so the compound (Y) is $M_2^{(I)}\ CO_3$.

(Here $M^{(I)}$ is an alkali metal).

(iv) As CO_2, H_2O and CO_3^{2-} can be obtained by heating HCO_3^-, so the given reactions are

$$\underset{X}{2M^{(I)}\ HCO_3} \xrightarrow{\Delta} \underset{(A)}{CO_2} + \underset{(B)}{H_2O} + \underset{(Y)}{M_2^{(I)}CO_3}$$

$$\underset{Y}{2M_2^{(I)}\ CO_3} + BaCl_2 \rightarrow BaCO_3 + 2M^{(I)}Cl$$

(v) From the data on the masses of the compounds, the molar mass of $M^{(I)}$ can be calculated and the metal $M^{(I)}$ can be identified.

Suppose the molar mass of $M^{(I)}$ is ‘m’.

$$\begin{array}{ccccc} 2M^{(I)}HCO_3 & \rightarrow & CO_2 & +H_2O & +M_2^{(I)}CO_3 \\ 2(61+m)g & & 44\ g & 18\ g & (60+2m)g \\ 22.02\ g & & 4.4\ g & 1.8\ g & 1.38\ g \end{array}$$

According to given data:

As 44 g of CO_2 is evolved from 2(61 + m)g of $M^{(I)}HCO_3$

So 4.4 g CO_2 will be evolved from

$$\frac{2(61+m)}{44}\times 4.4\ g \quad \text{of } M^{(I)}HCO_3$$

As 4.4 g CO_2 is evolved from 22.02 g of $M^{I}HCO_3$

$$\text{So} \quad \frac{2(61+m)}{44}\times 4.4 = 22.02$$

On solving, we get

m = 39 g

Thus, the metal $M^{(I)}$ is Potassium (K).

So X = $KHCO_3$
Y = K_2CO_3
Z = $BaCO_3$
A = CO_2
B = H_2O

27. In the following, identify the compounds reaction conditions represented by the (A), (B) and (C).

$$H_3C-CH=CH-CHO \xrightarrow{NaBH_4} (A) \xrightarrow{HCl,\ ZnCl_2} (B) \xrightarrow{KCN,\ H^+} (C)$$

[IIT1991]

Solution

$$CH_3-CH=CH-CHO \xrightarrow{NaBH_4}$$

$$\underset{(A)}{CH_3-CH=CH-CH_2OH} \xrightarrow{HCl,\ ZnCl_2}$$

$$\underset{(B)}{CH_3-CH=CH-CH_2Cl} \xrightarrow{KCN,\ H^+}$$

$$\underset{(C)}{CH_3-CH=CH-COOH}$$

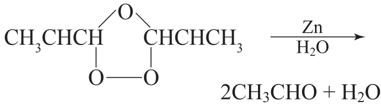
28. When gas A is passed through dry KOH at low temperature, a deep red coloured compound B and a gas C are obtained. The gas A, on reaction with but-2-ene, followed by treatment with Zn / H_2O yields acetaldehyde. Identify A, B and C.

[IIT1994]

Solution

The reaction of gas (A) with but-2-ene followed by treatment with Zn/H_2O gives CH_3CHO. This shows that the gas (A) is ozone (O_3).

$$CH_3CH=CHCH_3 + O_3 \longrightarrow$$



$$2CH_3CHO + H_2O_2$$

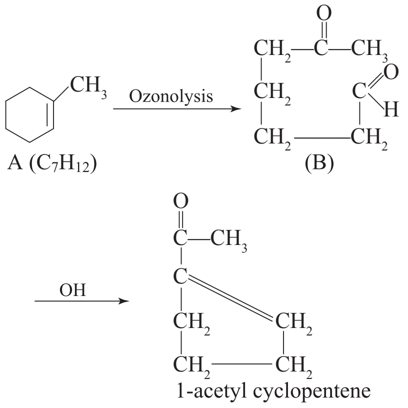
Reaction of O_3 with KOH:

$$3KOH + \underset{(A)}{2O_3} \rightarrow \underset{\substack{\text{Potassium} \\ \text{ozonide (B)} \\ \text{(Red colour)}}}{2KO_3} + KOH.H_2O + \tfrac{1}{2}\,O_2 \uparrow$$

29. A hydrocarbon A of the formula C_7H_{12} on ozonolysis gives a compound B which undergoes aldol condensation giving 1-acetylcyclopentene. Identify A and B

[IIT1997]

Solution



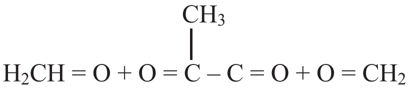
30. A monomer of a polymer on ozonolysis gives two moles of CH_2O and one mole of CH_3COCHO. Write the structure of monomer and write all – 'cis' configuration of polymer chain.

[IIT2005]

Solution

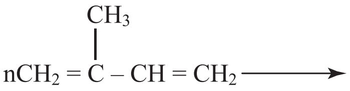
$$H_2C=\overset{\overset{CH_3}{|}}{C}-CH=CH_2 \longrightarrow$$

Monomer

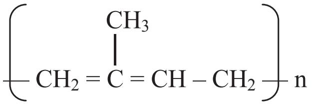


$$H_2CH=O+O=\overset{\overset{CH_3}{|}}{C}-C=O+O=CH_2$$

Thus the possible polymer should be

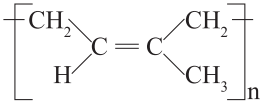


$$nCH_2=\overset{\overset{CH_3}{|}}{C}-CH=CH_2 \longrightarrow$$



$$\left[CH_2=\overset{\overset{CH_3}{|}}{C}=CH-CH_2 \right]_n$$

Structure of all cis configuration of the polymer.



All cis form

31. Identify X, Y and Z in the following synthetic scheme and write their structures.

$$CH_3CH_2C\equiv C-H \xrightarrow{\text{(i) } NaNH_2 \text{ (ii) } CH_3CH_2Br}$$

$$(X) \xrightarrow{H_2/Pd\text{-}BaSO_4} (Y) \xrightarrow{\text{alk. } KMnO_4} (Z)$$

Is the compound Z optically active? Justify your answer.

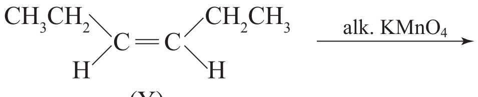
[IIT2002]

Solution

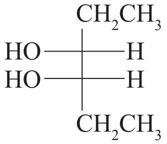
$$CH_3CH_2-C\equiv C-C \xrightarrow{\text{(i) } NaNH_2 \text{ (ii) } CH_3CH_2Br}$$

$$CH_3CH_2-C\equiv C-CH_2CH_3 \xrightarrow[\text{(cis-addition of H atoms)}]{H_2/Pd\text{-}BaSO_4}$$

(X)



(Y)



(Z)

(Z) is in meso form having plane of symmetry. The upper half molecule is mirror image of the lower half molecule. the molecule is, therefore optically inactive due to internal compensation.

ORGANIC COMPOUNDS CONTAINING HALOGENS

(HALOALKANES AND HALOARENES)

CHAPTER 4

CHAPTER CONTENTS

Introduction, Preprations and Properties of Halides Alkyl halides: Rearrangement reaction of alkyl carbocation, Grignard reagent, nucleophillic substitution reactions and elimination reactions. Haloarenes: Nucleophilic aromatic substitution in haloarenes and substituted haloarenes (excluding Benzyne mechanism and cine substitution) and various levels of multiple-choice questions

HALO ALKANES

These are halogen derivatives of hydrocarbons and these are of following types depending upon number of hydrogen atoms present in them.

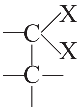
MONO HALIDES (R – X) These are mono halogen derivatives of alkanes having a general formula C_nH_{2n+1} X. and known as alkyl halides.

R – X may be of three types

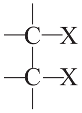
- Primary: R – CH_2X
- Secondary: R_2 CH.X
- Tertiary: R_3 C.X

DI HALIDES (C_N H_{2N} X_2) These are dihalogen derivatives and are of gem and vicinal types.

Gem



Vic



e.g.,

CH_3CHBr_2 — Ethylidine bromide

$BrCH_2CH_2Br$ — Ethylene bromide

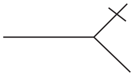
- α, ω or Terminal dihalides.
  For example, $BrCH_2 – CH_2 – CH_2 – CH_2Br$
  1,4-dibromo butane

TRI HALIDES (C_n H_{2n-1} X_3): These are trihalogen derivatives generally shown as CHX_3 (haloforms).

TETRA HALIDES These are tetrahalogen derivatives of alkanes CX_4 or CX_2Y_2.

Monohalides

- These are called haloalkanes. They may show chain, position and optical isomerisms

For example, C_2H_5Br Bromoethane.  2-Halo propane

Preparation of Monohalides

(1) By Direct Halogenation of Alkanes (For details see halogenation in alkane)

$$R-H + X-X \xrightarrow{hv} R-X + HX$$

For example,

$$CH_4 + Cl_2 \xrightarrow{-HCl} CH_3Cl \xrightarrow[-HCl]{Cl_2} CH_2Cl_2 \xrightarrow[-HCl]{Cl_2} CHCl_3 \xrightarrow[-HCl]{Cl_2} CCl_4$$

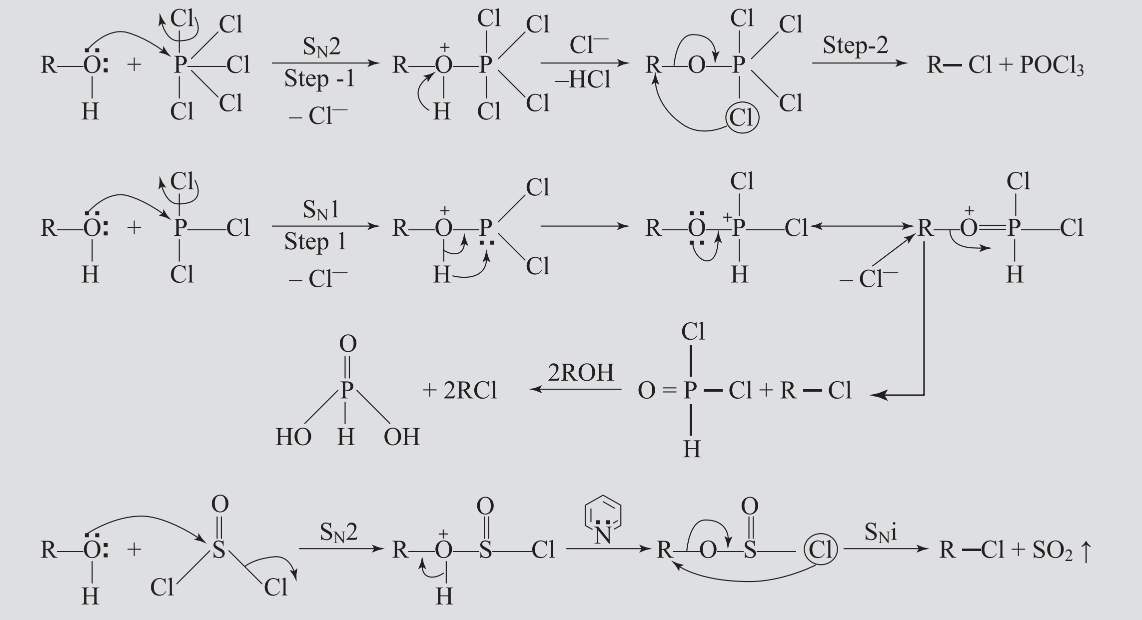
(2) From Alcohols

- $R-OH + PCl_5 \rightarrow R-Cl + POCl_3 + HCl$
- $3R-OH + PCl_3 \rightarrow 3R-Cl + H_3PO_3$
- $R-OH + SOCl_2 \xrightarrow{\text{pyridine}} R-Cl + SO_2 + HCl$

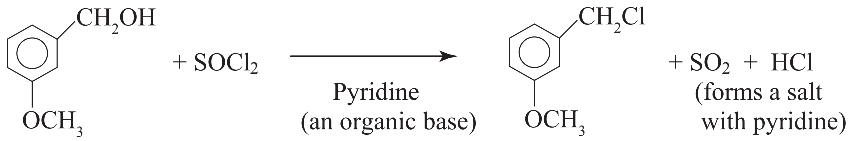
It is called Darzen's method. Here pyridine refluxes gaseous blproducts from here.

- $R-H + SO_2Cl_2 \xrightarrow[\text{or peroxide}]{hv} R-Cl + HCl + SO_2$

Mechanism



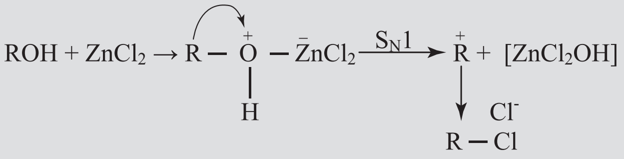
Example $3(CH_3)_2CHCH_2OH + PBr_3 \xrightarrow[\text{4hours}]{-10 \text{ to } 0^{o}C} 3(CH_3)_2CHCH_2Br + H_3PO_3$ 55 -60 %)



(3) By Groove's Method

$$R–OH + HX \xrightarrow{\text{anhy. } ZnCl_2} R–X + H_2O$$

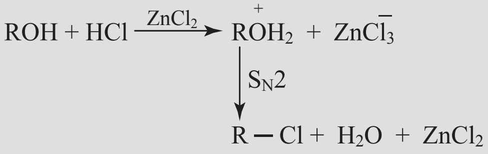
Mechanism



$$ROH + ZnCl_2 \rightarrow R-\underset{\substack{|\\ H}}{\overset{+}{O}}-\overset{-}{Zn}Cl_2 \xrightarrow{S_N1} \overset{+}{R} + [ZnCl_2OH]$$

$$\overset{+}{R} \xrightarrow{Cl^-} R-Cl$$

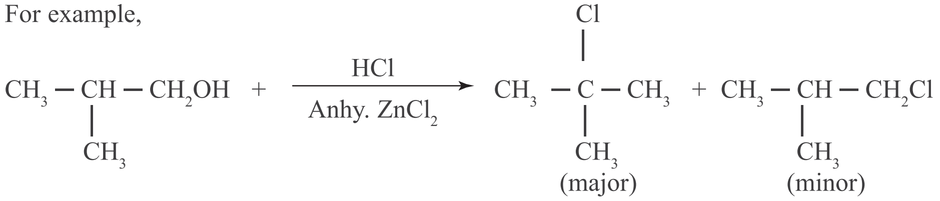
In case of lower conc. of $ZnCl_2$ no rearrangement occurs and S_N2 mechanism is follows



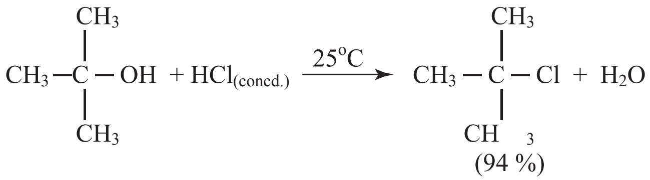
$$ROH + HCl \xrightarrow{ZnCl_2} \overset{+}{R}OH_2 + Zn\overline{Cl_3}$$

$$\overset{+}{R}OH_2 \xrightarrow{S_N2} R-Cl + H_2O + ZnCl_2$$

For example,



$$CH_3-\underset{\substack{|\\ CH_3}}{CH}-CH_2OH + \xrightarrow[\text{Anhy. } ZnCl_2]{HCl} \underset{\text{(major)}}{CH_3-\overset{\substack{Cl\\ |}}{\underset{\substack{|\\ CH_3}}{C}}-CH_3} + \underset{\text{(minor)}}{CH_3-\underset{\substack{|\\ CH_3}}{CH}-CH_2Cl}$$



$$CH_3-\overset{\substack{CH_3\\ |}}{\underset{\substack{|\\ CH_3}}{C}}-OH + HCl_{(concd.)} \xrightarrow{25^{o}C} \underset{(94\ \%)}{CH_3-\overset{\substack{CH_3\\ |}}{\underset{\substack{|\\ CH_3}}{C}}-Cl} + H_2O$$

$$CH_3CH_2CH_2CH_2\ OH + HBr(conc) \xrightarrow[\text{reflux}]{} \underset{(95\ \%)}{CH_3CH_2CH_2CH_2Br}$$

- Order of reactivity of HX with alcohols is:
  HI > HBr > HCl
- Order of reactivity of alcohols with Hx is.
  $t^o > s^o > p^o$
- In case of tertiary alcohols the reaction may take place in absence of $ZnCl_2$ also.

  For example,

  $(CH_3)_3C–OH + HCl \rightarrow (CH_3)_3C–Cl + H_2O$
  tert. Butyl alcohol tert. Butylchloride

(4) *Bromo And Iodo Alkanes*

$C_2H_5OH + KBr + H_2SO_4 \rightarrow C_2H_5Br + KHSO_4 + H_2O$

$CH_3CH_2OH \xrightarrow{kI/H_2SO_2} CH_3CH_2I + KHSO_4 + H_2O$

$C_2H_5OH + KI + H_3PO_4 \longrightarrow C_2H_5I + KH_2PO_4 + H_2O$

(5) Reaction of R –OH With ‘P + I_2

$6\ R–OH + 2P + 3I_2 \longrightarrow 6\ R–I + 2H_3PO_3$

For example,

$6\ C_2H_5OH + 2P + 3Br_2 \rightarrow 6C_2H_5Br + H_3PO_3$

(6) *By Finkelstein Reaction* It is specially used for iodo alkanes preparation.

$CH_3–CH_2Br + NaI \xrightarrow{acetone} CH_3CH_2I + NaBr$

(7) *Fluoroalkane*

- This reaction is called Swart reaction.

  $CH_3Cl + AgF \longrightarrow CH_3F + AgCl$

  $2CH_3Cl + Hg_2F_2 \longrightarrow 2CH_3F + Hg_2Cl_2$

(8) *Borodine Hundsdiecker Reaction or From Silver Salts of Acids*

- It is used mainly for preparing bromoalkanes from silver salts as follows:

  $RCOOAg + X_2 \xrightarrow{CCI_4} R\text{-}X + CO_2 + AgX$

- In case of iodine, an ester is formed and the reaction is called Birnbaum Simonini reaction.

  $2RCOOAg + I_2 \longrightarrow R – COOR + 2CO_2 + 2AgI$

Mechanism

$RCOOAg + X_2 \longrightarrow RCOOX + AgX$

$RCOOX \longrightarrow X^{\cdot} + RCOO^{\cdot} \longrightarrow R^{\cdot} + CO_2$

$R^{\cdot} + X_2 \longrightarrow R - X + X^{\cdot}$

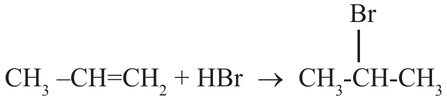
$R^{\cdot} + RCOOX \longrightarrow RX + RCOO^{\cdot}$

(9) From Ethers

$$R\text{–}O\text{–}R + PCl_5 \longrightarrow 2R\text{–}Cl + POCl_3$$

$$R\text{–}O\text{–}R' + PCl_5 \longrightarrow R - Cl + R' - Cl + POCl_3$$

(10) From Alkenes Alkenes react with HX according to Markonikoff's or anti-Markonikoff's rule to give haloalkanes as follows:

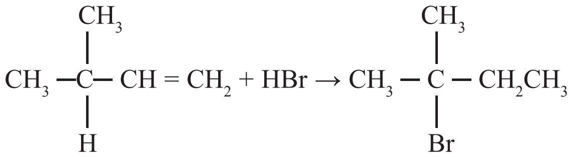


$$CH_3\text{–}CH{=}CH_2 + HBr \rightarrow CH_3\text{-}\overset{\overset{\displaystyle Br}{|}}{C}H\text{-}CH_3$$

It is according to MarkownoKoff's rule.

$$CH_3\text{–}CH{=}CH_2 + HBr \xrightarrow{\text{benzoyl peroxide}} \underset{10\%}{CH_3\text{– }CH_2\text{–}CH_2Br}$$

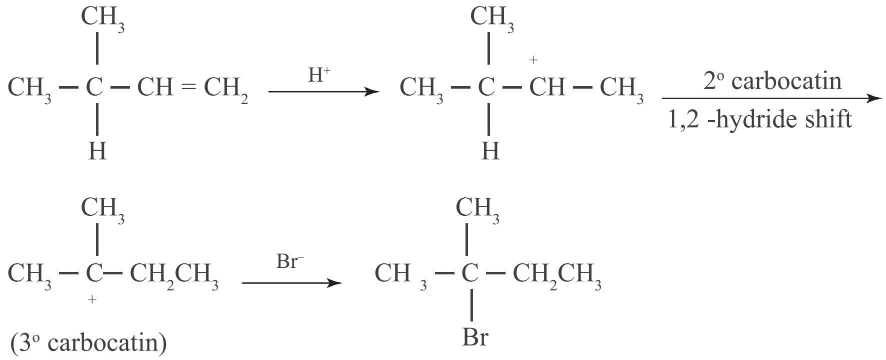
It is according to anti-MarkownoKoff's rule.



$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-CH=CH_2 + HBr \rightarrow CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle Br}{|}}{C}}-CH_2CH_3$$

3- Methyl but -1- ene 2- bromo-2-methyl butane

This can be explained by 1,2- hydride shift to attain greater stability of carbocation.



$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-CH=CH_2 \xrightarrow{H^+} CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{+}{C}H-CH_3 \xrightarrow[\text{1,2 -hydride shift}]{2^o\text{ carbocatin}}$$

$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{+}{C}}-CH_2CH_3 \xrightarrow{Br^-} CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle Br}{|}}{C}}-CH_2CH_3$$

(3° carbocatin)
More stable than 2°

2- Bromo-2- methyl butane

REMEMBER

$$\underset{\text{Propane}}{CH_3 - CH = CH_2} + SO_2Cl_2 \xrightarrow[\text{UV light}]{200°C} \underset{\text{3- Chloroprop -1-ene}}{ClCH_2CH = CH_2}$$

(11) From Primary Amines

$$R - NH_2 + \underset{\substack{\text{Nitrosyl}\\ \text{Chloride}}}{NOCl} \longrightarrow R\text{–}Cl + N_2 + H_2O$$

(12) By Rydone Methods

An alcohol on heating with halogen in presence of triphenyl phosphate $(PhO)_3PO$ produces alkyl halides.

$$R-CH_2OH + Br_2 + (C_6H_5O)_3PO \xrightarrow{\text{Heat}} R-CH_2Br + C_6H_5OH + (C_6H_5O)_2POBr$$

Physical Properties

(1) Lower members (CH_3X, C_2H_5X) are colourless gases while higher members are colorless liquids up to C_{18} and C_{18} onwards members are colourless solids.

(2) The alkyl halides are polar in nature and have dipole moment value 2.05 to 2.15 Debye, yet they are insoluble in water because they can neither form hydrogen bonds with water nor they can break already exisiting hydrogen bonds in water.

Dipole moment in decreasing order:

$RCl > RF > RBr > RI$

$CH_3Cl > CH_3F > CH_3Br > CH_3I$

(3) Alkyl chlorides are generlly lighter than water but alkyl bromides and iodides are heavier than water. The relative density of alkyl halides follow the order

$R-I > R-Br > R-Cl.$

It is explained on the basis of alrge van der Waal's forces of attraction for iodides due to larger surface area and so on.

(4) The boiling point of haloalkanes are higher thant the alkanes of comparable masses . It is due to the fact that, halolakens are polar in nature, and there are presaent dipole - dipole attractive forces in them, wheres only weak van der Waal's forces of attraction are present in alkanes Boiling point and density increases with the increase in molecular weight.

or $C_4H_9Cl > C_3H_7Cl > C_2H_5Cl > CH_3Cl$

$RI > RBr > RCl > RF.$

The order of the boiling points in a group of isomeric alkyl halides is
Primary > Secondary > Tertiary

- The volatility has the following order:
  Chloride > bromide > iodide

  $R-Cl > R-Br > R-I$

(5) Alkyl chlorides burn with green-edged flames.

(6) The bottles conttaining alkyl iodide turn violet on standing.

$$\underset{\text{Alkyl iodide}}{2R-I} \xrightarrow[\text{standing}]{\text{On}} R-R + \underset{\text{Violet}}{I_2}$$

Chemical Properties

Relative Reactivity of Haloalkanes As the C – X – is polar so these are reactive compounds and on the basis of electronegativity, the relative reactvity of haloalkanes towards nucleophilic substitution reaction appears to be $R-F > R-Cl > R-Br > R-I$ But actual order is $R-I > R-Br > R-Cl > R-F$
It is explained on the basis of bond dissociation energy as follows:

H_3C-I	H_3C-Br	H_3C-Cl	H_3C-F
234 kj mole^{-1}	293 kj mole^{-1}	351 kj mole^{-1}	452 kj mole^{-1}

Since $C-I$ bond has the minimum bond dissociation energy while $C-F$ has maximum. Therefore, $C-I$ bond is broken most easily and so on. Thus order of reacitivity is

$R-I > R-Br > R-Cl > R-F$
$R_3CX > R_2CHX > RCH_2\,X$
$CH_3X > C_2H_5HX > C_3H_7X > \ldots.$

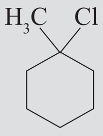
Halomethane	Bond length (in pm)	Bond dissociation energy (kj/mol)
H_3C-F	139	452
H_3C-Cl	178	351
H_3C-Br	193	293
H_3C-I	214	234

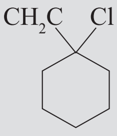
(1) *Nucleophilic Substitution Reactions* Alkyl halides undergo nucleophilic substitution reactions as follows:

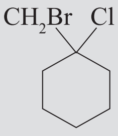
$$\overset{+\delta}{R} - \overset{-\delta}{X} + \underset{\text{Stronger Nucleophile}}{Z^-} \longrightarrow R - Z + X^-$$

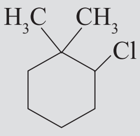
REMEMBER

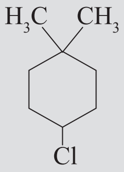
Write the following alkyl halides in decreasing order of S_N2 reactivity. Explain your reasoning.


(A)


(B)


(C)


(D)


(D)

Solution
C > B > E > D >> A. C and B are both primary, and bromide is a more reactive nucleofuge than chloride. E and D are both secondary, but nucleophillic attack on D is hindered by the two nearby CH_3 groups. A is tertiary, and therefore unreactive under S_N2 conditions.

For example,

- $R-X \xrightarrow{\text{aq. KOH}} R-OH + HX$
- $R-X \xrightarrow{\text{AgOH}} R-OH + AgX$
- $R-X \xrightarrow{\text{alc. KCN}} R-CN + KX$

Here $R-CN$ is the major product as KCN being ionic provides CN^- ion so attack is from carbon atom side.

- $R-X \xrightarrow{\text{AgCN}} R-NC + AgX$

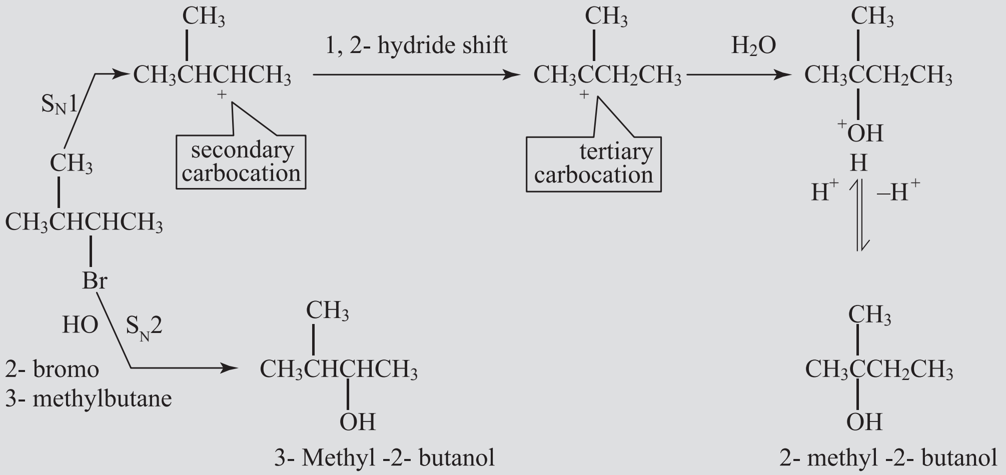
Here major product is RNC as AgCN being covalent can not furnish CN^- ion so here the attack is from nitrogen atom side.

- $R-X \xrightarrow{AgNO_2} R-NO_2 + AgX$
  Nitro alkane
- $R-X \xrightarrow{KNO_2} R-O-NO + KX$
  Alkyl nitrite
- $R-X \xrightarrow{NaN_3} R-N_3 + NaX$
  Azides
- $R-X \xrightarrow{NaSH} R-SH + NaX$
  Thiols
- $R-X \xrightarrow{R'COOAg} R'COOR + AgX$
- $R-X \xrightarrow{R'ONa} R'-O-R + NaX$

  It is called Williamson synthesis. It is the best method to prepare all kind of ethers.
- $R-X \xrightarrow[C_2H_5OH/H_2O]{R'SNa} R'-S-R + NaX$
- $R-X \xrightarrow{Na_2S} R-S-R + 2NaX$
  Thio ether
- $R-X \xrightarrow[\text{Anhy. AlCl}_3]{C_6H_6} C_6H_5-R + HX$

  It is called Friedal Craft's reaction.
- $R-X \xrightarrow{\text{moist } Ag_2O} R-OH$
- $2R-X + \underset{\text{dry}}{Ag_2O} \longrightarrow \underset{\text{Ether}}{R-O-R} + 2AgX$
- $R-X + NaC \equiv CR' \longrightarrow R-C \equiv C-R' + NaX$
  Alkyne

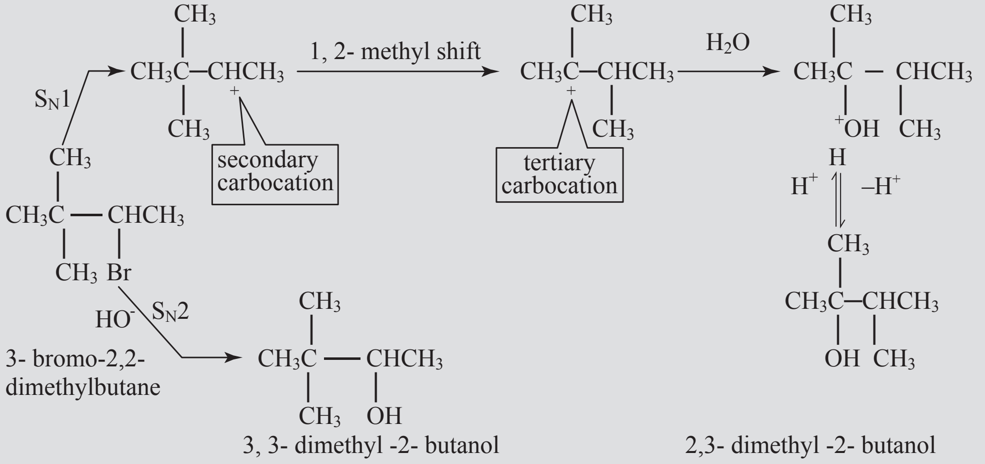
REMEMBER



It means by SN[1] and SN[2] mechanisms it gives two different products.

REMEMBER

3-Bremo 2,2 de-methyl on hydrolysis gives two different products as follows.

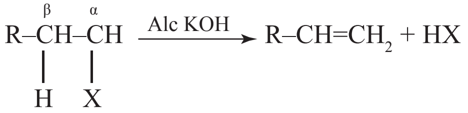


3- bromo-2,2-dimethylbutane

3, 3- dimethyl -2- butanol

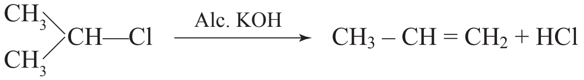
2,3- dimethyl -2- butanol

(2) ***Dehydrohalogenation*** It involves α, β-elimination following E_1 and E_2 mechanisms. Here α-β-elimination reaction takes place as follows:



$$\mathrm{R{-}\underset{H}{\overset{\beta}{CH}}{-}\underset{X}{\overset{\alpha}{CH}} \xrightarrow{Alc\ KOH} R{-}CH{=}CH_2 + HX}$$

For example,



$$\mathrm{\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH{-}Cl \xrightarrow{Alc.\ KOH} CH_3 - CH = CH_2 + HCl}$$

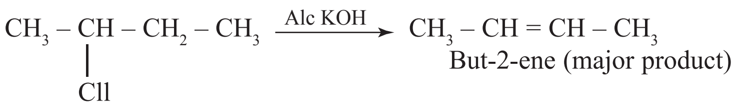
Saytzeff's Rule According to it, "Removal of β-H-atom takes place from β-carbon atom with more alkyl groups or less H-atoms so that a more stable alkene is formed".

Relative reactivities of alkyl halides in an E_1 reaction = relative stabilities of carbocation formed

3° benzylic > 3° allylic > 2° benzylic > 2° allylic > 3° > 1° benzylic ≈ 1° allylic ≈ 2° > 1° > vinyl

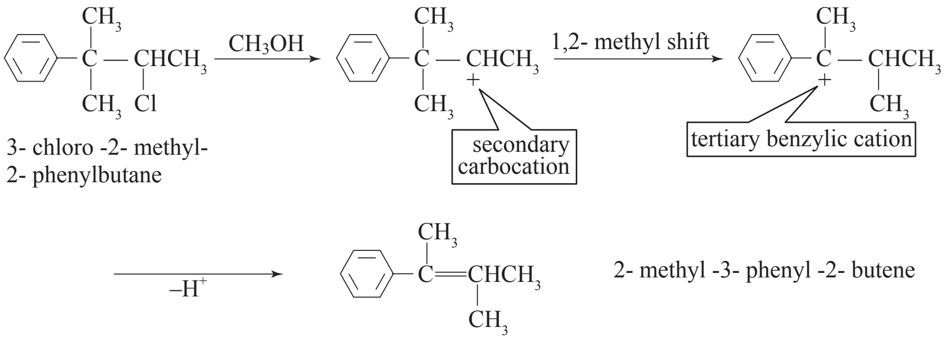
increasing reactivity and stability of R–X.

For example,



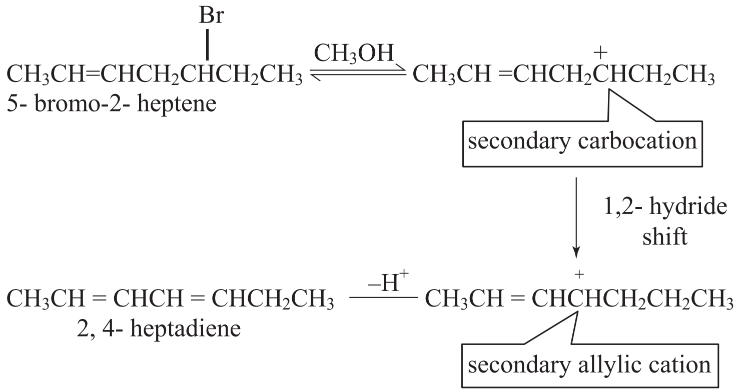
$$\mathrm{CH_3 - \underset{Cll}{CH} - CH_2 - CH_3 \xrightarrow{Alc\ KOH} CH_3 - CH = CH - CH_3}$$

But-2-ene (major product)



3- chloro -2- methyl-2- phenylbutane

2- methyl -3- phenyl -2- butene



$$CH_3CH{=}CHCH_2\overset{Br}{\overset{|}{C}}HCH_2CH_3 \overset{CH_3OH}{\rightleftharpoons} CH_3CH{=}CHCH_2\overset{+}{C}HCH_2CH_3$$

5- bromo-2- heptene

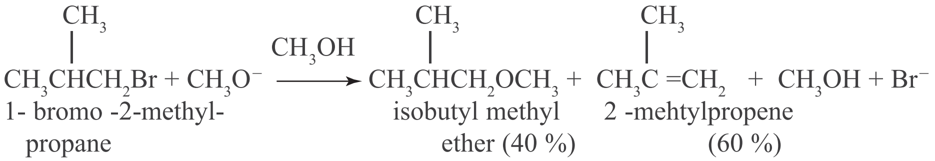
secondary carbocation

1,2- hydride shift

$$CH_3CH = CHCH = CHCH_2CH_3 \xleftarrow{-H^+} CH_3CH = CH\overset{+}{C}HCH_2CH_2CH_3$$

2, 4- heptadiene

secondary allylic cation

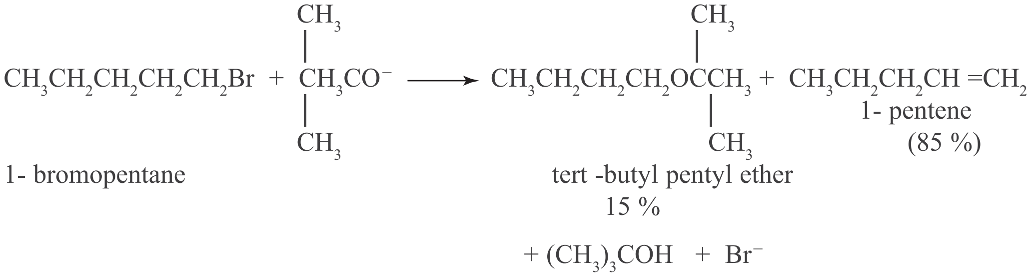


$$CH_3\overset{CH_3}{\overset{|}{C}}HCH_2Br + CH_3O^- \xrightarrow{CH_3OH} CH_3\overset{CH_3}{\overset{|}{C}}HCH_2OCH_3 + CH_3\overset{CH_3}{\overset{|}{C}} = CH_2 + CH_3OH + Br^-$$

1- bromo -2-methyl- propane

isobutyl methyl ether (40 %)

2 -mehtylpropene (60 %)



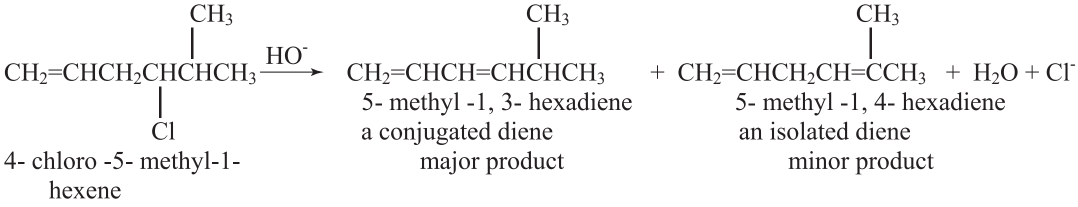
$$CH_3CH_2CH_2CH_2CH_2Br + CH_3\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}O^- \longrightarrow CH_3CH_2CH_2CH_2O\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}CH_3 + CH_3CH_2CH_2CH = CH_2$$

$$+ (CH_3)_3COH + Br^-$$

1- bromopentane

tert -butyl pentyl ether 15 %

1- pentene (85 %)

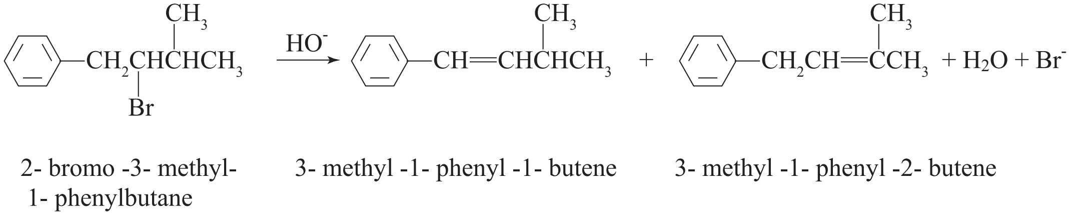


$$CH_2{=}CHCH_2\underset{Cl}{\underset{|}{C}}H\overset{CH_3}{\overset{|}{C}}HCH_3 \xrightarrow{HO^-} CH_2{=}CHCH{=}CH\overset{CH_3}{\overset{|}{C}}HCH_3 + CH_2{=}CHCH_2CH{=}\overset{CH_3}{\overset{|}{C}}CH_3 + H_2O + Cl^-$$

4- chloro -5- methyl-1- hexene

5- methyl -1, 3- hexadiene
a conjugated diene
major product

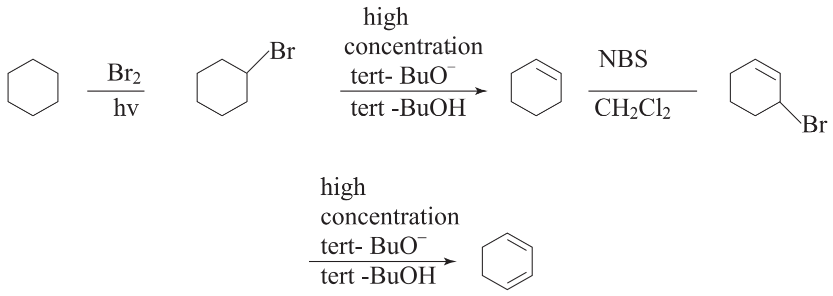
5- methyl -1, 4- hexadiene
an isolated diene
minor product

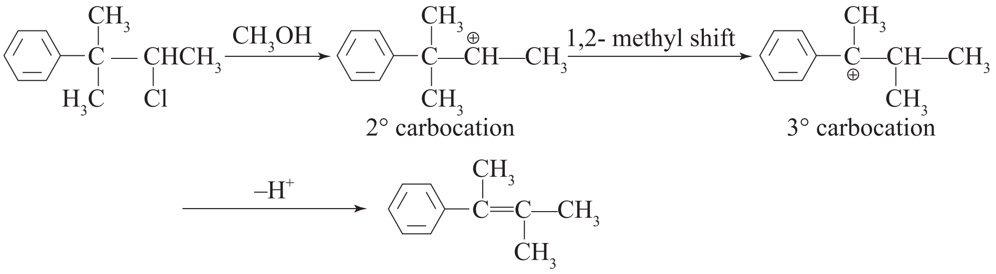


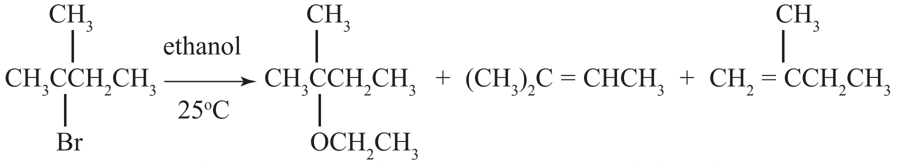
2- bromo -3- methyl- 1- phenylbutane

3- methyl -1- phenyl -1- butene

3- methyl -1- phenyl -2- butene







$$\underset{\underset{\text{- butane}}{\text{2- Brom -2 methyl}}}{CH_3\overset{\overset{CH_3}{|}}{\underset{\underset{Br}{|}}{C}}CH_2CH_3} \xrightarrow[25^{o}C]{\text{ethanol}} \underset{\text{2- Ethoxy -2- methylbutane}}{CH_3\overset{\overset{CH_3}{|}}{\underset{\underset{OCH_2CH_3}{|}}{C}}CH_2CH_3} + \underset{\text{2- Methyl -2- butene}}{(CH_3)_2C = CHCH_3} + \underset{\text{2- Methyl -1- butene}}{CH_2 = \overset{\overset{CH_3}{|}}{C}CH_2CH_3}$$

2- Brom -2 methyl - butane

2- Ethoxy -2- methylbutane (major product in absence of sodium ethoxide)

2- Methyl -2- butene

2- Methyl -1- butene

(Alkene mixture is major product in presence of sodium ethoxide)

(3) With Metals

(a) With Na [Wurtz Reaction]

$$R–X + 2Na + X–R \xrightarrow[\text{dry either}]{} R – R + 2NaX$$

(b) With Zn [Frankland Reaction]

$$R–X + Zn + X–R \xrightarrow{\Delta} R – R + ZnX_2$$

(c) With Mg

$$R–X + Mg \xrightarrow{\text{Dry ether}} \underset{\text{Grignard reagent}}{R – Mg – X}$$

(d) With Lead Sodium Alloy

$$4C_2H_5Br + 4Pb\ (Na) \longrightarrow \underset{\text{T.E.L.}}{(C_2H_5)_4Pb} + 4NaBr + 3Pb$$

- Tetra ethyl lead (TEL) is an antiknocking substance.

(e) With Lithium

$$RX + 2Li \xrightarrow{\text{ether}} R - Li + LiX$$

(4) Reduction

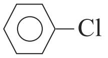
$$R - X + 2\,[H] \xrightarrow[\text{Or Zn/HCI}]{\text{LiAIH}_4} R - H + HX$$

$$R\text{-}X + 2HI \xrightarrow{\text{Red 'P'}} R\text{-}H + HX + I_2$$

(5) Heating Effect

$$R–CH_2–CH_2–X \xrightarrow{560°C} R - CH = CH_2 + HX$$

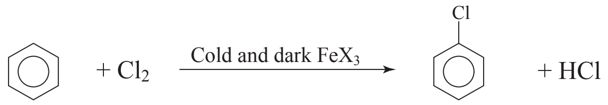
CHLORO BENZENE



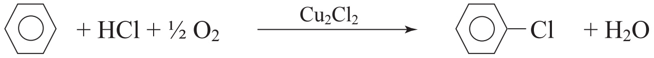
or C_6H_5Cl

Methods of Preparation

From Benzene



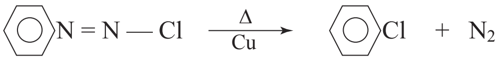
Commercial Method or Raschig Method



From Alcohol

From Benzene Diazonium Chloride or Sand Mayer's Reaction

Gatterman Reaction



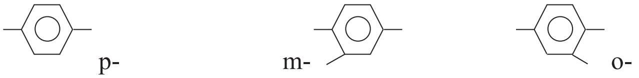
Physical Properties

(1) Aryl halides are colourless liquids and colourless solids with charactristic odour . Chloro benzene is a colourless liquid with a pleasant smell and a boiling point of 132^{o}C. It is heavier than water and insoluble in it.

(2) The boiling piont of alryl halides follow the order:

Ar — I > Ar — Br > Ar — Cl > AR — F

(3) The melting point of *p* - isomer is more than *o*- and *m*- isoemr.

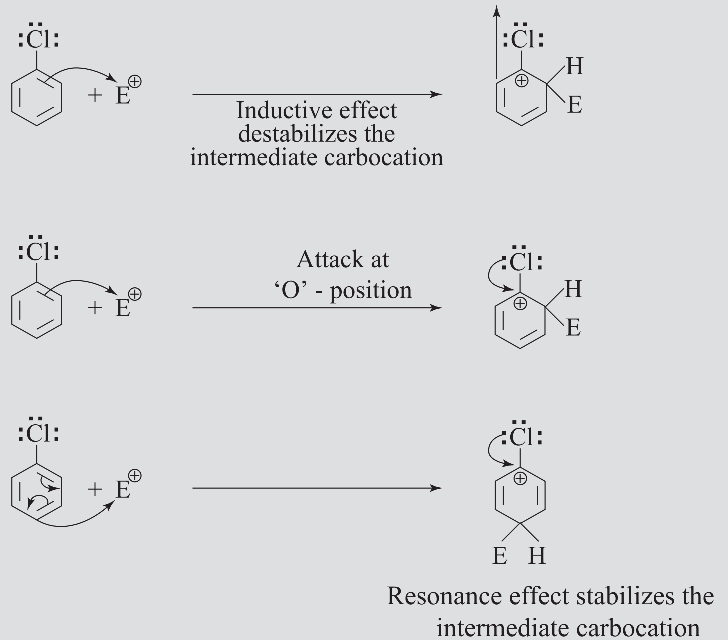


As p-isomer is more stable and symmetrical than o -and m- isomers. Therefore, it fits well into the crystal lattice and more energy is required to break it. Hence its melting point is more.

Chemical Properties

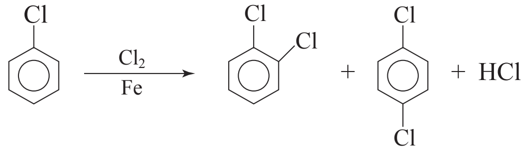
(A) Due to Benzene ring The Cl^- atom present in the ring deactivates the ring but it is o- and p- directing. The rate of electrophilic substitution will be slower than that of benzene.

Chlorine withdraws electrons through inductive effect and releases electrons through resonance. Through inductive effect, chlorine destabilizes the intermediate carbocation formed during the electrophilic substitution.



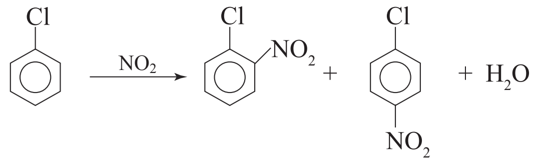
Through resonance, halogen tends to stabilize the carbocation and the effect is more pronounced at ortho- and para-position. The inductive effect is stronger than resonance and causes net electron withdrawal and thus causes net deactivation. The resonance effect tends to oppose the inductive effect for the attack at ortho-and para-positions and hence makes the deactivation less for ortho-and para-attack. Reactivity is thus controlled by the stronger inductive effect and orientation is controlled by resonance effect.

Halogenation



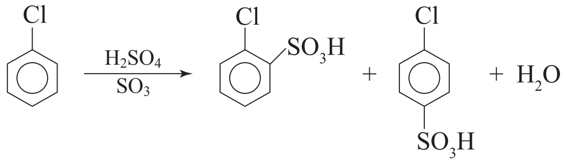
ortho, para dichloro benzene

Nitration



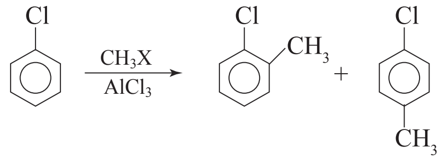
ortho, para nitrochloro benzene

Sulphonation



ortho, para chloro
benzene sulphonic acid

Friedel Craft Alkylation



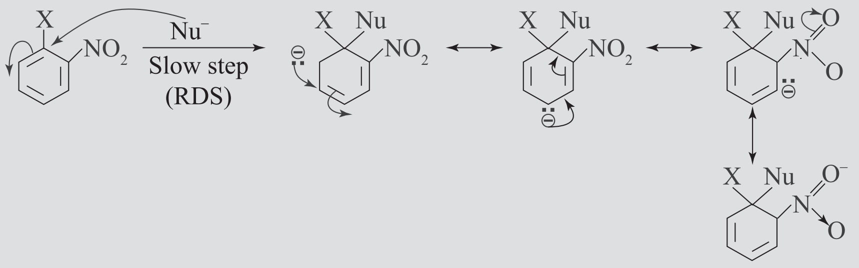
ortho, para methyl chloro benzene

DUE TO CHLORINE (NUCLEOPHILIC SUBSTITUTION)

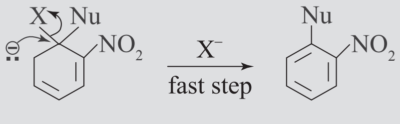
- *Reactivity of Chlorine Atom in Chloro Benzene* The reactivity of Cl^- atom in chlorobenzene is very low because C – Cl bond in chloro benzene acquires a double bond character and resonance stabilized so more energy is required to break a double bond than a single bond hence lower reactivity. When electron withdrawing groups like NO_2, CN etc. are attached on ortho and para positions.The reactivity of Cl- atom is enhanced and it can be easily substituted by stronger nucleophiles.

Mechanism

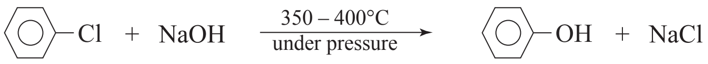
Step 1

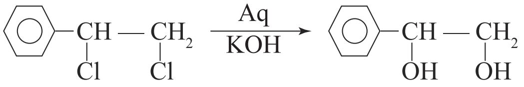


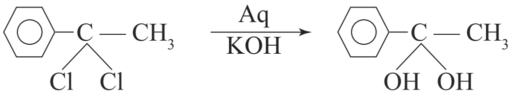
Step 2

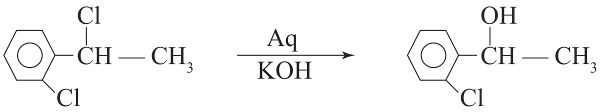


- *Substitution by –OH Group*



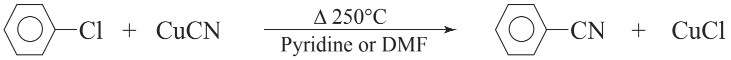




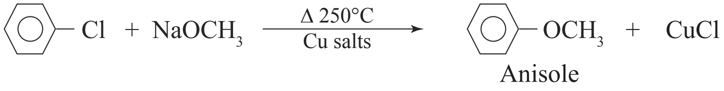


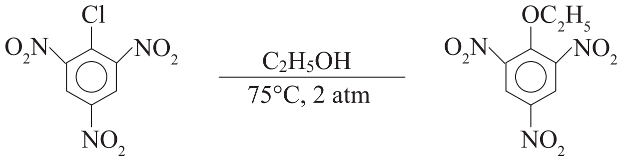
- *Substitution by NH_2 Group*

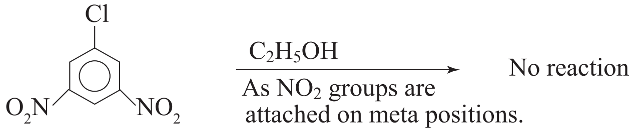
- *Substitution by CN Group*



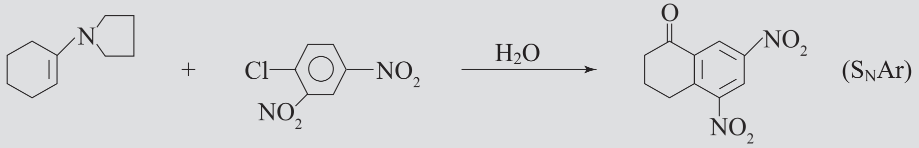
- *Substitution by O-R Group*



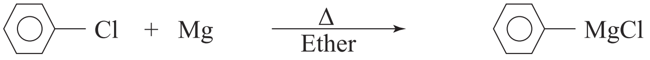




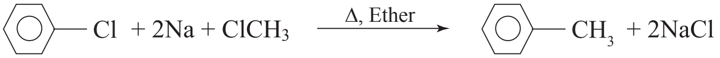
REMEMBER



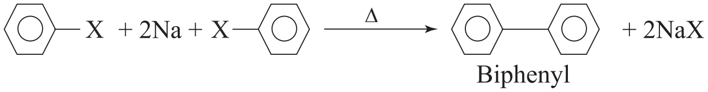
- *With Magnesium*



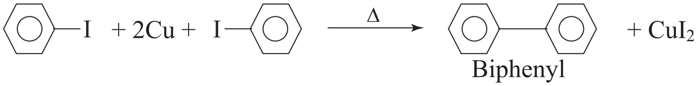
- *Wurtz Fitting Reaction*



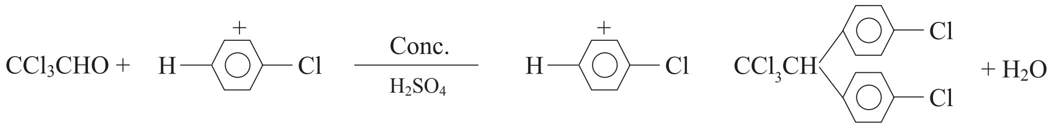
- *Fittig Reaction*



- *Ullmann Reaction*



- *With Chloral:* Chloral on heating with chlorobenzene in presence of conc. H_2SO_4 gives DDT (p, p-dichloro diphenyl trichloro ethane).



DDT

- It is an off-white crystalline powder and was used as an insecticide.

ENHANCE YOUR KNOWLEDGE

- It has been observed that presence of bulky groups in primary halides (inspite of more positive I.E.) causes steric hinderance and bring them less reactive towards SN^2 mechanism.

  $CH_3X > C_2H_5X > C_3H_7X$

- Halothane ($CF_3CHClBr$) is a common inhalative Anaesthesia.
- Antiseptic action of CHI_3 is due to free I_2.
- CF_4 (Freon-11), CF_3Cl (Freon-13), $CFCl_3$ (Freon-11).
- Per fluoro carbons (P.F.Cs) has general formula C_nH_{2n+2}.
- The halogen derivatives of the aromatic hydrocarbons in which the halogen atom is present in the side chain are called Aryl alkyl halides or aralkyl halides.

For example, $Ar - CH_2 - X$

  - CCl_4 is used as a medicine for hookworms.
  - CF_4 is freon-14, CF_3Cl is freon-13, CF_2Cl_2 is freon-12 and $CFCl_3$ is freon-11.
  - Per fluorocarbons have a general formula $C_n\,F_{2n+2}$.

For example,

$$C_6H_{14} + 14F_2 \xrightarrow{573\text{ K, }CoF_2} C_6F_{14} + 16\,HF$$

- Halothane ($CF_3CHClBr$) is used as a inhalative anaesthetic agent.
- Chloretone is a hypnotic or sleep inducing drug.
- Westron is tetrachloro ethane while Westrosol is trichloro ethylene.

Teflon $(- CF_2 - CF_2 -)n$

- It is a polymer of tetrafluoro ethylene .
- It is chemically inert thermostatic plastic.
- It is used for electrical insulation and in gasket materials.

$$CHCl_3 \xrightarrow[HF]{SbF_3} CHF_2Cl \xrightarrow[HF]{800^{o}C} \underset{\text{Tetrafluoroethylene}}{CF_2 = CF_2} \;\; nCF_2 = CF_2 \longrightarrow \underset{\text{Teflon}}{(- CF_2 - CF_2 -)n}$$

MULTIPLE-CHOICE QUESTIONS

Straight Objective Type Questions (Single Choice only)

1. n-Propyl bromide on treatment with ethanolic potassium hydroxide produces
(a) Propane (b) Propene
(c) Propyne (d) Propanol

2. Which is the best solvent to use for the solvolysis reaction of t- butyl chloride?
(a) Water
(b) Carbon tetrachloride
(c) Formic acid
(d) Heptane

3. 1-Chlorobutane on reaction with alcoholic potash gives
(a) 1-Butene (b) 1-Butanol
(c) 2-Butene (d) 2-Butanol.

4. Correct order of B. P. for the alkyl halide is
(a) $C_2H_5Cl > C_2H_5Br > C_2H_5I$
(b) $C_2H_5I > C_2H_5Br > C_2H_5Cl$
(c) $C_2H_5I > C_2H_5Cl > C_2H_5Br$
(d) $C_2H_5Br > C_2H_5I > C_2H_5Cl$

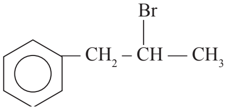
5. Chlorination of toluene in presence of light and heat followed by treatment with aqueous NaOH gives
(a) o-Cresol
(b) p-Cresol
(c) 2, 4-Dihydroxytoluene
(d) Benzoic acid.

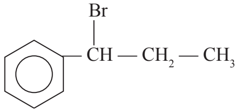
6. Which of the following represents the correct order of densities?
(a) $CCl_4 > CHCl_3 > CH_2Cl_2 > CH_3Cl > H_2O$
(b) $CCl_4 > CHCl_3 > CH_2Cl_2 > H_2O > CH_3Cl$
(c) $H_2O > CH_3Cl > CH_2Cl_2 > CHCl_3 > CCl_4$
(d) $CCl_4 > CHCl_3 > H_2O > CH_2Cl_2 > CH_3Cl$

7. Which of the following has the highest normal boiling point?
(a) iodobenzene (b) bromobenzene
(c) chlorobenzene (d) fluorobenzene

8. Among the following alkyl halides, choose the one with the lowest boiling point.
(a) *t*-butyl chloride (b) *n*-butyl chloride
(c) *t*-butyl bromide (d) *n*-butyl iodide

9. Propyl benzene reacts with bromine in presence of light or heat to give

(a)


(b)


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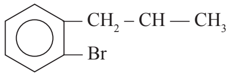

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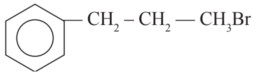
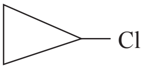


10. The compound most reactive towards SN^1 reaction is
(a) $Me_3C - CH_2Cl$ (b) $MeOCH_2Cl$
(c) $PhCH_2CH_2Cl$ (d)


11. The starting substance for the preparation of iodoform is any one of the following, except
(a) $CH_3CH(OH)CH_3$ (b) CH_3CH_2OH
(c) HCH_2OH (d) CH_3COOH_3

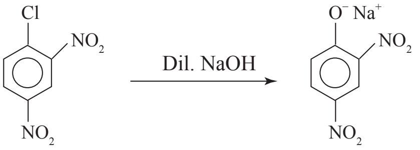
12. The reaction of –bromobenzyl chloride with NaCN in ethanol leads to:
(a) 4-bromo-2-cyanobenzyl chloride
(b) 4-cyanobenzyl cyanide
(c) 4-cyanobenzyl chloride
(d) 4-bromobenzyl cyanide

13. Which of the following reagents could be used to convert cyclohexanol to chlorocyclohexane?
(a) Cl_2, light (b) $SOCl_2$
(c) PBr_3 (d) none of these

14. Which of the following bases would give the best yield for the substitution product when reacted with 2^- chloropropane?
(a) CH_3COO- (b) OH^-
(c) NH_2^- (d) $CH_3CH_2O^-$

15. Arrange the following compounds in order of increasing dipole moment: Toluene (I), m-dichlorobenzene (II), o-dichlorobenzene (III), and p-dichlorobenzene (IV).
(a) I < IV < II < III (b) IV < I < II < III
(c) IV < I < III < II (d) IV < II < I < III.

16. The following transformation proceeds through



(a) benzyne intermediate
(b) oxirane

(c) electrophillic – addition
(d) activated nucleophillic substitution

17. Which of the following is the best nucleophile is an S_N2 reaction where competition from E2 is unimportant?

(a) $HCOO^-$ (b) H_2O
(c) Cl^- (d) OH^-

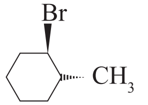
18. Which of the following compounds will undergo an S_N2 reaction most readily?

(a) $(CH_3)_3CCH_2I$
(b) $(CH_3)_3CCl$
(c) $(CH_3)_2CHI$
(d) $(CH_3)_2CHCH_2CH_2CH_2I$

19. $CH_3CD_2CHBrCH_2CD_3$ on reaction with alc. KOH gives:

(a) $CH_3CD_2CH = CHCD_3$
(b) $CH_3CD = C = CHCD$
(c) $CD_3CD_2CH = CHCH_3$
(d) $CH_3CD = CHCH_2CD_3$

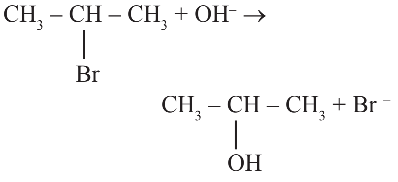
20. What is the product of the reaction of the following compound with alcoholic potassium hydroxide?



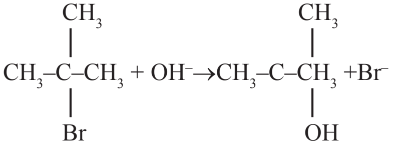
(a) 1- methylcyclohexane only
(b) 1- Methylcyclohexane only
(c) 3- methylocyclohexene (major product), 1- methylcyclohexene (minor product)
(d) 3- methylhexene only

21. Which of the following is example of SN^2 reaction?

(a) $CH_3Br + OH^- \rightarrow CH_3OH + Br^-$

(b) 
$CH_3 - \underset{\displaystyle Br}{\underset{|}{CH}} - CH_3 + OH^- \rightarrow CH_3 - \underset{\displaystyle OH}{\underset{|}{CH}} - CH_3 + Br^-$

(c) $CH_3 - CH_2 - OH \xrightarrow{-H_2O} H_2C = CH_2$

(d) 
$CH_3{-}\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle Br}{\underset{|}{C}}}}{-}CH_3 + OH^- \rightarrow CH_3{-}\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle OH}{\underset{|}{C}}}}{-}CH_3 + Br^-$

22. Toluene when refluxed with Br_2 in the presence of light mainly gives

(a) p- bromotoluene
(b) benzyl bromide
(c) o-bromotoluene
(d) mixture of o- and p-bromotoluene

23. The pesticide DDT slowly charges to:

(a) p, p'-dichlorodiphenyldichloroethene
(b) p, p'-dichlorodiphenyldichloroethane
(c) p, p'-dichlorodiphenylethene
(d) CCl_3-CHO and chlorobenzene

24. When chlorine is passed through propene at 400°C, which of the following is formed?

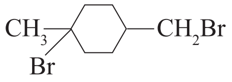
(a) allyl chloride (b) PVC
(c) vinyl chloride (d) 1,2-dichloroethane

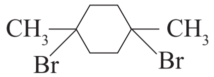
25. The conversion of 2,3-dibromobutane to 2-butene with Zn and alcohol is

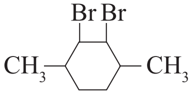
(a) β-Elimination
(b) Redox reaction
(c) Both β-elimination and redox reaction
(d) α-Elimination

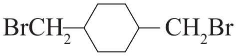
26. 

(A) is:

(a) 

(b) 

(c) 

(d) 

27. Nucleophilicity order is correctly represented by

(a) $NH_2^- > F^- > HO^- > CH_3^-$
(b) $CH_3^- > NH_2^- > HO^- > F^-$
(c) $CH_3^- < NH_2^- < HO^- < F^-$
(d) $CH_3^- \approx NH_2^- > OH^- \approx F^-$

28. In SN^1 reaction, the racemization takes place. It is due to:

(a) conversion of configuration
(b) retention of configuration
(c) inversion of configuration
(d) both (a) and (b)

29. Arrange the following halides in the decreasing order of SN^1 reactivity:

(I) $CH_3CH_2CH_2Cl$,
(II) $CH_2 = CHCH(Cl)CH_3$
(III) $CH_3CH_2CH(Cl)CH_3$

(a) I > II > III (b) II > III > I
(c) II > I > III (d) III > II > I

30. o-Methoxybromobenzene is treated with sodamide and then with ammonia. The product formed is

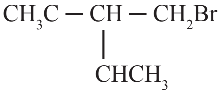
(a) methoxyaniline (b) m-methoxyaniline
(c) aniline (d) o-methoxyaniline

31. Which of the following undergoes E_2 elimination in the presence of a strong base to yield one product?
(a) 3- bromo -2- methylpentane
(b) 1 - bromo -1- methylcyclohexane
(c) 1- bromo -3, 3- dimethylbutane
(d) 3- bromo -3- methylpentane

32. Isopropyl chloride undergoes hydrolysis by
(a) SN^1 and SN^2 mechanisms
(b) neither SN^1 nor SN^2 mechanisms
(c) SN^1 mechanism only
(d) SN^2 mechanism only

33. Which one of the following is most reactive towards nucleophillic substitution reaction?
(a) C_6H_5Cl (b) $CH_2 = CH - Cl$
(c) $ClCH_2 - CH = CH_2$ (d) $CH_3CH = CH - Cl$

34. Which of the following will have the maximum dipole moment?
(a) CH_3Cl (b) CH_3Br
(c) CH_3I (d) CH_3F

35. Most reactive alkyl halide towards E2 mechanism is
(a) $CH_3C - CH_2Br$
(b) $CH_3CHCHBrCH_3$
(c) $CH_3CH_2 - CH_2CH_2Br$
(d) 
$CH_3C - \underset{\displaystyle CHCH_3}{\underset{|}{CH}} - CH_2Br$

36. Most reactive halide towards SN^1 reaction is
(a) sec-butyl chloride
(b) tert-butyl chloride
(c) n-butyl chloride
(d) allyl chloride

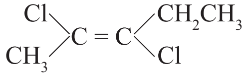
37. The order of reactivity of alkyl halides towards elimination reaction is
(a) 1° > 2° > 3° (b) 2° > 1° > 3°
(c) 3° > 2° > 1° (d) 3° > 1° > 2°

38. The reactivity order of halides for dehydrohalogenation is
(a) R – F > R – Cl > R – Br > R – I
(b) R – I > R – Br > R – Cl > R – F
(c) R – I > R – Cl > R – Br > R – F
(d) R – F > R – I > R – Br > R – Cl

39. A set of compounds in which the reactivity of halogen atom in the ascending order is
(a) chloroethane, chlorobenzene, vinyl chloride
(b) chlorobenzene, vinyl chloride, chloroethane
(c) vinyl chloride, chloroethane, chlorobenzene
(d) vinyl chloride, chlorobenzene, chloroethane

40. What is the major product of the following reaction?

$$CH_3 - C \equiv C - CH_2CH_3 \xrightarrow{Cl_2\ (1\ mole)} ?$$

(a) $CH_3CH_2 - CCl_2 - CH_2CH_3$
(b) $CH_3 - CCl_2CH_2CH_2CH_3$
(c) $CH_3 - CCl_2 - CCl_2 - CH_2CH_3$
(d) 

41. Allyl chloride on dehydrochlorination gives
(a) propylene (b) acetone
(c) propadiene (d) allyl alcohol

42. Which of the following most readily undergoes S_N1 displacements?
(a) 1- Bromopentane
(b) 2- Bromopentane
(c) 2- Bromo-2- methylbutane
(d) 1- Bromo-2- methylbutane

43. The most reactive nucleophiles among the following is
(a) $C_6H_5O^-$ (b) $(CH_3)_3CO^-$
(c) $(CH_3)_2CHO^-$ (d) CH_3O^-

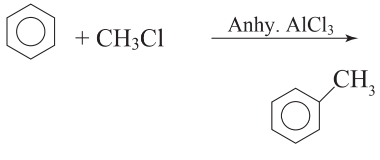
44. Which of the following are arranged in the decreasing order of dipole moment?
(a) CH_3Cl, CH_3Br, CH_3F (b) CH_3Cl, CH_3F, CH_3Br
(c) CH_3Br, CH_3Cl, CH_3F (d) CH_3Br, CH_3F, CH_3Cl

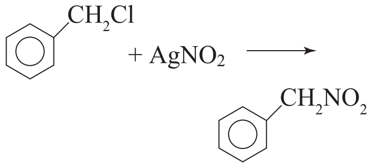
45. Consider the following reactions:

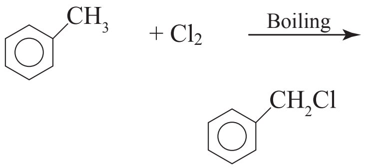
$$X + HCl \xrightarrow[\text{(addition)}]{\text{anhyd. AlCl}_3} \underset{Y}{C_2H_5Cl} \xrightarrow[\text{(substitution)}]{\text{anhyd. ZnCl}_2/\text{HCl}}$$

Y can be converted to X on heating with …….. at ………. temperature.
(a) Cu, 300°C
(b) Al_2O_3, 350°C
(c) $NaOH/I_2$, 60°C
(d) $Ca(OH)_2 + CaOCl_2$, 60°C

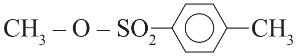
46. Which one of the following is a free radical substitution reaction?
(a) $CH_3CHO + HCN \rightarrow CH_3CH(OH)CN$

(b) 

(c) 

(d)


47. Which of the following substrate is most reactive towards methoxide ion (Me – O$^{\ominus}$)?

(a)


(b) $CH_3 – I$

(c) $CH_3 – Cl$

(d) $CH_3 – O – SO_2 – CF_3$

48. Identify A and B in the following reaction:

$$C_2H_5Cl \xrightarrow{A} C_6H_5OH \xrightarrow{B} C_2H_5Cl$$

(a) A = $AgNO_2$; B = KNO_2

(b) A = aq. NaOH ; B = $AgNO_2$

(c) A = alc. KOH /Δ ; B = aq. NaOH

(d) A = aq. KOH ; B = AgOH

49. Which of the following is least reactive in a nucleophillic substitution reaction?

(a) $(CH_3)_3C – Cl$ (b) $CH_2 = CHCl$

(c) CH_3CH_2Cl (d) $CH_2 = CHCH_2Cl$

50. 1,2-dibromoethane reacts with alcoholic KOH to yield a product X. The hybridization state of the carbons present in X, respectively are

(a) sp^2, sp^2 (b) sp, sp

(c) sp^3, sp^2 (d) sp^3, sp^3

51. What is the major products of the reaction of 2-bromopentane with sodium ethoxide in ethanol?

(a) trans-2- pentene

(b) 2- ethoxypentane

(c) cis -2 pentene

(d) both A and C

52. Identify A and B in the following reaction:

$$A \xrightarrow{\text{Aq. NaOH, }\Delta} C_6H_5OH \xleftarrow{\text{AgOH}} B$$

(a) A = C_2H_4, B = C_2H_5Cl

(b) A = C_2H_5Cl, B = C_2H_5Cl

(c) A = C_2H_2, B = C_2H_6

(d) A = C_2H_5Cl, B = C_2H_4

53. Among the following the strongest nucleophiles is

(a) C_2H_5SH (b) CH_3COO^-

(c) CH_3NH_2 (d) $NCCH_2^-$

54. Which of the following sets of reagents will convert 1- bromo -2- phenylethane to 1- phenylethanol?

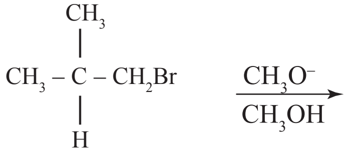
(a) H_2SO_4 and heat

(b) 1. $NaOCH_2CH_3$/ CH_3CH_2OH, 2. BH_3/diglyme, 3. $H2O_2$, OH^-

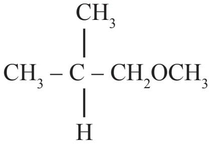
(c) 1. $NaOC(CH_3)_3/(CH_3)_3COH$, 2. $Hg(OAc)_2$ /THF –H_2O, 3. $NaBH_4$, OH^-

(d) $NaNH_2/NH_3$ 2. Br_2 /light, 3. H^+/H_2O

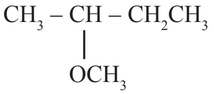
55. The major product formed in the following reaction is



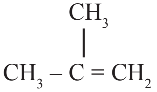
$$CH_3 – \overset{CH_3}{\underset{H}{C}} – CH_2Br \xrightarrow[CH_3OH]{CH_3O^-}$$

(a)


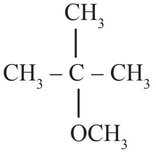
$$CH_3 – \overset{CH_3}{\underset{H}{C}} – CH_2OCH_3$$

(b)


$$CH_3 – \underset{OCH_3}{CH} – CH_2CH_3$$

(c)


$$CH_3 – \overset{CH_3}{C} = CH_2$$

(d)


$$CH_3 – \overset{CH_3}{\underset{OCH_3}{C}} – CH_3$$

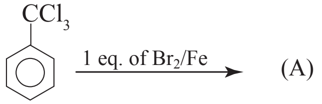
56. The major product obtained on treatment of $CH_3CH_2CH(F)CH_3$ with CH_3O^-/CH_3OH is

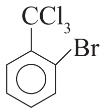
(a) $CH_3CH_2CH(OCH_3)CH_3$ (b) $CH_3CH = CHCH_3$

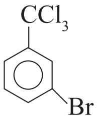
(c) $CH_3CH_2CH = CH_2$

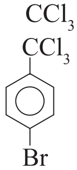
(d) $CH_3CH_2CH_2CH_2OCH_3$

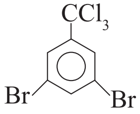
57. Compound (A) is



(a)


(b)


(c)


(d)


58. Fluorobenzene (C_6H_5F) can be synthesized in the laboratory

(a) by heating petrol with HF and KF.

(b) from aniline by diazotization followed by heating the diazonium salt with HBF_4.

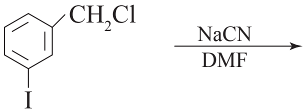
(c) by direct fluorination of benzene with F_2 gas.

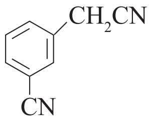
(d) by reacting bromobenzene with NaF solution.

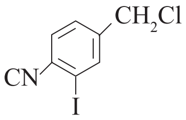
59. An alkyl bromide produces a single alkene when it reacts with sodium ethoxide and ethanol. This alkene undergoes hydrogenation and produces 2- methylbutane. What is the identify of the alkyl bromide?

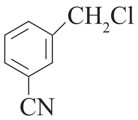
(a) 1- bromobutane
(b) 1- bromo- 2- methylbutane
(c) 2- bromo-2- methylbutane
(d) 1- bromo-2, 2- dimethylpropane

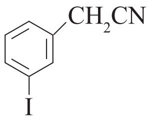
60. The structure of the major product formed in the given reaction:



(a) 

(b) 

(c) 

(d) 

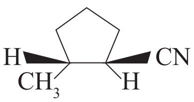
61. In the reaction,

$$R - X \xrightarrow{\text{alc. KCN}} A \xrightarrow{\text{dil. HCl}} B$$

The product B is

(a) alkyl chloride (b) aldehyde
(c) carboxylic acid (d) ketone

62. Which of the following reacts under S_N2 conditions with sodium cyanide, NaCN, to produce the following product?



(a) trans-1-iodo-2-methylcyclopentane
(b) cis-1-iodo-2-methylcyclopentane
(c) cis-2- methylcyclopentanole
(d) trans -2- methylcyclopentanole

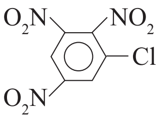
63. Which of the following compounds has the highest boiling point?

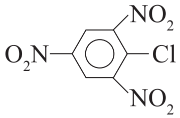
(a) $CH_3CH_2CH_2Cl$
(b) $CH_3CH_2CH_2CH_2Cl$
(c) $CH_3CH(CH_3)CH_2Cl$
(d) $(CH_3)_3CCl$

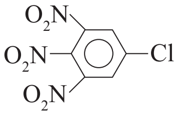
64. Which of the following sequence of reactions (reagents) can be used for the conservation of $C_6H_5CH_2CH_3$ into C_6H_5 CH $=CH_2$?

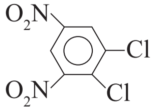
(a) $SOCl_2$; H_2O (b) SO_2Cl_2 ; alc. KOH
(c) Cl_2/hv ; H_2O (d) $SOCl_2$; alc KOH

65. Which chloroderivative of nitrobenzenes among the following would undergo hydrolysis, most readily with aqueous NaOH?

(a) 

(b) 

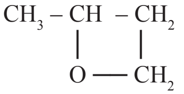
(c) 

(d) 

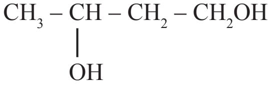
66. The correct increasing order of the reactivity of halides for SN_1 reaction is

(a) $CH_3–CH_2–X < (CH_3)_2CH–X < CH_2=CH–CH_2X < PhCH_2 – X$
(b) $(CH_3)_2CH–X < CH_3 – CH_2 – X < CH_2 = CH – CH_2 –X < PhCH_2 – X$
(c) $PhCH_2 – X < (CH_3)_2CH –X < CH_3–CH_2– X < CH_2 = CH – CH_2 – X$
(d) $CH_2 = CH – CH_2 – X < PhCH_2 – X < (CH_3)_2CH X < CH_3–CH_2– X$

67. The major product formed in the following reaction is $CH_3CH(Cl)CH_2 – CH_2OH \xrightarrow{\text{aq. KOH}}$

(a) $CH_3CH = CH – CH_2OH$
(b) $CH_2 = CH – CH_2 – CH_2OH$
(c) 

$$\begin{array}{l} CH_3 - CH\ \ - CH_2 \\ \qquad\quad\ |\qquad\ \ | \\ \qquad\quad O - CH_2 \end{array}$$

(d) 

$$\begin{array}{l} CH_3 - CH - CH_2 - CH_2OH \\ \qquad\quad\ | \\ \qquad\quad OH \end{array}$$

68. HBr reacts with $CH_2 = CH – OCH_3$ under anhydrous conditions at room temperature to give

(a) $BrCH_2CHO$ and CH_3OH
(b) CH_3CHO and CH_3Br
(c) $CH_3 – CHBr – OCH_3$
(d) $BrCH_2 – CH_2 – OCH_3$

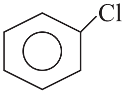
69. Replacement of Cl of chlorobenzene to give phenol requires drastic conditions but chlorine of 2, 4-dinitrochlorobenzene is readily replaced because

(a) $–NO_2$ makes the ring electron rich at ortho and para positions
(b) $–NO_2$ withdraws electrons at meta – position

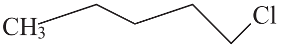
(c) $-NO_2$ donate electrons at meta-position
(d) $-NO_2$ withdraws electrons at ortho and para positions

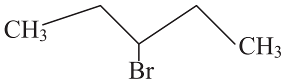
70. The organic chloro compound, which shows complete stereochemical inversion during a SN^2 reaction, is
(a) $(C_2H_5)_2$ CHCl
(b) $(CH_3)_3CCl$
(c) $(CH_3)_2CHCl$
(d) CH_3Cl

71. Which of the following shows S_N1 reaction most readily?

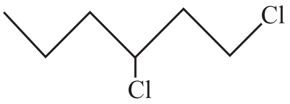
(a) 

(b) 

(c) 

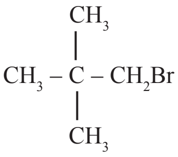
(d) 

72. Consider the following alkyl halide.

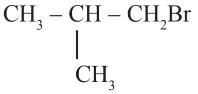


If one mole of this dibromide is mixed with one mole of NaI in acetone, what is the principal product of the reaction?
(a) 1- chloro -3- iodohexane
(b) 3- chloro-1- iodohexane
(c) 1,3- diiodohexane
(d) Both A and B

73. In a SN^2 substitution reaction of the type
$R - Br + Cl^- \xrightarrow{\text{DMF}} R - Cl + Br^-$
Which one of the following has the highest relative rate?

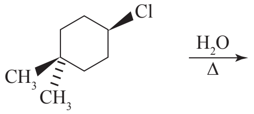
(a) 
$CH_3 - \overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}} - CH_2Br$

(b) CH_3CH_2Br
(c) $CH_3 - CH_2 - CH_2Br$

(d) 
$CH_3 - \underset{\underset{\large CH_3}{|}}{CH} - CH_2Br$

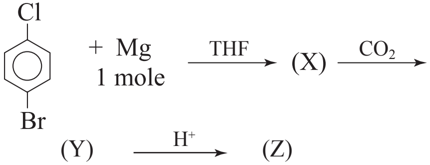
74. When 2, 4-dinitrochlorobenzene is treated with sodium hydroxide at 100°C followed by protonation:
(a) 2, 4-dinitrophenol is formed via an electrophilic aromatic substitution mechanism.
(b) 3, 5-dinitrophenol is formed via an electrophilic aromatic substitution mechanism.
(c) 2, 4-dinitrophenol is formed via an elimination-addition nucleophilic aromatic substitution mechanism.
(d) 2, 4-dinitrophenol is formed via an addition-elimination nucleophilic aromatic substitution mechanism.

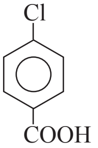
75. Predict the most likely mechanism for the reaction shown below.

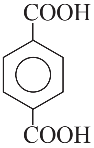


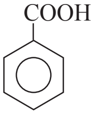
(a) S_N1
(b) S_N2
(c) E1
(d) E2

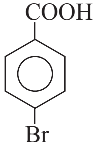
76. Identify (Z) in the following reaction:



(a) 

(b) 

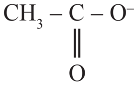
(c) 

(d) 

Brainteasers Objective Type Questions (Single choice only)

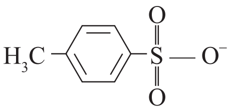
77. How many structural isomers of C_3H_6ClBr are possible and how many of them are optically active respectively?
(a) 5, 2
(b) 5, 3
(c) 4, 2
(d) 3, 2

78. The decreasing order of nucleophilicity among the nucleophiles

(1) 
$CH_3 - \underset{\underset{\large O}{\|}}{C} - O^-$

(2) CH_3O^-

(3) CN^-

(4) 

(a) 2 > 3 > 1 > 4
(b) 3 > 2 > 1 > 4
(c) 1 > 2 > 3 > 4
(d) 4 > 3 > 2 > 1

79. Consider the following haloalkanes:

1. CH_3F 2. CH_3Cl
3. CH_3Br 4. CH_3I

The increasing order of reactivity in nucleophillic substitution reaction is

(a) $4 < 3 < 2 < 1$ (b) $1 < 3 < 2 < 4$
(c) $1 < 2 < 3 < 4$ (d) $1 < 2 < 4 < 3$

80. In the following groups

(1) –OAc (2) –OMe
(3) $-OSO_2Me$ (4) $-OSO_2CF_3$

The order of leaving group ability is

(a) $1 > 2 > 3 > 4$ (b) $4 > 3 > 1 > 2$
(c) $4 > 2 > 1 > 3$ (d) $2 > 3 > 4 > 1$

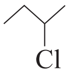
81. Arrange the following:

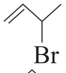
(1) $CH_3CH_2CH_2Cl$
(2) $CH_3CH_2 - CHCl–CH_3$
(3) $(CH_3)_2CHCH_2Cl$
(4) $(CH_3)_3C –Cl$

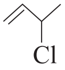
In order of decreasing tendency towards S_N2 reaction

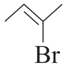
(a) $1 > 3 > 2 > 4$ (b) $4 > 4 > 3 > 1$
(c) $2 > 1 > 3 > 4$ (d) $1 > 2 > 4 > 3$

82. Arrange the given alkyl halides in the increasing reactivity towards nucleophilic substitution reactions.

(I)


(II)


(III)


(IV)


(a) II > III > I > IV (b) I > III > IV > II
(c) II > I > III > IV (d) IV > I > II > III

83. For the following:

(1) I^- (2) Cl^-
(3) Br^-

the increasing order of nucleophilicity would be

(a) $I^- < Br^- < Cl^-$ (b) $Cl^- < Br^- < I^-$
(c) $I^- < Cl^- < Br^-$ (d) $Br^- < Cl^- < I^-$

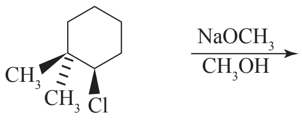
84. $CH_3Br + Nu^- \rightarrow CH_3 - Nu + Br^-$

The decreasing order of the rate of the above reaction with nucleophiles (Nu^-) a to d is [Nu^- =

(a) PhO^-
(b) AcO^-
(c) HO^-
(d) CH_3O^-]

(a) d > c > a > b (b) d > c > b > a
(c) a > b > c > d (d) b > d > c > a

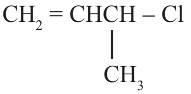
85. Predict the most likely mechanism for the reaction shown below.

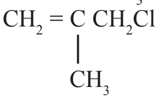


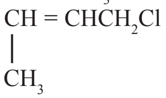
(a) S_N1
(b) E1cb
(c) E1
(d) E2

86. Which is the correct decreasing order of relative rates for solvolysis of the following allylic chlorides in formic acid containing small amount of water?

(I) $CH_2 = CHCH_2 - Cl$

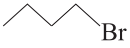
(II)

$CH_2 = CH\underset{\displaystyle CH_3}{\underset{|}{CH}} - Cl$

(III)

$CH_2 = \underset{\displaystyle CH_3}{\underset{|}{C}}\ CH_2Cl$

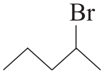
(IV)

$\underset{\displaystyle CH_3}{\underset{|}{CH}} = CHCH_2Cl$

(a) I > II > III > IV
(b) II > I > IV > III
(c) II > IV > I > III
(d) III > IV > II > I

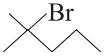
87. Dehydrobromination of the following is in the order:



I



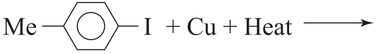
II



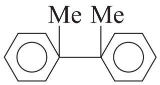
III

(a) III > II > I (b) I > II > III
(c) II > III > I (d) II > I > III

88. The product in the reaction



is

(a)


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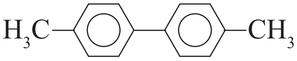
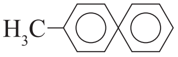


(c)


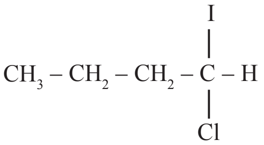
(d) none

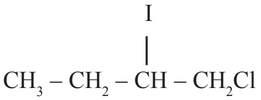
89. Predict the product C obtained in the following reaction butyne-1.

$CH_3CH_2 - C \equiv CH + HCl \longrightarrow B \xrightarrow{HI} C$

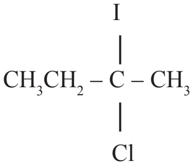
(a)

$CH_3 - \underset{\displaystyle Cl}{\underset{|}{CH}} - CH_2\ CH_2\ I$

(b)

$CH_3 - CH_2 - CH_2 - \overset{\displaystyle I}{\overset{|}{\underset{\displaystyle Cl}{\underset{|}{C}}}} - H$

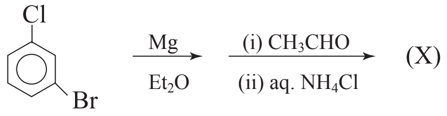
(c) 

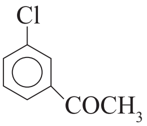
$CH_3-CH_2-\overset{\overset{I}{|}}{CH}-CH_2Cl$

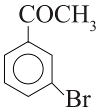
(d) 

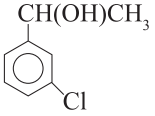
$CH_3CH_2-\underset{\underset{Cl}{|}}{\overset{\overset{I}{|}}{C}}-CH_3$

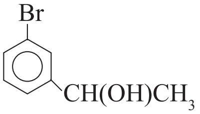
90. The product (X) of the following reaction is



(a) 

(b) 

(c) 

(d) 

91. A dihalogen derivative 'X' of a hydrocarbon with three carbon atoms reacts with alcoholic KOH and produces another hydrocarbon which forms a red precipitate with ammonia cal Cu_2Cl_2. 'X' gives an aldehyde on reaction with aqueous KOH. The compound 'X' is

(a) 1,2-Dichloropropane
(b) 1,3-Dichloropropane
(c) 1,3-Dichloropropane
(d) 1,1-Dichloropropane
(e) 2,2-Dichloropropane

92. Identify Z in the following series:

$$C_2H_5I \xrightarrow{\text{Alc. KOH}} X \xrightarrow{Br_2} Y \xrightarrow{\text{KCN}} Z$$

(a) CH_3CH_2CN (b) $NCCH_2-CH_2CN$
(c) $BrCH_2-CH_2CN$ (d) $BrCH=CHCN$.

93. The compound

$$C_7H_8 \xrightarrow{3Cl_2/\Delta} A \xrightarrow{Br_2/Fe} B \xrightarrow{Zn/HCI} C$$

The compound C is
(a) p-bromotoluene
(b) o-bromotoluene
(c) m-bromotoluene
(d) 3-bromo-2, 4, 6-trichlorotoluene

94. 1,2-Dibromopropane on treatment with X moles of $NaNH_2$ followed by treatment with ethyl bromide gives a pentyne. The value of X is

(a) Four (b) Three
(c) Two (d) One

95. The SN^1 reactivity of the following halides will be in the order:

(1) $(CH_3)_3CBr$ (2) $(C_6H_5)_2CHBr$
(3) $(C_6H_5)_2C(CH_3)Br$ (4) $(CH_3)_2CHBr$
(5) C_2H_5Br
(a) (3) > (2) > (1) > (4) > (5)
(b) (5) > (1) > (2) > (4) > (3)
(c) (1) > (3) > (5) > (2) > (4)
(d) (5) > (4) > (1) > (2) > (3)

96. Two isomeric alkenes (A) and (B) having molecular formula C_5H_9Cl on adding H_2, (A) gives optically inactive compound while (B) gives a chiral compound. The two isomers are:

(a) A is 1-chloro-1-pentene and B is 5-chloro-1-pentene
(b) A is 3-chloro-2-pentene and B is 1-chloro-2-pentene
(c) A is 4-chloro-1-pentene and B is 2-chloro-2-pentene
(d) A is 3-chloro-1-pentene and B is 4-chloro-2-pentene

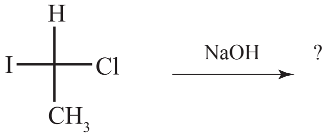
97. When 2,2-dimethylbutane is subjected to free-radical chlorination, __________ distinct monochlorinated products are possible and __________ of these contain asymmetric carbon atoms.

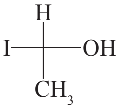
(a) 4, 2 (b) 4, 0
(c) 5, 0 (d) 5, 2

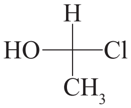
98. The relative reactivity of

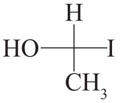
(I) Benzyl chloride
(II) p-methoxy benzyl chloride
(III) p-nitrobenzyl chloride
towards SN^1 reaction follows the order
(a) I > II > III (b) II > III > I
(c) II > I > III (d) III > II > I

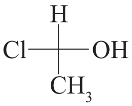
99. The product of the reaction given below is



(a) 

(b) 

(c) 

(d) 

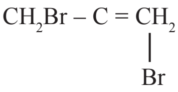
100. An alkyl chloride produces a single alkene on reaction with sodium ethoxide and ethanol. The alkene further undergoes hydrogenation to yield-2-methylbutane. Identify the alkyl chloride from amongst the following:
(a) $ClCH_2CH(CH_3)CH_2CH_3$
(b) $ClCH_2C(CH_3)_2CH_3$
(c) $ClCH_2CH_2CH_2CH_3$
(d) $CH_3C(Cl)(CH_3)CH_2CH_3$

101. Chloroethane reacts with Y to form NaCl and Z. One mole of Z reacts with two moles of HI to form water and iodoethane. Which of the following is Y?
(a) CH_3CHO (b) $C_2H_5OC_2H_5$
(c) C_2H_5ONa (d) CH_3COOH

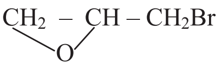
102. The rate for the substitution reaction of 2- bromobutane and HO^- in 75% ethanol 25 % water at 30°C is rate = 3.20×10^{-5} [2- bromobutane] [HO^-] + 1.5×10^{-6} [2- bromobutane]
What per cent of the reaction takes place by the S_N2 mechanism when:
a. $[HO^-] = 1.00$ M?
b. $[HO^-] = 0.001$ M?
(a) 96 % (b) 94 %
(c) 92 % (d) 93%

103. Allyl bromide, A is made to react with $Br_2(CCl_4)$ at 5°C. The product B is treated with NaOH to yield C. What is C?

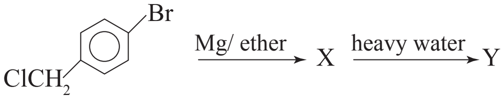
(a) $BrCH_2 – CH = CHBr$

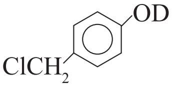
(b) 
$$CH_2Br-\underset{\substack{|\\ Br}}{C}=CH_2$$

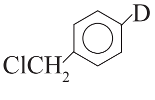
(c) $BrCH = C = CH_2$

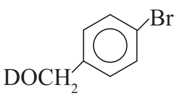
(d) 

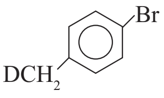
104. The final product X, Y obtained in this reaction is



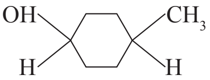
(a) 

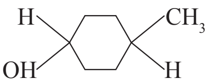
(b) 

(c) 

(d) 

105. 

(a) 

(b) 

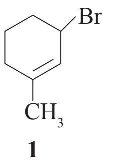
(c) Both (d) None

106. Bottles containing C_6H_5I and $C_6H_5CH_2I$ lost their original labels. They were labeled A and B for testing. A and B were separately taken in test tubes and boiled with NaOH solution. The end solution in each tube was made acidic with dilute HNO_3 and some $AgNO_3$. solution added. Solution B gave a yellow precipitate. Which one of the following statements is true for the experiment?
(a) A was $C_6H_5CH_2I$
(b) A was C_6H_5I
(c) B was C_6H_5I
(d) Addition of HNO_3 was unnecessary

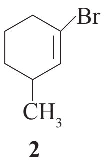
107. The decreasing order of reactivity of m-nitrobromobenzene (I); 2,4,6-trinitrobromo-benzene (II); p-nitrobromobenzene (III); and 2,4-dinitrobromobenzene (IV) towards OH^- ions is
(a) I > II > III > IV (b) II > IV > I > III
(c) II > IV > III > I (d) IV > II > III > I

108. Consider the following compounds:
I. DDT II. Gammexane
III. Carbon tetrachloride IV. chlorobenzene
The correct sequence of these compounds in the increasing order of percentage of chlorine in them is
(a) I, II, III, IV (b) IV, I, II, III
(c) IV, II, I, III (d) III, I, II, IV

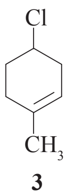
109. Rank the following molecules in order of increasing relative rate of S_N1 solvolysis with methanol and heat (slowest to fastest reacting).



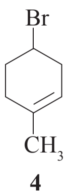
1



2



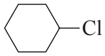
3

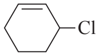


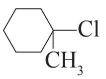
4

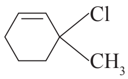
(a) 3 < 2 < 4 < 1 (b) 2 < 3 < 4 < 1
(c) 4 < 3 < 2 < 1 (d) 2 < 3 < 4 < 1

110. Which of the following compounds will be most reactive for SN^1 reactions?

(a) 

(b) 

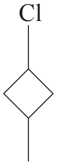
(c) 

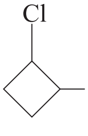
(d) 

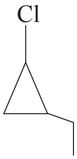
111. At higher temperature, iodoform reaction is given by:

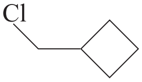
(a) $CH_3CO_2CH_3$ (b) $CH_3CO_2C_6H_5$
(c) $CH_3CO_2C_2H_5$ (d) $C_6H_5CO_2CH_3$

112. An unknown compound Ahas the formula C_5H_9Cl. It does not react with bromine in carbon tetrachloride. When treated with a strong base it produces a single compound, B, with the formula C_5H_8 that reacts with bromine in carbon tetrachloride. Ozonolysis of compound B, using ozone followed by dimethylsulfide, produces a compound with the formula $C_5H_8O_2$. Which of the following is the structure of A?

(a) 

(b) 

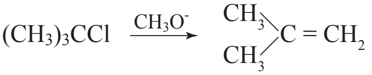
(c) 

(d) 

113. An alkyl bromide produces a single alkene when it reacts with sodium ethoxide and ethanol. This alkene on hydrogenation produces 2-methyl-butane. What is the identity of the alkyl halide?

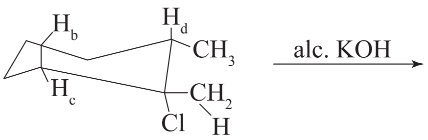
(a) 1-Bromo-2-methyl butane
(b) 2-Bromo-2-methyl butane
(c) 2-Bromopentane
(d) 1-Bromobutane

114. The reaction



$$(CH_3)_3CCl \xrightarrow{CH_3O^-} \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=CH_2$$

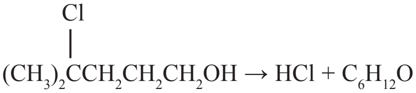
(a) S_N1 (b) S_N2
(c) E2 (d) E1

115. For 

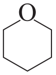
alkene (X), (X) contains:

(a) H_b, H_a, H_d but not H_c
(b) H_b, H_c, H_d but not H_a
(c) H_a, H_b, H_c but not H_d
(d) H_c, H_a, H_d but not H_b

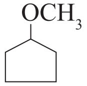
116. Formulate the structure of the most likely product of the following reaction of 4- chloro-4-methyl-1-pentanol in neutral polar solution.

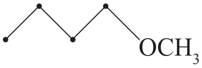


$$(CH_3)_2\overset{\overset{Cl}{|}}{C}CH_2CH_2CH_2OH \rightarrow HCl + C_6H_{12}O$$

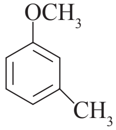
(a) 

(b) 

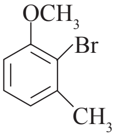
(c) 

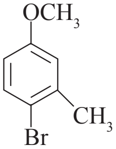
(d) 

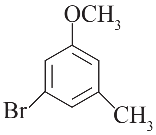
117. The major product obtained on the monobromination (with $Br_2/FeBr_3$) of the following compound A is

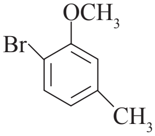


(A)

(a) 

(b) 

(c) 

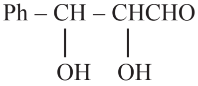
(d) 

118. Consider the following reaction,

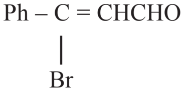
$$Ph\underset{\underset{Br}{|}}{CH} - \underset{\underset{Br}{|}}{CH}CHO \xrightarrow[\Delta]{K_2CO_3}$$

Here the structure of the major product is:

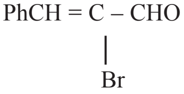
(a) $PhC \equiv CCHO$

(b) 

$$Ph - \underset{\underset{OH}{|}}{CH} - \underset{\underset{OH}{|}}{CH}CHO$$

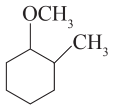
(c) 

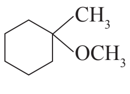
$$Ph - \underset{\underset{Br}{|}}{C} = CHCHO$$

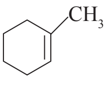
(d) 

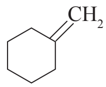
$$PhCH = \underset{\underset{Br}{|}}{C} - CHO$$

119. When (cis)-1-bromo-2 methylcyclohexane is treated with methanol and heat, four different products are formed–two by substitution and two by elimination.

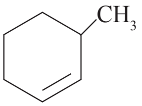








Which of the following conditions would change the outcome of this reaction by promoting the production of 3-methylhexene as the major product?

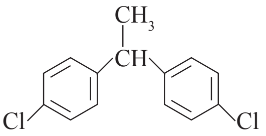


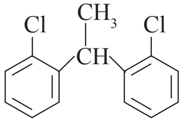
(a) KOH, ethanol and heat
(b) water/acetone and heat
(c) tert-butoxide/tert-butyl alcohol
(d) tert-butyl alcohol and heat

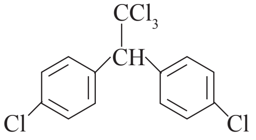
120. The reaction $CH_3Cl + OH^- \rightarrow CH_3OH + Cl^-$ is first order in both chloromethane and hydroxide. Given the rate constant $k = 3.5 \times 10^{-3}$ mol L $^{-1}$ s^{-1}, what is the observed rate at the following concentrations?
$[CH_3Cl] = 0.50$ mol L^{-1}; $[OH^-] = 0.015$ mol L^{-1}
(a) 2.6×10^{-6} mol L $^{-1}$s^{-1}
(b) 2.6×10^{-3} mol L $^{-1}$s^{-1}
(c) 1.75×10^{-3} mol L $^{-1}$s^{-1}
(d) 2.6×10^{-5} mol L $^{-1}$s^{-1}

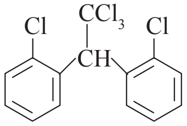
121. When 2- methylpentane undergoes single monochlorination. The total number of products formed and optically active ones are respectively
(a) 5, 2 (b) 5, 3
(c) 4, 2 (d) 4, 3

122. Which one of the following compound is the product of the reaction?

(a)


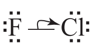
(b)


(c)


(d)


123. Only one of the following process will occur measurably at room temperature. Which one is that?

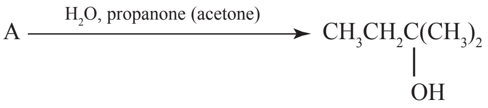
(a)


(b)


(c)

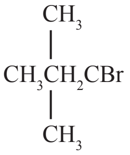

(d)


124. In this transformation



$$A \xrightarrow{H_2O,\ \text{propanone (acetone)}} CH_3CH_2\underset{\displaystyle OH}{\underset{|}{C}}(CH_3)_2$$

What is the best structure for A?

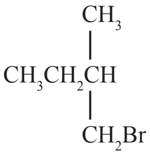
(a)


$$CH_3CH_2\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}Br$$

(b) $BrCH_2CH_2CH(CH_3)_2$

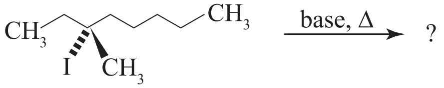
(c)


$$CH_3\underset{\displaystyle Br}{\underset{|}{C}}HCH(CH_3)_2$$

(d)


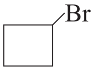
$$CH_3CH_2\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_2Br}{\underset{|}{C}}}}H$$

125. How many distinct alkene products are possible when the alkyl iodide below undergoes E2 elimination?



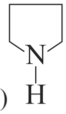
(a) 1
(b) 2
(c) 3
(d) 5

126. $NH_2(CH_2)_4Br$ when is heated one gets:

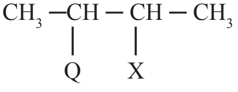
(a)


(b) $NH_2(CH_2)_8NH_2$

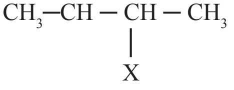
(c) $NH_2(CH_2)_2CH = CH_2$

(d)


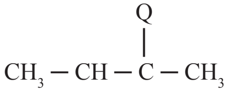
127. The correct order of S_N2/E2 ratio for the % yield of product of the following halide is
(I) $CH_3 - CH_2 - X$

(II)


$$CH_3 - \underset{\displaystyle Q}{\underset{|}{C}}H - \underset{\displaystyle X}{\underset{|}{C}}H - CH_3$$

(III)


$$CH_3 - CH - \underset{\displaystyle X}{\underset{|}{C}}H - CH_3$$

(IV)


$$CH_3 - CH - \overset{\displaystyle Q}{\overset{|}{C}} - CH_3$$

(a) I > III > II > IV

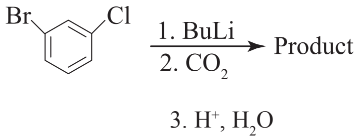
(b) I > II > III > IV
(c) III > I > II > IV
(d) IV > II > I > III

128. Which reaction intermediate is involved in the following reaction?

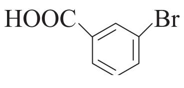
2- methylbutane $\xrightarrow{Br_2,\ hv}$ 2- bromo -3-methylbutane
(not the major product)

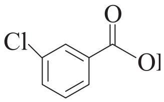
(a) A tertiary carbocation
(b) A secondary carbocation
(c) A tertiary radical
(d) A secondary radical

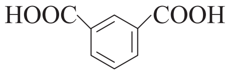
129.



Here the product is?

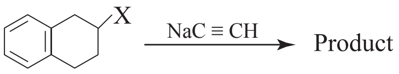
(a)


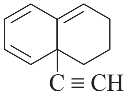
(b)


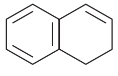
(c)


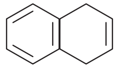
(d) All of these

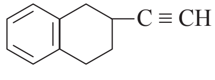
130. What are the probable products formed in this reaction?



(I)


(II)


(III)


(IV)


(a) I , III, IV
(b) II , III , IV
(c) II, IV
(d) III, IV

Decisive Thinking Objective Type Questions (One or more than one choice)

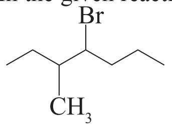
131. Which of the following is/are true about S_N2 reactions?

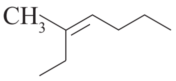
(a) They follow a two -step bimolecular mechanism
(b) They do not undergo rearrangements.
(c) Methyl and primary substrates react faster than secondary and tertiary substrates.
(d) The rate of the reactions depend on both the substrate and nucleophile concentration.

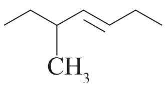
132. Which of the following statements correctly describe(s) E1 reactions of alkyl halides (RX)?

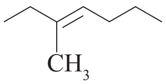
(a) Rearrangements are sometimes seen
(b) Rate = k[base][RX]
(c) Rate = k[RX]
(d) The reactions occur in two or more distinct steps

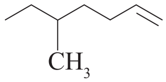
133. In the given reaction the products formed can be:



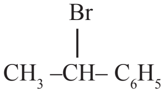
(a)


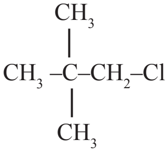
(b)


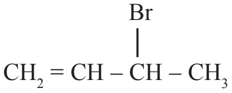
(c)


(d)


134. Which of the following compounds will give SN^1 reaction in polar protic solvent:

(a)

$CH_3-\underset{}{\overset{Br}{\overset{|}{C}}}H-C_6H_5$

(b)

$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-Cl$

(c)

$CH_2 = CH - \overset{\overset{Br}{|}}{CH} - CH_3$

(d) CH_3Cl

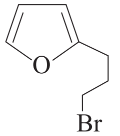
135. In which of the following, order is/are correct?

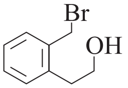
(a) MeBr > Me$_2$CHBr>(Me)$_3$C─Br >Et$_3$C─Br(S_N2)
(b) MeI > MeBr > MeCl > MeF(S_N2)
(c) PhCH$_2$Br > PhCHBrMe > PhCBrMe$_2$ > PhCBrMePh(S_N1)
(d) Me$_3$CBr > MeCHBr > Me$_2$CHCH$_2$Br > MeCH$_2$CH$_2$CH$_2$Br (E2)

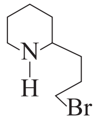
136. Which of the following phrases are correctly linked with S_N1 reaction?

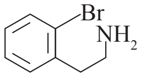
(a) Rate is affected by polarity of solvent
(b) Rearrangement is possible
(c) The strength of the nucleophile is important in determining rate
(d) The reactivity series is tertiary > secondary > primary

137. Which of the following substrates can not give intramolecular SN^2 reaction?

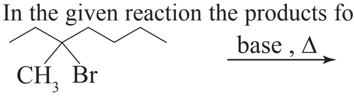
(a) 

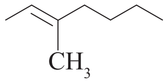
(b) 

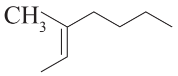
(c) 

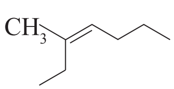
(d) 

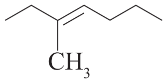
138. In the given reaction the products formed can be



(a) 

(b) 

(c) 

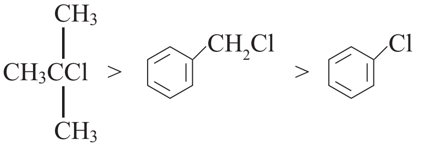
(d) 

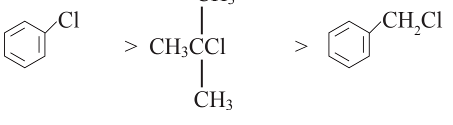
139. Which of the following statements about benzyl chloride is/are correct?

(a) It is a lachrymatory liquid and answers Beilstein's test.
(b) It gives a white precipitate with alcoholic silver nitrate.
(c) It is less reactive than alkyl halides.
(d) It can be oxidized to benzaldehyde by boiling with copper nitrate solution.

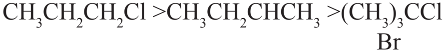
140. Which of the following order is/are correct here?

S_N1 reactivity:

(a) 

(b) 

SN^2 reactivity:

(c) 

$CH_3CH_2CH_2Cl > CH_3CH_2\overset{\displaystyle Cl}{\overset{|}{C}}HCH_3 > (CH_3)_3CCl$

SN^2 reactivity:

(d) 

$CH_3Br > (CH_3)_2CHCH_2Br > (CH_3)_2CH\overset{\displaystyle Br}{\overset{|}{C}}HCH_3$

141. The incorrect is/are:

(a) $(CH_3)_3CBr + CN^- \rightarrow E1$
(b) $(CH_3)_3CBr + H_2O \rightarrow E2$
(c) $CH_3CHBrCH_3 + O^-H \rightarrow SN^2$
(d) $CH_3CH_2CH_2Cl + I^- \rightarrow S_N1$

142. Select the correct statements:

(a) CH_3CH I. CH_3 is a secondary alkyl halide
(b) Acetylene is formed when $CH_2 = CH - Cl$ is heated with water.
(c) Iodoform gives a precipitate with $AgNO_3$ solution on heating whereas chloroform does not.
(d) Freon (CCl_2F_2) is prepared by the action of CCl_4 and SbF_3 in the presence of $SbCl_5$ as a catalyst.

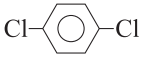
143. Which of the following compounds is/are chiral?

(a) 2-chloropentane
(b) 1-chloropentane
(c) 3-chloro-2-methylpentane
(d) 1-chloro-2-methylpentane

144. Which one of the following is/are correct order of boiling points of the alkyl/aryl halides?

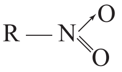
(a) $CH_3(CH_2)_3Cl > CH_3(CH_2)_2Cl$
(b) $(CH_3)_3CCl > (CH_3)_2CHCH_2Cl$
(c) $CHCl_3 > CH_2Cl_2$
(d) $C_6H_5Br > C_6H_5Cl$

145. Consider the following halogen containing compounds

(a) $CHCl_3$ (b) CCl_4
(c) CH_2Cl_2 (d) 

The compounds with a net zero dipole moment are

146. Which of the following pair is correctly matched?

	Reaction	Product
(a)	RX + AgCN	RNC
(b)	RX + KCN	RCN
(c)	RX + KNO_2	
(d)	RX + $AgNO_2$	R – O – N = O

147. The products of reaction of alcoholic silver nitrile with ethyl bromide are

(a) Ethyl alcohol (b) Ethene
(c) Nitroethane (d) Ethyl nitrile

148. In which of the following reactions, the given product is/are according to expectation?

(a) $Me_3CO^- K^+ + MeBr \xrightarrow{Me_3COH} Me_3COMe$

(b) $t\text{-}BuBr + KCN \xrightarrow{EtOH–H_2O} Me_2C = CH_2$

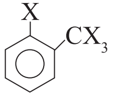
(c) $n\text{-}BuBr + KCN \xrightarrow{EtOH–H_2O} n\text{-}BuCN$

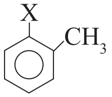
(d) $Me_3CBr + MeO^- K^+ \xrightarrow{MeOH} Me_3COMe$

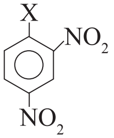
149. Aryl halides are less reactive towards nucleophilic substitution reactions as compared to alkyl halides due to:

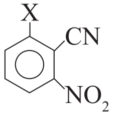
(a) The formation of less stable carbonium ion
(b) Resonance stabilization
(c) Longer carbon-halogen bond
(d) sp^2 – Hybridised carbon attached to halogen.

150. In which of the following compounds X- atom can be easily substituted by a stronger nucleophile?

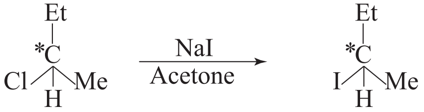
(a) 

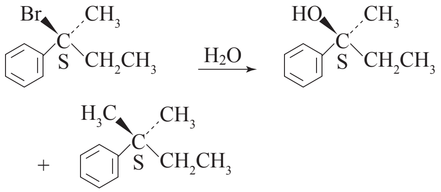
(b) 

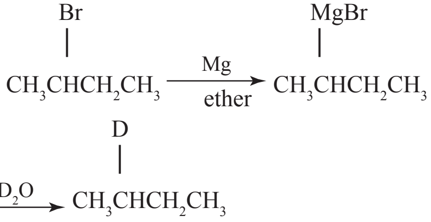
(c) 

(d) 

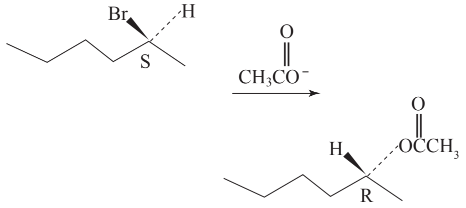
151. Which of the following reactions is/are not correct?

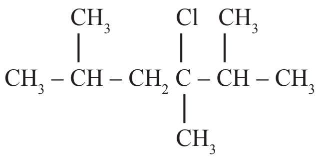
(a) 

(b) 

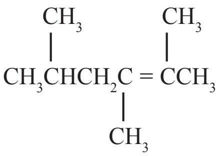
(c) 

$CH_3\underset{}{\overset{Br}{C}}HCH_2CH_3 \xrightarrow[\text{ether}]{Mg} CH_3\overset{MgBr}{C}HCH_2CH_3 \xrightarrow{D_2O} CH_3\overset{D}{C}HCH_2CH_3$

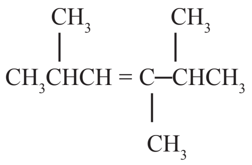
(d) 

152. 

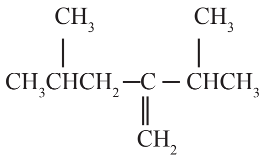
$CH_3-\overset{CH_3}{CH}-CH_2\,\underset{CH_3}{\overset{Cl}{C}}-\overset{CH_3}{CH}-CH_3$

(a) 

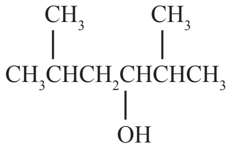
$CH_3\overset{CH_3}{C}HCH_2\underset{CH_3}{C}=\overset{CH_3}{C}CH_3$

(b) 

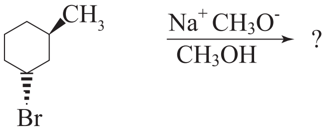
$CH_3\overset{CH_3}{C}HCH=\underset{CH_3}{C}-\overset{CH_3}{C}HCH_3$

(c) 

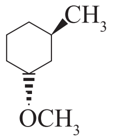
$CH_3\overset{CH_3}{C}HCH_2-\underset{CH_2}{\underset{\|}{C}}-\overset{CH_3}{C}HCH_3$

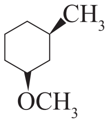
(d) 

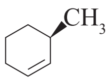
$CH_3\overset{CH_3}{C}HCH_2\underset{OH}{C}H\overset{CH_3}{C}HCH_3$

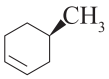
153. 

Here the product can be?

(a) 

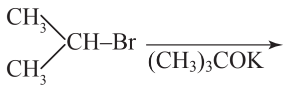
(b) 

(c) 

(d) 

154. Which of the following statements are correct here?

(a) $CH_3Br \xrightarrow[\text{in aq. HCOOH}]{-OH}$ can show S_N1 reaction

(b) 

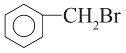
follow Hoffmann's rule

(c) Walden inversion is always by S_N1 mechanism

(d) $R-X \xrightarrow[\text{Acetone}]{\text{NaI}}$ S_N2 mechanism is followed

155. Which of the following statements are correct here?

(a) $Cl-CH_2-O-C_2H_5$ shows S_N1 mechanism Reactions

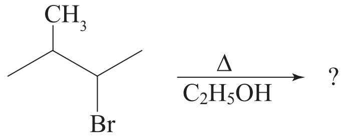
(b) 

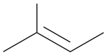
can show S_N1 mechanism Reactions also

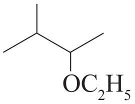
(c) S_N1 reactions are favoured by steric factors

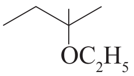
(d) S_N2 reactions are stereo specific and stereo selective

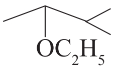
156.



(a) 

(b) 

(c) 

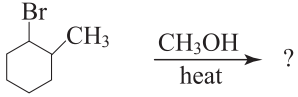
(d) 

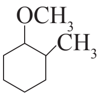
157. 

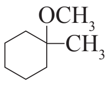
Which of the following is/are correct here regarding this reaction?

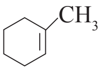
(a) It is a free radical addition reaction
(b) Here product is γ- Lindane
(c) It is an explosive reaction
(d) The product is a famous insecticide

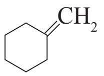
158. When1-bromo-2-methylcyclohexane undergoes solvolysis in methanol, the major product formed are?



(a) 

(b) 

(c) 

(d) 

Linked-Comprehension Type Questions

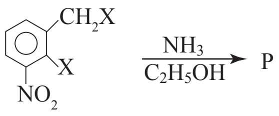
Comprehension 1

Allyl halides have extremely very low reactivity towards nucleophillic substitution reactions mainly because of

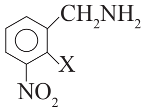
(1) Resonance stabilization of (= bond) between C and X atoms.
(2) Sp^2 hybridisation states of cabon atom.
(3) Un stability of phenyl cation (no S_N1 is possible).
(4) Repulsion between nucleophile and electron rich arenes.

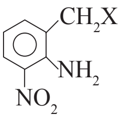
The presence of a strong electron withdrawing group like $-NO_2$ at ortho and para position facilitates the attack of nucleophile on haloarenes. As the carbanion formed here is stabilized by resonance.

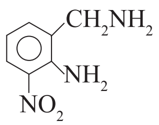
159.

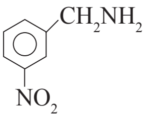


Here (P) can be given as:

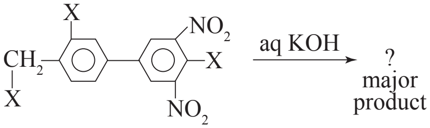
(a) 

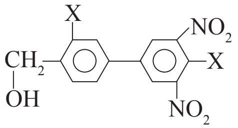
(b) 

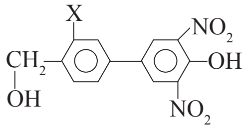
(c) 

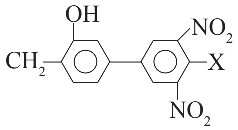
(d) 

160. Here the product can be?



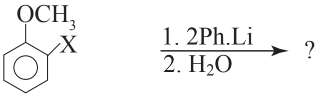
(a) 

(b) 

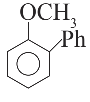
(c) 

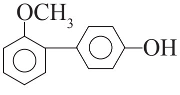
(d) None of these

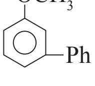
161.

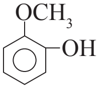


Here product formed is?

(a) 

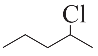
(b) 

(c) 

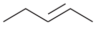
(d) 

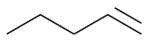
Comprehension 2

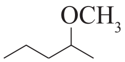
Halides undergo nucleophillic substitution and elimination reactions and form organometallic compounds. Through these reactions, a variety of useful classes of organic compounds can be prepared. The C– X bond being polar is the site for nucleophillic substitution reactions, which can take place by S_N2 or S_N1 mechanism depending upon the structure of the halide and reaction conditions. Halides containing C^{sp2}-X bond are unreactive under comparable conditions. Electron withdrawing groups at ortho and para positions increase the reactivity of aryl halides in nucleophillic substitution reactions.

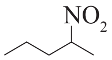
162.  $\xrightarrow[CH_3OH]{AgNO_3}$?

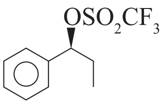
Here the major product is?

(a) 

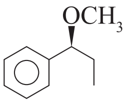
(b) 

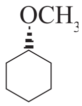
(c) 

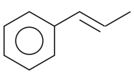
(d) 

163.  $\xrightarrow[CH_3OH]{\Delta}$ Product?

Here the product formed is?

(a) 

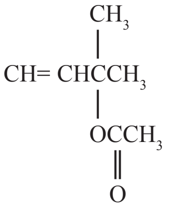
(b) 

(c) 

(d) All of these

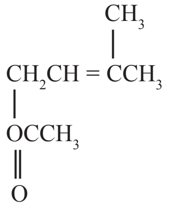
164. 3- Bromo -3-methyl -1- butene forms two substitution products when it is added to a solution of sodium acetate in acetic acid. Select the correct statements:

(1) Here reaction is carried out by S_N1 mechanism
(2) Sodium acetate is a stronger nucleophile
(3) The kinetically controlled product is



$$CH{=}CH\overset{\displaystyle CH_3 \atop |}{\underset{| \atop \displaystyle OCCH_3 \atop \| \atop O}{C}}CH_3$$

(4) The thermodynamically controlled product is



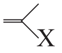
$$\underset{| \atop \displaystyle OCCH_3 \atop \| \atop O}{CH_2}CH = \overset{\displaystyle CH_3 \atop |}{C}CH_3$$

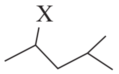
(a) 1, 2, 4
(b) 1, 3, 4
(c) 3, 4
(d) 1, 2, 3

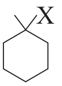
Comprehension 3

Water, alcohol can serve as not only solvents but also as nucleophiles. When a solvent can act like a nucleophile the reaction is called solvolysis. It is a case of nucleophillic reaction which can take place by either S_N1 or S_N2 mechanisms. If solvent is polar and halides is tertiary or secondary S_N1 mechanism is followed but if it is a primary halide S_N2 mechanism if favoured.

165. Which of the following shows the correct decreasing order of solvolysis with aqueous ethanol?

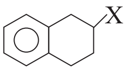
(1) 

(2) 

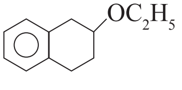
(3) 

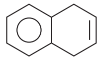
(4) 

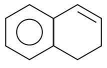
(a) 3 > 2 > 1 > 4
(b) 3 > 2 > 4 > 1
(c) 2 > 3 > 4 > 1
(d) 3 > 1 > 4 > 2

166.  $\xrightarrow[C_2H_5ONa]{\Delta}$ (P) major product

Here (P) is?

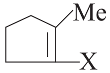
(a) 

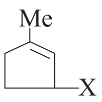
(b) 

(c) 

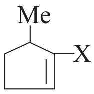
(d) Both B and C

167. Which of these compounds can undergo solvolysis by S_N1 mechanism most fast here?

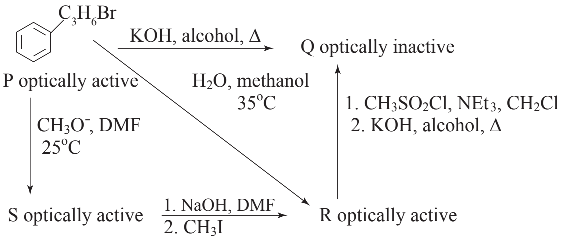
(a) 

(b) 

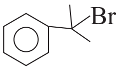
(c) 

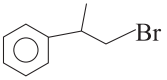
(d) 

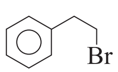
Comprehension 4

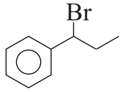


168. Here the compound (P) can be?

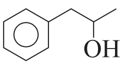
(a) 

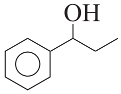
(b) 

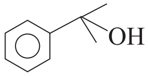
(c) 

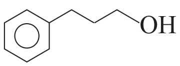
(d) 

169. Here compound (R) can be given as?

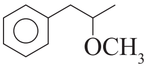
(a) 

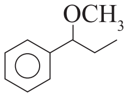
(b) 

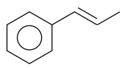
(c) 

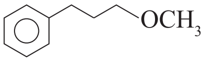
(d) 

170. Here the compound S can be given as?

(a) 

(b) 

(c) 

(d) 

Assertion-Reason Type Questions

In the following question two statements (Assertion) A and Reason (R) are given Mark.

(a) if A and R both are correct and R is the correct explanation of A;
(b) if A and R both are correct but R is not the correct explanation of A;
(c) A is true but R is false;
(d) A is false but R is true,

171. **(A):** The effect of electron withdrawing group at ortho and para position increases the reactivity of haloarenes but at meta position
(R): As at meta position negative charge can not be stabilized by such a group in any resonating structure

172. **(A):** Alkyl iodides darken on standing.
(R): Alkyl iodides are prepared by Finkelstein reaction.

173. **(A):** 2-chloro-3-methylbutane on treatment with alcoholic potash gives 2-methyl-butene-2 as major product.
(R): The reaction occurs according to Saytzeff rule.

174. **(A):** Primary benzylic halides are more reactive than primary alkyl halides towards SN^1 reactions.
(R): Reactivity depends upon the nature of the nucleophile and the solvent.

175. **(A):** Isopropyl chloride is more reactive than CH_3Br in SN^2 reactions.
(R): SN^2 reactions are always accompanied by inversion of configuration.

176. **(A):** o-dichloro benzene has higher metlting point than p-dichloro-benzene.
(R): Stronger the Van der Waal's forces of attraction, higher is the melting point.

177. **(A):** Addition of Br_2 to cis-but-2-ene is stereoselective.
(R): SN^2 reactions are stereospecific as well as stereoselective.

178. **(A):** SN^2 reaction of an optically active alkyl halide with an aqueous solution of KOH gives an alcohol with opposite sign of rotation.
(R): SN^2 reactions proceed with inversion of configuration.

179. **(A):** Benzyl chloride is more reactive than p-chlorotoluene towards aqueous NaOH.
(R): The C – Cl bond in benzyl chloride is more polar than C – Cl bond in p-chlorotoluene.

180. **(A):** Tertiary haloalkanes are more reactive than primary haloalkanes towards elimination reactions.
(R): The +I-effect of the alkyl gropus weakens the C – X bond.

181. **(A):** Rate of reaction is dependent only on the concentration of nucleophile in SN^1 reactions.
(R): Polar solvent favours SN^1 reaction.

182. **(A):** The carbon halogen bond in an aryl halide is shorter than the carbon halogen bond in an alkyl halide.
(R): A bond formed of an sp^3 orbital should be shorter than the corresponding bond involving an sp^2 orbital.

183. **(A):** SN^2 reaction of CH_3 – Br is faster in DMSO than in H_2O.
(R): DMSO has greater capability to solvate nucleophile.

184. **(A):** In SN^1 mechanism, the product with inversion of configuration is obtained in higher amount compared to the product with the retention of configuration.

(R): Front side attack of nucleophile is hindered due to the presence of leaving group in the vicinity.

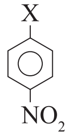
185. **(A):** Bromobenzene upon reaction with Br_2/Fe gives 1, 4-dibromobenzene as the major product.

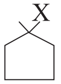
(R): In bromobenzene, the inductive effect of the bromo group is more dominant than the mesomeric effect in directing the incoming electrophile. **[IIT 2008]**

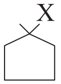
Matrix-Match Type Questions

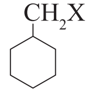
186. Match The following:

Column I

(a)  $\xrightarrow[FeX_3]{X_2}$

(b)  $\xrightarrow[KOH]{alc}$

(c)  $\xrightarrow[KOH]{aq}$

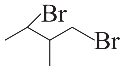
(d)  $\xrightarrow[KOH]{aq}$

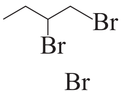
Column II

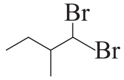
(p) S_N2
(q) S_N1
(r) E_1
(s) Electrophilic substitution

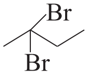
187. Match the following:

Column I

(a) 

(b) 

(c) 

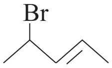
(d) 

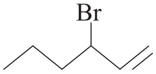
Column II

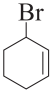
(p) Gem di- halide
(q) Vic di- halide
(r) Optically active
(s) Isomer of 1,3 -di butane

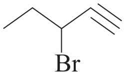
188. Match the following:

Column I

(a) 

(b) 

(c) 

(d) 

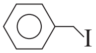
Column II

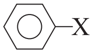
(p) Can show geometrical isomerism
(q) Can show optical isomerism
(r) If C^+ is formed it will be resonance stabilized
(s) On heating with alk. KOH gives penta 1, 3 di-ene

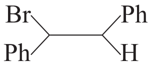
189. Match the following:

List I (Compounds)

(a) $(CH_3)_3CX$

(b) 

(c) 

(d) 

List II (Properties indicated)

(p) Fairly reactive towards E_2
(q) White precipitate with aqueous $AgNO_3$
(r) Yellow precipitate with $AgNO_3$
(s) Unreactive towards SN reactions
(t) Fairly reactive towards SN reactions

190. Match the following:

Column I (Reactants)

(a) $CH_3(CH_2)_3OH \xrightarrow{NaBr,\ H_2SO_4,\ \Delta}$

(b) $(CH_3)_3COH \xrightarrow[\text{room temp.}]{\text{Conc. HCl}}$

(c) $CH_3CH(OH)(CH_2)_2CH_3 \xrightarrow{PBr_3}$

(d) $Me_2CHCH_2OH \xrightarrow{SOCl_2}$

Column II (Alkyl halides)

(p) $CH_3CHBr(CH_2)_2CH_3$
(q) Me_2CHCH_2Cl
(r) $(CH_3)_3CCl$
(s) $CH_3(CH_2)_3Br$

191. Match the following:

List I

(Halo alkane)

(a) Iodoform

(b) BHC

(c) Freon-14

(d) Halothanes

List II

(applications)

(p) CF_4

(q) antiseptic

(r) moth repellent

(s) inhalative anesthetic

(t) termite pesticide

192. Match the following:

Column I (Reactants)

(a) $CH_3CH_2CH_2CH_2Br$ + alc. KOH

(b) $CH_3CH_2CH(Br)CH_3$ + alc. KOH

(c) $(CH_3)_3CBr$ + alc. KOH

(d) $CH_3CH_2CH_2CH_2Br$ + aq. KOH

Column II (Products)

(p) butan-2-ol

(q) trans-but-2-ene

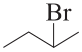
(r) but-1-ene

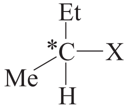
(s) 2-methylprop-1-ene

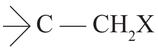
(t) α, β -elimination

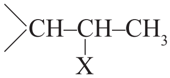
193. Match the following:

Column I

(a)  $\xrightarrow{\text{aq. KOH}}$?

(b)  $\xrightarrow[\text{Acetone}]{\text{NaI}}$?

(c)  $\xrightarrow{\text{aq. KOH}}$?

(d)  $\xrightarrow[\text{alc. KOH}]{\Delta}$?

Column II

(p) S_N1

(q) E_1

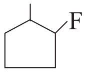
(r) S_N2

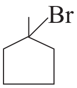
(s) Methyl shift

(t) Change of configuration

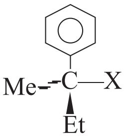
194. Match the following:

Column I

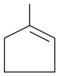
(a)  $\xrightarrow{\text{alc. KOH}}$

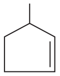
(b)  $\xrightarrow{\text{alc. KOH}}$

(c) $CH_3-CHDCl \xrightarrow{OH}$

(d)  $\xrightarrow{H_2O}$

Column II

(p) 

(q) 

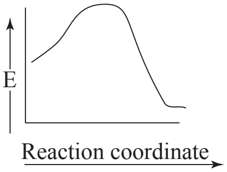
(r) S_N2

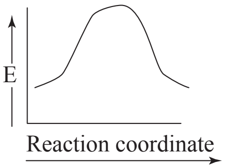
(s) S_N1

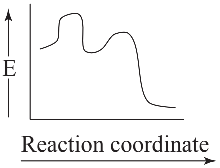
(t) Racemisation

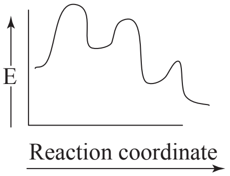
195. Which of the following is/are correctly matched?

Column I

(a) 

(b) 

(c) 

(d) 

Column II

(p) $(CH_3)_3CCl + (C_6H_5)_3P \rightarrow$

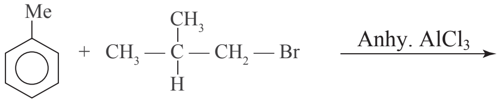
(q) $(CH_3)_2CHI + KBr \rightarrow$

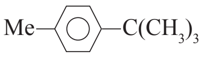
(r) $(CH_3)_3CBr + HOCH_2CH_3 \rightarrow$

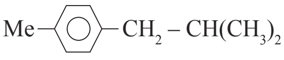
(s) $CH_3CH_2Br + NaOCH_2CH_3 \rightarrow$

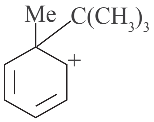
The IIT-JEE Corner

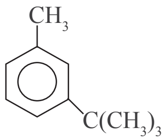
196. Select the correct product in the reaction:



(a) 

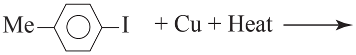
(b) 

(c) 

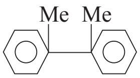
(d) 

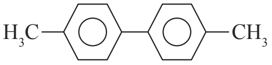
[IIT 1997]

197. The product in the reaction:



is

(a) 

(b) 

(c) 

(d) none **[IIT 1997]**

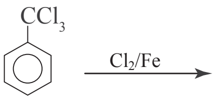
198. The major product in the reaction:

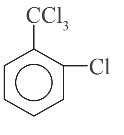
$CH_3 - CH_2 - Br \xrightarrow{AgCN}$, is

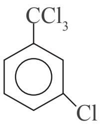
(a) $CH_3 - CH_2 - CN$ (b) $CH_3 - CH_2Ag$
(c) $CH_3 - CH_2NC$ (d) None

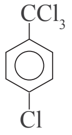
[IIT 1997]

199. Predict the major product.



(a) 

(b) 

(c) 

(d) all the three

[IIT 1997]

200. In the reaction of p-chlorotoluene with KNH_2 in liquid NH_3, the major product is

(a) o-toluidine (b) m-toluidine
(c) p-toluidine (d) p-chloroaniline.

[IIT 1997]

201. During debromination of meso-dibromobutane, the major compound formed is

(a) n-butane (b) 1-butane
(c) cis-2-butene (d) trans-2-butene.

[IIT 1997]

202. Which of the following will react with water:

(a) $CHCl_3$ (b) Cl_3CCHO
(c) CCl_4 (d) $ClCH_2CH_2Cl$

[IIT 1998]

203. Toluene when treated with Br_2/Fe, gives p-bromotoluene as the major product because the methyl group

1. is para-directing
2. is m-directing
3. activates the ring by hyperconjugation
4. deactivates the ring

(a) 1, 3 (b) 1, 2, 3
(c) 1, 2 (d) none

[IIT 1999]

204. A solution of (+)–2-chloro-2-phenylethane in toluene racemises slowly in the presence of small amount of $SbCl_5$, due to the formation of

(a) carbanion (b) carbene
(c) free radical (d) carbocation

[IIT 1999]

205. The order of reactivities of the following alklyl halides for a SN^2 reaction is

(a) RF > RCl > RBr > RI
(b) RF > RBr > RCl > RI
(c) RCl > RBr > RF > RI
(d) RI > RBr > RCl > RF

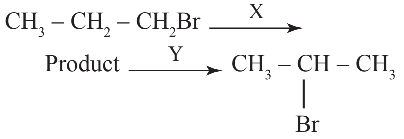
[IIT 2000]

206. An SN^2 reaction at an asymmetric carbon of a compound always gives

(a) an enantiomer of substrate
(b) a product with opposite optical rotation
(c) a mixture of diastereomers
(d) a single stereoisomer

[IIT 2001]

207. Identify the set of reagents/reaction conditions 'X' and 'Y' in the following set of transformations



$$CH_3-CH_2-CH_2Br \xrightarrow{X} \text{Product} \xrightarrow{Y} CH_3-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_3$$

(a) X = dilute aqueous NaOH, 20°C ;
Y = HBr/acetic acid, 20°C.

(b) X = concentrated alcoholic NaOH, 80°C ;
Y = HBr/acetic acid, 20°C.

(c) X = dilute aqueous NaOH, 20°C ;
Y = $Br_2/CHCl_3$, 0°C.

(d) X = concentrated alcoholic NaOH, 80°C ;
Y = $Br_2/CHCl_3$, 0°C.

[IIT 2002]

208. $CH_3NH_2 + CHCl_3 + KOH \rightarrow$ Nitrogen containing compound + KCl + H_2O. Nitrogen containing compound is. **[IIT 2006]**

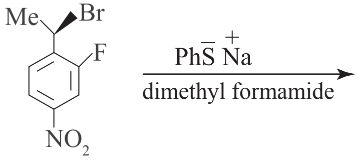
(a) $CH-C\equiv N$

(b) $CH_3-NH-CH_3$

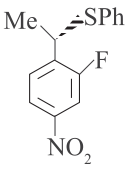
(c) $CH_3-\overset{-}{N}\equiv\overset{+}{C}$

(d) $CH_3\overset{+}{N}\equiv\overset{-}{C}$

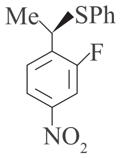
209. The major product of the following reaction is **[IIT 2008]**



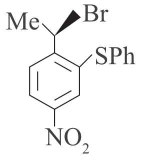
(a)



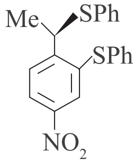
(b)



(c)



(d)



ANSWERS

Straight Objective Type Questions

1. (b) **2.** (a) **3.** (a) **4.** (b) **5.** (d) **6.** (b) **7.** (a) **8.** (a) **9.** (b) **10.** (b) **11.** (c) **12.** (d)
13. (b) **14.** (a) **15.** (b) **16.** (d) **17.** (d) **18.** (d) **19.** (a) **20.** (d) **21.** (a) **22.** (b) **23.** (a) **24.** (a)
25. (c) **26.** (d) **27.** (b) **28.** (d) **29.** (b) **30.** (b) **31.** (c) **32.** (a) **33.** (c) **34.** (a) **35.** (b) **36.** (b)
37. (c) **38.** (b) **39.** (b) **40.** (d) **41.** (c) **42.** (c) **43.** (d) **44.** (b) **45.** (b) **46.** (d) **47.** (d) **48.** (d)
49. (b) **50.** (b) **51.** (d) **52.** (b) **53.** (a) **54.** (c) **55.** (c) **56.** (c) **57.** (b) **58.** (b) **59.** (b) **60.** (d)
61. (c) **62.** (b) **63.** (b) **64.** (b) **65.** (b) **66.** (a) **67.** (d) **68.** (c) **69.** (d) **70.** (d) **71.** (b) **72.** (b)
73. (b) **74.** (d) **75.** (a) **76.** (a)

Brainteasers Objective Type Questions

77. (b) **78.** (b) **79.** (c) **80.** (b) **81.** (a) **82.** (a) **83.** (b) **84.** (b) **85.** (d) **86.** (c) **87.** (a) **88.** (b)
89. (d) **90.** (c) **91.** (d) **92.** (b) **93.** (c) **94.** (b) **95.** (a) **96.** (d) **97.** (a) **98.** (c) **99.** (d) **100.** (a)
101. (c) **102.** (a) **103.** (b) **104.** (d) **105.** (b) **106.** (b) **107.** (c) **108.** (b) **109.** (b) **110.** (d) **111.** (c) **112.** (a)
113. (a) **114.** (c) **115.** (c) **116.** (b) **117.** (b) **118.** (d) **119.** (c) **120.** (d) **121.** (b) **122.** (c) **123.** (a) **124.** (a)
125. (d) **126.** (d) **127.** (a) **128.** (d) **129.** (b) **130.** (b)

Decisive Thinking Objective Type Questions

131. (b), (c), (d) **132.** (a), (c), (d) **133.** (a), (b), (c) **134.** (a), (b), (c) **135.** (a), (b), (d)
136. (a), (b), (d) **137.** (a), (d) **138.** (a), (b), (c), (d) **139.** (a), (b), (d) **140.** (a), (c), (d)
141. (a), (c), (d) **142.** (a), (c), (d) **143.** (a), (c), (d) **144.** (a), (c), (d) **145.** (b), (d)
146. (a), (b) **147.** (c), (d) **148.** (a), (b), (c) **149.** (b), (d) **150.** (a), (c), (d)
151. (b), (c), (d) **152.** (a), (b, (c) **153.** (a), (b), (c), (d) **154.** (a), (b), (d) **155.** (a), (b), (d)
156. (a), (b), (d) **157.** (a), (b), (d)

Linked-Comprehension Type Questions

Comprehension 1-5

159. (c) **160.** (b) **161.** (c) **162.** (b) **163.** (d) **164.** (b) **165.** (b) **166.** (c) **167.** (c) **168.** (d) **169**. (b) **170.** (b)

Assertion-Reason Type Questions

171. (a) **172.** (c) **173.** (a) **174.** (b) **175.** (d) **176.** (d) **177.** (b) **178.** (a) **179**. (a) **180.** (b)
181. (d) **182**. (c) **183.** (c) **184.** (a) **185.** (c)

Matrix-Match Type Questions

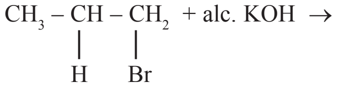
186. (a)- (s), (b) - (r), (c)- (q), (d)- (p)
187. (a)- (q, r), (b)- (q, r, t), (c)- (p, r), (d)- (p, t)
188. (a)- (p, q, r), (b)- (q, s, r), ((c))- (p, q, r), (d)- (q)
189. (a)- (t), b-(r, t), (c)-(s), (d)-(p, t)
190. (a)- (s), (b)- (r), (c)- (p), (d)- (q)
191. (a)- (q), (b)- (t), (c)- (p), (d)- (s),
192. (a)- (r, t), (b)- (q, t), (c)- (s, t), (d)- (p)
193. (a)- (p), (b)- (r, t), (c)- (q, s), (d)- (q)
194. (a)- (q), (b)- (p), (c)- (r), (d)- (s, t)
195. (a) -(s), (b)-(q), (c)- (p), (d) (r)

The IIT-JEE Corner

196. (a) **197.** (b) **198.** (c) **199.** (b) **200.** (b) **201.** (d) **202.** (b) **203.** (a) **204.** (d) **205.** (d) **206.** (d) **207.** (b)
208. (d) **209.** (a)

HINTS AND EXPLANATIONS

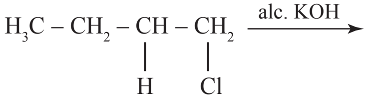
Straight Objective Type Questions

1. 

$CH_3-\underset{H}{CH}-\underset{Br}{CH_2}$ + alc. KOH $\rightarrow$

$CH_3-CH=CH_2+KBr+H_2O$

2. The solvolysis of t-butyl chloride follows an S_N1 mechnasim. The transition state is polar because of the ionization of t-butyl chloride; thus the best solvent for solvolysis is the most polar (has the highest dielectric constant), water.

3. 

$H_3C-CH_2-\underset{H}{CH}-\underset{Cl}{CH_2}\xrightarrow{\text{alc. KOH}}$

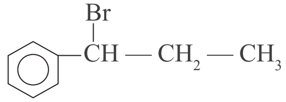
$CH_3-CH_2-CH=CH_2+KCl+H_2O$

But-1-ene

4. For a given alkyl group boiling point increases with the increase in the atomic mass of the halogen atom present.

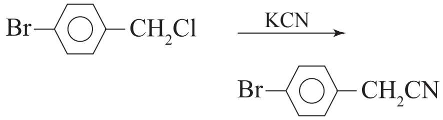
7. Iodobenzene has the highest boiling point because it has the greatest number of polarizable electrons, which produces the strongest London forces.

9. Bromination (electrophillic substitution) of side chain occurs at the benzylic position (the one α to Ph) giving the product.



11. CH_3OH does not give iodoform.

12.



4-bromobenzyl cyanide

13. $SOCl_2$ is the only listed reagent that will effect this conversation. (Alcohol reaction)

14. Acetate, CH_3COO^-, is a weak base and thus would not initiate an elimination reaction. All of the other bases listed are strong bases that yield high percents of the elimination products, propene.1

15. The reaction occurs by activated nucleophillic substitution.

17. OH^- is the best nucleophile because it is the strongest base listed. Neucleophilicity often parallels basicity.

20. 3- methylcycloxene is the only product of the reaction because of the position of the methyl group. For E2 dehydrohalogenation to occurs, the H atom that is removed must be anti-coplanar to the halogen atom. The methyl group prevents the removal of the H atom that would produce 1- mehylcyclohexene.

21. Only 1° alkyl halides, that is, CH_3Br undergoes SN^2 reaction.

22. In presence of heat and light, toluene undergoes side chain bromination.

$$C_6H_5CH_3\xrightarrow{Br_2,\ hv}C_6H_5CH_2Br$$

23. $(p-Cl-C_6H_4-)_2CH-CCl_3\longrightarrow$

$(p-Cl-C_6H_4-)_2C=CCl_2+HCl$

p, p'-dichlorodiphenyldichloroethene

24. At high temperature that is, 400°C substitution occurs in preference to addition.

$$CH_3CH=CH_2\xrightarrow[-HCl]{Cl_2,\ 400^oC}ClCH_2CH=CH_2$$

25. The conversion of 2,3-dibromobutane to 2-butene with Zn and alcohol is β-elimination.

$$CH_3-\underset{\beta}{CHBr}-\underset{\alpha}{CHBr}-CH_3\xrightarrow[-ZnBr_2]{\text{Zn/alcohol}}$$

$CH_3-CH=CH-CH_3$

2-Butene

28. Both the retention and inversion of configuration.

29. Reactivity decreases in the order: allylic > 2° > 1° halides. so the correct order is II > III > I.

31. 1- Bromo -3, 3- dimethylbutane only has one adjacent C atom with a H atom that can be abstracted; thus, it only produces one product,3 , 3- dimethyl - butene.

32. Isopropyl being 2° alkyl halide can undergo hydrolysis either by SN^1 to SN^2 reaction.

34. CH_3Cl has higher dipole moment than CH_3F due to much longer C – C bond length than C – F bond length.

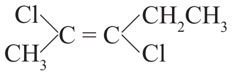
36. Since the order of stability of carbocations decreases in the order: tert-butyl > allyl > sec-butyl > n-butyl, so tert-butyl chloride is the most reactive.

37. Reactivity towards elimination reactions:
3° > 2° > 1°

38. R – I > R – Br > R – Cl > R – F

39. Chlorobenzene (less reactive), vinyl chloride (more reactive), chloroethane (most reactive).

40. $CH_3 - C \equiv C - CH_2CH_3 \xrightarrow[\text{Trans addition}]{Cl_2}$



41. $\underset{\text{Allyl chloride}}{Cl - CH_2 - CH = CH_2} \xrightarrow[-HCl]{KOH(alc.)\ \Delta} \underset{\text{Propadiene}}{CH_2 = C = CH_2}$

42. 2- Bromo -2- methylbutane undergoes S_N1 reactions most readily it is the only tertiary chloride listed. The others are primary and secondary chlorides.

43. As due to +I effect of the CH_3 groups, $(CH_3)_2CHO^-$ and $(CH_3)_3CO^-$ are stronger, bases but due to steric hindrance both are weaker nucleophiles than CH_3O^-. Further due to resonance $C_6H_5O^-$ is the weaker nucleophile.

44. CH_3Cl, CH_3F, CH_3Br

46. At higher temperature the reaction of toluene with chlorine is an example of free radical substitution.

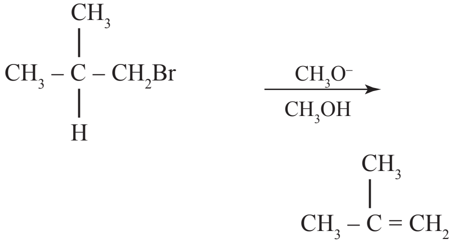
49. Chlorine of vinyl chloride (CH_2 = CHCl) is non-reactive (less reactive) towards nucleophile in nucleophillic substitution reaction.

51. Secondary bromides more readily undergo elimination reactions with strong bases such as sodium ethoxide; thus, the major products are both cis- and trans-2- pentene.

53. C_2H_5SH ($C_2H_5S^-$) is the strongest nucleophile.

54. In the first reaction, $NaOC(CH_3)_3/(CH_3)_3COH^-$ converts the bromide to styrene through an E2 elimination. Next, $Hg(OAc)_2$ /THF -H_2O followed by $NaBH_4$, OH^- produces the desired product through Markovnikov addition of water across the double bond.

55.

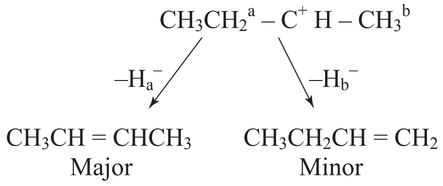


$$CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} - CH_2Br \xrightarrow[CH_3OH]{CH_3O^-} CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{C} = CH_2$$

It is an example of nucleophillic substitution.

56. According to Saytzeff's rule,

$CH_3CH_2CH(F)CH_3 \xrightarrow{CH_3O^-/CH_3OH}$

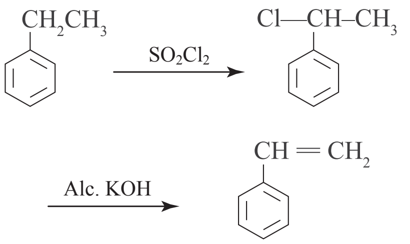


59. 1- bromo-2- methylbutane undergoes dehydrohalogenation and produces 2- methyl -1- butene, which undergoes hydrogenation to produces 2- methylbutane.

61. $R - X \xrightarrow{\text{alc. KCN}} R - CN \xrightarrow{\text{dil. HCl}} \underset{\text{Carboxylic acid}}{R - COOH}$

62. To obtain the trans product cis- 1- iodo-2- methylcyclopentane must be used as the substrate. The good nucleophili, CN^-, would do an S_N2 displacement of the iodide.

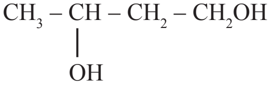
64.



66. Reactivity of halides towards SN^1 mechanism is

Benzyl > allyl > 3° > 2° > 1°

67. $CH_3CH(Cl)CH_2 - CH_2OH \xrightarrow{\text{aq. KOH}}$



$$CH_3 - \underset{\underset{\displaystyle OH}{|}}{CH} - CH_2 - CH_2OH$$

69. NO_2 group withdraws electrons from o- and p-positions and hence activates the Cl towards nucleophillic substitution reactions.

70. For a SN^2 reaction, the C-atom is least hindered towards the attack of nucleophile in the case of a primary halide that is, CH_3Cl.

71. That is the only tertiary substrate.

72. 3- chloro 1- iodohexane is the principle product because the I^- is a good nucleophile and will more readily attack the less hindered primary C atom. With only mole of iodide available, the major product will be the monosubstituted product and not the disubstituted one.

73. As primary is more reactive than secondary and tertiary alkyl halides so CH_3CH_2Br has the highest relative rate.

Brainteasers Objective Type Questions (Single choice only)

77. $\underset{*}{\mathrm{B}}\mathrm{rClCHCH_2CH_3}$
1-bromo -1-chloropropane (2)

$\mathrm{BrCH_2\overset{*}{C}HClCH_3}$
1- bromo-2- chloropropane (2)

$\mathrm{ClCH_2\overset{*}{C}HBrCH_3}$
2- bromo-1- chloropropane (2)

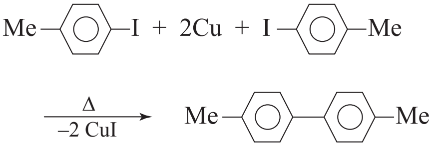
$\mathrm{CH_3CBrClCH_3}$
2- bromo-2- chloropropane

$\mathrm{BrCH_2CH_2CH_2Cl}$
1- bromo-3- chloropropane

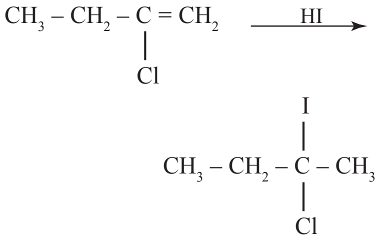
83. As nucleophilicity increases with increase of mass in a group that is, $\mathrm{Cl^- < Br^- < I^-}$

84. $\mathrm{C_6H_5O^-}$ that is, possess less nucleophilicity due to stabilized nature of phenoxide ion. $\mathrm{CH_3OH}$ is weaker acid than $\mathrm{CH_3COOH}$

88. This is Ullmann's reaction.



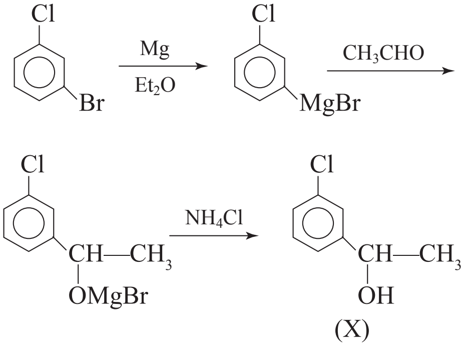
89. $\mathrm{CH_3-CH_2-C\equiv CH + HCl} \longrightarrow$



$$\mathrm{CH_3-CH_2-\underset{Cl}{C}=CH_2} \xrightarrow{\text{HI}}$$

$$\mathrm{CH_3-CH_2-\overset{I}{\underset{Cl}{C}}-CH_3}$$

90.



(X)

91. The reaction sequence is as follows:

$$\underset{\text{Aldehyde}}{\mathrm{CH_3CH_2CHO}} \xrightarrow{\text{aq.KOH}} \underset{\text{1 , 1-dichloropropane}}{\mathrm{CH_3CH_2CHCl_2}} \xrightarrow{\text{alc.KOH}}$$

$$\underset{\text{hydrocarbon}}{\mathrm{CH_3-C\equiv CH + 2KCl + H_2O}}$$

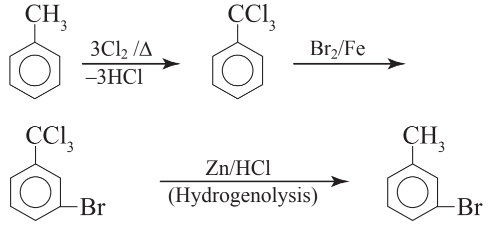
$$\Big\downarrow \mathrm{Cu_2Cl_2/NH_3}$$

Red ppt.

92. $\mathrm{C_2H_5I} \xrightarrow[\text{–HI}]{\text{alc. KOH}} \mathrm{CH_2=CH_2} \xrightarrow{\mathrm{Br_2}}$

$\mathrm{BrCH_2-CH_2Br} \xrightarrow{\text{KCN}} \mathrm{NCCH_2-CH_2CN}$

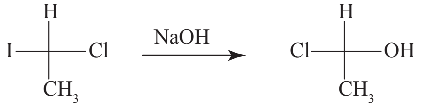
93.



94. $\mathrm{CH_3-CHBr-CH_2Br + 2NaNH_2 \rightarrow}$
$\mathrm{CH_3-C\equiv CH + 2NaBr + 2NH_3}$
$\mathrm{CH_3-C\equiv CH + NaNH_2 \rightarrow}$
$\mathrm{CH_3-C\equiv C^-\,Na^+ + NH_3}$
$\mathrm{CH_3-C\equiv C^-\,Na^+ + CH_3CH_2Br \rightarrow}$
$\mathrm{CH_3-C\equiv C-CH_2CH_3 + NaBr}$
2-pentyne

96. $\mathrm{CH_2=CH-{}^*CHCl-CH_2CH_3} \xrightarrow[\mathrm{H_2}]{}$
3-chloro-1-pentene (A)
(Optically active)
$\mathrm{CH_3CH_2-CHCl-CH_2CH_3}$
3-chloropentane
(Optically inactive)
$\mathrm{CH_3CH=CH-{}^*CHCl-CH_3} \xrightarrow{\mathrm{H_2}}$
4-chloro-2-pentene (B)
(Optically active)
$\mathrm{CH_3CH_2CH_2-{}^*CHCl-CH_3}$
2-chloropentane
(Optically active)

99.



100. $\mathrm{Cl-CH_2-CH(CH_3)-CH_2CH_3} \xrightarrow[\text{EtOH}]{\text{NaOEt}}$

$CH_2 = C(CH_3) - CH_2CH_3 \xrightarrow{H_2\ catalyst}$

$CH_3 - CH(CH_3) - CH_2CH_3$
2-Methylbutane

101. $CH_3 - CH_2Cl + C_2H_5ONa \longrightarrow$
(Y)
$C_2H_5OC_2H_5 + NaCl \xrightarrow{2HI}$
(Z)
$CH_3 - CH_2 - I + H_2O$

102. percentage by $S_N2 = \dfrac{S_N2}{S_N2 + S_N1} \times 100$
$= 3.20 \times 10^{-5}$ [2- bromobutane]
$\dfrac{(1.00) \times 100)}{3.20 \times 10^{-5}\ [\text{2- bromobutane}]}$
$(1.00) + 1.5 \times 10^{-6}$ [2- bromobutane]

$$= \frac{3.20 \times 10^{-5})}{3.20 \times 10^{-5} + 0.15 \times 10^{-5}} \times 100$$
$$= \frac{3.20 \times 10^{-5}}{3.35 \times 10^{-5}} \times 100$$
$$= 96\ \%$$

106. 3 As B gives yellow precipitate with $AgNO_3/HNO_3$, B must be $C_6H_5CH_2I$ and hence A is C_6H_5I.

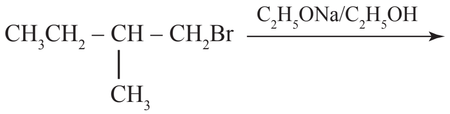
107. Reactivity decreases as the number of NO_2 groups at o- and p- position w.r.t. to Br decreases. m-nitrobromobenzene is, however, less reactive than the p-nitrobromobenzene since the NO_2 group at m-position cannot stabilize the intermediate carbanion by resonance. So the order is II > IV > III > I.

108. IV (C_6H_5Cl, Cl = 31.5 %), I(DDT, Cl = 53.7 %), II ($C_6H_6Cl_6$, Cl = 73.19 %), III (CCl_4, Cl = 92.2 %).

111. At higher temperature, $CH_3CO_2C_2H_5$ undergoes hydrolysis to give ethanol which gives iodoform test.
$CH_3CO_2C_2H_5 + NaOH \rightarrow CH_3CO_2Na + C_2H_5OH$
$C_2H_5OH \xrightarrow{I_2/NaOH} CHI_3$
Other esters upon hydrolysis give either CH_3OH or C_6H_5OH both of which do not give iodoform test.

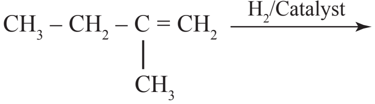
112. 1- Chloro-3- methylcyclobutane is the only one of the listed compounds that fits the description. Another compound that has these same chemical properties is chlorocyclopentane.

113.

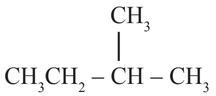


$CH_3CH_2 - \underset{\displaystyle CH_3}{\underset{|}{CH}} - CH_2Br \xrightarrow{C_2H_5ONa/C_2H_5OH}$

1-Bromo-2-methylbutane



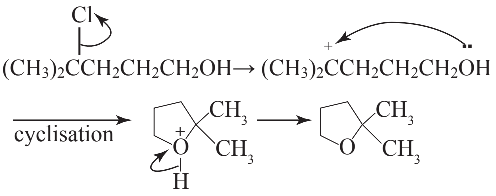
$CH_3 - CH_2 - \underset{\displaystyle CH_3}{\underset{|}{C}} = CH_2 \xrightarrow{H_2/Catalyst}$



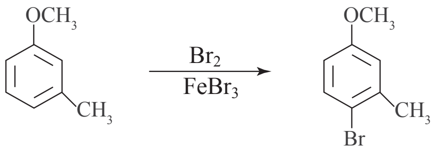
$CH_3CH_2 - \overset{\displaystyle CH_3}{\overset{|}{CH}} - CH_3$

2-Methylbutane

116. The reaction occurs as follows:

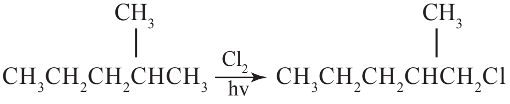


117.



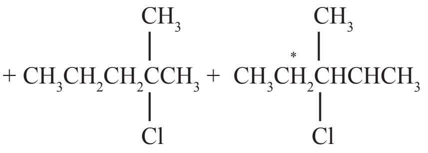
(A)
As methyl group is ortho- or para-directing.

121.



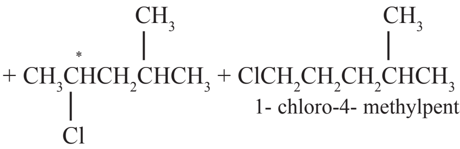
$CH_3CH_2CH_2\overset{\displaystyle CH_3}{\overset{|}{C}}HCH_3 \xrightarrow[hv]{Cl_2} CH_3CH_2CH_2\overset{\displaystyle CH_3}{\overset{|}{C}}HCH_2Cl$

1- chloro-2-methylpentane



$+ CH_3CH_2CH_2\underset{\displaystyle Cl}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}CH_3 + CH_3CH_2\overset{*}{C}H\underset{\displaystyle Cl}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}HCH_3$

2- chloro- 2-methylpentane 3- chloro-2-methylpentane

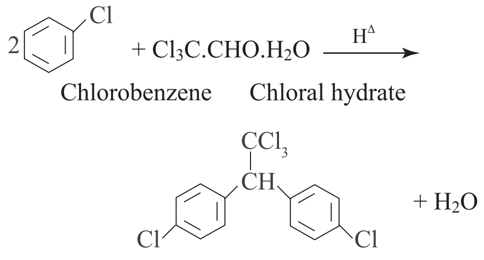


$+ CH_3\underset{\displaystyle Cl}{\underset{|}{\overset{*}{C}}}HCH_2\overset{\displaystyle CH_3}{\overset{|}{C}}HCH_3 + ClCH_2CH_2CH_2\overset{\displaystyle CH_3}{\overset{|}{C}}HCH_3$

1- chloro-4- methylpentane

2- chloro-4- methylpentane

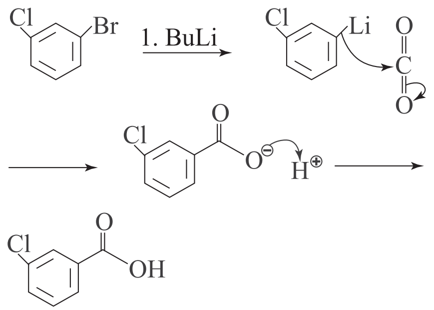
122.



Chlorobenzene Chloral hydrate

2, 2-bis-(4-chlorophenyl)
1, 1, 1-trichloroethane

129.



Decisive Thinking Objective Type Questions

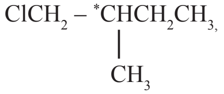
131. S_N2 reactions follow a one-step bimolecular mechanism.

139. As benzyl chloride is more reactive than alkyl halides.

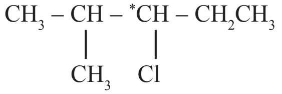
142. As Vinyl chloride ($CH_2 = CH – Cl$) does not undergo dehydrochlorination on boiling with water to produce acetylene.

143. $CH_3CH_2CH_2CH_2Cl$ does not have a chiral carbon and hence is not optically active while all others have chiral carbon atoms and hence are optically active.

$CH_3 – {}^*CHCl – CH_2CH_3$,



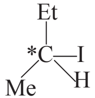
$$ClCH_2 – {}^*\underset{CH_3}{\underset{|}{C}}HCH_2CH_3,$$



$$CH_3 – \underset{CH_3}{\underset{|}{CH}} – {}^*\underset{Cl}{\underset{|}{CH}} – CH_2CH_3$$

147. $\underset{(alc.)}{C_2H_5Br + AgNO_2} \rightarrow \underset{(major)}{C_2H_5NO_2} + \underset{(minor)}{C_2H_5ONO}$

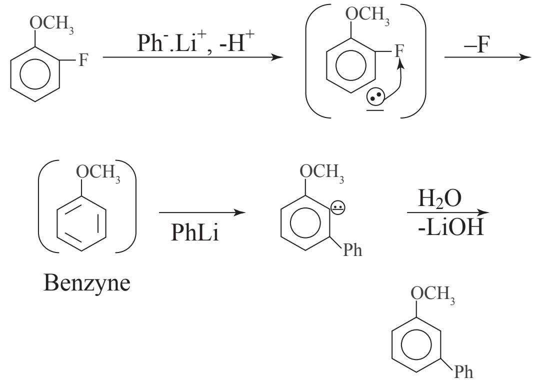
151. As this reaction is according to SN^2 mechanism so the product must be.



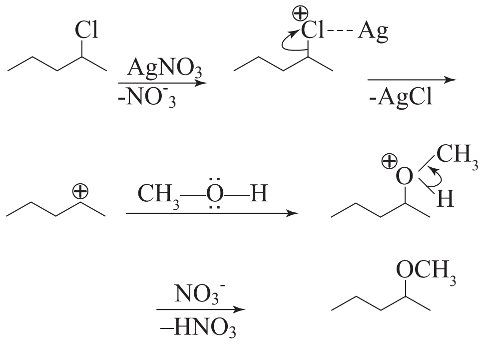
154. As Walden inversion always occurs by S_N2 mechanism.

Linked-Comprehension Type Questions

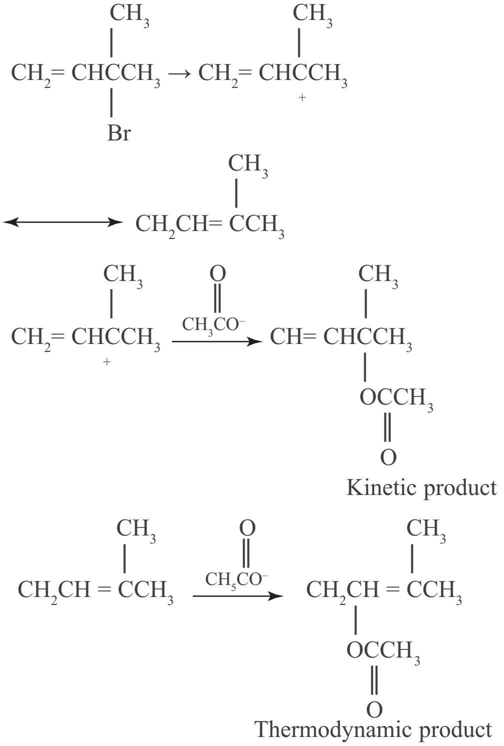
161.



162.



164. Sodium acetate is a poor nucleophile, so we can assume the reaction takes place primarily by an S_N1 pathway the thermodynamically controlled product



$$CH_2{=}\,CH\overset{CH_3}{\underset{Br}{C}}CH_3 \rightarrow CH_2{=}\,CH\overset{CH_3}{\underset{+}{C}}CH_3 \longleftrightarrow CH_2CH{=}\,\overset{CH_3}{C}CH_3$$

$$CH_2{=}\,CH\overset{CH_3}{\underset{+}{C}}CH_3 \xrightarrow{CH_3\overset{O}{\overset{\|}{C}}O^-} CH{=}\,CH\overset{CH_3}{\underset{\underset{\underset{O}{\|}}{OCCH_3}}{C}}CH_3$$

Kinetic product

$$CH_2CH = \overset{CH_3}{C}CH_3 \xrightarrow{CH_3\overset{O}{\overset{\|}{C}}O^-} \underset{\underset{\underset{O}{\|}}{OCCH_3}}{CH_2}CH = \overset{CH_3}{C}CH_3$$

Thermodynamic product

167. C^+ formed is (C) is not only t° but also allyl.

Assertion-Reason Type Questions

171. Assertion is wrong and reason is correct. The solvolysis of I by SN^2 process is slower than II due to steric hindrance.

172. Iodides being less stable lose $\mathbf{I_2}$**.** the liberated I_2 is absorbed by iodides to darken their colour.

175. As the size of the alkyl groups increases, the SN^2 reactivity decreases further C – Cl bond is stronger and more difficult to cleave than C – Br bond. So CH_2Br is more reactive than $(CH_3)_2CHCl$.

176. Among dichloro benzenes, the p-isomer being symmetrical packs closely in the crystal lattice and hence has much higher melting point than o-and m-isomers.

181. In SN^1 reaction, the rate of reaction is dependent only on the concentration of alkyl halide that is, rate = k[RX].

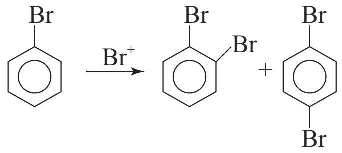
182. A bond formed of an sp^3 orbital should be larger than the corresponding bond involving an sp^2 orbital.

185. Bromonezene show both- I effect as well as +M effect; while mesomeric effect domicates the –I character and becomes the directing factor for incoming electrophile.

Formation of electrophile takes palce.

$Br-Br + FeBr_3 \rightarrow Br^+ + FeBr_4^-$

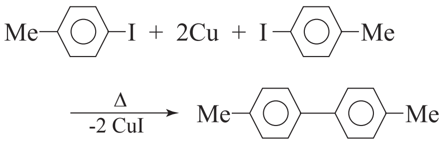
Bromobezene acts as an *ortho-para* directors for upcoming electrophiles.



1,4-dibromobenzene (major product)

The IIT JEE Corner

197. This is Ullmann's reaction.



199. Because $-CCl_3$ is electron withdrawing group and is meta directing.

200. The benzyne formed as an intermediate gives a more stable carbanion when the nucleophillic attack by the amide occurs at the m-position than at the p-position.

201. Addition of Br_2 to trans-but-2-ene gives meso-2, 3-dibromobutane. So debromination of meso-2,3-dibromobutane will give trans but-2-ene here.

203. Due to hyperconjugation the ring is activated and ortho-para positions becomes positions of maximum electron density. Therefore electrophile (^+Br) attack at these positions.

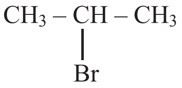
204. $SbCl_2$ is used for the formation of carbocation.

205. As with the decrease in size of halogen, C – X bond energy increases and so reactivity of alkyl halide decreases.

206. In SN^2 reaction, inversion of configuration occurs and only a single stereoisomer is obtained.

207. $CH_3-CH_2-CH_2Br \xrightarrow[\substack{\text{(X)} \\ \text{dehydrohalogenation}}]{\text{conc. alc. NaOH, 80}^\circ\text{C}}$

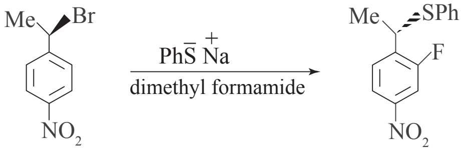
$$CH_3-CH=CH_2 \xrightarrow[\substack{\text{Acetic acid } 20^\circ\text{C} \\ \text{(Y)}}]{\text{HBr}}$$



$$CH_3-\underset{\underset{Br}{|}}{CH}-CH_3$$

208. Isocyanide test/Carbylamine reaction

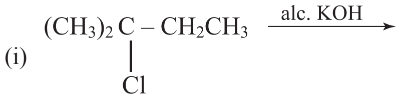
209.



As nucleophillic substitution on alkyl halide is easier than on aryl halides. Substitution reaction is of S_N2 type that leads the formation of inversion product.

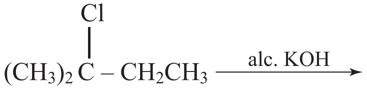
SUBJECTIVE SOLVED EXAMPLES

1. Complete the following reaction with appropriate structure.

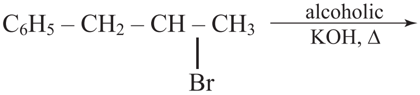

(i) $(CH_3)_2\underset{\displaystyle Cl}{\underset{|}{C}} - CH_2CH_3 \xrightarrow{\text{alc. KOH}}$

[IIT 1992]

Solution


$(CH_3)_2\overset{\displaystyle Cl}{\overset{|}{C}} - CH_2CH_3 \xrightarrow{\text{alc. KOH}}$

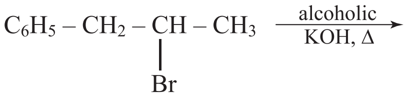
$(CH_3)_2CHCH_2C(CH_3)_3$


$C_6H_5 - CH_2 - \underset{\displaystyle Br}{\underset{|}{CH}} - CH_3 \xrightarrow[\text{KOH, }\Delta]{\text{alcoholic}}$

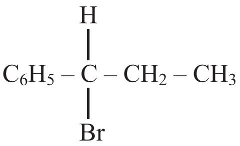
(ii) (A) $\xrightarrow{\text{HBr}}$ (B)

[IIT 1993]

Solution

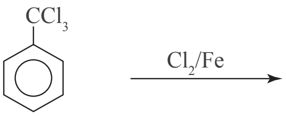

$C_6H_5 - CH_2 - \underset{\displaystyle Br}{\underset{|}{CH}} - CH_3 \xrightarrow[\text{KOH, }\Delta]{\text{alcoholic}}$

$C_6H_5CH = CH - CH_3 \xrightarrow{\text{HBr}}$


$C_6H_5 - \overset{\displaystyle H}{\overset{|}{\underset{\displaystyle Br}{\underset{|}{C}}}} - CH_2 - CH_3$

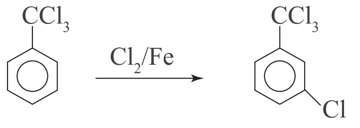
$C_6H_5CH_2C^+HCH_3$ and $C_6H_5C^+HCH_2CH_3$ carbocations are formed on addition of HBr on $C_6H_5CH = CHCH_3$, the latter is stabilized due to resonance and hence Br^- adds on it forming $C_6H_5CHBr.CH_2CH_3$ as the final product.

(iii)



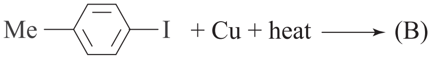
[IIT 1997]

Solution



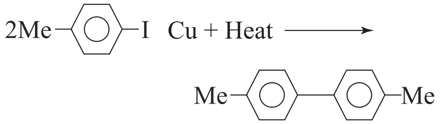
(meta product)

(iv)

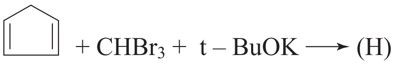


[IIT 1997]

Solution

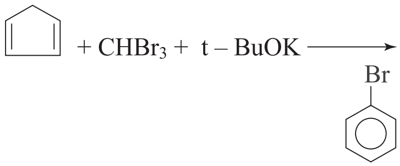


(v)



[IIT 1997]

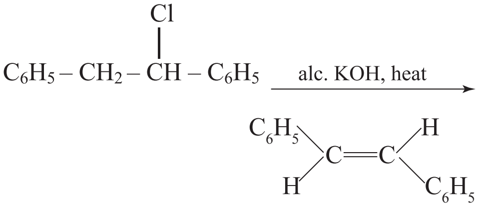
Solution



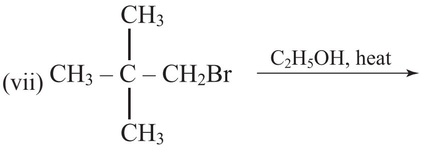
(vi) $C_6H_5CH_2CHClC_6H_5 \xrightarrow{\text{alc. KOH, heat}}$ 2 products

[IIT 1998]

Solution

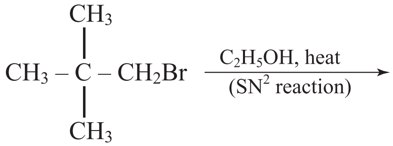


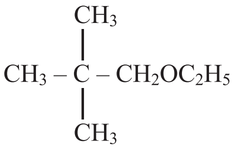
cis and trans-Stilbene
(trans is major product)


(vii) $CH_3 - \overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}} - CH_2Br \xrightarrow{C_2H_5OH\text{, heat}}$

[IIT 2000]

Solution


$CH_3 - \overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}} - CH_2Br \xrightarrow[(SN^2\text{ reaction})]{C_2H_5OH\text{, heat}}$



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2OC_2H_5$$

2. State the conditions under which the following preparation are carried out. Give the necessary equations which need not be balanced:
   (i) Lead tetraethyl from sodium-lead alloy

Solution

$4C_2H_5Br + 4(Na - Pb)$

$Pb(C_2H_5)_4 + 4NaBr + 3Pb$

(ii) Methyl chloride from aluminium carbide

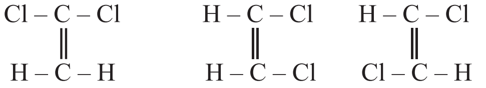
Solution

$$Al_4C_3 \xrightarrow{H_2O} CH_4 \xrightarrow{Cl_2,\ sunlight} CH_3Cl$$

3. Write the structure of all the possible isomers of dichloroethene. Which of them will have zero dipole moment?

Solution

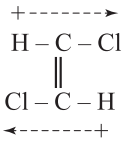
Dichloroethene exists in three isomeric form.



$$\begin{array}{c} Cl-C-Cl \\ \| \\ H-C-H \end{array} \qquad \begin{array}{c} H-C-Cl \\ \| \\ H-C-Cl \end{array} \qquad \begin{array}{c} H-C-Cl \\ \| \\ Cl-C-H \end{array}$$

1,1-dichloro ethene (cis)-1,2-dichloro ethene (trans)-1,2-di chloroethene

trans-1,2-dichloroethene has zero dipole moment as follows:



$$\begin{array}{c} +\text{-------}\rightarrow \\ H-C-Cl \\ \| \\ Cl-C-H \\ \leftarrow\text{-------}+ \end{array}$$

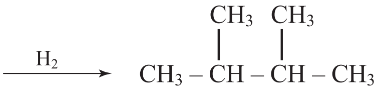
4. An alkyl halide, X of formula $C_6H_{13}Cl$ on treatment with potassium tertiary butoxide gives two isomeric alkenes Y and Z (C_6H_{12}). Both alkenes on hydrogenation give 2,3-dimethylbutane. Predict the structures of X, Y and Z.

[IIT 1996]

Solution

Summary:

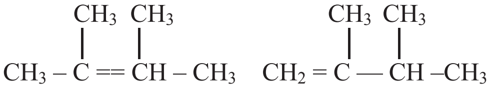
$$\underset{(X)}{C_6H_{13}Cl} \xrightarrow{(CH_3)_3COK} \underset{(Y\ \&\ Z)}{\text{Two isomeric alkenes}}$$



$$\xrightarrow{H_2} CH_3-\overset{\overset{CH_3}{|}}{C}H-\overset{\overset{CH_3}{|}}{C}H-CH_3$$

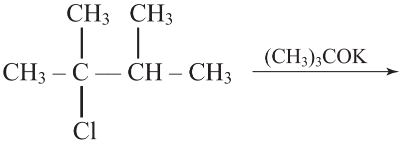
2,3-Dimethylbutane

Two isomeric precursors of 2,3-dimethylbutane are



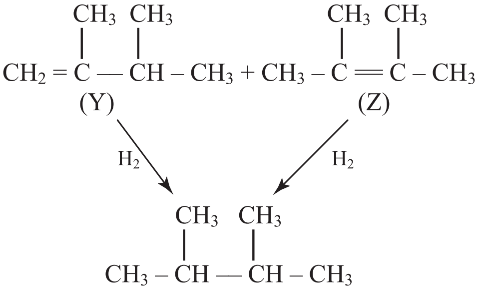
$$CH_3-\overset{\overset{CH_3}{|}}{C}=\overset{\overset{CH_3}{|}}{C}H-CH_3 \qquad CH_2=\overset{\overset{CH_3}{|}}{C}-\overset{\overset{CH_3}{|}}{C}H-CH_3$$

So the precursor of Y and Z should have following structure:



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{Cl}{|}}{C}}-\overset{\overset{CH_3}{|}}{C}H-CH_3 \xrightarrow{(CH_3)_3COK}$$

(X)



$$\underset{(Y)}{CH_2=\overset{\overset{CH_3}{|}}{C}-\overset{\overset{CH_3}{|}}{C}H-CH_3} + \underset{(Z)}{CH_3-\overset{\overset{CH_3}{|}}{C}=\overset{\overset{CH_3}{|}}{C}-CH_3}$$

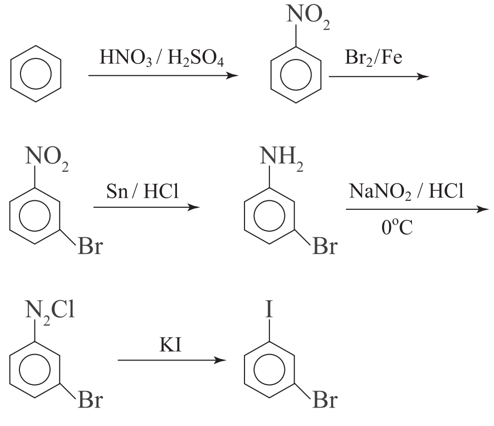
$$\xrightarrow{H_2} CH_3-\overset{\overset{CH_3}{|}}{C}H-\overset{\overset{CH_3}{|}}{C}H-CH_3$$

2,3-Dimethylbutane

5. How will you prepare m-bromoiodobenzene from benzene (in not more than 5-7 steps)?

[IIT 1996]

Solution



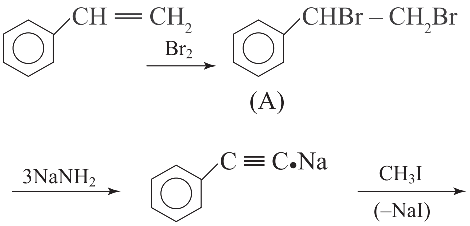
6. Complete the following reactions with appropriate structures of products / reagents.

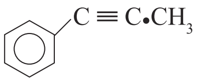
$$C_6H_5CH = CH_2 \xrightarrow{Br_2} (A)$$

(i) $\xrightarrow[\text{(ii) } CH_3I]{\text{(i) } NaNH_2 \text{ (3.0 equiv.)}}$ (B)

[IIT 1998]

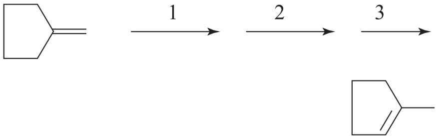
Solution





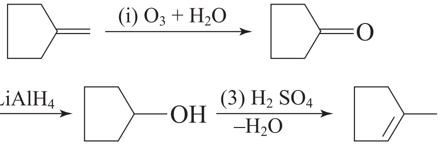
(B)

(ii)



[IIT 1999]

Solution



ORGANIC COMPOUNDS CONTAINING OXYGEN-1

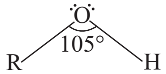
(ALCOHOLS, PHENOL AND ETHER)

CHAPTER 5

CHAPTER CONTENTS

Introduction, Preparations, Properties of Alcohols Phenols and Ethers
Alcohols : Esterification, dehydration and oxidation, reaction with sodium, phosphorus halides, Anhydrous $ZnCl_2$-Conc. HCl, conversion of alcohols into aldehydes and ketones.
Phenols: Acidity, electrophilic substitution reactions (halogenation, nitration and sulfonation); Reimer-Tiemann reaction, Kolbe reaction.
Ethers: Preparation by Williamson's synthesis and various level of multiple-choice questions

ALCOHOLS



- These are hydroxy derivatives of alkanes or these are alkyl derivatives of water with a general formula R – OH.

TYPES OF ALCOHOLS Alcohols are of the following types:

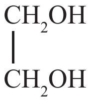
(1) Mono Hydric Alcohol These are alcohols with only one –OH group. Their general formula is

$C_n H_{2n+1} OH$.

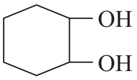
They are further of following types:

(a) Primary alcohol (1^o) RCH_2OH e.g., CH_3OH methyl alcohol (Methanol)
(b) Secondary alcohol (2^o) R_2CHOH e.g., $(CH_3)_2CHOH$ isopropyl alcohol (Propan-2-ol)
(c) Tertiary alcohol (3^o) $R_3C.OH$ e.g., $(CH_3)_3COH$ tertiary butyl alcohol (2-methyl-propan-2-ol)

(2) Di Hydric Alcohol These are alcohols having two –OH groups.
For example, Glycol, cyclo hexan 1, 2 di-ol



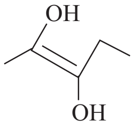
$$\begin{array}{c} CH_2OH \\ | \\ CH_2OH \end{array}$$



(3) Tri Hydric Alcohol These are alcohols having three –OH groups.
For example, Glycerol (Propan 1, 2, 3 tri-ol)

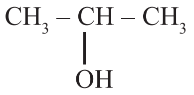
$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

NOMENCLATURE OF ALCOHOLS Alcohols are named as Alkanol.
For example,



2'E'-pent 2-en, 2,3-di-ol

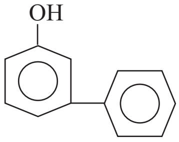
$CH_3 – CH_2 – CH_2OH$ Propanol



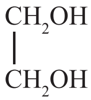
$$\begin{array}{l} CH_3 – CH – CH_3 \\ \quad\quad\ | \\ \quad\quad OH \end{array}$$

Propan-2-ol

$(CH_3)_3COH$ 2-Methyl-butan-2-ol

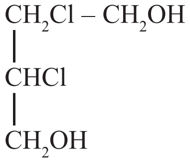


3-Phenyl hydroxy benzene



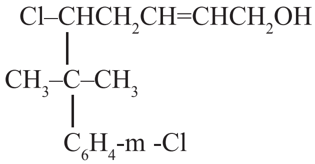
$$\begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array}$$

Ethan-1, 2-diol



$$\begin{array}{l} CH_2Cl – CH_2OH \\ | \\ CHCl \\ | \\ CH_2OH \end{array}$$

2, 3-dichloro butan-1, 4-diol



$$\begin{array}{l} Cl–CHCH_2CH{=}CHCH_2OH \\ \quad\ | \\ CH_3–C–CH_3 \\ \quad\ | \\ \quad C_6H_4\text{-m -Cl} \end{array}$$

5- chloro -6- methyl -6- (3- chloro phenyl) -2- hepten -1-ol

ISOMERISM SHOWN BY ALCOHOLS Alcohol may show chain, position and functional isomerism.

For example,

(1) Butan-1-ol and 2-methylpropan-1-ol are chain isomers
(2) Propan-1-ol and propan-2-ol are position isomers.
(3) Benzyl alcohol and Anisol are functional isomers.

GENERAL METHODS OF PREPARATION

Alcohols are prepared by following methods:

From Alkanes (R – H) (only by tertiary alkanes)

$$R_3C – H \xrightarrow[OH^-]{KMnO_4} R_3C – OH$$

$$(CH_3)_3C – H \xrightarrow[OH^-]{KMnO_4} (CH_3)_3C – OH$$

2-Methyl propane Tertiary butyl alcohol (2-methylpropan-2-ol)

- Here pink colour of $KMnO_4$ disappears.

From Haloalkanes (R – X) Alkyl halides on hydrolysis by aqueous alkali like NaOH, KOH or moist Ag_2O give alcohol as follows by substitution reaction.

$$\underset{\substack{\text{or}\\ \text{KOH}}}{R - X + AgOH\ (aq)} \rightarrow \underset{\substack{\text{or}\\ \text{KX}}}{R - OH + AgX}$$

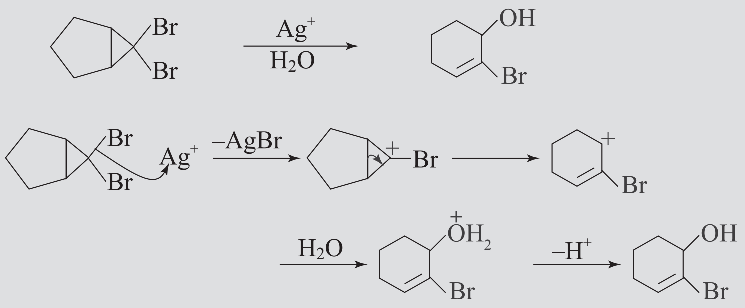
$$CH_3\,Br + \underset{\text{Aq.}}{KOH} \rightarrow CH_3OH + KBr$$

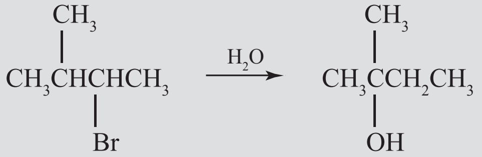
- This method is suitable only for primary alkyl halide as secondary alkyl halide gives a mixture of alcohol and alkene and tertiary alkyl halide gives only alkene.

For example, $\underset{\substack{\text{propyl bromide}\\ (\text{s}^{\text{o}}\ \text{halide})}}{(CH_3)_2\,CHBr} \xrightarrow{\text{aq KOH}} \underset{\text{isopropyl alcohol}}{(CH_3)_2CHOH} + \underset{\text{Propene}}{CH_3 - CH = CH_2} + KBr + H_2O$

$$\underset{\substack{\text{Tertiary butyl bromide}\\ (\text{t}^{\text{o}}\ \text{halide})}}{(CH_3)_3\,CBr} \xrightarrow{\text{aq KOH}} \underset{\text{Isobutene}}{(CH_3)_2\,C = CH_2} + KBr + H_2O$$

Mechanism

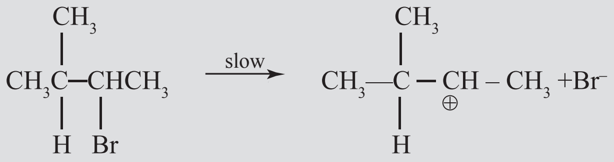




$$CH_3\overset{\overset{CH_3}{|}}{C}H\underset{\underset{Br}{|}}{C}HCH_3 \xrightarrow{H_2O} CH_3\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}CH_2CH_3$$

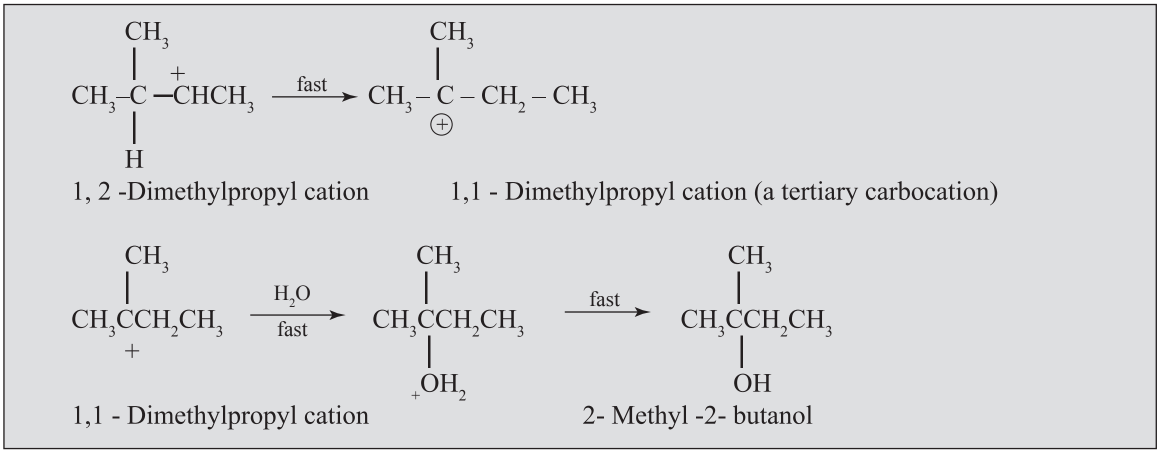
2- Bromo -3- methylbutane 2 - Methyl -2- butanol (93 %)

Mechanism



$$CH_3\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{C}}-\underset{\underset{Br}{|}}{C}HCH_3 \xrightarrow{\text{slow}} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{C}}-\underset{\oplus}{CH}-CH_3 + Br^-$$

2- Bromo -3- methylbutane 1, 2- Dimethylpropyl cation (a secondary carbocation)



1, 2 -Dimethylpropyl cation 1,1 - Dimethylpropyl cation (a tertiary carbocation)

1,1 - Dimethylpropyl cation 2- Methyl -2- butanol

From Ether (R – O – R) Ethers on hydrolysis by dilute acids give alcohol.

$$R - O - R + H.OH \xrightarrow[\text{Dil. } H_2SO_4]{\Delta} 2R - OH$$

For example,

$$\underset{\text{Dimethyl ether}}{CH_3 - O - CH_3} + H.OH \xrightarrow[\text{Dil. } H_2SO_4]{\Delta} \underset{\text{Methanol}}{2CH_3 - OH}$$

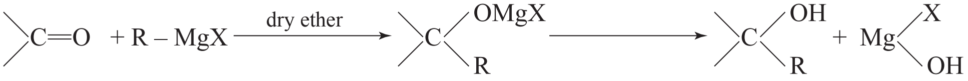
- If alkyl groups are different, two types of alcohols will be formed.

For example,

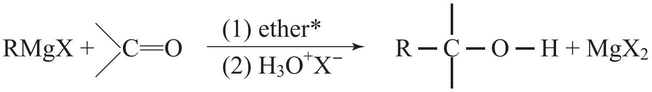
$$\underset{\text{Ethylpropyl ether}}{C_2H_5 - O - C_3H_7} + H.OH \xrightarrow[\text{Dil. } H_2SO_4]{\Delta} \underset{\text{ethanol}}{C_2H_5 - OH} + \underset{\text{Propyl alcohol}}{C_3H_7OH}$$

From Grignard's Reagent

(a) ***With Carbonyl Compound*** It is the best method to prepare 1°, 2°, 3° type of alcohols. Here Grignard reagent reacts with carbonyl compounds to form an intermediate compound which on hydrolysis gives alcohol. One must remember that formaldehyde gives primary alcohol here, while rest of the aldehydes give secondary alcohols and ketones give tertiary alcohols.

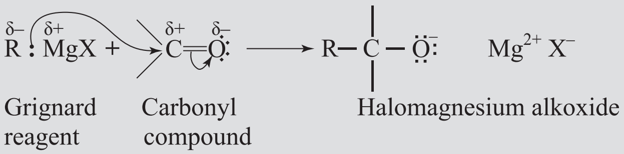


(Or)

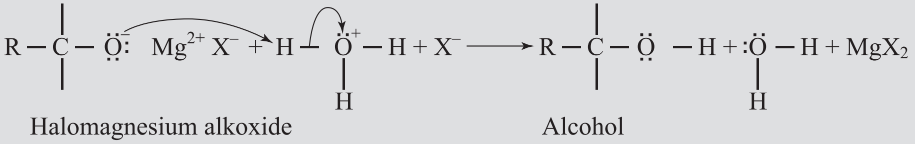


Mechanism

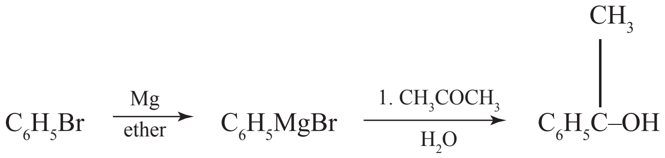
Step 1



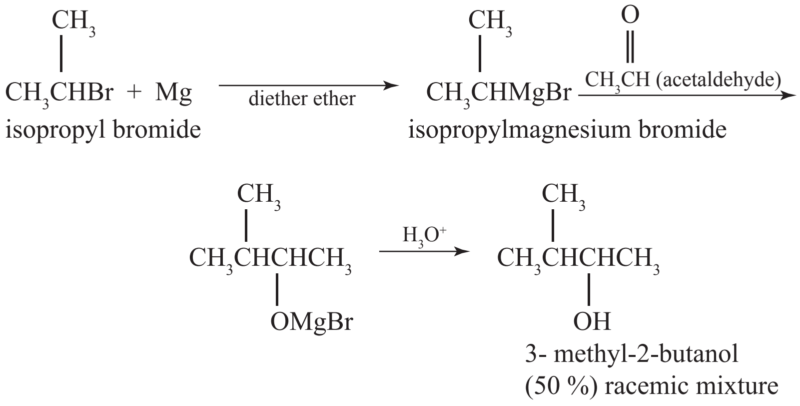
Step 2



e.g.,

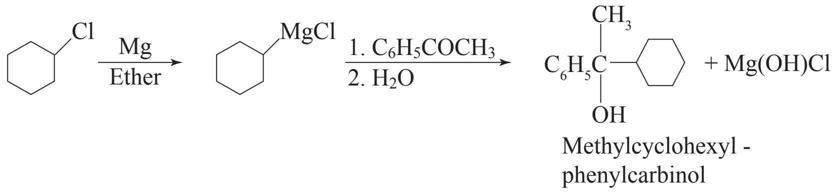


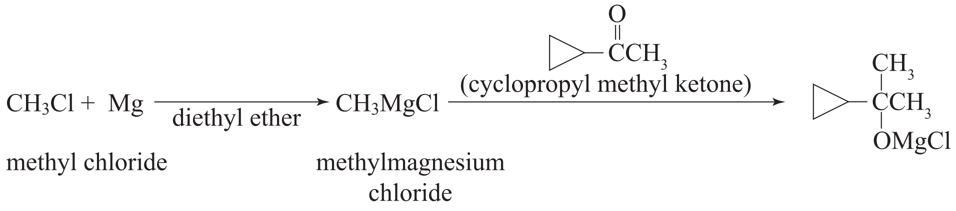
$$C_6H_5Br \xrightarrow[\text{ether}]{Mg} C_6H_5MgBr \xrightarrow[H_2O]{1.\ CH_3COCH_3} C_6H_5\overset{\overset{CH_3}{|}}{C}\text{–}OH$$

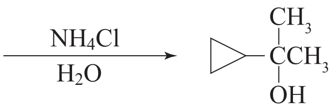


$$\underset{\text{isopropyl bromide}}{CH_3\overset{\overset{CH_3}{|}}{C}HBr} + Mg \xrightarrow{\text{diether ether}} \underset{\text{isopropylmagnesium bromide}}{CH_3\overset{\overset{CH_3}{|}}{C}HMgBr} \xrightarrow{CH_3\overset{\overset{O}{\|}}{C}H\ \text{(acetaldehyde)}}$$

$$CH_3\overset{\overset{CH_3}{|}}{C}H\underset{\underset{OMgBr}{|}}{C}HCH_3 \xrightarrow{H_3O^+} \underset{\substack{\text{3- methyl-2-butanol} \\ \text{(50 \%) racemic mixture}}}{CH_3\overset{\overset{CH_3}{|}}{C}H\underset{\underset{OH}{|}}{C}HCH_3}$$

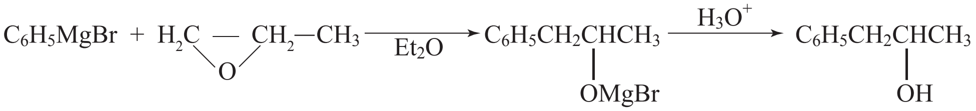






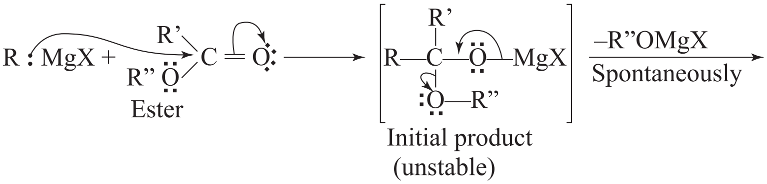
2- cyclopropyl -2- propanol
(68%)

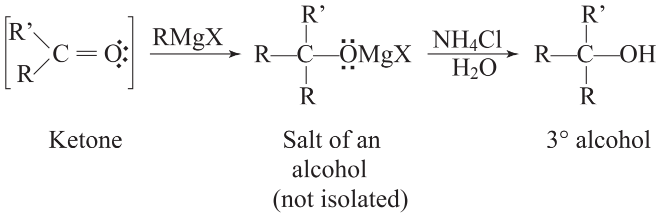
(b) ***From Epoxy ethers***



Grignard reagent reacts primarily at the less-substituted ring carbon atom of substituted oxiranes.

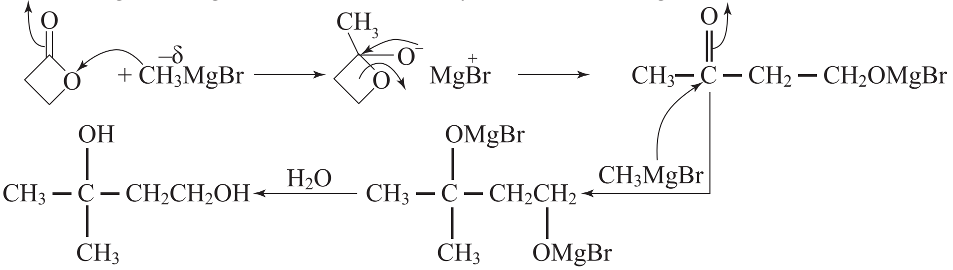
(c) ***From Esters*** Grignard reagent reacts with esters to give tertiary alcohol as follows:





For example,

Grignard reagent can also attack on cyclic esters first to give ketones then 3^o alcohol.



By the Reduction of Carbonyl Compound (R – CHO and R – CO – R) Carbonyl compounds on reduction give alcohol by using reducing agents like $LiAlH_4$, $NaBH_4$, Zn/HCl, H_2/Ni etc.

- Aldehydes on reduction give primary alcohols as follows:

$$R-CHO + H_2 \xrightarrow[\text{or } LiAlH_4]{Ni} R-CH_2OH$$

Primary alcohol

For example,

$$\underset{\text{Ethanal}}{CH_3CHO} + H_2 \xrightarrow[\text{or Na/}C_2H_5OH]{\text{Ni}} \underset{\text{Ethanol}}{CH_3CH_2OH}$$

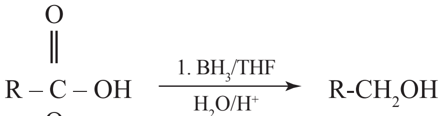
- Ketones on reduction give secondary alcohols.

$$R-CO-R' + H_2 \xrightarrow[\text{or LiAlH}_4]{\text{Ni}} R_2CHOH$$

For example,

$$\underset{\text{Propan-2-one}}{CH_3-CO-CH_3} + H_2 \xrightarrow[\text{or LiAlH}_4]{\text{Ni}} \underset{\text{Propan-2-ol}}{(CH_3)_2CHOH}$$

By the Reduction of Acids and Acid Derivatives (R – COOH, R – COX , R – COOR) These undergo reduction into alcohols with the help of $LiAlH_4$ or $NaBH_4$ reducing agents as follows:



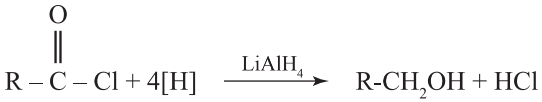
$$R-\overset{\overset{O}{\|}}{C}-OH \xrightarrow[H_2O/H^+]{1.\ BH_3/THF} R\text{-}CH_2OH$$

$$R-\overset{\overset{O}{\|}}{C}-OH + 4[H] \xrightarrow{LiAlH_4} R\text{-}CH_2OH + H_2O$$

Here R may be H, CH_3, C_2H_5 etc.

For example, $CH_3COOH + 4[H] \xrightarrow{LiAlH_4} CH_3CH_2OH + H_3O$

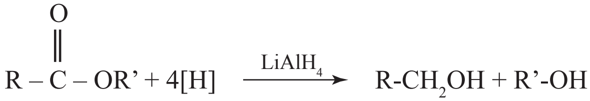
Ethanol



$$\underset{\text{Acid chloride}}{R-\overset{\overset{O}{\|}}{C}-Cl} + 4[H] \xrightarrow{LiAlH_4} \underset{\text{Alcohol}}{R\text{-}CH_2OH} + HCl$$

For example,

$$\underset{\text{Acetyl chloride}}{CH_3COCl} + 4[H] \xrightarrow{LiAlH_4} CH_3CH_2OH + HCl$$



$$\underset{\text{Ester}}{R-\overset{\overset{O}{\|}}{C}-OR'} + 4[H] \xrightarrow{LiAlH_4} R\text{-}CH_2OH + R'\text{-}OH$$

For example,

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + 4[H] \xrightarrow{LiAlH_4} 2C_2H_5OH$$

From Primary Amines Primary amines react with nitrous acid to give alcohols.

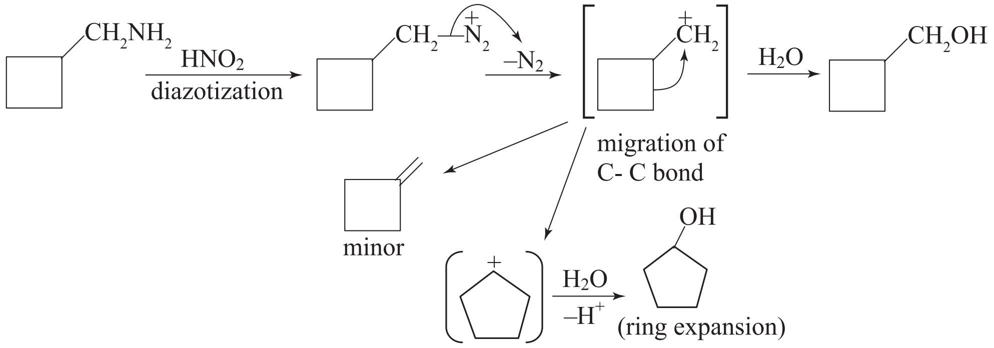
$$R-CH_2NH_2 + HNO_2 \rightarrow R-CH_2OH + N_2 + H_2O$$

Example,

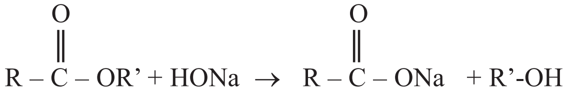
(1) $\underset{\text{Methyl amine}}{CH_3NH_2} + HNO_2 \rightarrow CH_3OH + N_2 + H_2O$

(2) $(CH_3)_2\,CHNH_2 + HNO_2 \rightarrow (CH_3)_2CHOH + N_2 + H_2O$
Isopropyl amine Isopropyl alcohol

(3)

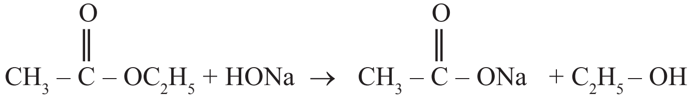


By Hydrolysis of Esters Esters on hydrolysis by dilute acid or alkali give alcohols as follows:



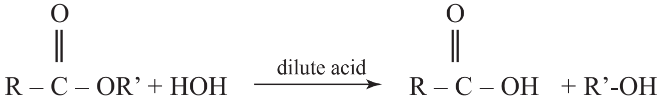
$$R-\overset{\overset{O}{\|}}{C}-OR' + HONa \rightarrow R-\overset{\overset{O}{\|}}{C}-ONa + R'\text{-}OH$$

For example,



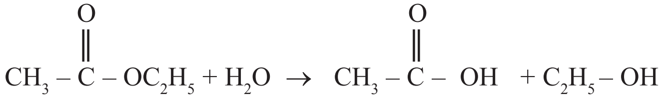
$$CH_3-\overset{\overset{O}{\|}}{C}-OC_2H_5 + HONa \rightarrow CH_3-\overset{\overset{O}{\|}}{C}-ONa + C_2H_5-OH$$

Ethyl acetate Sodium acetate



$$R-\overset{\overset{O}{\|}}{C}-OR' + HOH \xrightarrow{\text{dilute acid}} R-\overset{\overset{O}{\|}}{C}-OH + R'\text{-}OH$$

For example,



$$CH_3-\overset{\overset{O}{\|}}{C}-OC_2H_5 + H_2O \rightarrow CH_3-\overset{\overset{O}{\|}}{C}-OH + C_2H_5-OH$$

Ethyl acetate Acetic acid

Industrial Preparation

By the Hydrolysis of Alkene Alkenes undergo hydrolysis to give alcohols following MarkowniKoff's addition.

(a) ***Indirect Hydrolysis*** Here alkenes are hydrolyzed by dilute acid like H_2SO_4 into alcohols as follows:

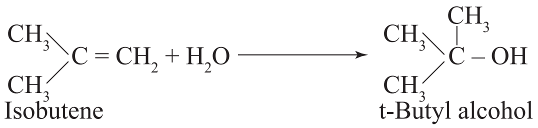
For example, (1)

$CH_3-CH=CH_2 + H.HSO_4 \rightarrow CH_3-CH_2-CH_2H.SO_4 \xrightarrow{HOH} CH_3-CH_2-CH_2OH + H_2SO_4$
Propene Propanol

(b) ***Direct Hydrolysis*** It occurs according to Markownikoff's rule.

For example,

$$R - CH = CH_2 + H.OH \xrightarrow{\text{dil. } H_2SO_4} R\text{-}CHOH - CH_3$$



$$(CH_3)_2C = CH_2 + H_2O \longrightarrow (CH_3)_2C(CH_3) - OH$$

Isobutene t-Butyl alcohol

Oxo Process Here alkene is treated with carbon monoxide and hydrogen in presence of cobalt carbonyl to give aldehyde which on reduction by Zn-Cu or Ni gives alcohol.

For example,

$$R\text{–}HC = CH_2 + CO + H_2 \xrightarrow[\text{High temperature High Pressure}]{[Co(CO)_4]_2} R\text{-}CH_2 - CH_2 - CHO \xrightarrow{H_2/Ni} R\text{–}CH_2\text{–}CH_2\text{–}CH_2\text{– }OH$$

Some Specific Preparations

Methyl Alcohol [CH_3OH]

- $CH_4 + O_2 \xrightarrow[\Delta,\ 200 \text{ atm 'P' } 300^oC]{\text{cu-tube}} CH_3OH$
- $\underset{\text{water gas}}{CO + H_1} + H_2 \xrightarrow[\Delta]{\text{oxides of Cu, Zn}} CH_3OH$
- CH_3OH is also obtained by the fractional distillation of pyroligneous acid (obtained by distillation of wood).
- Pyroligneous acid has 6 – 10 per cent CH_3COOH, 1 – 3 per cent CH_3OH [64°], 0.1 – 0.5 % CH_3COCH_3 [56°]
- When pyroligneous acid is treated with calcium hydroxide. Acetic acid is removed in the form of calcium acetate precipitate. The liquor having methyl alcohol and acetone on fractional distillation gives methyl alcohol as acetone is removed first as it is more volatile than methyl alcohol.

Ethyl Alcohol [C_2H_5OH]

From Starch and Sugar (Carbohydrates):

- **From Sugar**
  Molasses having nearly 20 per cent sugar is diluted upto 10 – 20 per cent by adding 5 – 6 times of water. Now add a little conc. H_2SO_4, yeast and keep the solution for 2 – 3 days at 298 K for fermentation. As a result of fermentation, ethanol is formed as follows:

  $$\underset{\text{Sugar}}{C_{12}H_{22}O_{11}} + H.OH \xrightarrow[\text{in yeast}]{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

  $$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow[\text{in yeast}]{\text{Zymase}} 2C_2H_5OH + 2CO_2 \uparrow$$

- **From Starch**
  Here starchy substances are treated with steam and malt (a source of diastase) is added to prepare ethyl alcohol as follows:

$$\underset{\text{Starch}}{2(C_6H_{10}O_5)n + nH_2O} \xrightarrow{\text{diastase}} \underset{\text{Maltose}}{nC_{12}H_{22}O_{11}} \xrightarrow[\text{Maltase}]{H_2O\text{ yeast}} 2C_6H_{12}O_6$$

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow[\text{in yeast}]{\text{Zymase}} 2C_2H_5OH + 2CO_2\uparrow$$

Physical Properties

- Lower Alcohols (methanol, ethanol) are colourless and sweet smelling, liquids while higher alcohols are colourless, odourless, waxy solids.
- Alcohols are highly soluble in water in any proportion due to intermolecular hydrogen bonding with water molecules however their solubility decreases with increase of molecular weight.

  For example, $CH_3OH > C_2H_5OH > C_3H_7OH > C_4H_9$ ……
- Boiling points of alcohols are greater than corresponding ethers or alkyl halides due to presence of inter-molecular hydrogen bonding in alcohols alcohol there is present inter-molecular hydrogen bonding, so alcohols exists as associated molecules.

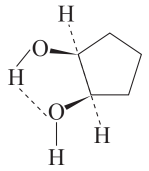
  

  $$\cdots\cdots \underset{\substack{|\\R}}{H-O} \cdots\cdots \underset{\substack{|\\R}}{H-O} \cdots\cdots \underset{\substack{|\\R}}{H-O} \cdots\cdots \underset{\substack{|\\R}}{H-O}$$

  Therefore , more energy is required to break these hydrogen bonds, so the boiling point of alcohols is higher, on the other hand in alkanes and haloalkanes only weak van der Waal's forces of attraction and dipole-dipole attractive forces are present respectivily, which can be easily broken in comparison to hydrogen bonds.

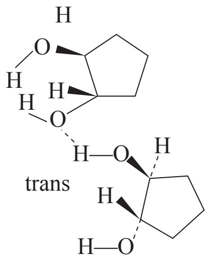
  For example, - $C_2H_5OH > CH_3OCH_3$ or C_2H_5X
- Boiling point ∝ molecular weight or surface area.

  For example, - $\underset{\text{Neobutyl alcohol}}{CH_3\,CH_2\,CH_2\,CH_2OH} > \underset{\text{Isobutyl alcohol}}{(CH_3)_2CHOH} > \underset{\text{n-propyl alcohol}}{CH_3\,CH_2\,CH_2OH}$



cis

Intramolecular H- bond
(a)



Intramolecular H- bond
(b)

- Alcohols can not be dried over anhydrous calcium chloride , because they form solid derivatives with $CaCl_2$ such as $CaCl_2 . 4CH_3OH$, $CaCl_2 . 4\,C_2H_5OH$, called as alcoholates or alcohols of crystallization.

CHEMICAL PROPERTIES Alcohol gives following type of reactions:

(A) Reactions With Cleavage of – O $\vdots$ H Bond or due to H⁺ These reactions show acidic nature of alcohols. Alcohols are very-very weak acidic in nature and considered as neutral practically.

$$R\rightarrow\ddot{\underset{..}{O}}-H \rightleftharpoons R-\ddot{\underset{..}{O}}\!:^{\ominus} + H^{\oplus}$$

In alcohols, due to the presence of an electron releasing alkyl group, electron density is increased on the oxygen atom, which hinders the release of a proton, so alcohols are weakly acidic in nature. Morover, if proton release, alkoxide ion is formed, it is not resonance stabilized, hence, it is unstable and the equilibrium shifts towards backward direction.

Order of reactivity and acidity The order of reactivity of reactions of the type involving O–H cleavage is

$CH_3OH > 1^o > 2^o > 3^o$ alcohols.

(i) With Metals Alcohols reacts with active metals like Na, K etc. to give metal alkoxides which react with haloalkanes to form ethers.

$$2R - OH + 2Na \rightarrow 2R - ONa + H_2\uparrow \xrightarrow[R'X]{} R\text{-}O\text{-}R' + NaX$$

For example, $2CH_3 - OH + 2Na \rightarrow \underset{\text{Sodium methoxide}}{2CH_3 - ONa} + H_2\uparrow$

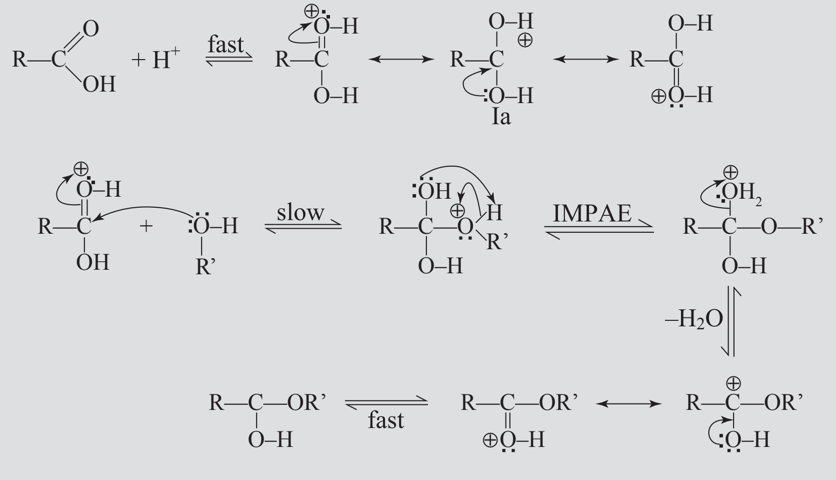
$$CH_3ONa + C_2H_5Cl \longrightarrow \underset{\text{Methyl ethyl ether}}{CH_3 - O - C_2H_5} + NaCl$$

(ii) Ester Formation Alcohols give esters with acids and acid derivatives as follows:

$$R'–OH + R\text{-}COOH \xrightarrow{\text{dil. acid}} R\text{-}COOR' + H_2O$$

For example, $CH_3 - COOH + HO\text{-}C_2H_5 \rightarrow \underset{\text{Ethylacetate}}{CH_3 - COOC_2H_5} + H_2O$

Mechanism



(iii) With Grignard Reagent Alcohols react with Grignard reagent to give alkanes.

$$R - OH + R'MgX \rightarrow R'H + R–OMgX$$

For example,

$$C_2H_5 - OH + CH_3MgBr \rightarrow CH_4 + C_2H_5–OMgBr$$

(B) Reaction Due to –OH Group (Cleavage of C — OH type)

(i) With HX Here alcohol reacts with HX to give alkyl halide.

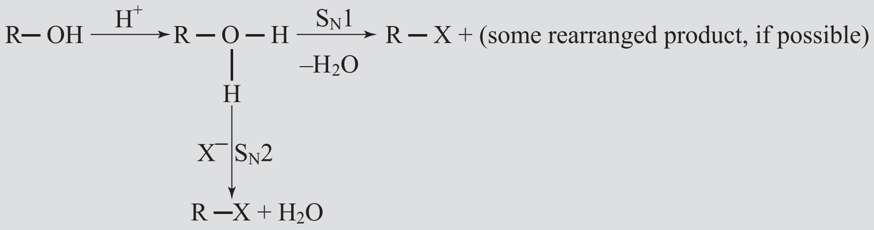
$$R\text{-}OH + HX \xrightarrow{\text{Anhy. } ZnCl_2} R\text{-}X + H_2O$$

$$C_2H_5OH + HBr \xrightarrow{\text{Anhy. } ZnCl_2} C_2H_5Br + H_2O$$

- Here anhydrous $ZnCl_2$ is catalyst, dehydrating agent and prevents reverse reaction.
- Here reactivity order for alcohol is tertiary > secondary > primary.

Here reactivity order for HX is HI > HBr > HCl > HF

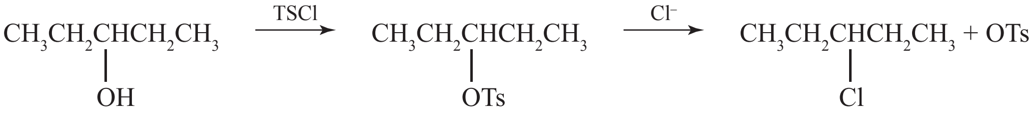
Mechanism



$$R-OH \xrightarrow{H^+} R-\underset{H}{\underset{|}{O}}-H \xrightarrow[-H_2O]{S_N1} R-X + \text{(some rearranged product, if possible)}$$

$$R-\underset{H}{\underset{|}{O}}-H \xrightarrow[S_N2]{X^-} R-X + H_2O$$

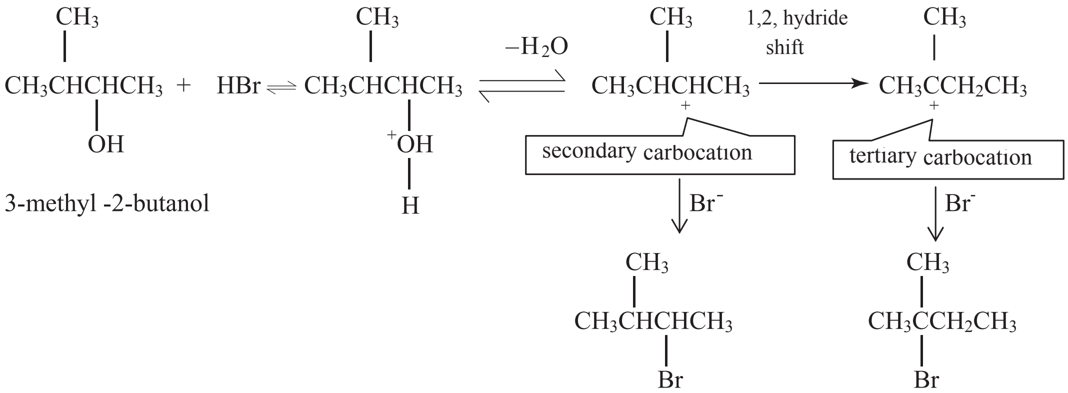
For example,



$$CH_3CH_2\underset{OH}{\underset{|}{C}}HCH_2CH_3 \xrightarrow{TSCl} CH_3CH_2\underset{OTs}{\underset{|}{C}}HCH_2CH_3 \xrightarrow{Cl^-} CH_3CH_2\underset{Cl}{\underset{|}{C}}HCH_2CH_3 + OTs$$

3- Pantanol 3- chloropentane

For example,



$$CH_3\overset{CH_3}{\overset{|}{C}}H\underset{OH}{\underset{|}{C}}HCH_3 + HBr \rightleftharpoons CH_3\overset{CH_3}{\overset{|}{C}}H\underset{H}{\underset{|}{\underset{{}^+OH}{\underset{|}{C}}}}HCH_3 \underset{}{\overset{-H_2O}{\rightleftharpoons}} CH_3\overset{CH_3}{\overset{|}{C}}H\overset{+}{C}HCH_3 \xrightarrow{\text{1,2, hydride shift}} CH_3\overset{CH_3}{\overset{|}{\overset{+}{C}}}CH_2CH_3$$

$$CH_3\overset{CH_3}{\overset{|}{C}}H\underset{Br}{\underset{|}{C}}HCH_3 \qquad CH_3\overset{CH_3}{\overset{|}{\underset{Br}{\underset{|}{C}}}}CH_2CH_3$$

3-methyl -2-butanol

2- bromo -3-methyl-butane minor product

2- bromo -2- methyl-butane major product

(ii) *With PX_5, PX_3, $SOCl_2$*

$$R–OH + PX_5 \xrightarrow{\Delta} R\text{-}X + POX_3 + HX$$

For example,

$$C_2H_5 – OH + PCl_5 \xrightarrow{\Delta} C_2H_5Cl + POCl_3 + HCl$$

$$3R\text{-}OH + PX_3 \xrightarrow{\Delta} 3R\text{-}X + H_3PO_3$$

For example,

$$3C_2H_5 – OH + PCl_3 \xrightarrow{\Delta} 3C_2H_5Cl + H_3PO_3$$

$$R–OH + SOCl_2 \xrightarrow{\text{pyridine}} R–Cl + SO_2 + HCl$$

For example,

$$C_2H_5 – OH + SOCl_2 \xrightarrow{\text{pyridine}} C_2H_5Cl + SO_2 + HCl$$

- Here pyridine reflux gaseous biproducts SO_2 and HCl from here so it is a better method and known as Dorzen's method.
- An alcohol cannot give such reactions with Cl_2 or S_2Cl_2 .

(iii) *With NH_3* When an alcohol reacts with ammonia over heated alumina a primary amine is obtained.

$$R–OH + NH_3 \xrightarrow[350^oC]{\Delta\, Al_2O_3} R\text{-}NH_2 + H_2O$$

For example,

$$C_2H_5OH + NH_3 \xrightarrow[350^oC]{\Delta\, Al_2O_3} C_2H_5NH_2 + H_2O$$

(C) Reaction of Whole R –OH

(i) *Dehydration* Alcohols can be dehydrated into alkenes or ether depending upon the nature of dehydrating agent, temperature and amount of alcohol. Some common dehydrating agents are conc. H_2SO_4 , conc. H_3PO_4, Al_2O_3 etc.

(a) ***When Alcohol is in Excess, H_2SO_4 is Dehydrating Agent and Temperature is 140°C*** Ether is formed here as follows:

$$R – OH + H_2SO_4 \xrightarrow{100^o–110^oC} RHSO_4 + H_2O$$

$$RHSO_4 + R\text{-}OH \xrightarrow{140^o} R – O – R + H_2SO_4$$

For example,

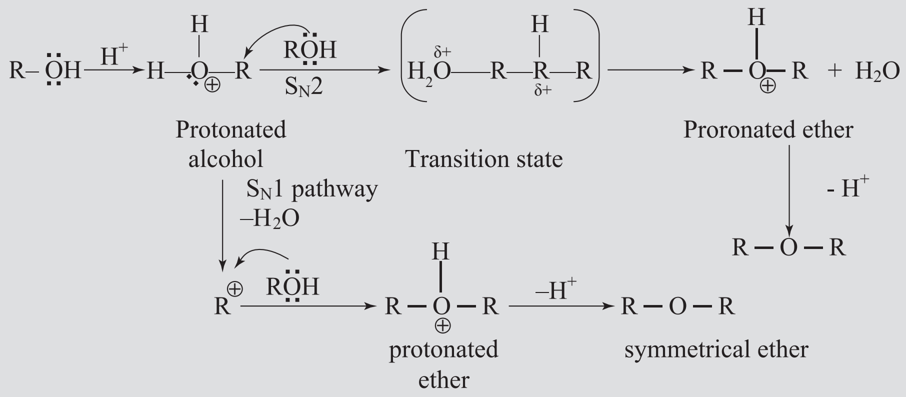
$$C_2H_5 – OH + H_2SO_4 \xrightarrow{100^o–110^oC} C_2H_5HSO_4 + H_2O$$

Ethyl hydrogen sulphate

$$C_2H_5HSO_4 + C_2H_5\text{-}OH \xrightarrow{140^o} C_2H_5 – O – C_2H_5 + H_2SO_4$$

Diethyether

Mechanism



(b) ***When H_2SO_4 is in Excess and Temperature is 170°C*** An alkene is formed here.

$$C_2H_5-OH+H_2SO_4 \xrightarrow{100^\circ\text{–}110^\circ C} C_2H_5\,HSO_4+H_2O$$

Ethyl hydrogen sulphate

$$C_2H_5HSO_4 \xrightarrow{170^\circ} C_2H_4 + H_2SO_4$$

Ethene

$$CH_3-OH+H_2SO_4 \xrightarrow{100^\circ\text{–}110^\circ C} CH_3HSO_4 + H_2O$$

Methyl hydrogen sulphate

$$2CH_3HSO_4 \xrightarrow{170^\circ} (CH_3)_2SO_4 + H_2SO_4$$

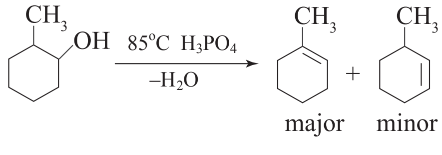
Dimethyl sulphate

- Here removal of β-hydrogen atom takes place from the β-carbon atom having less number of hydrogen atom to give a more stable alkene as a major product that is, according to Saytzeff rule.

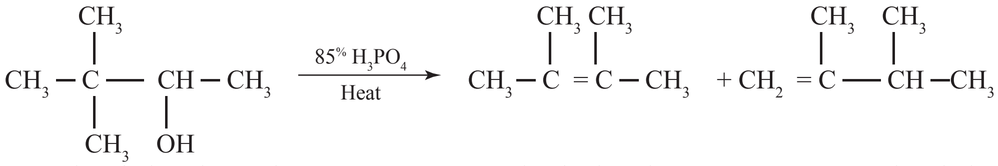
  For example,

$$CH_3-CH_2-CHOH-CH_3 \xrightarrow{\text{conc. } H_2SO_4} CH_3-CH= CH-CH_3$$

But-2-ene



Rearrangement During Dehydration:

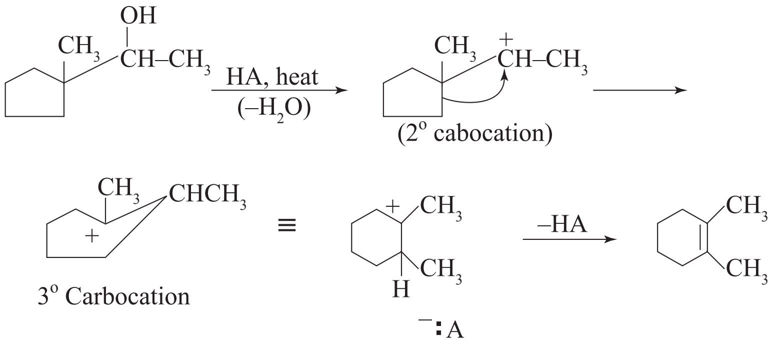


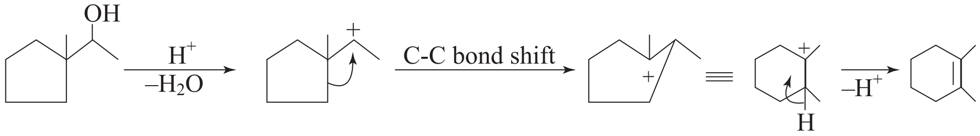
$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-\underset{\displaystyle OH}{CH}-CH_3 \xrightarrow[\text{Heat}]{85\%\ H_3PO_4} CH_3-\overset{CH_3}{C}=\overset{CH_3}{C}-CH_3 + CH_2=\overset{CH_3}{C}-\overset{CH_3}{CH}-CH_3$$

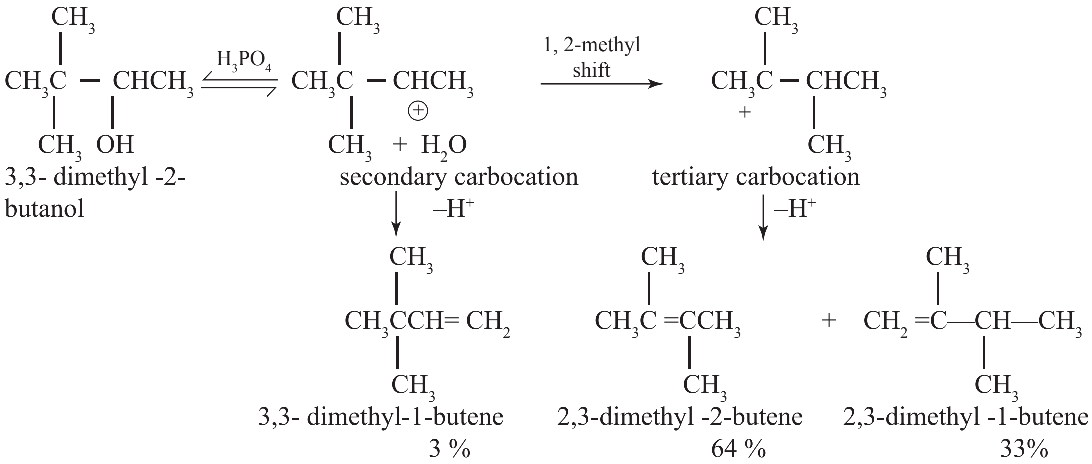
3,3 -Dimethyl -2- butanol

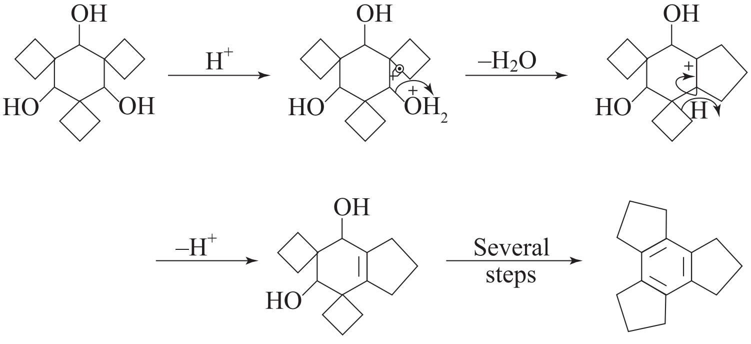
2,3- Dimehtyl -2- butene
(major product)

2,3- Dimethyl -1- butene
(minor product)


OH
CH_3
$CH–CH_3$
HA, heat
$(–H_2O)$
CH_3
$\overset{+}{C}H–CH_3$
(2° cabocation)
CH_3
$CHCH_3$
3° Carbocation
≡
CH_3
CH_3
H
$^{-}$:A
–HA
CH_3
CH_3

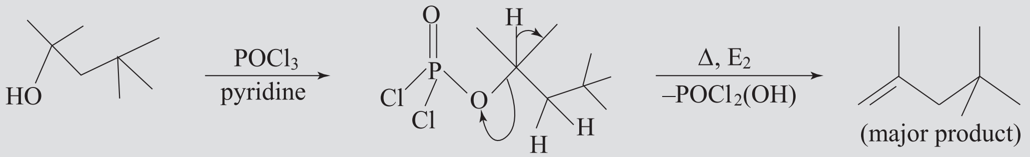

OH
H^+
$–H_2O$
C-C bond shift
≡
H
$–H^+$


CH_3
$CH_3C – CHCH_3$
CH_3 OH
3,3- dimethyl -2-butanol
H_3PO_4
$CH_3C – CHCH_3$
CH_3 + H_2O
secondary carbocation
1, 2-methyl shift
$CH_3C – CHCH_3$
tertiary carbocation
$–H^+$
$CH_3CCH= CH_2$
3,3- dimethyl-1-butene
3 %
$–H^+$
$CH_3C =CCH_3$
2,3-dimethyl -2-butene
64 %
$CH_2 =C—CH—CH_3$
2,3-dimethyl -1-butene
33%


OH
HO
OH
H^+
OH
HO
$\overset{+}{O}H_2$
$–H_2O$
OH
HO
H
$–H^+$
OH
HO
Several steps

REMEMBER

The E2 eliminations of 3° alcohols under relativitly non-acidic conditions may be accomplished by treating with phosphrous oxy chloride, $POCl_3$ in pyridine.
For example,



(c) When Vapours of Alcohol are Passed Over Heated Alumina (Al_2O_3) or Thoria (ThO_2)

(i) At 250°C Ether is formed

$$R-OH + R-OH \xrightarrow[250^{\circ}C]{Al_2O_3} R-O-R + H_2O$$

For example,

$$2C_2H_5OH \xrightarrow[250^{\circ}C]{Al_2O_3} C_2H_5-O-C_2H_5 + H_2O$$

- If both the alcohols are different then three types of ethers will be formed.

For example,

$$CH_3OH + C_2H_5OH \xrightarrow[350^{\circ}C]{Al_2O_3} CH_3-O-CH_3 + C_2H_5-O-C_2H_5 + CH_3-O-C_2H_5 + H_2O$$

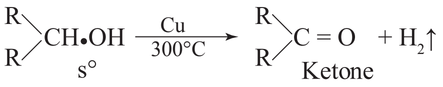
(d) When Vapours of Alcohol are Passed Over Heated Alumina (Al_2O_3) or Thoria (ThO_2)

(i) At 350°C Alkene is formed

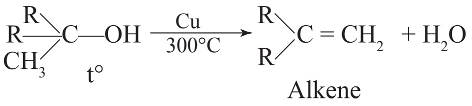
$$C_2H_5OH \xrightarrow[350^{\circ}C]{Al_2O_3} C_2H_4 + H_2O$$

(ii) Dehydrogenation (Cu / 300°C)
It is a test of p°, s°, t° alcohols as different products are formed here.

$$\underset{p^{\circ}}{R-CH_2OH} \xrightarrow{Cu/300^{\circ}C} \underset{\text{Al dehyde}}{R-CHO + H_2\uparrow}$$



$$\underset{s^{\circ}}{R_2CH{\cdot}OH} \xrightarrow[300^{\circ}C]{Cu} \underset{\text{Ketone}}{R_2C=O} + H_2\uparrow$$



$$\underset{t^{\circ}}{R_2(CH_3)C-OH} \xrightarrow[300^{\circ}C]{Cu} \underset{\text{Alkene}}{R_2C=CH_2} + H_2O$$

Oxidation It is a test of different alcohols as p°, s°, t° alcohols give different products during oxidation.

(i) Primary alcohols give acids having same number of carbon atoms with acidic $KMnO_4$ or $K_2Cr_2O_7$.

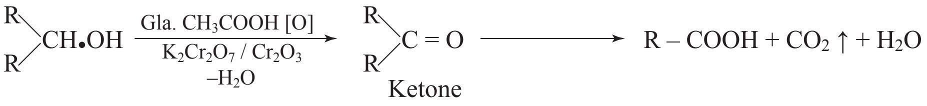
$$R-CH_2OH \xrightarrow[-H_2O]{[O]\text{ acidic }KMnO_4} R-CHO \xrightarrow{[O\}\text{ acidic }KMnO_4} \underset{\text{Acid}}{R-COOH}$$

e.g.,

$$CH_3CH_2OH \xrightarrow[-H_2O]{[O]\text{ acidic }KMnO_4} CH_3-CHO \xrightarrow{[O\}\text{ acidic }KMnO_4} \underset{\text{Acetic acid}}{CH_3COOH}$$

- During the oxidation the colour of oxidizing agent disappears.

(ii) Secondary alcohol on oxidation gives ketone which undergo further oxidation under drastic conditions by strong oxidizing agents like HNO_3 to give acid with one carbon atom less than alcohol.

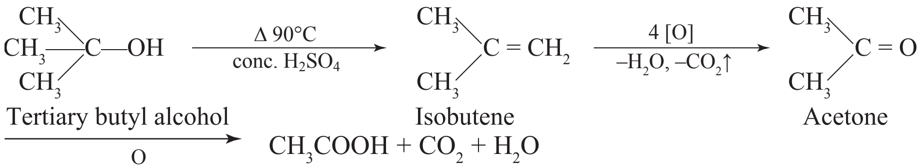


$$R_2CH\cdot OH \xrightarrow[K_2Cr_2O_7 / Cr_2O_3,\ -H_2O]{\text{Gla. }CH_3COOH\ [O]} \underset{\text{Ketone}}{R_2C=O} \longrightarrow R-COOH + CO_2\uparrow + H_2O$$

$$(CH_3)_2CHOH \xrightarrow[K_2Cr_2O_7/Cr_2O_3]{\text{Gla. }CH_3COOH\ [O]} CH_3-CO-CH_3 \longrightarrow CH_3COOH + CO_2 + H_2O$$

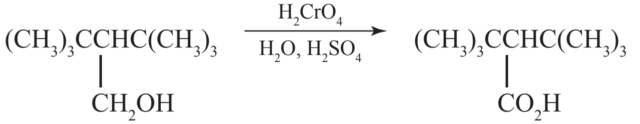
Isopropyl Alcohol

(iii) Tertiary alcohol cannot undergo oxidation by mild oxidizing agent as above however it can be oxidized under drastic conditions by strong oxidizing agents and the final product acid will have two carbon atom less than alcohol.



$$(CH_3)_3C-OH \xrightarrow[\text{conc. }H_2SO_4]{\Delta\ 90°C} (CH_3)_2C=CH_2 \xrightarrow[-H_2O,\ -CO_2\uparrow]{4\ [O]} (CH_3)_2C=O \xrightarrow[O]{} CH_3COOH + CO_2 + H_2O$$

Tertiary butyl alcohol Isobutene Acetone



$$(CH_3)_3CCH(CH_2OH)C(CH_3)_3 \xrightarrow[H_2O,\ H_2SO_4]{H_2CrO_4} (CH_3)_3CCH(CO_2H)C(CH_3)_3$$

2- tert - Butyl -3, 3-dimethyl -1- butanol

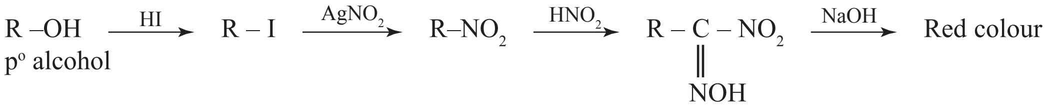
2- tert -Butyl -3, 3-dimehtylbutanoic acid (82 %)

Test of Primary, Secondary, Tertiary Alcohols

(i) *Lucas Method*

- Concentrated HCl + Anhy. $ZnCl_2$ is Lucas reagent.
- The reactivity of alcohols towards Lucas reagent is $t^o > s^o > p^o$
- $\underset{\text{Primary alcohol}}{R-CH_2OH} \xrightarrow{\text{Lucas .Reagent}}$ No reaction in cold.
- $\underset{\text{Secondary alcohol}}{R_2CHOH} \xrightarrow{\text{Lucas .Reagent}}$ Formation of ppt. after 5-10 minutes.
- $\underset{\text{Tertiary alcohol}}{R_3C.OH} \xrightarrow{\text{Lucas .Reagent}}$ An oily layer (turbidity) is formed in cold at once.

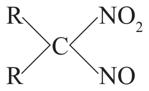
(2) ***Victor Mayer Method*** Here primary, secondary and tertiary alcohols give different colours during the experiment.



$$\underset{\text{p° alcohol}}{R-OH} \xrightarrow{HI} R-I \xrightarrow{AgNO_2} R-NO_2 \xrightarrow{HNO_2} \underset{\displaystyle NOH}{\underset{\|}{R-C-NO_2}} \xrightarrow{NaOH} \text{Red colour}$$

$$R_2CHOH \xrightarrow{HI} R_2\,CHI \xrightarrow{AgNO_2} R_2\,CHNO_2 \xrightarrow{HNO_2}$$

s° alcohol



$\xrightarrow{NaOH}$ Blue colour

$$R_3COH \xrightarrow{HI} R_3CI \xrightarrow{AgNO_2} R_3\,CNO_2 \xrightarrow{HNO_2} \text{No reaction} \xrightarrow{NaOH} \text{Colourless}$$

t° alcohol

(3) ***Dichromate test*** This test based on the fact that three types of monohydric alcohols give different oxidation products on oxidations as follows:

Primary alcohol
RCH_2OH
[O] $\downarrow$ $Na_2Cr_2O_7 + H_2SO_4$
$RCHO$
[O] $\downarrow$ $Na_2Cr_2O_7 + H_2SO_4$
$RCOOH$
Acid (Orange solution becomes green)

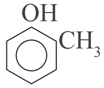
Secondary alcohol
R_2CHOH
[O $\downarrow$ $Na_2Cr_2O_7 + H_2SO_4$
R_2CO
Ketone (Orange solution becomes green)

Tertiary alcohol
R_3COH
[O] $\downarrow$ $Na_2Cr_2O_7 + H_2SO_4$
No reaction (Solution remians orange)

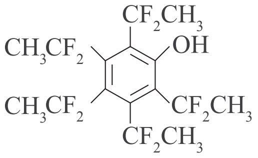
PHENOL OR HYDROXY COMPOUNDS

- These are hydroxy derivatives of benzene and are of following types:

Phenol

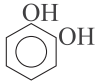


o-cresol

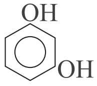


Pentakis (1,1 -difluoroethyl) phenol

Di Hydroxy



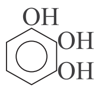
Catechol



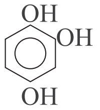
Resorcinol

Quinol or Hydroquinone

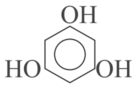
Tri Hydroxy



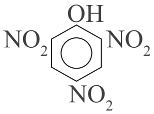
Pyrogallol



Hydroxy quinol

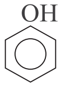


Phloro glucinol



Picric acid

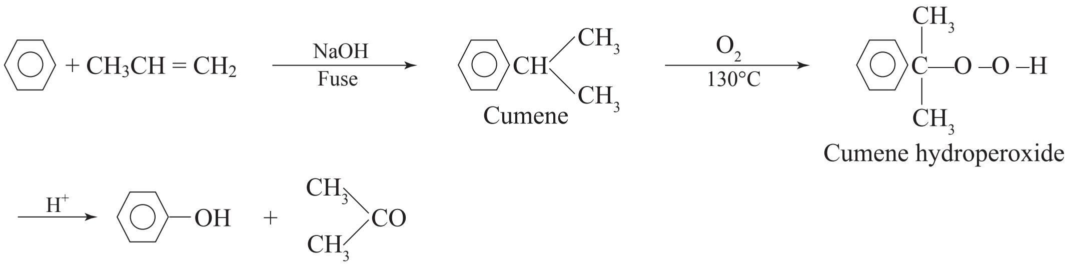
PHENOL OR HYDROXY BENZENE OR CARBOLIC ACID



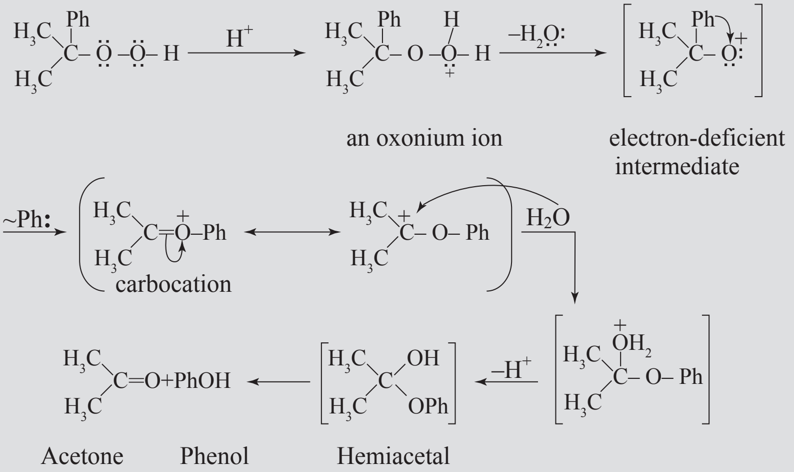
- Phenol was discovered by Runge by the middle oil fraction of coal tar distillation. Phenol is acidic, antiseptic and also disinfectant. It is soluble in aqueous NaOH and KOH but insoluble in aq. $NaHCO_3$ [while acids (benzoic acid) are soluble in NaOH or KOH, aqueous $NaHCO_3$] It gives violet colour with aq. $FeCl_3$ which is of $(C_6H_5O)_3$ Fe.

Methods of Preparation

- **From Middle Oil Fraction of Coal Tar** The middle oil fraction mainly contains phenol (acidic) and Naphthalene (neutral). The mixture is dissolved in NaOH in which phenol is soluble and Naphthalene is insoluble. The aqueous solution on acidification gives phenol.
- **Industrial Method or From Cumene**



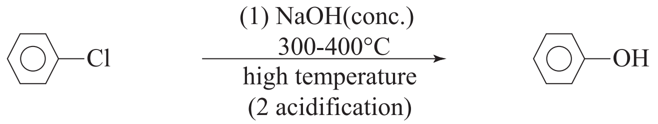
Mechanism



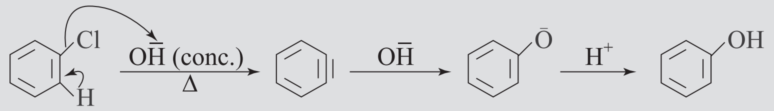
- **Lab Method**

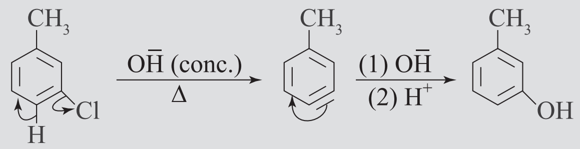
$$C_6H_5SO_3H \xrightarrow[\text{Fuse}]{NaOH} C_6H_5SO_3Na \xrightarrow[\Delta]{NaOH} C_6H_5OH + Na_2CO_3$$

- **Commercial or (Dow's Method) Process**

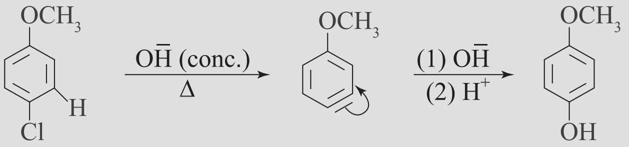


Mechanism



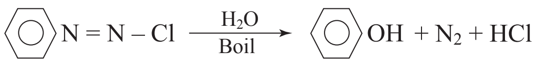


(CH3 is electron
releasing group)



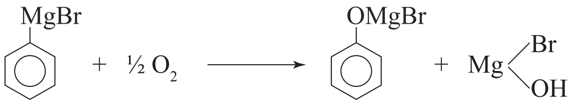
(OCH shows - I effect)

- **From Benzene Diazonium Chloride**

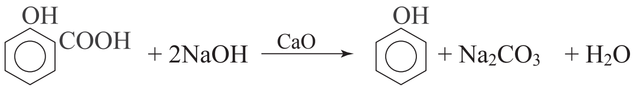


Phenol

- **From Grignard Reagent**

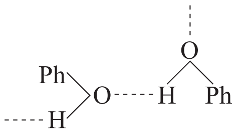


- **From Salicylic Acid**

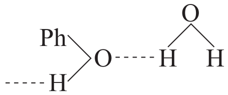


PHYSICAL PROPERTIES

1. It is a crystalline, deliquescent solid with a melting point of 42°C and a boiling point of 182°C. It attains pink colour in air and light.
2. Phenols are, in general, insoluble in water and soluble in organic sovents, however, phenol itself and some dihydric and trihydric phenols are soluble in water due to the presence of hydrogen bonding.

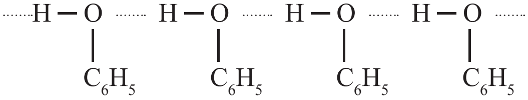


Intermolecular hydrogen bonding in phenols



Hydrogen bonding between phenol and water molecules

3. The boiling point of phenols are higher than the hydrocarbon of camparable masses. This is due to the presence of inter-molecular hydrogen bonding, for example, the b.p. of phenol is more than that of toluene.

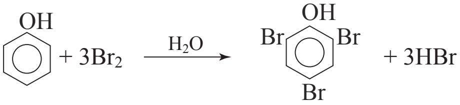


$$\cdots\mathrm{H}-\underset{\substack{|\\ C_6H_5}}{\mathrm{O}}\cdots\mathrm{H}-\underset{\substack{|\\ C_6H_5}}{\mathrm{O}}\cdots\mathrm{H}-\underset{\substack{|\\ C_6H_5}}{\mathrm{O}}\cdots\mathrm{H}-\underset{\substack{|\\ C_6H_5}}{\mathrm{O}}\cdots$$

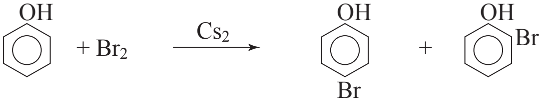
CHEMICAL PROPERTIES

Electrophilic Subsitution In phenol the -OH group is highly ring activating so electrophilic substitution is easier and at a higher rate than that of benzene.

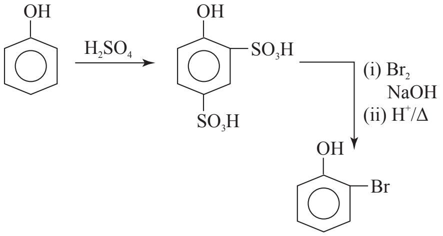
- **Halogenation**



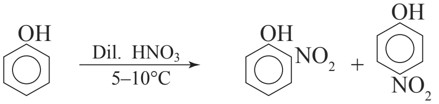
2, 4,6- Tri bromo phenol



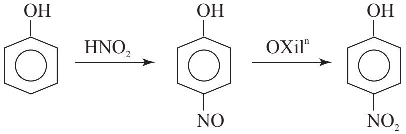
o- and p-bromophenol



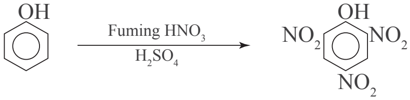
- **Nitration**



masor

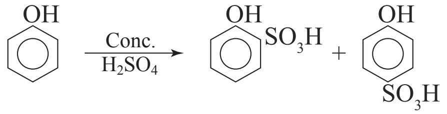


- A mixture of ortho and para nitrophenol can be separated by steam distillation because o-nitro phenol is volatile in steam due to chelation. (Intramolecular H-bonding).



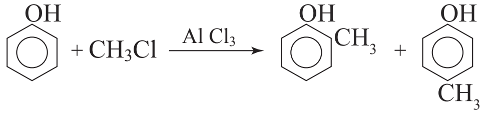
2, 4, 6 tri nitro phenol
Picric acid (explosive)

- **Sulphonation**



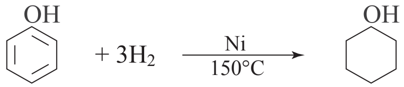
o, p-hydroxybenzene sulphonic acid

- At low temperature ortho isomer is dominating while at high temperature para isomer is dominating here.
- **Friedal Craft Reaction**



o & p cresols

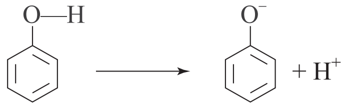
- Here the yield of the product is poor as ring alkylation takes place to avoid it $AlCl_3$ must be used in a proper amount.
- **Hydrogenation**



Cyclo hexanol

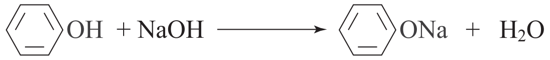
Reaction Due to OH Group

- **Acidic Nature**



Phenoxide or phenolate ion

- Phenol is acidic in nature due to phenoxide ion formation which is resonance stabilized.
- **Salt Formation**



- **Ether Formation**

Anisole

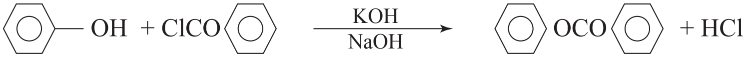
- 

Anisole

- **Acetylation**

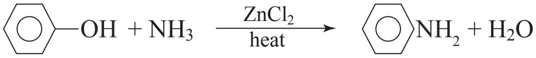
phenyl acetate

- **Benzylation (Schotten – Baumann Reacion)**

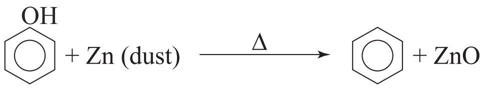


Phenyl Benzoate

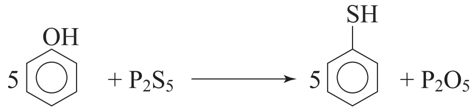
- **With Ammonia**



- It is called Bucherer reaction.
- **With Zinc Dust**

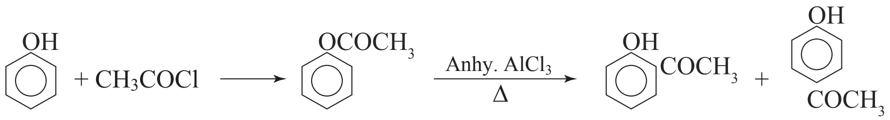


- **With P_2S_5** Phenol on heating with phosphorous penta sulphide gives thiophenol.

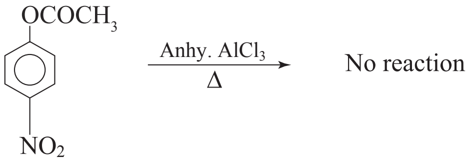


Other Reactions

(1) Fries Migration When phenol is acylated and the formed ester is further heated with lewis acid like anhydrous $AlCl_3$ etc. ortho and para acylphenols are formed. This rearrangement is called Fries migration or Fries rearrangement. Here at low temperature, para product is dominating and if in the ester ortho or para position is associated with electron withdrawing group the reaction is not possible.

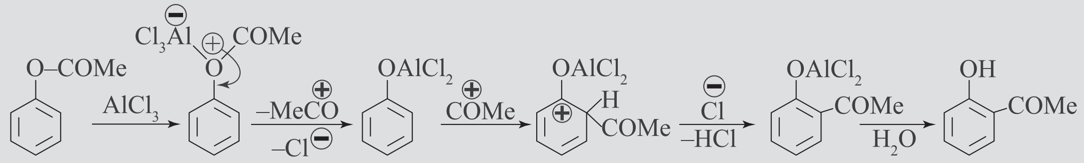


o- & p-hydroxy acetophenone

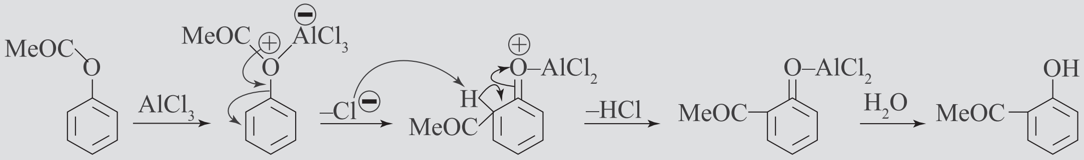


Mechanism

Two-step Mechanism

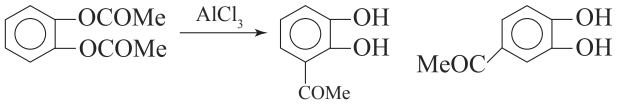


Single-step Mechanism



For example,

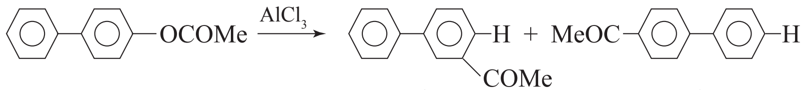
(i) Esters of catechol give acyl catechols



2, 3- Dihydroxy - acetophenone (minor)

2, 3- Dihydroxy - acetophenone (major)

(ii) Diphenyl esters also undergo Fries rearrangement predominantly in the same ring



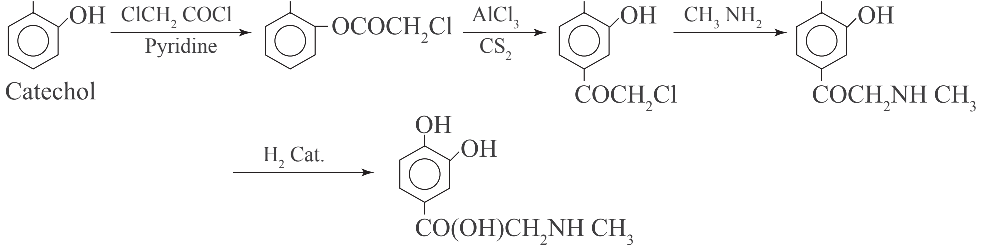
Major

Minor

4- Hydroxy -3- Methoxybiphenyl

4- Hydroxy -4'- Methoxybiphenyl

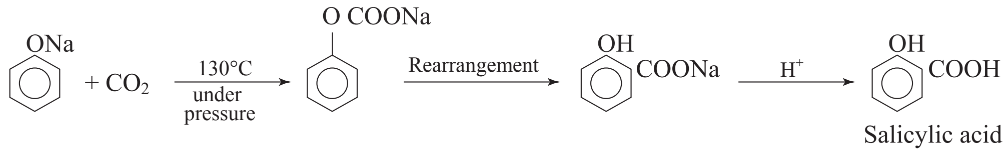
(iii) A very useful application is in the synthesis of (±) adrenaline which is a heart stimulatent.



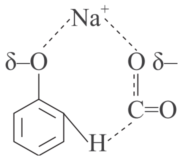
Catechol

± Adrenaline

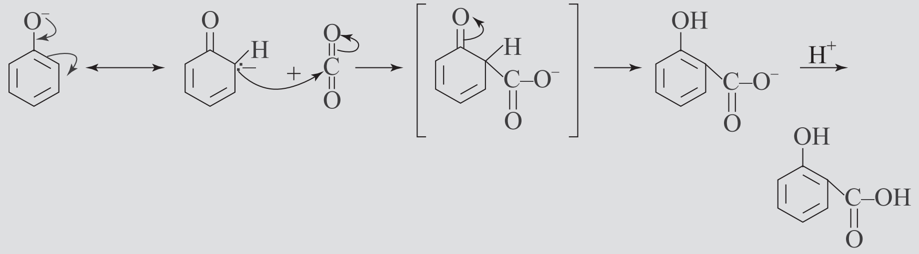
(2) Kolbe's Reaction When CO_2 is passed through sodium phenoxide under pressure(6 -7 atm) and at 125°C and the formed intermediate undergoes rearrangement to give salicylic acid, the process is called Kolbe's reaction.



- Here if we take potassium or other metal phenoxide the major product para hydroxy benzoic acid. In case of sodium phenoxide the major product ortho hydroxy benzoic acid due to chelation as shown below:

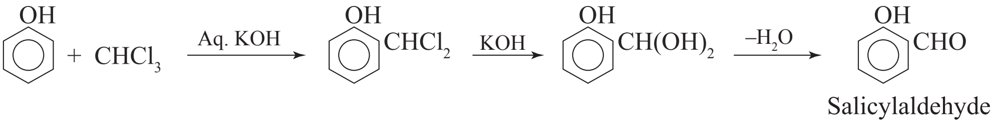


Mechanism

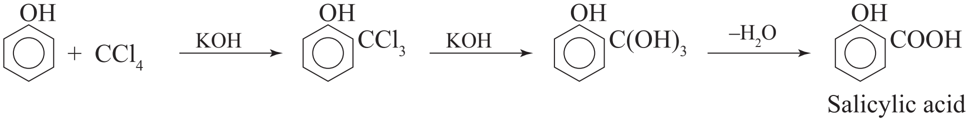


(3) Reimer Tiemann Reaction In this reaction phenol is treated with chloroform or CCl_4 in alkali solution to get salicyldehyde and salicylic acid respectively and in this reaction the reaction intermediate is di chloro carbene ($:CCl_2$)

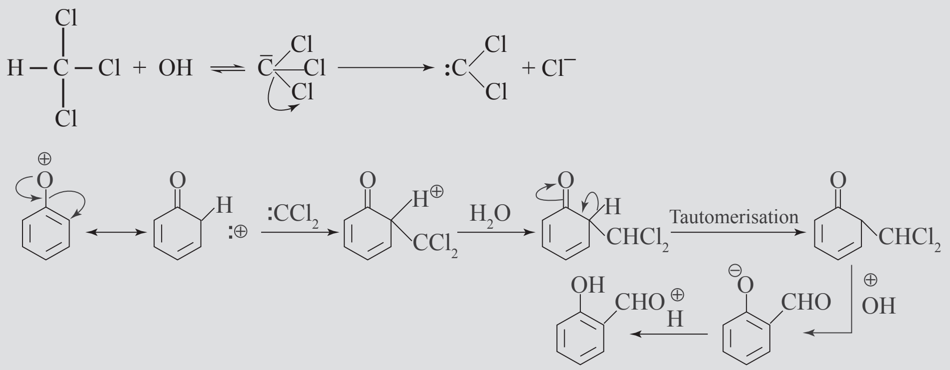
- Phenol gives salicylaldehyde with chloroform and KOH or NaOH. Salicylaldehyde is Steam volatile and does not give pink colour with Schiff reagent due to chelation.



- Phenol on reaction with carbon tetrachloride gives salicylic acid or ortho hydroxy benzoic acid.

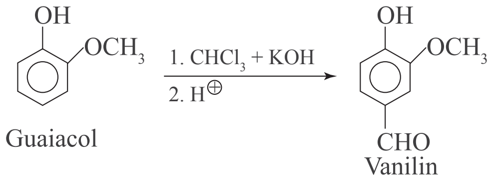


Mechanism

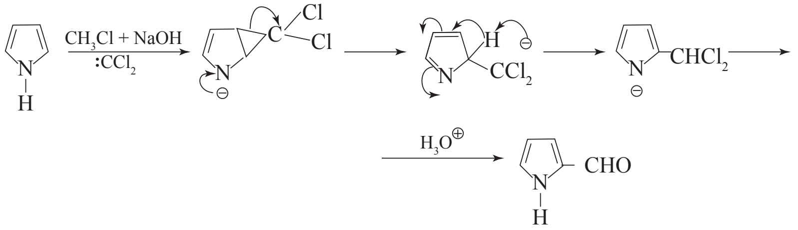


For examples,

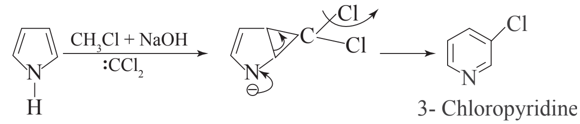
(i) Preparation of vanillin



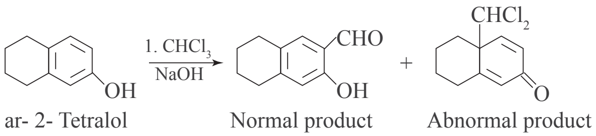
(2)

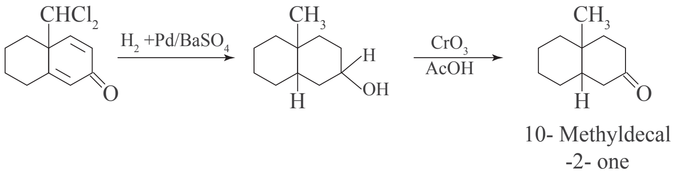


(3) Ring expansion case



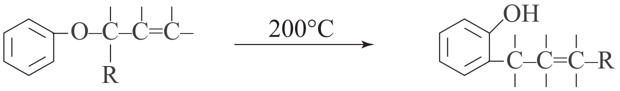
(iii) Certain phenolic compounds also exhibit normal and abnormal RTR



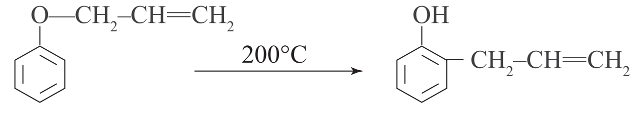


(4) Claisen Reaction (Claisen-rearrangement): Allyl aryl ehters when heated rearrange to *o*- allyl phenols in a reaction called Claisen rearrangement. It involves migration of allyl group to ortho position but if both ortho positions are filled, the allyl group migrates to para-position (This is often called paraclaisen rearrangement). The reaction sometimes need either haet or catalyst like HCl, H_2SO_4, $ZnCl_2$, BF_3 or $AlCl_3$.

In general, it may be represented as below:



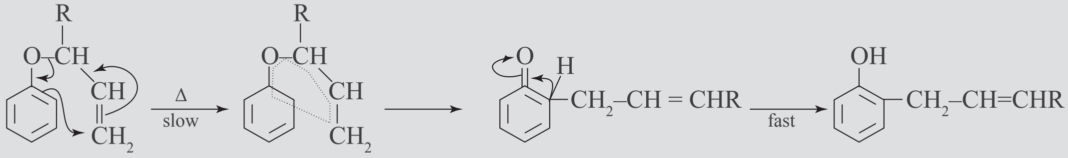
For example,



Allyl aryl ether

o- Allyl phenol

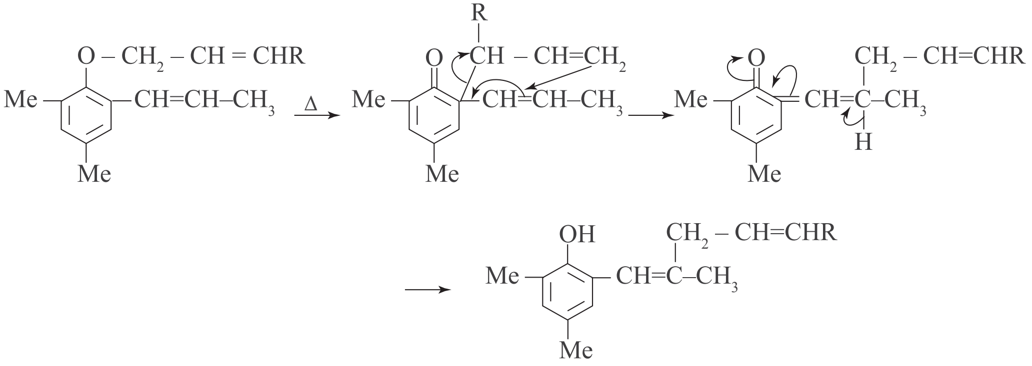
Mechanism



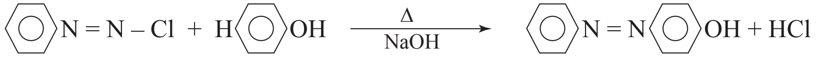
Transition state

Dienone (I) intermediate

For examples,



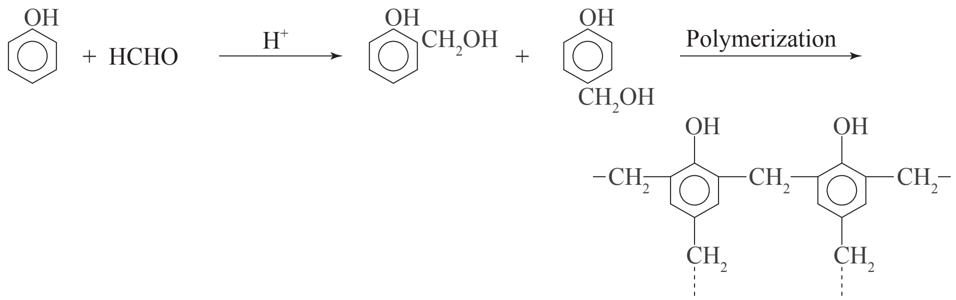
(5) With Benzene Diazonium Chloride (Coupling Reaction)



p-hydroxy azo benzene

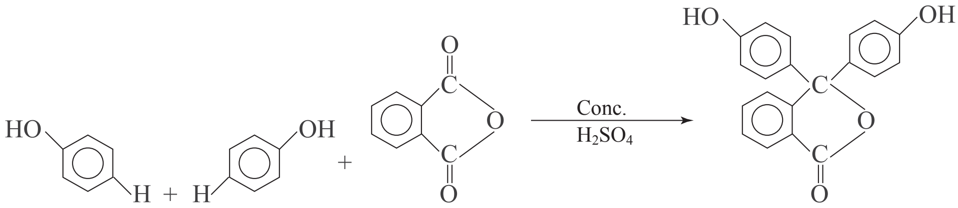
(6) Condensation Reactions

(i) With Formaldehyde Phenol on condensation with formaldehyde in presence of acid or alkali gives a three dimensional polymer 'Bakelite' (a resin and thermo setting plastic). This reaction is called Lederer-Manasse reaction.



(Bakelite) Plastic
Thermosetting plastic

(ii) Condensation With Phthalic Anhydride Phenol on condensation with phthaleic anhydride in presence of sulphuric acid gives phenolphthalene a dye and an indicator.

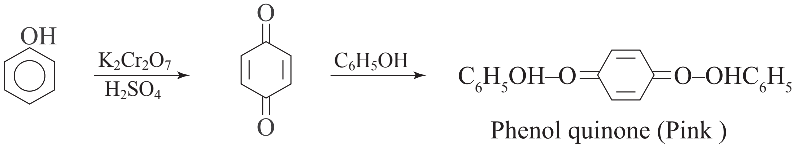


Phenolphthalein (indicator)

(7) Oxidation of Phenol

Phenol gives different products on oxidation as follows:

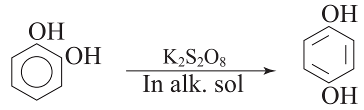
(i) With $K_2Cr_2O_7$ or By Air or by jone's reagent ($CrO_3 + H_2O$)



p-benzo quinone

Phenol quinone (Pink)

(ii) With $K_2S_2O_8$ or Elbs Per Sulphate Oxidation



Catechol

Quinoline or Hydroquinone

REMEMBER

- These are strong reducing agent used and in photography as developer.
- They are antioxidants, free radicals inhibitors.

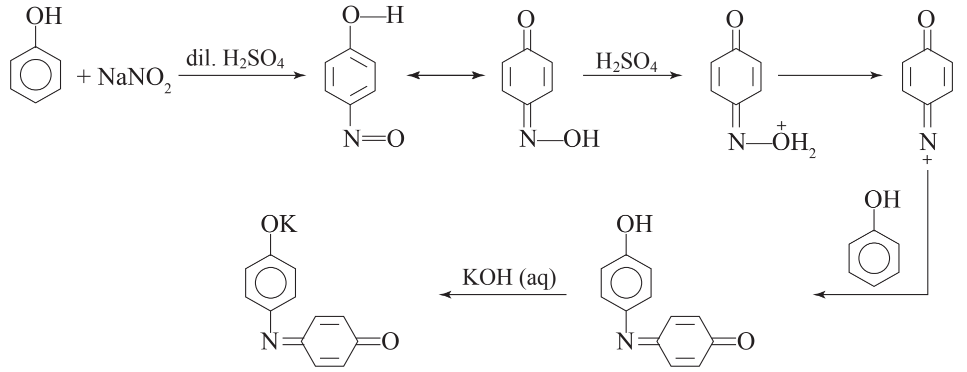
Test of Phenol

With Neutral $FeCl_3$ Phenol on reaction with neutral ferric chloride gives violet colour of ferric phenoxide

$$C_6H_5OH \xrightarrow{FeCl_3} \underset{\text{Violet colour}}{(C_6H_5O)_3Fe}$$

- **Liebermann's Nitroso Reaction**

$$\underset{\text{In } H_2SO_4}{C_6H_5OH} \xrightarrow[\text{in excess of } H_2O]{NaNO_2} \text{Red colouration} \xrightarrow[\text{excess}]{NaOH} \text{Blue colouration}$$



Indophenol (blue) Indophenol (red)

- **Can Test**

  Treat a few drops of ceric ammonium nitrate with 3-4 ml of hot aqueous solution of the organic compound. A green or brown precipitate is formed.

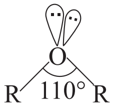
$$\underset{\text{CAN}}{(NH_4)_2[Ce(NO_3)_6]} + \underset{\text{Phenol}}{2C_6H_5OH} \rightarrow \underset{\text{green or brown ppt.}}{[Ce(NO_3)_4\,(C_6H_5OH)_2]} + 2NH_4NO_3$$

- Phenol gives blue colour with ammonia and sodium hypo chlorite.

Uses of Phenol

- Phenol is used widely as an antiseptic in ointments, soaps etc.
- Dettol is 2, 4-Dichloro-3,5-dimethyl phenol.
- Phenol is used in the manufacture of dyes like Phenolphthalene, Alizarine and Azodyes.
- In the manufacture of famous drugs like Aspirin, Phenacetin etc.
- In the manufacture of Bakelite.
- Phenol is used as the starting material for the manufacture of the drugs aspirin, phenacetin, salol, salicyclic acid etc.

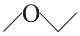
ETHERS (R – O –R)



- These are di alkyl or aryl derivatives of H_2O having a general formula $C_n H_{2n+2}O$.
- Ethers are called simple ethers when both the alkyl or aryl groups are same.

  For example, $C_2H_5 – O – C_2H_5$, $C_6H_5 – O – C_6H_5$
- Ethers are called mixed ethers when both the alkyl or aryl groups are different.

  Example,

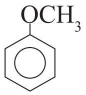


Methyl ethyl ether , $CH_3 – O – C_6H_5$ (Anisole)

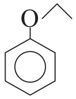
Nomenclature of Ethers Ethers are named as alkoxy alkane. Here alkoxy is for less carbon alkyl group while alkane is for more carbon alkyl group.

Example, $C_2H_5 – O – C_2H_5$, $CH_3 – O – CH_2 – CH_2 – CH_3$ $CH_3 – CH_2 – O – CH_2 – CH.(CH_3)_2$

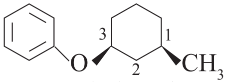
Ethoxy ethane Methoxy propane Ethoxy 2-methyl propane



Methoxy benzene



Ethoxy benzene



cis -1- methyl -3 phenoxy cyclohexane

Isomerism Shown by Ethers:

- Ethers are functional isomers of alcohols and ethers themselves show metamerism.

  Example,

  $C_2H_5 – O – C_2H_5$ and $CH_3 – O – CH_2 – CH_2 – CH_3$ are metamers.

  $C_6H_5 – CH_2 – OH$ and $C_6H_5 – O – CH_3$ are functional isomers.

METHODS OF PREPARATION Ethers are prepared as follows:

(1) From Williamson Synthesis It is the best method to prepare all type of ethers that is, simple, mixed or aromatic ethers. Here alkyl halides are treated with sodium alkoxide in presence of magnesium to give ethers. It involves SN^2 mechanism during the attack of $R – O^-$ on $R – X$ that is, back side attack occurs here.

Mechanism

$$R – X + R – ONa \xrightarrow{\Delta\ Mg} R – O – R + NaX$$

$$R – OH + Na \longrightarrow R – ONa + H^+$$

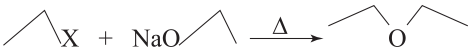
$$R – ONa \longrightarrow R – O^- + Na^+$$

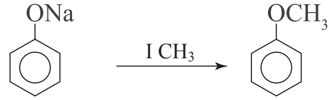
$$R – O^- + R' – X \xrightarrow{\Delta} (R –O \text{-----} R' – X) \xrightarrow{X^-} R – O – R' + Br^-$$

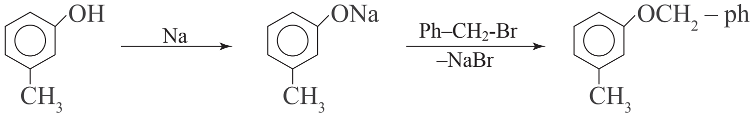
Unstable Transition state

Example,

$$\underset{\text{Sodium ethoxide}}{C_2H_5-ONa} + C_2H_5Br \xrightarrow{\Delta\ Mg} \underset{\text{Di ethyl ether}}{C_2H_5-O-C_2H_5} + NaBr$$

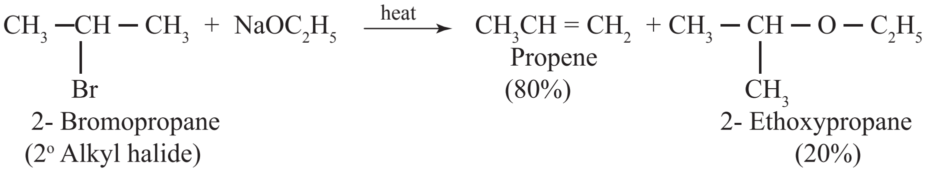




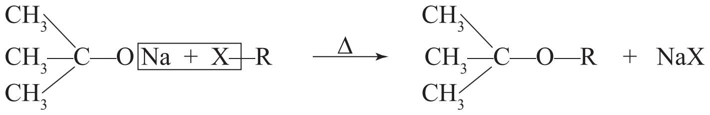


Limitations: The reactivity of primary (1°) alkyl halides is in the order, $CH_3 > CH_3CH_2 > CH_3CH_2CH_2$ and the tendency of alklyl halides to undergo elimination is 3° > 2° > 1°. So for better yield, the alkyl halide must be primary while alkoxide should be secondary or tertiary. Due to steric hindrance, secondary alkyl halides also prefer to undergo elimination rather than substitution. In case of tertiary halides, an alkene is formed, however, when alkoxide is tertiary, ether is formed as main product.

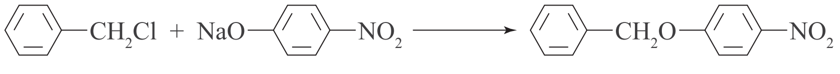
Example,



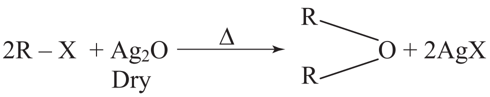
$$\underset{\substack{\text{2- Bromopropane}\\(2^{\circ}\text{ Alkyl halide})}}{CH_3-\underset{Br}{\underset{|}{CH}}-CH_3} + NaOC_2H_5 \xrightarrow{heat} \underset{\substack{\text{Propene}\\(80\%)}}{CH_3CH=CH_2} + \underset{\substack{\text{2- Ethoxypropane}\\(20\%)}}{CH_3-\underset{CH_3}{\underset{|}{CH}}-O-C_2H_5}$$



Aromatic halides cannot be used in Williamson ether synthesis. However, if strong electron withdrawing group at ortho and para-positions are present, then reaction takes place. For example,



(2) From R – X When alkyl or aryl halide is treated with dry silver oxide ether is formed as follows:



Example,

$$2C_2H_5Br + \text{dry } Ag_2O \xrightarrow{\Delta} C_2H_5-O-C_2H_5$$

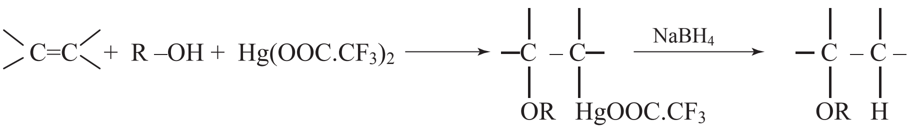
(3) From Alcohols Alcohols on dehydration give ethers depending upon amount of alcohol and temperature.

(a) By the dehydration of alcohols using concentrated sulphuric acid at 140°C. Here ethers are formed as follows:

$$R - OH + H_2SO_4 \xrightarrow{\Delta} R - HSO_4 + H_2O$$

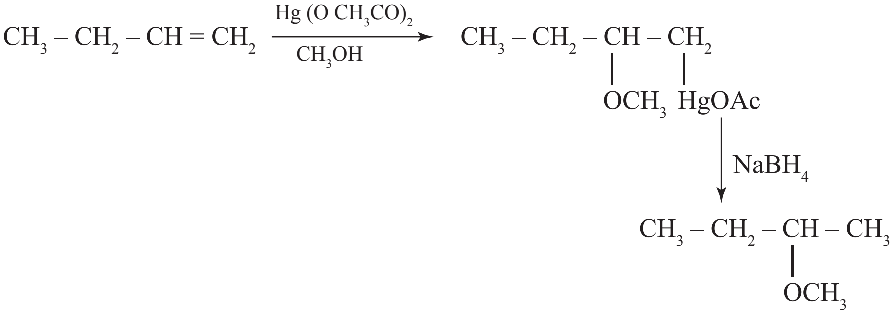
$$R - HSO_4 + R - OH \xrightarrow[140^oC]{\Delta} R - O - R + H_2SO_4$$

(4) By Alkoxy Mercuration-Demercuration Here alkenes undergo alkoxylation with alcohols with the help of trifluoro mercuric acetate (mercuration) followed by reduction with $NaBH_4$ (demercuration). Here addition takes place according to Markownikoff's rule as follows:



$$>C=C< + R-OH + Hg(OOC.CF_3)_2 \longrightarrow -\underset{OR}{\overset{|}{\underset{|}{C}}} - \underset{HgOOC.CF_3}{\overset{|}{\underset{|}{C}}}- \xrightarrow{NaBH_4} -\underset{OR}{\overset{|}{\underset{|}{C}}} - \underset{H}{\overset{|}{\underset{|}{C}}}-$$

Example,



$$CH_3 - CH_2 - CH = CH_2 \xrightarrow[CH_3OH]{Hg\,(O\,CH_3CO)_2} CH_3 - CH_2 - \underset{OCH_3}{\underset{|}{CH}} - \underset{HgOAc}{\underset{|}{CH_2}} \xrightarrow{NaBH_4} CH_3 - CH_2 - \underset{OCH_3}{\underset{|}{CH}} - CH_3$$

2 – Methoxy butane

(5) From Grignard Reagent

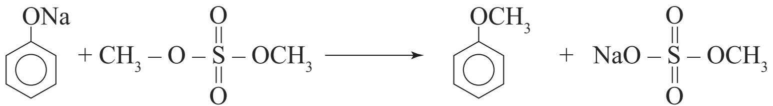
$$R - O - CH_2X + X'\,Mg - R' \longrightarrow R - O - CH_2 - R' + X - Mg - X'$$

Example,

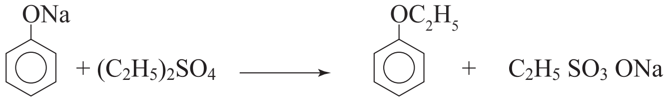
$$C_2H_5 - O - CH_2Cl + Br - Mg - C_2H_5 \longrightarrow C_2H_5 - O - CH_2 - CH_2 - CH_3 + MgBrCl$$

Methoxy propane

(6) For Aromatic Ethers Aromatic ethers can be prepared by the reaction of sodium phenoxide with dialkyl sulphate as follows:



Anisole

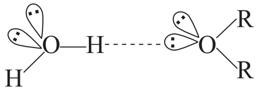


Phenetole

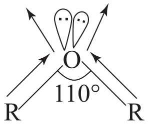
PHYSICAL PROPERTIES

- First two members that is, dimethyl ether and diethyl ether are gases, rest ethers are liquids and aromatic ethers are solid also.
- Ethers have lower boiling points than their isomeric alcohols as they do not have hydrogen bonding like alcohols.

  For example, $C_2H_5OH > CH_3 - O - CH_3$



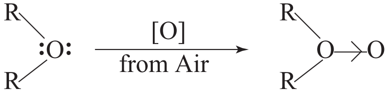
- Ethers are partially soluble in H_2O due to formation of hydrogen bonding with water as follows:
- Ethers are weak lewis bases or Bronsted bases as central atom oxygen has two lone pair of electrons to donate.
- Ethers have some value of Dipole Moment also due to presence of lone pair of electrons on oxygen atom.



- In an ether oxygen atom is sp^3 hybridized and the shape of ether is bent with a bond angle of 110°. The angle is expended due to the dominance of repulsive forces of bulkier alkyl groups over the lone pair electronic repulsion.

CHEMICAL REACTIONS

1 Peroxide Formation Ether can form peroxide in the presence of light and air and when these peroxides are heated, an explosion occurs. The presence of peroxide in ether can be easily detected by shaking small volume of ether with aq. KI solution. Ether are made peroxide free by washing ether with $FeSO_4$ solution.

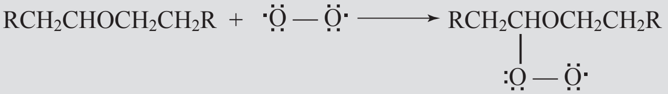


Mechanism

Initiation step:

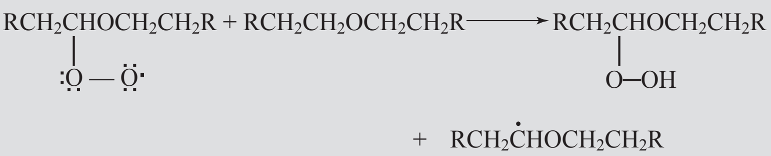
$$RCH_2CH_2OCH_2CH_2R + \cdot\ddot{\underset{..}{O}}-\ddot{\underset{..}{O}}\cdot \longrightarrow RCH_2\dot{C}HOCH_2CH_2R + H:\ddot{\underset{..}{O}}-\ddot{\underset{..}{O}}\cdot$$

Propagation step 1:



$$RCH_2CHOCH_2CH_2R + \cdot\ddot{\underset{..}{O}}-\ddot{\underset{..}{O}}\cdot \longrightarrow \begin{array}{c} RCH_2CHOCH_2CH_2R \\ | \\ :\underset{..}{O}-\ddot{\underset{..}{O}}\cdot \end{array}$$

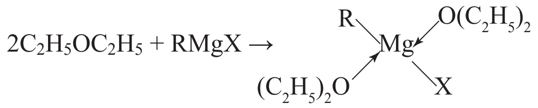
Propagation step 2:

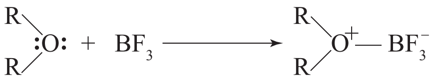


$$\begin{array}{c} RCH_2CHOCH_2CH_2R \\ | \\ :\underset{..}{O}-\ddot{\underset{..}{O}}\cdot \end{array} + RCH_2CH_2OCH_2CH_2R \longrightarrow \begin{array}{c} RCH_2CHOCH_2CH_2R \\ | \\ O-OH \end{array}$$

$$+ \ RCH_2\dot{C}HOCH_2CH_2R$$

2 With Lewis Acids Ethers can form coordination complexes with Lewis acids like BF_3, $AlCl_3$, RMgX, etc. As the ether (having lone pair of electrons) are Lewis bases, so they easily coordinate to form complexes known as etherates.





Stable complexes

3 With Sulphuric Acid

- **With Dil. Sulphuric Acid** Ethers on heating with it, give alcohols in case of mixed ether two type of alcohols will be formed.

$$R-O-R + H-OH \xrightarrow{\text{Dil. } H_2SO_4} 2R-OH$$

For example,

$$C_2H_5-O-C_2H_5 + H-OH \xrightarrow{\text{Dil. } H_2SO_4} 2C_2H_5-OH$$

$$R-O-R' + H-OH \xrightarrow{\text{Dil. } H_2SO_4} R-OH + R'-OH$$

For example,

$$CH_3-O-C_2H_5 + H-OH \xrightarrow{\text{Dil. } H_2SO_4} CH_3-OH + C_2H_5-OH$$

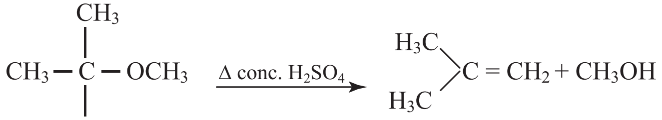
REMEMBER

- If temperature is low Oxonium salt is formed.

$$C_2H_5OC_2H_5 + H_2SO_4 \rightarrow [(C_2H_5)_2OH]^+ HSO_4^-$$

- **With Hot and Concentrated Sulphuric Acid** It is given by secondary and tertiary ethers mainly. Here ethers undergo elimination to give an alkene and an alcohol.

For example,



Isobutene

Methyl tertiary butyl ether

4 Reaction With Halogen Acids Ethers can be cleaved when treated with HI, HBr as follows:

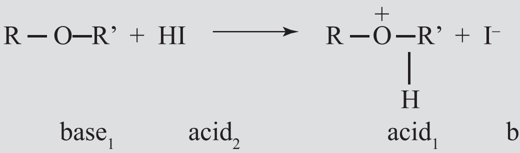
$$R-O-R + \underset{\text{Dil \& cold}}{H-X} \longrightarrow R-X + R-OH$$

$$\underset{\text{Hot \& excess}}{R - O - R + 2H - X} \xrightarrow{\Delta} 2R - X + H_2O$$

- Reactivity of halogen acids for this reaction decreases as HI > HBr > HCl.

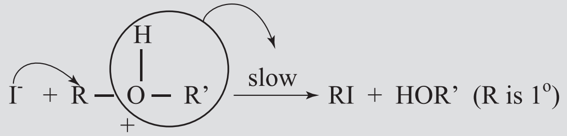
Mechanism

(a) **Step 1**



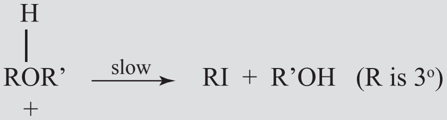
$$\underset{\text{base}_1}{R - O - R'} + \underset{\text{acid}_2}{HI} \longrightarrow \underset{\text{acid}_1}{R - \overset{+}{\underset{|\atop H}{O}} - R'} + \underset{\text{base}_2}{I^-}$$

Step 2 for S_N2



$$I^- + R - \overset{H}{\underset{+}{O}} - R' \xrightarrow{\text{slow}} RI + HOR' \ (R \text{ is } 1^o)$$

Step3 for S_N1



$$\overset{H}{\underset{+}{ROR'}} \xrightarrow{\text{slow}} RI + R'OH \quad (R \text{ is } 3^o)$$

Step 4 for S_N1 $R^+ + I^- \longrightarrow RI$

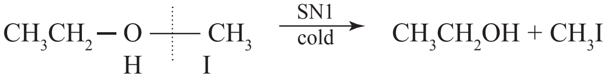
For example,

$$\underset{\text{Cold}}{C_2H_5 - OC_2H_5 + HI} \longrightarrow C_2H_5OH + C_2H_5I$$

$$\underset{\text{Hot}}{C_2H_5 - OC_2H_5 + 2HI} \longrightarrow 2C_2H_5I + H_2O$$

- **When a mixed ether is used in this reaction X^- is taken with smaller alkyl group**.

For example,

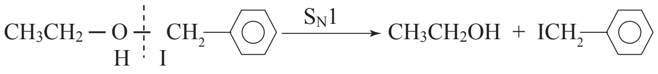


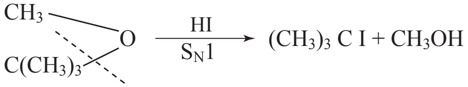
$$CH_3CH_2 - \underset{H}{O} \vdots \underset{I}{CH_3} \xrightarrow[\text{cold}]{SN1} CH_3CH_2OH + CH_3I$$

$$\underset{\text{Anisole w}}{C_6H_5 - O\ CH_3} + HI \longrightarrow C_6H_5 - OH + CH_3\ I$$

$$CH_3I \xrightarrow{AgNO_3} \underset{\text{Yellow ppt.}}{AgI}$$

- This method is called Zeisel method. It is used to find number of alkoxy groups in an ether.





Here I^- is taken with larger alkyl group as there is formation of more stable carbocation (Benzyl and t°).

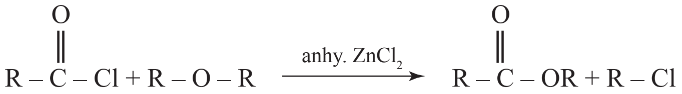
REMEMBER

- Cyclic ethers can be cleaved by heating at 100ºC.

  For example,

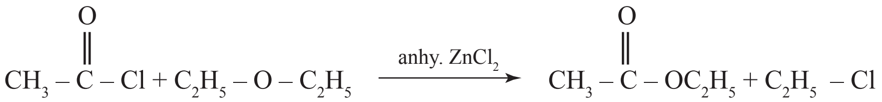
1,4-Dibromobutane

5. **Acylation by R – COCl or (R – CO)$_2$ O** When ethers are treated with acid chlorides or acid anhydrides in presence of anhydrous $ZnCl_2$ esters are formed. When mixed ether is taken a mixture of esters will be formed.



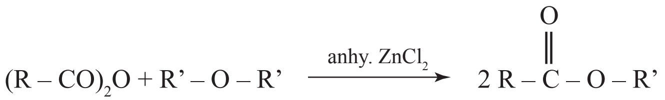
$$R-\overset{O}{\overset{\|}{C}}-Cl + R-O-R \xrightarrow{\text{anhy. } ZnCl_2} R-\overset{O}{\overset{\|}{C}}-OR + R-Cl$$

For example,



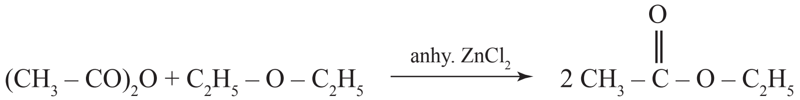
$$CH_3-\overset{O}{\overset{\|}{C}}-Cl + C_2H_5-O-C_2H_5 \xrightarrow{\text{anhy. } ZnCl_2} CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5 + C_2H_5-Cl$$

Acetyl chloride Ethyl acetate



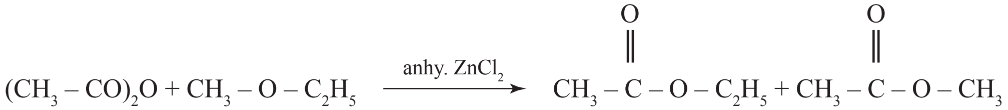
$$(R-CO)_2O + R'-O-R' \xrightarrow{\text{anhy. } ZnCl_2} 2\,R-\overset{O}{\overset{\|}{C}}-O-R'$$

For example,



$$(CH_3-CO)_2O + C_2H_5-O-C_2H_5 \xrightarrow{\text{anhy. } ZnCl_2} 2\,CH_3-\overset{O}{\overset{\|}{C}}-O-C_2H_5$$

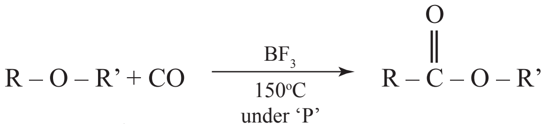
Acetic anhydride Ethyl acetate

- 

$$(CH_3-CO)_2O + CH_3-O-C_2H_5 \xrightarrow{\text{anhy. } ZnCl_2} CH_3-\overset{O}{\overset{\|}{C}}-O-C_2H_5 + CH_3-\overset{O}{\overset{\|}{C}}-O-CH_3$$

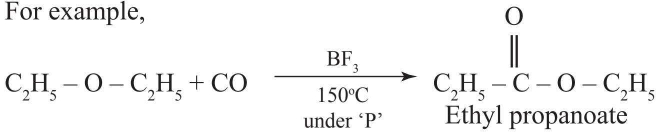
Ethyl acetate Methyl acetate

6. **With Carbon Monoxide** Ethers reacts with carbon monoxide to form esters as follows:



$$R-O-R' + CO \xrightarrow[\substack{150^{o}C \\ \text{under 'P'}}]{BF_3} R-\overset{O}{\overset{\|}{C}}-O-R'$$

For example,



$$C_2H_5-O-C_2H_5 + CO \xrightarrow[\substack{150^{o}C \\ \text{under 'P'}}]{BF_3} C_2H_5-\overset{O}{\overset{\|}{C}}-O-C_2H_5$$

Ethyl propanoate

7. **With PCl_5**

$$R - O - R + PCl_5 \xrightarrow{\Delta} 2\,R - Cl + 2POCl_3$$

For example,

$$C_2H_5 - O - C_2H_5 + PCl_5 \xrightarrow{\Delta} 2C_2H_5 - Cl + 2POCl_3$$

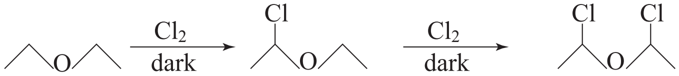
$$R - O - R' + PCl_5 \xrightarrow{\Delta} R - Cl + R' - Cl + 2POCl_3$$

For example,

$$CH_3 - O - C_2H_5 + PCl_5 \xrightarrow{\Delta} CH_3 - Cl + C_2H_5 - Cl + 2POCl_3$$

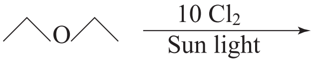
8. **Halogenation** Ethers react with chlorine as follows:

(i) In dark:



1,1' Dichloro diethyl ether

(ii) In Sunlight with excess of chlorine:



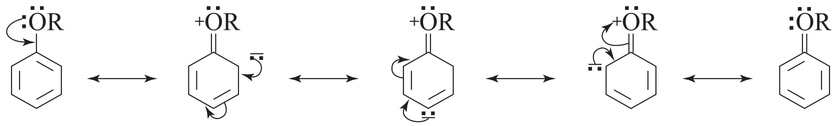
$CCl_5 - O - CCl_5$

Perchloro diethyl ether

9. **Dehydration of Ether**

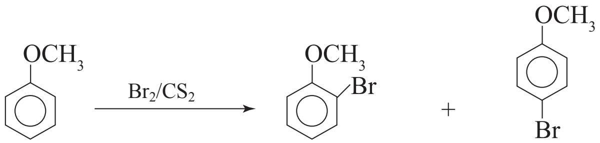
$$C_2H_5 - O - C_2H_5 \xrightarrow[360^\circ C]{Al_2O_3} 2CH_2 = CH_2 + H_2O$$

10. **Electrophillic Substitution Reaction of Aromatic Ethers** Aromatic ethers like anisole gives such reactions like nitration, halogenation etc., like phenols, the alkoxy group (─OR) in aromatic ethers is ortho and para directing and activates the ring towards electrophilic substitution reactions.



Resonating structures of alkoxybenzene

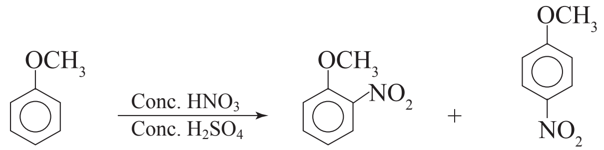
- **Bromination**



(31%) (67%)

Ortho bromoanisole Para bromoanisole

- **Nitration**

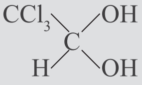


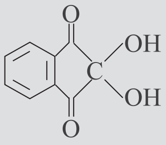
(31%) Ortho nitroanisole (67%) Para nitroanisole

ENHANCE YOUR KNOWLEDGE

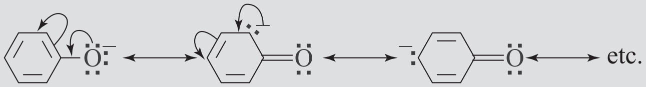
- Alcohols show chain, position and functional isomerism e.g., C_2H_5OH and CH_3OCH_3 are functional isomers.
- Reaction of R – OH with Na shows acidic nature of R – OH

  $C_6H_5OH > H_2O > R-OH$ [acidic nature]
- R – OH + Ceric ammonium nitrate → Red colour
- CH_3OH is called carbinol or wood sprit. (60% CH_3OH)
- C_2H_5OH is called grain alcohol.
- 100 per cent C_2H_5OH is absolute alcohol.
- 20 per cent C_2H_5OH + 80 per cent gasoline is power alcohol. It is used in motor vehicles as a fuel.
- 95.47 per cent C_2H_5OH + 4.53 per cent H_2O is reactified sprit.
- Isopropyl alcohol is rubbing alcohol.
- C_2H_5OH is made undrinkable by mixing it with CH_3OH, petrol, rubber etc. (denatured or methylated sprit.)
- Decreasing order of dehydration of alcohols is $t^o > s^o > p^o$
- Decreasing order of reactivity of alcohols towards Lucas reagent $t^o > s^o > p^o$
- Capacity towards H-bond formation of alcohols is $p^o > s^o > t^o$
- Reactivity of alcohols towards ester formation with organic acids : $p^o > s^o > t^o$
- Order of R – OH for ester formation with inorganic acids: $t^o > s^o > p^o$
- CH_3OH does not give iodoform reaction.
- A mixture of 95.57 per cent C_2H_5OH and 4.43 per cent H_2O boils at constant temperature that is Azotropic mixture.
- $\underset{C_2H_5OH}{\text{Wine}} \xrightarrow[\text{open}]{\text{oxidation}} \underset{CH_3COOH}{\text{Soure}}$
- Proof sprit is 57 per cent by volume C_2H_5OH or 49 per cent by weight of C_2H_5OH.
- Both these hydrates are stable due to **intramolecular hydrogen bonding**.

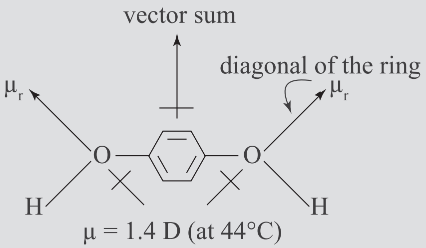




- Glycerol trinitrate is colourless. Oily liquid and an inorganic ester known as Nobel's oil, which is used in the treatment of Asthma and Pectoris.
- Ethers are used as solvents and anesthetic agents and Ether's anesthetic nature was given by Dr William Mortan.
- Poly ethers (Carbo waxes) have high solubility in H_2O due to multiple hydrogen bond formation with H_2O.
- We can use $R - OSO_2 R'$ also in place of $R - X$ in Williamson synthesis.
- PhO^- a weker nucleophillic than RO^- as The nucleophillic pairs of electrons on oxygen are involved in resonance in the case of PhO^-. This resonance interaction decreases their availability to participate in nucleophillic processes. No such resonance is possible in the case of the alkoxide ion. It is also this resonance interaction that makes phenoxide less basic than alkoxide, as well as making phenols more acidic than alcohols.



- p- Dihydroxybenzene is found to have appreciable amount of dipole moment (1.4 D at 44 °C). From the molecular diagram of the compound, it can be easily understood that the two O- H bonds are not along the diagonal of the ring, so the resultant group moments (μ_r) (one for each -OH group) are not opposite direction. They result a net dipole moment for the molecule (μ 1.4 D)



Estimation of the number of methoxy group in a compound (Zeisel's Method):
The reaction between an ether and hydroiodic acid is used in the estimation of number of methoxy or ethoxy group in a compound.
A known weight of the compound of molecular mass M is treated with 57 per cent HI.

$$R - OCH_3 + HI \rightarrow ROH + H_3C - I$$

Methoxy or ethyl iodide thus liberated is absorbed in the alcoholic silver nitrate solution, and silver iodide is precipitated. The precipitate filtered, washed dried and weighed.

$$CH_3I + AgNO_3 + H_2O \rightarrow CH_3OH + AgI \downarrow + HNO_3$$

One mole of silver iodide precipitate corresponds to the presence of one methoxy or one ehtoxy group, as the case may be.

In the above case.

w g of compound gives AgI = w g

M g of compound gives AgI $= \frac{W}{w} \times M$

No. of moles $= \frac{\text{Given mass}}{\text{Molar mass}}$

Molar mass of AgI = 108 + 127 = 235

No. of moles of AgI $= \frac{W}{w} \times \frac{M}{235}$ = x moles of AgI

Hence, number of methoxy group present in the molecule = x.

MULTIPLE-CHOICE QUESTIONS

Straight Objective Type Questions (Single Choice only)

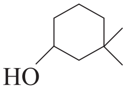
1. Which of the following is most soluble in water?
(a) isobutyl alcohol
(b) n-butyl alcohol
(c) sec-butyl alcohol
(d) tert-butyl alcohol

2. Ethyl alcohol exhibits acidic character on reacting it with
(a) hydrogen chloride (b) acetic acid
(c) sodium metal (d) acidic $K_2Cr_2O_7$

3. Phenol can be distinguished from ethyl alcohol by all reagents except
(a) Na (b) $FeCl_3$
(c) Br_2/H_2O (d) NaOH

4. In the Libermann's nitroso reaction, sequential changes in the colour of phenol occurs as
(a) brown or red → green → deep blue
(b) red → deep blue → green
(c) red → green → white
(d) white → red → green

5. The IUPAC name of



is
(a) 3,3-dimethyl-1-hydroxycyclohexane
(b) 1,1-dimethyl-3-hydroxycyclohexane
(c) 3,3-dimethyl-1-cyclohexanol
(d) 1,1-dimethyl-3-cyclohexanol.

6. Among the following the most stable compound is
(a) cis-1, 2-cyclohexanediol
(b) trans-1, 2-cyclohexanediol
(c) cis-1, 3-cyclohexenediol
(d) trans-1,3-cyclohexanediol

7. Which of the following compounds is resistant to nucleophillic attack by hydroxyl ions?
(a) acetonitrile
(b) diethyl ether
(c) acetamide
(d) methyl acetate

8. Ethanol and dimethyl ether form a pair of functional isomers. The boiling point of ethanol is higher than that of dimethyl ether due to the presence of
(a) H-bonding in dimethyl ether
(b) H-bonding in ethanol
(c) CH_3 group in ethanol
(d) CH_3 group in dimethyl ether

9. Which of the following has lowest solubility in water?
(a) $(CH_3)_2CHOH$ (b) $(CH_3)_3COH$
(c) C_2H_5OH (d) MeOH

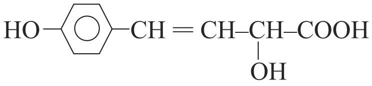
10. Which of the following has maximum hydrogen bonding?
(a) ethyl amine (b) ammonia
(c) ethyl alcohol (d) diethyl ether

11. The correct order of boiling points for primary (1°), secondary (2°) and tertiary (3°) alcohols is
(a) $1^{\circ} > 2^{\circ} > 3^{\circ}$ (b) $3^{\circ} > 2^{\circ} > 1^{\circ}$
(c) $2^{\circ} > 1^{\circ} > 3^{\circ}$ (d) $2^{\circ} > 3^{\circ} > 1^{\circ}$

12. Which of the following is most acidic?
(a) o-cresol (b) phenol
(c) p-nitrophenol (d) anisole

13. The ionization constant of phenol is higher than that of ethanol because
(a) phenoxide ion is a stronger base than ethoxide ion
(b) phenoxide ion is stabilized through delocalization
(c) phenoxide ion is less stable than ethoxide ion
(d) phenoxide ion is bulkler than ethoxide ion.

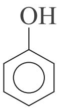
14. Which of the following will exhibit highest boiling point?
(a) $CH_3CH_2CH_2CH_2CH_2OH$
(b) $CH_3CH_2OCH_2CH_3$
(c) $CH_3CH_2C(CH_3)_2OH$
(d) $CH_3CH_2CH_2CH(CH_3)OH$

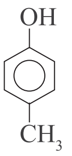
15.  will show
(a) Optical isomerism
(b) Geometrical isomerism
(c) Neither geometrical nor optical isomerism
(d) Geometrical and optical isomerism

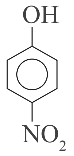
[DCE 2000]

16. *o*-Nitrophenol (X) and *p*-nitrophenol (Y) are two compounds. The melting point relationship between the two is
(a) X > Y (b) X = Y
(c) X < Y (d) X > > Y

17. The correct acidic order of the following is

(I) 

(II) 

(III) 

(a) I > II > III (b) III > I > II
(c) II > III > I (d) I > III > II

18. Which one of the following compounds will be most readily attacked by an electrophile?
(a) phenol (b) toluene
(c) benzene (d) chlorobenzene

19. Which of the following is the most suitable method for removing the traces of water from ethanol?
(a) heating with sodium metal
(b) passing dry HCl gas through it
(c) distilling it
(d) reacting with Mg

20. What will be the bond angle C – O – H in alcohol if C and O-atom possess sp^3-hybridization?
(a) $108^{\circ}.30'$ (b) 109°
(c) $111^{\circ}.42'$ (d) $109^{\circ}\ 28'$

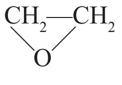
21. A compound with molecular formula $C_4H_{10}O_3$ is converted by the action of acetyl chloride to a compound of molecular mass 190. The original compound ($C_4H_{10}O_3$) has
(a) four –OH groups (b) three –OH groups
(c) two –OH groups (d) one –OH groups

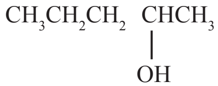
22. The molecule with maximum boiling point is
(a) $CH_3 - CHCl - CH_3$
(b) $CH_3 - CHOH - CH_2CH_2OH$
(c) $CH_3CH_2CH_2CH_2Cl$
(d) $CH_3 - CHOH - CH_3$

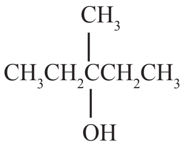
23. An ether is more volatile than an alcohol having the same molecular formula. This is due to
(a) dipolar character of ethers
(b) alcohols having resonance structures
(c) inter-molecular hydrogen bonding in ethers
(d) inter molecular hydrogen bonding in alcohols

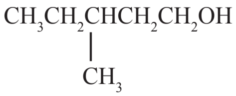
24. An alkaline solution of and citrate ions is called
(a) silver chloride; Tollen's reagent
(b) cupric sulphate; Benedict's solution
(c) silver nitrate; Fehling's solution
(d) cupric sulphate; Schiff's reagents

25. Periodic acid oxidizes
(a) 1, 4-diols (b) 1, 3-diols
(c) 1, 2-diols (d) β-ketoaldehyde

26. When one of the following compounds will react with Grignard reagent to yield a primary alcohol containing two more carbons?
(a) CH_3CHO (b) 
(c) HCHO (d) CH_3COCH_3

27. Among the following compounds which can be dehydrated very easily?
(a) $CH_3CH_2CH_2CH_2CH_2OH$
(b) 
$CH_3CH_2CH_2\ \underset{OH}{\underset{|}{CH}}CH_3$

(c) 
$CH_3CH_2\overset{CH_3}{\underset{OH}{C}}CH_2CH_3$

(d) 
$CH_3CH_2\underset{CH_3}{CH}CH_2CH_2OH$

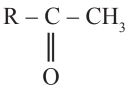
28. Phenol reacts with bromine water in carbon disulphide at low temperature to give
(a) o-bromophenol
(b) o- and p-bromophenols
(c) p-bromophenol
(d) 2, 4, 6-tribromophenol

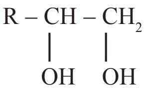
29. The compound which gives the most stable carbonium ion on dehydration is
(a) $(CH_3)_2\ CHCH_2OH$
(b) $(CH_3)_3COH$
(c) $CH_3CH_2CH_2CH_2OH$
(d) $CH_3CHOHCH_2CH_3$

30. The best reagent to convert pent-3-en-2-ol into pent-3-en–2-one is
(a) acidic permanganate
(b) acidic dichromate
(c) chromic anhydride in glacial acetic acid
(d) pyridinium chloro-chromate

31. Acid catalysed hydration of alkenes except ethene leads to the formation of
(a) primary alcohol
(b) secondary or tertiary alcohol
(c) mixture of primary and secondary alcohols
(d) mixture of secondary and tertiary alcohols

32. Alkene $R - CH = CH_2$ react with B_2H_6 in the presence of H_2O_2 to give

(a) 
$R - \underset{\underset{O}{\|}}{C} - CH_3$

(b) 
$R - \underset{OH}{\underset{|}{CH}} - \underset{OH}{\underset{|}{CH_2}}$

(c) $R - CH_2 - CHO$ (d) $R - CH_2 - CH_2 - OH$

33. Phenol, p-Methylphenol, m-Nitrophenol and p-Nitrophenol follows order of increasing acidic strength
(a) Phenol, p-Methylphenol, p-Nitrophenol, m-Nitrophenol
(b) p-Methylphenol, Phenol, m-Nitrophenol, p-Nitrophenol
(c) p-Methylphenol, m-Nitrophenol, Phenol, p-Nitrophenol
(d) m-Nitrophenol, p-Nitrophenol, Phenol, p-Methylphenol

34. o-Xylene $\xrightarrow{HNO_3}$ X $\xrightarrow[H_2SO_4]{phenol}$ Y
The product Y is
(a) phthalic acid
(b) isophthalic acid
(c) phenolphthalein
(d) o-Hydroxybenzenesulphonic acid

35. Phenol is less acidic than
(a) o-nitrophenol (b) p-methylphenol
(c) methanol (d) ethanol

36. The compound which gives the most stable carbonium ion on dehydration is
(a) $CH_3CH_2CH_2CH_2OH$ (b) $(CH_3)_3COH$
(c) $(CH_3)_2CHCH_2OH$ (d) $CH_3CHOHCH_2CH_3$

37. An organic compound 'X' on treatment with acidified $K_2Cr_2O_7$ gives a compound 'Y' which reacts with I_2 and sodium carbonate to form tri-iodomethane. The compound 'X' is
(a) $CH_3CHOHCH_3$ (b) CH_3CHO
(c) CH_3COCH_3 (d) CH_3OH

38. The compound obtained by the reaction of ethene with diborane followed by hydrolysis with alkaline hydrogen peroxide is
(a) ethanal (b) ethanol
(c) triethyl boride (d) propanol

39. Heating methyl phenyl ether with HI gives
(a) methanol + iodobenzene
(b) methyl alcohol + benzyl alcohol
(c) methyl iodide + phenol
(d) methyl iodide + iodobenzene

40. $CH_2 = CH_2 \xrightarrow[Ag]{O_2}$ X $\xrightarrow[473\ K]{steam}$ Y
The compound Y is
(a) ethylene glycol (b) epoxyethane
(c) ethanal (d) ethanol

41. Diethyl ether is heated with one mole of HI, which is formed
(a) ethyl alcohol and ethyl iodide
(b) ethyl iodide only
(c) ethyl alcohol only
(d) ethyl iodide and ethane

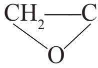
42. 1-phenylethanol can be prepared by the reaction of benzaldehyde with
(a) methyl iodide and magnesium
(b) methyl bromide and aluminium bromide
(c) ethyl iodide and magnesium
(d) methyl bromide

43. Conversion of cyclohexene to cyclohexanol can be conveniently achieved by

(a) hyboration – hydrolysis
(b) hydroboration – oxidation
(c) NaOH – H_2O
(d) Br_2 – H_2O

44. The alcohol that produces turbidity immediately with $ZnCl_2$/conc. HCl at room temperature:
(a) 1-hydroxy-2-methyl propane
(b) 2-hydroxy-2-methyl propane
(c) 2-hydroxy butane
(d) 1-hydrobutane

45. Reaction of



with RMgX followed by hydrolysis will lead to produce
(a) RCHOHR (b) $RCHOHCH_3$
(c) R_2CHCH_2OH (d) RCH_2CH_2OH

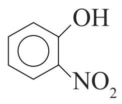
46. An organic compound (A) reacts with sodium metal and forms (B). On heating with conc. H_2SO_4 (A) gives diethyl ether. (A) and (B) are respectively
(a) C_2H_5OH & C_2H_5ONa
(b) C_3H_7OH & CH_3ONa
(c) CH_3OH & CH_3ONa
(d) C_4H_9OH & C_4H_9ONa

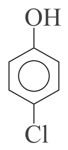
47. An aromatic ether is not cleaved by HI ever at 525 K. The compound is
(a) $C_6H_5OC_6H_5$ (b) $C_6H_5OC_3H_7$
(c) $C_6H_5OCH_3$ (d) tetrahydrofuran

48. The alcohol which does not give a stable compound on dehydration is
(a) methyl alcohol (b) ethyl alcohol
(c) n-butyl alcohol (d) n-propyl alcohol

49. tert-butyl methyl ether on heating with HI of one molar concentration gives
(a) $CH_3I + (CH_3)_3COH$ (b) $CH_3OH + (CH_3)_3Cl$
(c) $CH_3I + (CH_3)_3Cl$ (d) none of these

50. Which of the following is the strongest acid?

(a)


(b)


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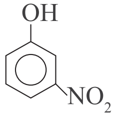

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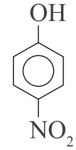


51. Ethylene reacts with 1 per cent cold alkaline $KMnO_4$ to form
(a) ethylene glycol (b) oxalic acid
(c) HCHO (d) ethyl alcohol

52. What is the product obtained when chlorine reacts with ethyl alcohol in the presence of NaOH?
(a) CH_3Cl (b) $CHCl_3$
(c) C_2H_5Cl (d) CCl_3CHO

53. The compound when reacts fastest with Lucas reagent at room temperature is
(a) butan-1-ol (b) butan-2-ol
(c) 2-methylpropan-2-o (d) 2-methylpropan-1-ol

54. Product C in the reaction,

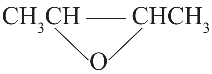
$$C_2H_5Br \xrightarrow{\text{aq. NaOH}} A \xrightarrow{\text{Na}} B \xrightarrow{CH_3I} C$$

Will be
(a) ethane (b) ethyl methyl ether
(c) ethyl iodide (d) propane

55. Isopropyl alcohol is obtained by reacting which of the following alkenes with concentrated H_2SO_4 followed by boiling with H_2O?
(a) 2-methylpropene (b) ethylene
(c) isoprene (d) propylene

56. The reaction of CH_3MgBr with acetone and hydrolysis of the resulting product gives
(a) $(CH_3)_3COH$ (b) $(CH_3)_2CHOH$
(c) $CH_3CH_2CH_2OH$ (d) $CH_3CH_2CH_2CH_2OH$

57. Which of the following compounds on reaction with CH_3MgBr will give a tertiary alcohol?

(a)


(b) $C_2H_5CO_2CH_3$
(c) C_6H_5CHO
(d) C_2H_5COOH

58. The reaction of Grignard reagent with formaldehyde followed by acidification gives
(a) an aldehyde (b) a ketone
(c) a carboxylic acid (d) aprimary alcohol

59. When diethyl ether is treated with excess of Cl_2 in the presence of sunlight, then the product formed is
(a) $CH_3CHCl – O – CH_2CH_3$
(b) $CH_3CHCl – O – CHClCH_3$
(c) $CCl_3CCl_2 – O – CCl_2CCl_3$
(d) $CH_3CCl_2 – O – CHClCH_3$

60. The two enzymes present in yeast that are responsible for the formation of ethyl alcohol from molasses in the fermentation process are
(a) invertase, maltase (b) zymase, diastase
(c) invertase, diastase (d) invertase, zymase

61. Oxymercuration-demercuration reaction of 1-methylcyclohexene gives
(a) trans-2-methyl cyclohexanol
(b) cis-2-methylcyclohexanol
(c) 1-methylcyclohexanol
(d) mixture of cis- and trans-2-methylcyclo-hexanol

62. The product of the following reaction is

$\xrightarrow[\text{(ii) } H_2O_2,\ OH^-]{\text{(i) } BH_3/THF}$

(a) 2-pentanol (b) pentane
(c) pentan-2-one (d) 1-pentanol

63. Acetic anhydride reacts wit diethyl ether in the presence of anhydrous $AlCl_3$ to give
(a) $CH_3COOCH_2CH_3$ (b) CH_3COOCH_3
(c) CH_3CH_2OH (d) $CH_3CH_2COOCH_3$

64. In the reaction sequence

$$\text{Glycerol} \xrightarrow{KHSO_4/\Delta} X \xrightarrow{\text{Zn-Hg/conc HCl}/\Delta} Y \xrightarrow{NBS/CCl_4} Z$$

Z will be
(a) 1,2-dibromopropane (b) 1-bromopropane
(c) 2-bromopropane (d) 3-bromopropene

65. The reagent required to convert propene to 1-propanol is
(a) B_2H_6 followed by H_2O_2/NaOH
(b) conc. H_2SO_4 followed by hydrolysis with boiling water
(c) HBr followed by hydrolysis with aqueous KOH
(d) $Hg(OCOCH_3)_2$ followed by reduction with $NaBH_4$.

66. The reagent used for the preparation of higher ethers from halogenated ethers is
(a) sodium alkoxide (b) grignard reagent
(c) conc H_2SO_4 (d) dry silver oxide

67. A compound is soluble in conc H_2SO_4. It does not decolourise bromine in carbon tetrachloride but is oxidized by chromic anhydride in aqueous sulphuric acid within two seconds, turning orange solution to blue, green and then opaque. The original compound is
(a) an alkane (b) an ether
(c) a tertiary alcohol (d) aprimary alcohol

68. An organic compound of molecular formula $C_4H_{10}O$ does not react with sodium. With excess of HI, it gives only one type of alkyl halide. The compound is
(a) 1-butanol (b) ethoxyethane
(c) 1-methoxypropane (d) 2methoxypropane

69. A compound of the formula $C_4H_{10}O$ reacts with sodium and undergoes oxidation to give a carbonyl compound which does not reduce Tollen's reagent, the original compound is
(a) sec-Butyl alcohol (b) n-butyl alcohol
(c) isobutyl alcohol (d) diethyl ether

70. Which of the following is correct?
(a) reduction of any aldehyde gives secondary alcohols
(b) reduction of vegetable oil with H_2SO_4 gives glycerine
(c) reaction of ethanolic iodine with NaOH gives iodoform
(d) sucrose on reaction with NaOH gives invert sugar.

71. Ethanol when reacted with PCl_5 gives A, $POCl_3$ and HCl. A reacts with silver nitrate to form B (major product) and AgCl. A and B respectively are
(a) C_2H_5Cl & $C_2H_5NO_2$
(b) C_2H_6 & $C_2H_5NO_2$
(c) C_2H_5Cl & $C_2H_5OC_2H_5$
(d) C_2H_6 & $C_2H_5OC_2H_5$

72. An organic compound A reacts with methyl magnesium iodide to form an addition product which on hydrolysis forms the compound B. Compound B gives blue colour salt in Victor meyer's test. The compounds A and B are respectively
(a) acetaldehyde, isopropyl alcohol
(b) acetone, isopropyl alcohol
(c) acetaldehyde, tertiary butyl alcohol
(d) acetaldehyde, ethyl alcohol

73. In the following reaction.

$$C_2H_5OC_2H_5 + 4H \xrightarrow{\text{Red P + HI}} 2X + H_2O$$

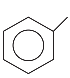
X is
(a) ethylene (b) propane
(c) ethane (d) butane

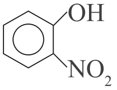
74. Which one of the following orders of acid strength is correct?
(a) RCOOH > HC ≡ CH > HOH > ROH
(b) RCOOH > ROH > HOH > HC ≡ CH
(c) RCOOH > HOH > ROH > HC ≡ CH
(d) RCOOH > HOH > HC ≡ CH > ROH

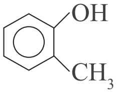
75. Which one of the following undergoes reaction with 50% sodium hydroxide solution to give the corresponding alcohol and acid?
(a) phenol
(b) benzaldehyde
(c) butanal
(d) benzoic acid

76. Which one of the following compounds is most acidic?

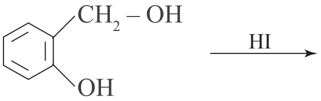
(a) $Cl - CH_2 - CH_2 - OH$

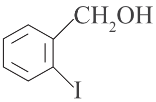
(b) 

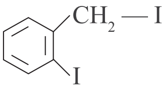
(c) 

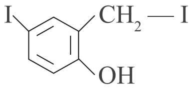
(d) 

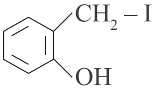
77. What is the major product of the following reaction?



(a) 

(b) 

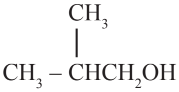
(c) 

(d) 

78. In the Victor-Meyer's test, the colour given by 1°, 2° and 3° alcohols are respectively
(a) red, colourless, blue
(b) red, blue, colourless
(c) colourless, red, blue
(d) red, blue, violet
(e) blue, red, violet

79. Among the following the one that gives positive iodoform test upon reaction with I_2 and NaOH is

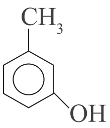
(a) $CH_3CH_2CH(OH)CH_2CH_3$ (b) $C_6H_5CH_2CH_2OH$

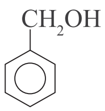
(c) 

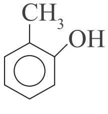
$CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{C}HCH_2OH$

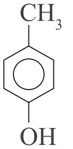
(d) $PhCHOHCH_3$

80. The structure of the compound that gives a tribromo derivative on treatment with bromine water is

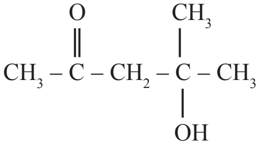
(a) 

(b) 

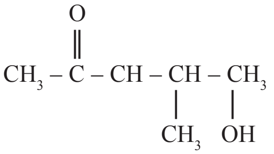
(c) 

(d) 

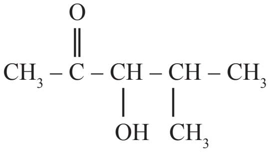
81. Which of the products is formed when acetone is reacted with barium hydroxide solution?

(a) 

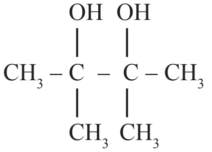
$CH_3 - \overset{\overset{\displaystyle O}{\|}}{C} - CH_2 - \underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}} - CH_3$

(b) 

$CH_3 - \overset{\overset{\displaystyle O}{\|}}{C} - \underset{\underset{\displaystyle CH_3}{|}}{CH} - \underset{\underset{\displaystyle OH}{|}}{CH} - CH_3$

(c) 

$CH_3 - \overset{\overset{\displaystyle O}{\|}}{C} - \underset{\underset{\displaystyle OH}{|}}{CH} - \underset{\underset{\displaystyle CH_3}{|}}{CH} - CH_3$

(d) 

$CH_3 - \underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}} - \underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}} - CH_3$

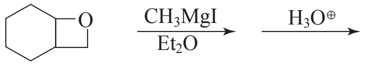
82. $CH_3CH_2OH \xrightarrow[\text{Step- 1}]{Cl_2,} CH_3CHO \xrightarrow[\text{Step- 2}]{3Cl_2}$

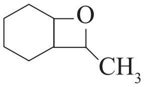
Cl_3CCHO

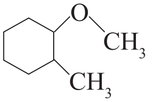
In the above reactions the role of Cl_2 in step -1 and step-2 respectively is
(a) oxidation, chlorination
(b) reduction, chlorination
(c) oxidation, addition
(d) reduction, substitution

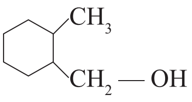
83. Which of the following compound would not evolve CO_2 when treated with $NaHCO_3$ solution?
(a) salicylic acid (b) phenol
(c) benzoic acid (d) 4-nitrobenzene acid

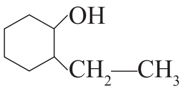
84. What is the major product of the following reaction?



(a) 

(b) 

(c) 

(d) 

85. The product formed on reaction of n-butanol with $SOCl_2$ in presence of pyridine is
(a) chlorobutanol (b) 1-chlorobutane
(c) chlorobutanone (d) 2-chlorobutane

86. Pentan-3-ol on reaction with aluminium tertiary butoxide in presence of acetone gives
(a) Pentan-3-one (b) Pentanoic acid
(c) Pentane (d) Pentanal

87. Which of the following compounds on reaction with ethyl magnesium iodide will form 2-methylbutan-2-ol?
(a) Acetaldehyde
(b) Acetone
(c) Formaldehyde
(d) Both formaldehyde and acetaldehyde

88. Phenol, when treated with bromine water gives a white precipitate due to the formation of
(a) o- and p-bromophenol
(b) 2, 4, 6-tribromophenol
(c) 3, 5-dibromophenol
(d) meta-bromophenol

89. The major product formed when a 3, 3-dimethylbutan-2-ol is heated with concentrated sulphuric acid is
(a) cis and trans isomers of 2, 3-dimethyl-1-butene
(b) 2, 3-dimethyl-1-butene
(c) 2, 3-dimethyl-2-butene
(d) cis and trans isomers of 3, 3-dimethyl-2-butene

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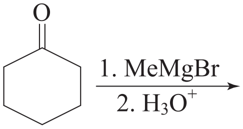
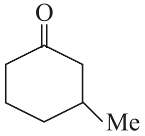
90. The correct order of increasing boiling points is
(a) isobutane < n-butane < n-butyl chloride < n-butanol
(b) isobutane < n-butyl chloride < n-butane < n-butanol
(c) n-butane < n-butanol < n-butyl chloride < isobutane
(d) n-butane < isobutane < n-butyl chloride < n-butanol

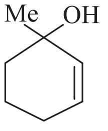
91. Bakelite is obtained from phenol by reacting with
(a) $(CH_2OH)_2$ (b) CH_3CHO
(c) CH_3COCH_3 (d) HCHO

92. Phenol, when it first reacts with concentrated sulphuric acid and then with concentrated nitric acid, gives
(a) 2, 4, 6-trinitrobenzene
(b) o-nitrophenol
(c) p-nitrophenol
(d) Nitrobenzene

93. Predict the product.



(a)


(b)


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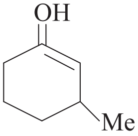

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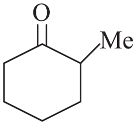
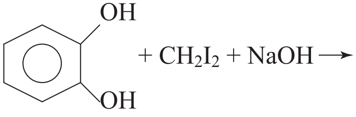
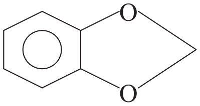


94. Identify the product in the following reaction



(a)


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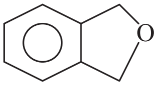

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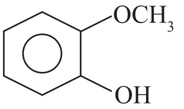

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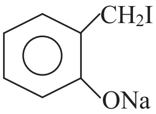


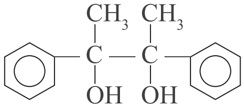
95. RCH_2CH_2OH can be converted to RCH_2CH_2COOH by the following sequence of steps –
(a) PBr_3, KCN, H_3O^+ (b) HCN, PBr_3, H_3O^+
(c) Pbr_3, KCN, H_2/P^+ (d) KCN, H_3O^+

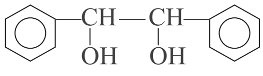
96. The final product B in the following reaction

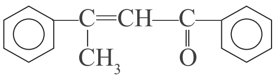
$$CH_3CH_2CH = CH_2 \xrightarrow[(C_6H_5CO_2)_2]{NBS,\ hv} A \xrightarrow[CH_2OH]{CH_3SNa} B$$

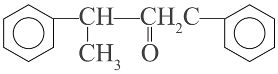
(a) Methyl 1-methylallylsulphide
(b) Allyl methyl sulphide
(c) n-Butyl methyl sulphide
(d) Diallyl sulphide

97. Acetophenone when reacted with a base, C_2H_5ONa, yields a stable compound which has the structure:

(a)


(b)


(c)


(d)


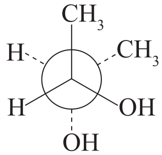
98. An organic compound (X) with molecular formula C_7H_8O is insoluble in aqueous $NaHCO_3$ but dissolves in NaOH. When treated with bromine water (X) rapidly gives (Y), $C_7H_5OBr_3$. The compound (X) and (Y) respectively are

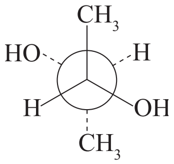
(a) o-cresol and 3,4,5-tribromo-2-methyl phenol
(b) Benzyl alcohol and 2,4,6-tribromo-3-methoxy benzene
(c) Methylbenzene and 2,4,6-tribromo-3-methoxy benzene
(d) m- cresol and 2,4,6-tribromo-3-methyl phenol

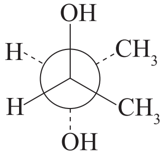
99. Which of the following organic compounds answers to both iodoform test and Fehling's test?

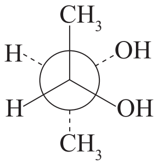
(a) Ethanal (b) Methanol
(c) Propanone (d) Ethanol

100. Which of the following is most stable conformation?

(a)


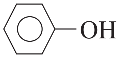
(b)


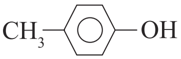
(c)


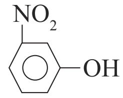
(d)


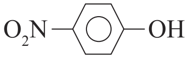
Brainteasers Objective Type Questions (Single choice only)

101. In the following compounds,

(I)


(II)


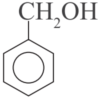
(III)


(IV)


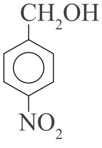
the order of acidity is

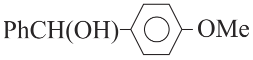
(a) III > IV > I > II (b) I > IV > III > II
(c) II > I > III > IV (d) IV > III > I > II

102. The increasing reactivity order of alcohol

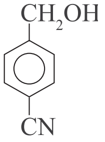
(I)


,

(II)


(III)


(IV) PhCH(OH)Ph,

(V)


towards reaction with HBr is

(a) II < I < III < IV < V
(b) II < V < I < IV < III
(c) V < II < I < IV < III
(d) II < V < IV < I < III

103. Which of the following facts explains as to why p-nitrophenol is more acidic than phenol?

I. –I effect of nitro group
II. Greater resonance effect of p-nitrophenoxy group
III. Steric effect of bulky nitro group

Select the correct answer using the codes given below:

(a) II and III (b) I and III
(c) I and II (d) II alone

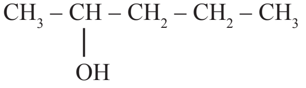
104. Under different conditions, nitration of phenol yields

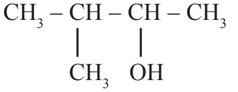
1. o-nitrophenol
2. p-nitrophenol
3. 2,4,5-trinitrophenol

The correct sequence of decreasing order of acidic nature of these phenols is

(a) 3, 2, 1 (b) 1, 2, 3
(c) 2, 1, 3 (d) 3, 1, 2

105. An alcohol $C_5H_{11}OH$ on dehydration gives an alkene, which on oxidation yield a mixture of a ketone and an acid. The alcohol is

(a)

$\underset{\displaystyle OH}{\underset{|}{CH_3-CH}}-CH_2-CH_2-CH_3$

(b)

$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$

(c) $(CH_3)_3CCH_2OH$
(d) $CH_3CH_2CH(OH)CH_2CH_3$

106. A polyhydric alcohol is benzoylated using benzoyl chloride in presence of sodium hydroxide. If molecular weight of polyhydric alcohol is 92 and that of its benzoyl derivative is 404, then the number of –OH groups present in polyhydric alcohol is

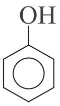
(a) 1 (b) 2
(c) 3 (d) 4

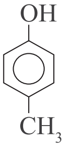
107. An organic compound C_3H_6O does not give a precipitate with 2,4-dinitrophenylhydrazine reagent and does not react with metallic sodium. It could be

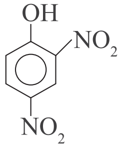
(a) $CH_3 - CH_2 - CHO$
(b) $CH_2 = CH - CH_2OH$
(c) $CH_3 - CO - CH_3$
(d) $CH_2 = CH - O - CH_3$

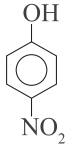
108. What amount of bromine will be required to convert 2g of phenol into 2,4,6-tribromophenol?
(a) 6.0 (b) 8.0
(c) 10.22 (d) 20.44

109. Strength of acidity is in order

(I) 

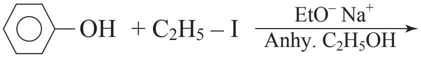
(II) 

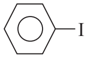
(III) 

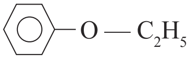
(IV) 

(a) I > IV > II > II (b) IV > III > I > II
(c) III > IV > I > II (d) II > I > III > IV

110. Product of the reaction would be



(a) $C_2H_5 - O - C_2H_5$
(b) $C_6H_5 - O - C_6H_5$
(c) 

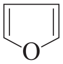
(d) 

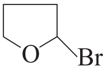
111. The reaction of elemental sulphur with Grignard reagent followed by acidification leads to the formation of
(a) sulphoxide
(b) mercaptan
(c) sulphonic acid
(d) thioester

112. In the reaction,
$H_3C - C \equiv CH \rightarrow H_3C - CH(OH) - CH_3$,
the reagent used would include
(a) Hg^{2+} / H_2SO_4
(b) Na in liquid NH_3, followed by CH_3Cl
(c) 1 mol of H_2 / Pt, followed by H_2SO_4/H_2O
(d) 2 mol of H_2/Pt, followed by aq. NaOH

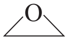
113. The reaction between HI and C_2H_4 in C_2H_5OH gives 'predominantly' C_2H_5I, whereas the reaction with HCl under the same conditions gives predominantly $(C_2H_5)_2O$. Identify the correct order of nucleophilicity of the nucleophiles involved in the above reactions.
(a) $I^- > EtO^- > Cl^-$ (b) $I^- > Cl^- > EtOH$
(c) $EtOH > Cl^- > I^-$ (d) $I^- > EtOH > Cl^-$

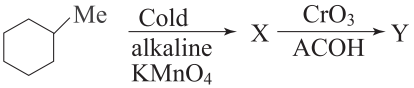
114. 

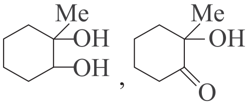
The structure of this product is
(a) 

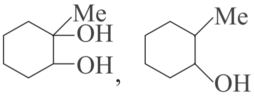
(b) 

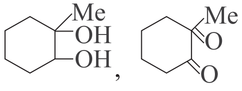
(c) $HO - CH_2CH_2CH_2CH_2Br$
(d) $BrCH_2CH_2CH_2CH_2Br$

115. 2-phenylethanol may be prepared by the reaction of phenylmagnesium bromide with
(a) HCHO (b) CH_3COCH_3
(c)  (d) CH_3CHO

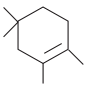
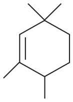
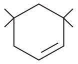
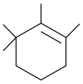
116. 

X and Y are:
(a) 

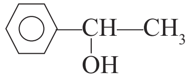
(b) 

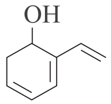
(c) 

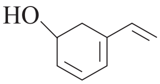
(d) No formation of X and Y

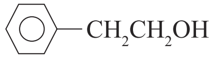
117. When 2,2,6,6-tetramethyl cyclohexanol is treated with an acid, an alkene is formed after rearrangement. The structure of the alkene can be given as:-
(a)  (b) 
(c)  (d) 

118. Compound (X) liberates hydrogen when treated with sodium metal. On oxidation, it gives a compound (Y) with the same number of carbons. Compound (Y) gives orange coloured crystalline 2,4-dinitrophenyl hydrazone derivative with 2,4-dinitrophenyl hydrazine hydrochloride. Compound (Y) on treatment with NaOH (aq) and iodine gives compound (Z). compound (Z) on treatment with dilute acid yields a compound, which is identified as benzoic acid. The structure of compound (X) is

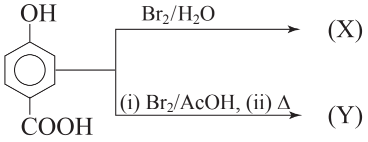
(a) 

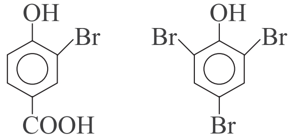
(b) 

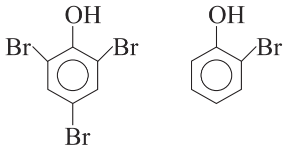
(c) 

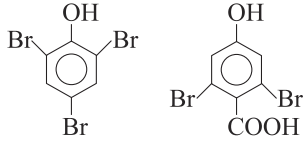
(d) 

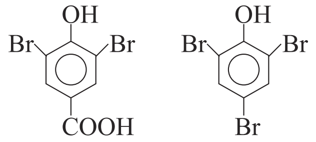
119. Products (X) and (Y) are respectively

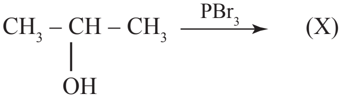


(a) 

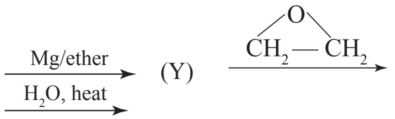
(b) 

(c) 

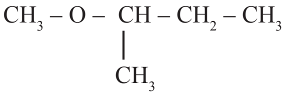
(d) 

120. 

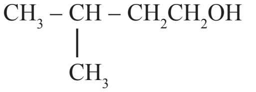
$$CH_3-\underset{OH}{\underset{|}{CH}}-CH_3 \xrightarrow{PBr_3} (X)$$



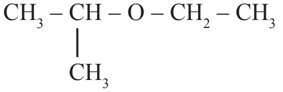
The final product is

(a) 

$$CH_3-O-\underset{CH_3}{\underset{|}{CH}}-CH_2-CH_3$$

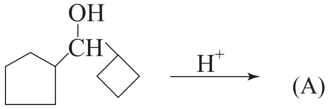
(b) 

$$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2CH_2OH$$

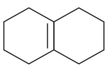
(c) 

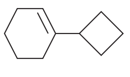
$$CH_3-\underset{CH_3}{\underset{|}{CH}}-O-CH_2-CH_3$$

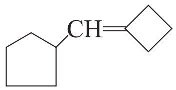
(d) None of these

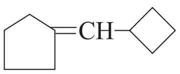
121. 

The product is:

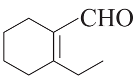
(a) 

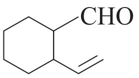
(b) 

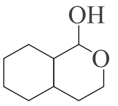
(c) 

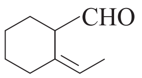
(d) 

122. Identify the product (X) in the following reaction:

(a) 

(b) 

(c) 

(d) 

123. $(H_3C)_3C\,CH_2OH + HBr \rightarrow$ Product. The most likely product is

(a) $(CH_3)_3C-CH_2Br$

(b) $(CH_3)_2\,C\,(OH).CHBr.CH_3$

(c) $(CH_3)_2\,C\,(OH)-CH_2CH_3$

(d) $(CH_3)_2C\,Br-CH_2CH_3$

124. A 0.12 g sample of a saturated monohydric alcohol when added to methyl magnesium iodide, liberates 44.48 ml of colourless gas at STP. The alcohol also gives yellow precipitate with I_2 and alkali. The possible structural formula of the alcohol is

(a) $CH_3CH(OH)C_2H_5$ (b) $CH_3CH_2CH_2OH$

(c) $CH_3CH(OH)CH_3$ (d) CH_3CH_2OH

125. Propan-1-ol can be prepared from propene

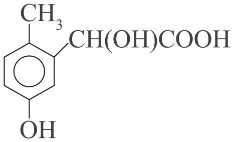
(a) B_2H_6 followed by H_2O_2

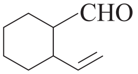
(b) CH_3COOH/H_2SO_4

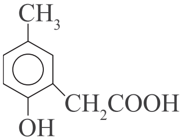
(c) H_2O/H_2SO_4

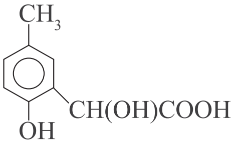
(d) $Hg(OAc)_2/H_2O$ followed by $NaBH_4$

126. p-cresol reacts with chloroform in alkaline medium to give the compound A which adds hydrogen cyanide to form, the compound B. The latter on acidic hydrolysis gives chiral carboxylic acid. The structure of the carboxylic acid is

(a) 

(b) 

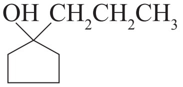
(c) 

(d) 

127. Identify X and Y in the following sequence of reactions:

$$CH_3CHO \xrightarrow{HNO_3} X \xrightarrow[\Delta]{P_4O_{10}} Y$$

	X	Y
(a)	CH_3CO_2OH	$(CH_3CO)_2O$
(b)	C_2H_5OH	CH_3CO_2H
(c)	CH_3CO_2H	$CH_3CO_2CH_3$
(d)	C_2H_5OH	C_2H_4

128. 

$$\xrightarrow{H_2SO_4} P \xrightarrow{B_2H_6} Q \xrightarrow{H_2O_2/OH^-} R$$

Here R is:

(a) ethyl cyclohexane

(b) 2- propyl cyclopentene

(c) 2- propyl cyclopentanol

(d) 1- Propyl cyclopentanol

129. Which is the method of choice fro preparing the ether $(CH_3CH_2)_3COCH_3$?

(a) $(CH_3CH_2)_3$ COH + CH_3MgBr

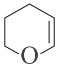
(b) CH_3Br+ $(CH_3CH_2)_3CO^-K^+$

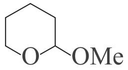
(c) $(CH_3CH_2)_3$ CBr + CH_3O^- K^+

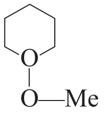
(d) $(CH_3CH_2)_3$ CMgBr + CH_3OH

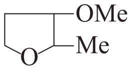
130. 3-Hydroxybutanal is formed when (X) reacts with (Y) in dilute (Z) solution. What are X, Y and Z?

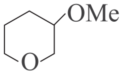
	X	Y	Z
(a)	CH_3CHO	CH_3CHO	NaOH
(b)	$(CH_3)_2CO$	$(CH_3)_2CO$	HCl
(c)	CH_3CHO	CH_3CHO	NaCl
(d)	CH_3CHO	$(CH_3)_2CO$	NaOH

131.  on reaction with MeOH in presence of H^+ gives mainly

(a) 

(b) 

(c) 

(d) 

132. Which among the following compounds will give a secondary alcohol on reacting with Grignard reagent followed by acid hydrolysis?

(I) HCHO

(II) C_2H_5CHO

(III) CH_3COCH_3

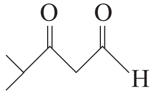
(IV) $HCOOC_2H_5$

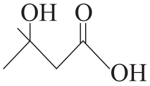
Select the correct answer using the codes given below:

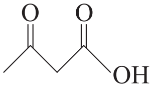
(a) III only (b) II only

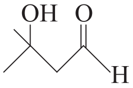
(c) I and IV (d) II and IV

133. What is the major product of this reaction?

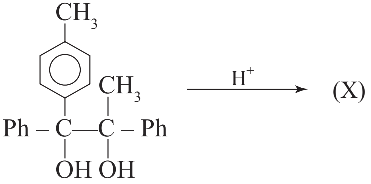
(a) 

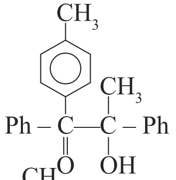
(b) 

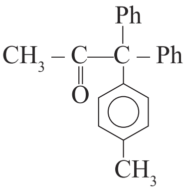
(c) 

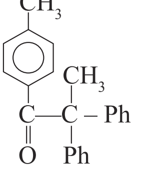
(d) 

134. Identify product (X) in the following reaction



(a) 

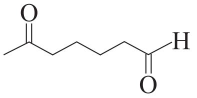
(b) 

(c) 

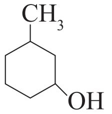
(d) None of these

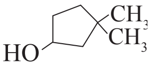
135. $C_7H_{14}O(P) \xrightarrow[\Delta]{H^+} C_7H_{12} \xrightarrow[2.\ H_2O_2/OH^-]{1.\ B_2H_6} C_7H_{14}O(R)$ (An isomer of P)

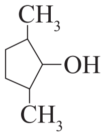
(A3° alcohol) (Q) $\downarrow$ 1. O_3, 2. Zn H_2O

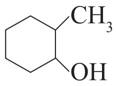


R can be:

(a) 

(b) 

(c) 

(d) 

136. In the following sequence of reactions,

$CH_3CH_2OH \xrightarrow{P + I_2} (A) \xrightarrow[Ether]{Mg}$

$(B) \xrightarrow{HCHO} (C) \xrightarrow{H_2O} (D)$

The compound (D) is:

(a) n-butyl alcohol (b) n-propyl alcohol
(c) propanal (d) butanal

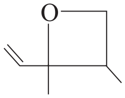
137. $HC \equiv CH \xrightarrow{HgSO_4/H_2SO_4}$

$\xrightarrow{(i)\ CH_3MgBr\ (ii)\ H_2O} \xrightarrow{PBr_3}$

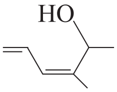
(a) $BrCH = CH - CH_3$ (b) $CH_2 = CH - Br$
(c) $CH_3CH_2CH_2Br$ (d) $CH_3CHBrCH_3$

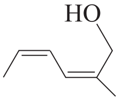
138. An iodo compound, Preacts with sodium acetylide (one mole) in presence of NH_3 to give the compound, Q. The latter by a reaction sequence: (I) with $NaNH_2$ in NH_3 (II) ethylene oxide followed by hydrolysis gives an saturated, 6-carbon primary alcohol R. Here the compound P is :

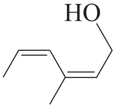
(a) C_2H_5I
(b) CH_3I
(c) $CH_3 - CHI - CH_2 - CH_3$
(d) n-C_3H_7I

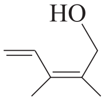
139. 

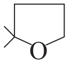
This strained ether on treatment with acid, is protonated on oxygen and ring opens to give a resonance stabilized carbocation. Which of the following diene given below when treated with acid will give the same carbocatoin.

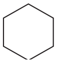
(a) 

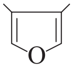
(b) 

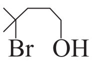
(c) 

(d) 

140.  on reaction with cold conc. HBr gives:

(a) 

(b) 

(c) 

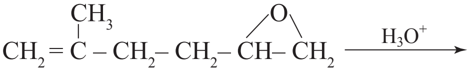
(d) 

141. The end product of the reaction

$C_2H_5OH \xrightarrow{PCl_5} A \xrightarrow{KCN} B$
$\xrightarrow{H_3O^+} C$ is

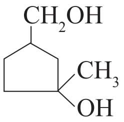
(a) propanol (b) propanoic acid
(c) propanamide (d) none of these

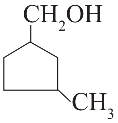
142. The major product for the reaction,

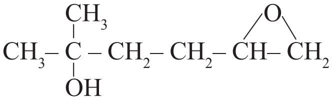


$CH_2 = \overset{CH_3}{\overset{|}{C}} - CH_2 - CH_2 - \overset{O}{CH - CH_2} \xrightarrow{H_3O^+}$

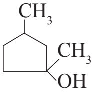
will be

(a) 

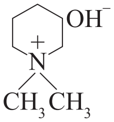
(b) 

(c) 

$CH_3 - \overset{CH_3}{\underset{OH}{C}} - CH_2 - CH_2 - \overset{O}{CH - CH_2}$

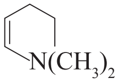
(d) 

143. In the following reaction,



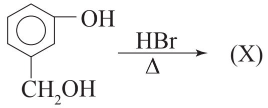
The organic product X has the structure

(a) 

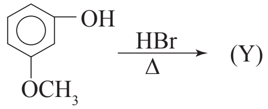
(b) 

(c) 

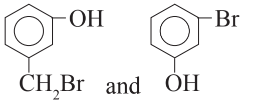
(d) 

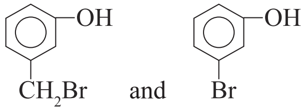
144. 

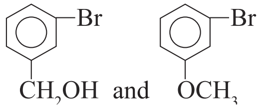
,

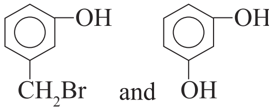


Here product (X) and (Y) are respectively:

(a) 

(b) 

(c) 

(d) 

145. Which compound on reaction with beaching powder gives chloroform?

(a) ethanol (b) methanal
(c) methanol (d) none of these

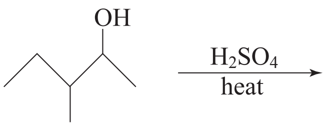
146. In the following sequence of reactions,

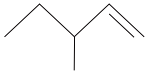
$$CH_3-CH(NH_2)-CH_3 \xrightarrow{HNO_2} A$$

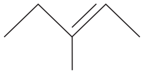
$$\xrightarrow{\text{oxidation}} B \xrightarrow[\text{(ii) } H^+/H_2O]{\text{(i) } CH_3MgI} C$$

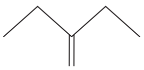
the compound C formed will be

(a) butanol-1
(b) 2-methylpropanol –1
(c) 2-methylpropanol –2
(d) butanol-2

147. 

(a) 

(b) 

(c) 

(d) All of these

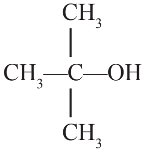
148. To prepare 3-ethylpentan-3-ol, the reagents needed are

(a) $CH_3CH_2MgBr + CH_3CH_2COCH_2CH_3$
(b) $CH_3CH_2CH_2MgBr + CH_3COCH_2CH_3$
(c) $CH_3MgBr + CH_3CH_2CH_2COCH_2CH_3$
(d) $CH_3CH_2MgBr + CH_3COCH_2CH_3$

149. Higher homologoues of ethers can be prepared by

(a) diazomethane
(b) grignard reagent
(c) alkyl halides
(d) none of these

150. Draw the structure of $C_4H_{10}O$ if the compound : (1) reacts with Na but fails to react with a strong oxidizing agent such as $K_2Cr_2O_7$; (2) gives a negative iodoform test; and (3) gives a positive Lucas test in 4 minutes.

(a) $CH_3-CH_2-CH_2-CH_2-OH$
(b) $(CH_3)_2CHCH_2OH$
(c) 

$CH_3-C(CH_3)_2-OH$

(d) $C_2H_5OC_2H_5$

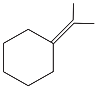
151. A sample of 6.75 mg of unknown alcohol is added to CH_3MgBr when 2.52 ml of CH_4 at STP is obtained. The unknown alcohol is

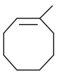
(a) methanol (b) ethanol
(c) 1- propanol (d) 1- pentanol

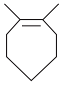
152. 

on dehydration mainly gives

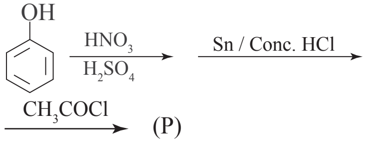
(a) 

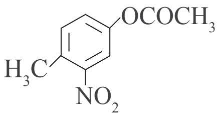
(b) 

(c) 

(d) 

153. The major product (P) in this reaction sequence is:



(a)


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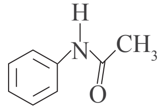
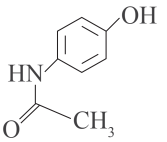
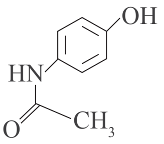
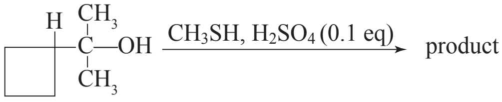


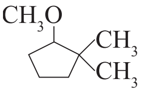
(c)


(d)


154. Treatment of alcohol P with acidic methanethiol gives product Q. Identify Q



(P)

(a)


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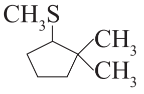

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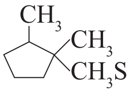

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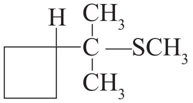


Decisive Thinking Objective Type Questions (One or more than one choice)

155. Which one/ones of the following reactions will yield 2-propanol?

(a) $CH_2 = CH - CH_3 + H_2O \xrightarrow{H^+}$

(b) $CH_3CHO \xrightarrow{\text{(i) } CH_3MgI, \text{ (ii) } H_2O}$

(c) $CH_2O \xrightarrow{\text{(i) } C_2H_5MgI, \text{ (ii) } H_2O}$

(d) $CH_2 = CH - CH_3 \xrightarrow{\text{Neutral } KMnO_4}$

156. Which of the following statements is/are correct here?

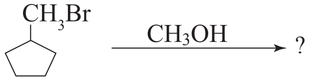
(a) Preparation of ether by intermolecular dehydration of alcohol follows S_N2 mechanism.

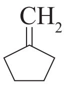
(b) The oxygen of the ether linkages makes ethers basic.

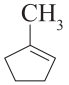
(c) Ethers can act both like bronsted acid and bronsted base.

(d) Di- ethyl ether and butanol -1 have almost same solubility in water.

157. Solvolysis of bromomethylcyclopentane in methanol gives a complex product mixture of ?



(a)


(b)


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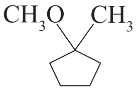

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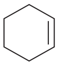
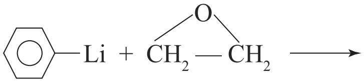
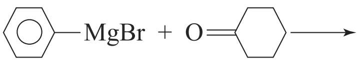
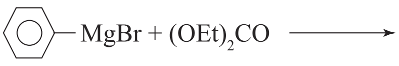


158. Which of the following reactions yield alcohol as the major product?

(a)

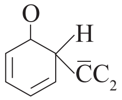

(b)


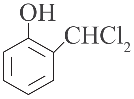
(c)


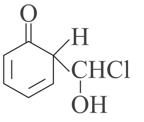
(d)


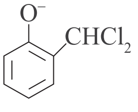
(excess)

159. When phenol is treated with $CHCl_3$ and NaOH followed by acidification, salicylaldehyde is obtained. Which of the following species are involved in the above mentioned reaction as intermediates?

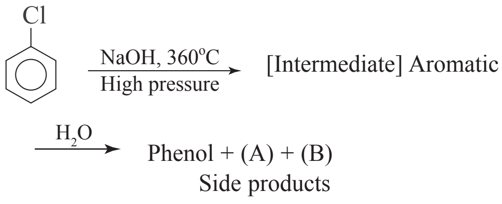
(a)


(b)


(c)


(d)


160. In the Dow process for the manufacture of phenol as follows



Which of these statement is/are correct:

(a) p-phenylphenol is also formed as by-product

(b) Phenol is formed via an intermediate that is aromatic.

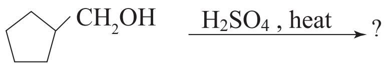
(c) Biphenylene is also formed as by- product.

(d) Diphenylether is also formed as by-product.

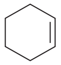
161. Which of the following can not be cleaved by HIO_4
(a) Ethan 1 , 2- di -ol (b) Butan 1, 2 -di -ol
(c) Propan 1, 3 -di -ol (d) 2-methoxy propanol

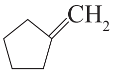
162. Which of the following reactions will result in the formation of anisole?
(a) sodium phenoxide is treated with methyl iodide
(b) phenol + dimethyl sulphate in presence of a base
(c) reaction of methylmagnesium iodide with phenol
(d) reaction of diazomethane with phenol

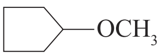
163. In this reaction

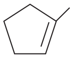
(1) 

The products formed are

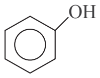
(a) 

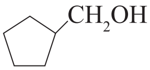
(b) 

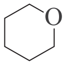
(c) 

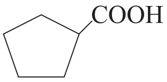
(d) 

164. Which of the following compounds can react with sodium metal?

(a) 

(b) 

(c) 

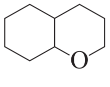
(d) 

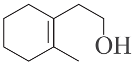
165. Which of the following given iodoform test?
(a) CH_3CH_2OH (b) $CH_3CH_2CH_2CH_2OH$
(c) $(CH_3)_2CHOH$ (d) CH_3COCH_3

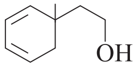
166. Which of the following are soluble in sodium bicarbonate?
(a) benzenesulphonic acid
(b) benzoic acid
(c) 2,4,6-trinitrophenol
(d) o-nitrophenol

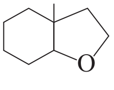
167. The chemicals used for preparing acetophenone are
(a) C_6H_6 (b) CH_3COCH_3
(c) CH_3COCl (d) Anhydrous $AlCl_3$

168. In the following dehydration reaction the product formed can be

(a) 

(b) 

(c) 

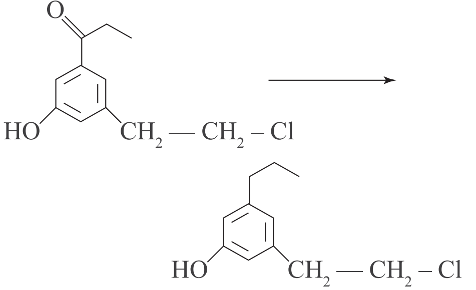
(d) 

169. In which of the following reactions ethyl chloride is/are formed?
(a) $C_2H_5OC_2H_5 + PCl_5 \xrightarrow{\Delta}$
(b) $CH_3OCH_3 + CH_3COCl \xrightarrow{AlCl_3}$
(c) $C_2H_5OC_2H_5 + Cl_2 \xrightarrow{hv}$
(d) $C_2H_5OH + PCl_3$

170. Which of the following is/are chiral?
(a) 3-bromopentane
(b) 2-hydroxypropanoic acid
(c) 2-butanol
(d) 2, 3-dibromopentane

171. Which statement is true regarding Fries rearrangement?
(a) In involves the formation of acylium ion as an intermediate which attacks the activated
(b) It is preferred for preparing o- and p-hydroxy ketones than the direct C-acylation of phenols
(c) A solvent must be needed for this rearrangement
(d) At low temperature 'para' is major while at higher temperature 'ortho' is major product.

172. Which of the following reagents may be used for the following conversion?



(a) $LiAlH_4$ (b) Zn – Hg/HCl
(c) $NH_2–NH_2/OH^–$ (d) H_2 /Pd

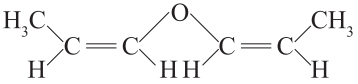
173. Phenol can be distinguished from ethanol by which reagents .
(a) $NaOH/I_2$
(b) neutral $FeCl_3$
(c) Br_2/H_2O
(d) phthalic anhydride/conc. H_2SO_4 & NaOH

174. The products obtained when benzyl phenyl ether is heated with HI in the mole ratio 1:1 are
(a) Phenol (b) Benzyl alcohol
(c) Benzyl iodide (d) Iodobenzene

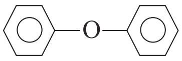
175. Victor meyer's test is/are by
(a) C_2H_5OH
(b) $(CH_3)_3COH$
(c) $CH_3CH_2CH_2OH$
(d) $(CH_3)_2CHOH$

176. Which of the following ethers can be synthesized directly by Williamson's synthesis?

(a) 

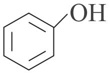
(b) 

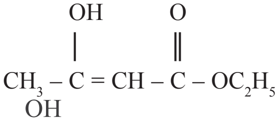
(c) $(CH_3)_2HC - O - C_2H_5$

(d) 

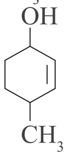
177. Which of the following reactions yield an alkyl halide?
(a) diethyl ether + RCOCl
(b) diethyl ether + PCl_5
(c) diethyl ether + HI
(d) diethyl ether + Cl_2

178. Characteristic dark colouration with neutral $FeCl_3$ solution is /are not given by

(a) 

(b) 

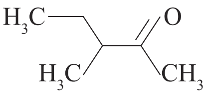
$CH_3 - \overset{\overset{\displaystyle OH}{|}}{C} = CH - \overset{\overset{\displaystyle O}{\|}}{C} - OC_2H_5$

(c) 

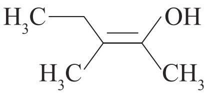
(d) CH_3CH_2OH

179. Which of the following is /are true is case of reaction with heated copper at 300°C?
(a) phenol → benzyl alcohol
(b) primary alcohol → aldehyde
(c) secondary alcohol → ketone
(d) tertiary alcohol → olefin.

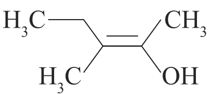
180. The correct statement(s) concerning the structures E, F and G is/are



(E)



(F)



(G)

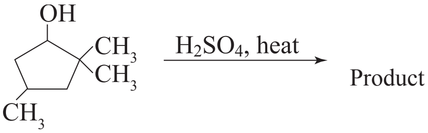
(a) E, F and G are resonance structure
(b) E, F and E, G are tautomers
(c) F and G are geometrical isomers
(d) F and G are diastereomes

[IIT 2008]

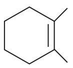
Linked-Comprehension Type Questions

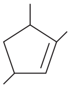
Comprehension 1

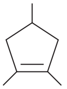
Alcohols undergo dehydration to give alkenes and ethers by eliminating water. The dehydrating agents used for this purpose are mainly con. H_2SO_4, H_3PO_4 etc. The mechanism of the reaction is given by E_1 mechanism. Alcohols may also undergo intermolecular dehydration to give cyclic ethers.

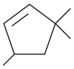
181. 

Here the product is ?

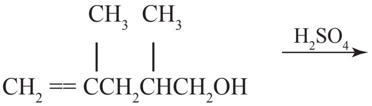
(a) 

(b) 

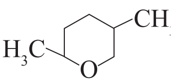
(c) 

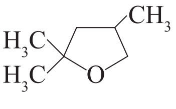
(d) 

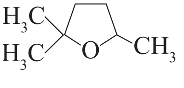
182. In the following reaction the product formed is ?

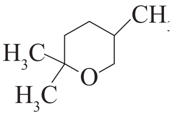


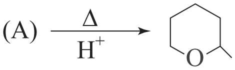
$CH_2 == \overset{\overset{\displaystyle CH_3}{|}}{C}CH_2\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_2OH \xrightarrow{H_2SO_4}$

(a) 

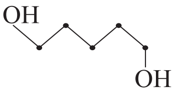
(b) 

(c) 

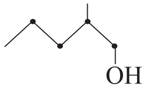
(d) 

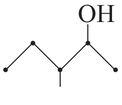
183. 

Here (A) can be ?

(a) 

(b) 

(c) 

(d) 

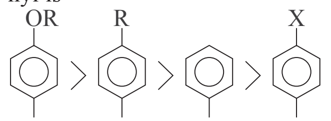
Comprehension 2

Pinacole pinocolone rearrangement involves the acid catalyzed elimination conversion of di- ols (1, 2 or vic) into carbonyl compounds. This pehomenon starts with the protonation of -OH group followed by H_2O elimination to give a carbocation alder rearrangement of stable carbocation formation finally H^+ is elimination to give carbonyl compound.

184. Which of the following is correct here about this rearrangement ?

(I) Migrating aptitude for substitutents is in $–C_6H_5 >$ -H > -R

(II) Migrating aptitude for substitutents is in phenyl is



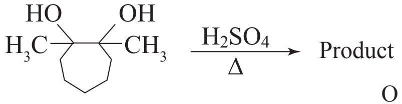
(III) The carbocation is stabilized by whitmore 1, 2 shift

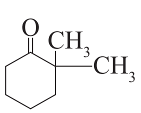
(IV) Steric hinderance may not effect the rate of migration here ?

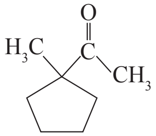
(a) I, III (b) I, II, III

(c) II, III, IV (d) I, II, III, IV

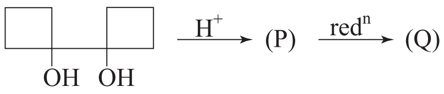
185. Proposes a mechanism for each of the following reactions:



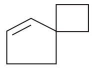
(a)


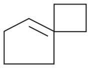
(b)


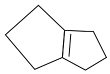
(c) None of these (d) Both A and B

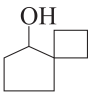
186.


In this sequence of reaction the final product (R) is ?

(a)


(b)


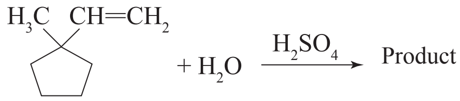
(c)


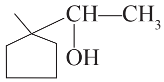
(d)


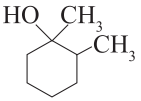
Comprehension 3

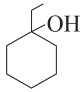
Alcohols can be synthesised from alkenes by acid catalysed hydration , oxymercuration - demercuration, hydroboration etc.

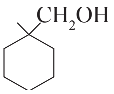
Alkyl halides can also be converted into alcohols by their hydrolysis using S_N1 or S_N2 mechanism. Carbonyl compounds, esters on reduction also give alcohols.

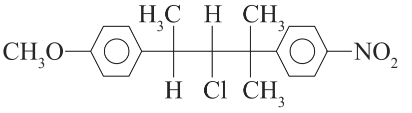
187.


(a)


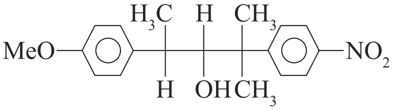
(b)


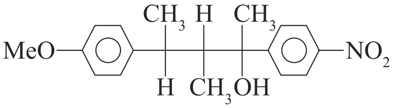
(c)


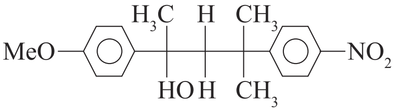
(d)


188.


on hydrolysis in presence of aqueous acetone gives

(I)


(II)


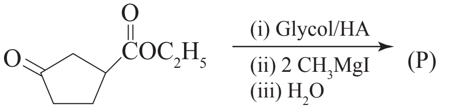
(III)


(a) (I) and (III)

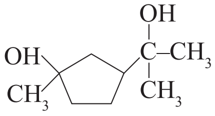
(b) (I) only

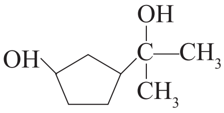
(c) (I) and (II)

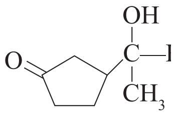
(d) (II) only

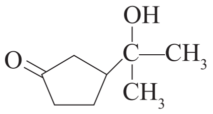
189.


Here the product (P) can be given as:

(a)


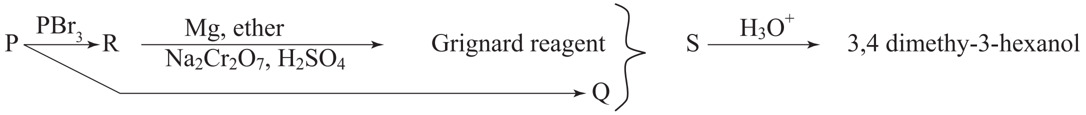
(b)


(c)


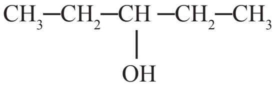
(d) 

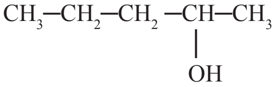
Comprehension 4

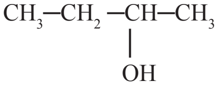
Compound Pis an optically active alcohol. Treatment with converts P into a ketone, Q. In a separate reaction, P is treated with PBr_3. converting P into compound R. Compound R is purified , and then it is allowed to react with magnesium in ether. Compound Q is added to the resulting solution of the Grignard reagent. After hydrolysis, this solution is found to contain 3, 4- dimethyl -3- hexanol.



190. The structure of compound A can be given as :

(a) 
$CH_3-CH_2-\underset{OH}{CH}-CH_2-CH_3$

(b) 
$CH_3-CH_2-CH_2-\underset{OH}{CH}-CH_3$

(c) 
$CH_3-CH_2-\underset{OH}{CH}-CH_3$

(d) $CH_3-CH_2-CH_2-CH_2OH$

191. Here compound B can be ?

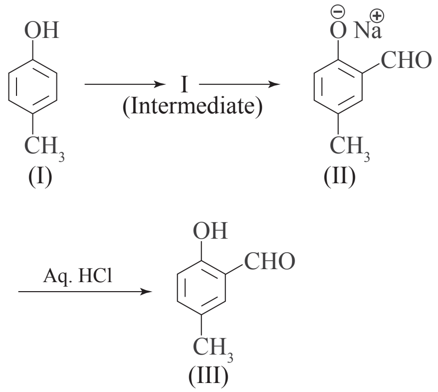
(a) Butanal (b) Butan 2- one
(c) Pentan 2- one (d) Pentan 3- one

192. Here compound C is ?

(a) 2- bromo pentane (b) 3- bromo pentane
(c) 2- bromo butane (d) May be A or B

Comprehension 5

Riemer-Tiemann reaction introduces an aldehyde group, on to the aromatic ring of phenol, ortho to the hydroxyl group. This reaction involves electrophillic aromatic substitution. This is a general method for the synthesis of substituted salicylaldehydes as depicted below:



193. The electrophile in this reaction is

(a) :CHCl (b) $^+CHCl_2$
(c) $:CCl_2$ (d) $.CCl_2$

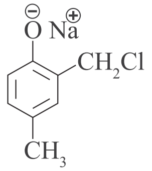
[IIT 2007]

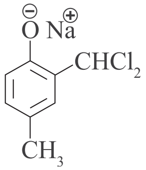
194. Which one of the following reagents is used in the above reaction?

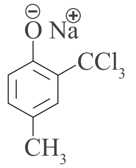
(a) aq. NaOH + CH_3Cl (b) aq. NaOH + CH_2Cl_2
(c) aq. NaOH + $CHCl_3$ (d) aq. NaOH + CCl_4

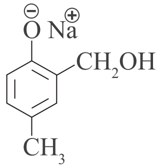
[IIT 2007]

195. The structure of the intermediate 'I' is

(a) 

(b) 

(c) 

(d) 

[IIT 2007]

Assertion-Reason Type Questions

In the following question two statements (Assertion) A and Reason (R) are given. Mark

(a) if A and R both are correct and R is the correct explanation of A
(b) if A and R both are correct but R is not the correct explanation of A
(c) A is true but R is false
(d) A is false but R is true

196. **(A):** The water solubility of the alcohols follow the order t-butyl alcohol > s-butyl alcohol > n-butyl alcohol.

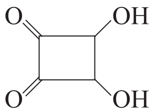
(R): Alcohols form H-bonding with water to show soluble nature.

197. (A): The order of acidic strength is
RCOOH > phenol > H_2O > C_2H_5OH
(R): As acid strength increases, pKa increases.

198. (A): Anhydrous $ZnCl_2$ is used in reaction of alcohols with HCl.
(R): $ZnCl_2$ forms a complex with oxygen of alcohol and converts –OH to a much better leaving group.

199. (A): An alcohol does not react with halide ions as such but on dissolution in strong acids it does react smoothly forming an alkyl halide.
(R): The strong acid accelerates the removal of proton from the –OH group of the alcohol.

200. (A):



This compound is almost as strong as H_2SO_4
(R): It contains a strained ring system

201. (A): The C – O bond length of aliphatic alcohols is less than aromatic alcohols.
(R): In aromatic alcohols C – O bond acquires π-bond character.

202. (A): The t-butoxide ion is a stronger base than OH^- or $C_2H_2O^-$ but a much poorer nucleophile.
(R): A negatively charged ion is always a more powerful nucleophile than its conjugate acid.

203. (A): Phenols cannot be converted into esters by direct reaction with carboxylic acids.
(R): Electron withdrawing groups increase the acidity of phenols.

204. (A): Phenol reacts with acyl halides in presence of pyridine to form phenyl acetate.
(R): Benzylation of phenol is carried out in the presence of NH_4OH.

205. (A): Phenol on oxidation with $KMnO_4$ gives meso tartaric acid.
(R): Pure phenol are colourless but turn pink due to oxidation due to phenoquinone (red)

206. (A): Treatment of phenol with nitrous acid yields p-benzoquinone monoxime.
(R): p-nitrosophenol and p-benzo quinine monoxime are tautomers.

207. (A): Phenols cannot be converted into esters by direct reaction with carboxylic acids whereas alcohols can be.
(R): The esterification reaction is exothermic for alcohols but slightly endothermic for phenols.

208. (A): Phenol is less acidic than p-nitrophenol
(R): Phenolate ion is more stable than P-nitrophenolate ion.

209. (A): 4-nitrophenol is more acidic than 2,4,6-trinitrophenol.
(R): Phenol is a weaker acid than carbonic acid.

210. (A): Both symmetrical and unsymmetrical ethers can be prepared with Williamsons' synthesis.
(R): Williamson's synthesis is an example of nucleophillic substitution reaction.

211. (A): Diphenyl ether is prepared by Ullmann reaction as shown below:

$$C_6H_5ONa + BrC_6H_5 \xrightarrow{\text{Cu, 483 K}} C_6H_5OC_6H_5 + NaBr$$

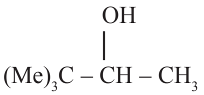
(R): Diphenyl ether is used as perfume.

212. (A): Ditertiary ether is very difficult to prepare.
(R): It is due to severe steric hindrance.

213. (A): Di-tert-butyl ether cannot be prepared by Williamson's synthesis.
(R): tert-Butyl bromide on treatment with sodium tert-butoxide preferentially undergoes elimination to form isobutylene and tert-butyl alcohol.

214. (A): $CH_3CH_2OCH_2Cl$ reacts faster when treated with water than $CH_3CH_2OCH_2CH_2CH_2Cl$ does.
(R): Carbonium ion formed by the ionization of $CH_3CH_2OCH_2Cl$ is stabilized by resonance.

215. (A): The dehydration of



$$(Me)_3C - \overset{\displaystyle OH}{\overset{|}{C}H} - CH_3$$

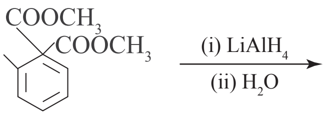
is presence of CS_2 and MeI.
(R): This reaction proceeds by formation of carbocation in first step.

Matrix-Match Type Questions

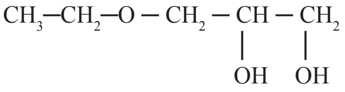
216. Match the following:

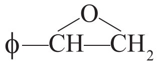
Column I (Reaction)

(a)



(b)

(c) 
$CH_3{-}CH_2{-}O-CH_2-\underset{\underset{OH}{|}}{CH}-\underset{\underset{OH}{|}}{CH_2}$

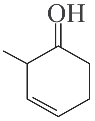
(d) 

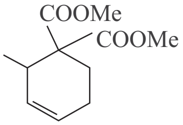
Column II (Product)

(p) 
$\phi-\underset{\underset{Cl}{|}}{CH}-CH_2OH$

(q) $CH_3-CH_2-O-CH_2{-}CHO$

(r) HCHO

(s) 

(t) 

217. Match the following:

List I

(a) Propane-1,2,3- triol
(b) Ethane-1,2-diol
(c) Tetrahydrofuran
(d) Power alcohol

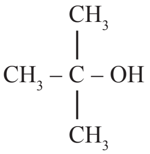
List II

(p) Cyclic ether
(q) absolute ethanol + petrol
(r) dynamite
(s) terylene

218. Match the following:

List I

(Compounds)

(a) $(CH_3)_2CH-OH$
(b) C_6H_5-OH
(c) HCHO
(d) 
$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH$

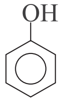
List II

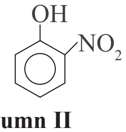
(Reagents)

(p) $FeCl_3$
(q) Victor Meyer's reagent
(r) Lucas reagent
(s) Fehling solution
(t) I_2 + NaOH

219. Match the following:

Column I

(a) 

(b) $C_2H_5-O-C_2H_5$
(c) C_2H_5OH
(d) 

Column II

(p) Brensted base as well as Lewis base
(q) Self- intermolecular
(r) Hydrogen bonding with water
(s) Intra molecular - bonding

220. Match the following:

Column I

(a) Resorcinol
(b) Guaicol
(c) Quinol
(d) Pyrogallol

Column II

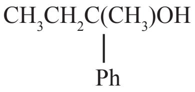
(p) m-Dihydroxy benzene
(q) Trihydroxy benzene
(r) p-dihydroxy benzene
(s) monomethyl ether

221. Match the following:

Column I

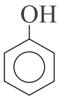
(a) $CH_3CH_2MgX + H_2CO$
(b) $CH_3CH_2CH_2COCH_3 + CH_3MgX$
(c) $CH_3MgX + H_2C-O-CH_2$
(d) $PhCH_2CHO + CH_3MgX$

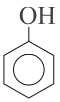
Column II

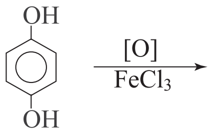
(p) $(CH_3)_2C(OH)CH_2CH_2CH_3$
(q) $CH_3CH_2CH_2OH$
(r) 
$CH_3CH_2\underset{\underset{Ph}{|}}{C}(CH_3)OH$
(s) $PhCH_2CH(OH)CH_3$

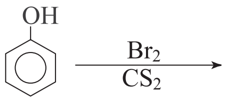
222. Match the following:

Column I

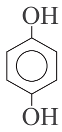
(a)  $\xrightarrow[CrO_2Cl_2]{(O)}$

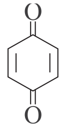
(b)  $\xrightarrow[\text{in alk. solution}]{K_2S_2O_8}$

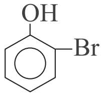
(c) 

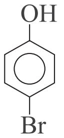
(d) 

Column II

(p) 

(q) 

(r) 

(s) 

223. Match the following:

List I

(Compounds)

(a) Ethanol.

(b) Iso propyl alcohol

(c) Phenol

(d) Formaldehyde

List II

(Reagent and reactions of response)

(p) Bakelite formation

(q) Ceric ammonium nitrate

(r) Haloform test

(s) $FeCl_3$

(t) Oily layer with lucas reagent

224. Match the following:

Column I

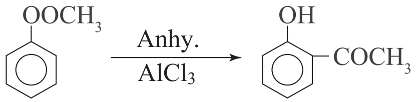
(a) Freis migration

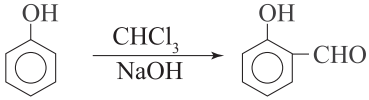
(b) Reimer - Tiemann reaction

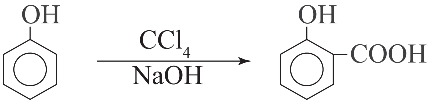
(c) Schotten Baumann reaction

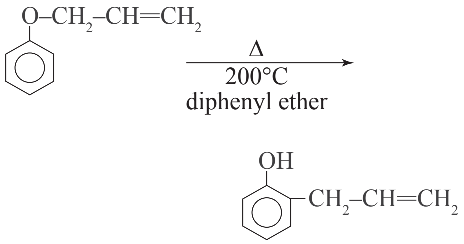
(d) Claisen rearrangement

Column II

(p) 

(q) 

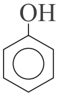
(r) 

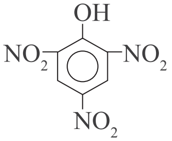
(s) 

(t) 

225. Match the following:

Column I (Compound)

(a) 

(b) 

(c) CH_3COOH

(d) C_2H_5OH

Column II (Possible reaction)

(p) Reaction with NaOH

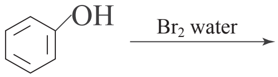
(q) Reaction with $NaHCO_3$

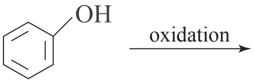
(r) Reaction with PCl_5

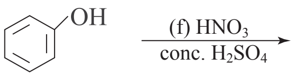
(s) Reaction with NH_3

226. Match the following:

Column I

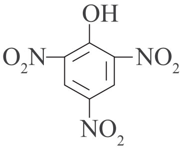
(a) 

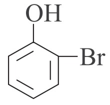
(b) 

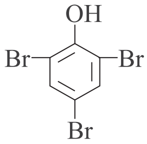
(c) 

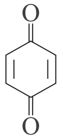
(d) 

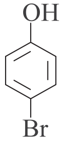
Column II

(p)  Picric acid

(q)  Ortho-bromophenol

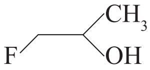
(r)  Tri-bromophenol

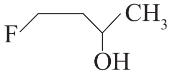
(s)  Parabenzoquinone

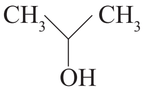
(t)  Para-bromophenol

The IIT-JEE Corner

227. The order of reactivity of the following alcohols

(I) 

(II) 

(III) 

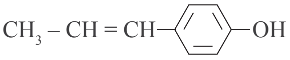
(IV) 

towards conc. HCl is

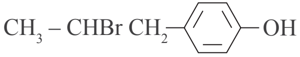
(a) I > II > III > IV
(b) I > III > II > IV
(c) IV > III > II > I
(d) IV > III > I > II

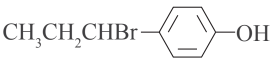
[IIT 1997]

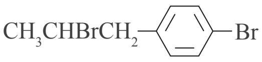
228. The reaction of

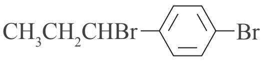


with HBr gives

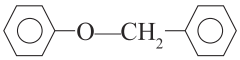
(a) 

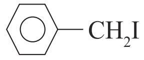
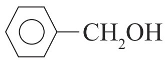
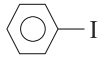
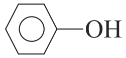
(b) 

(c) 

(d) 

[IIT 1998]

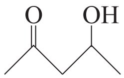
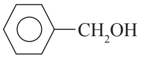
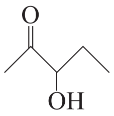
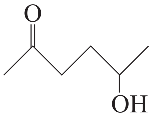
229. The ether  when treated with HI produces

(1) 
(2) 
(3) 
(4) 

(a) 1, 3
(b) 1, 2
(c) 1, 4
(d) all are formed

[IIT 1999]

230. Which of the following will be most readily dehydrated in acidic conditions?

(a) 
(b) 
(c) 
(d) 

[IIT 2000]

231. 1-Propanol and 2-propanol can be best distinguished by

(a) oxidation with $KMnO_4$ followed by reaction with Fehling solution
(b) oxidation with acidic dichromate followed by reaction with Fehling solution
(c) oxidation by heating with copper followed by reaction with Fehling solution
(d) oxidation with concentrated H_2SO_4 followed by reaction with Fehling solution.

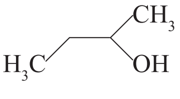
[IIT 2001]

232. Identify the correct order of boiling points of the following compounds

$CH_3CH_2CH_2CH_2OH$ (I)
$CH_3CH_2CH_2CHO$ (II)
$CH_3CH_2CH_2COOH$ (III)

(a) I > II > III
(b) III > I > II
(c) I > III > II(d)
III > II > I

[IIT 2002]

233.  $\xrightarrow[-H_2O]{H^+}$ F

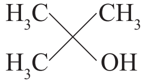
$\xrightarrow{Br_2, CCl_4}$ $C_4H_8Br_2$

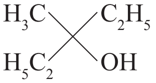
5 such products are possible
How many structures of F is possible?

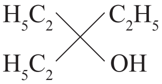
(a) 2
(b) 5
(c) 6
(d) 3

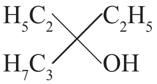
[IIT 2003]

234. Ethyl ester $\xrightarrow{CH_3MgBr\text{ (excess)}}$ P.
The product P will be

(a) 

(b) 

(c) 

(d) 

[IIT 2003]

235. $C_6H_5OH + C_2H_5I \xrightarrow[\text{Anhy. }(C_2H_5OH)]{^-O^-C_2H_5}$

(a) $C_6H_5OC_2H_5$ (b) $C_2H_5OC_2H_5$
(c) $C_6H_5OC_6H_5$ (d) C_6H_5I.

[IIT 2003]

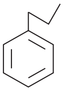
236. (I) 1,2-dihydroxy benzene
(II) 1,3-dihydroxy benzene
(III) 1,4-dihydroxy benzene
(IV) Hydroxy benzene

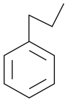
The increasing order of boiling points of above mentioned alcohols is :

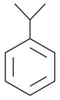
(a) I < II < III < IV
(b) I < II < IV < III
(c) IV < I < II < III
(d) IV < II < I < III

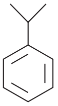
[IIT 2006]

237.  + Cl – CH_2CH_2 – CH_3 $\xrightarrow{AlCl_3}$ P

(a)  and CH_3CH_2CHO

(b)  and CH_3COCH_3

(c)  and CH_3COCH_3

(d)  and CH_3CH_2CHO

[IIT 2006]

ANSWERS

Straight Objective Type Questions

1. (d) **2**. (c) **3**. (a) **4**. (b) **5**. (c) **6**. (d) **7**. (d) **8**. (b) **9**. (b) **10**. (c)
11. (a) **12**. (c) **13**. (b) **14**. (a) **15**. (d) **16**. (c) **17**. (b) **18**. (a) **19**. (d) **20**. (b)
21. (c) **22**. (b) **23**. (d) **24**. (b) **25**. (c) **26**. (b) **27**. (c) **28**. (b) **29**. (b) **30**. (d)
31. (b) **32**. (d) **33**. (b) **34**. (c) **35**. (a) **36**. (b) **37**. (a) **38**. (b) **39**. (c) **40**. (a)
41. (a) **42**. (a) **43**. (b) **44**. (b) **45**. (d) **46**. (a) **47**. (a) **48**. (a) **49**. (b) **50**. (d)
51. (a) **52**. (b) **53**. (c) **54**. (b) **55**. (d) **56**. (a) **57**. (b) **58**. (d) **59**. (c) **60**. (c)
61. (c) **62**. (d) **63**. (a) **64**. (d) **65**. (a) **66**. (b) **67**. (d) **68**. (b) **69**. (a) **70**. (c)
71. (a) **72**. (a) **73**. (c) **74**. (c) **75**. (b) **76**. (c) **77**. (d) **78**. (b) **79**. (d) **80** . (a)
81. (a) **82**. (a) **83**. (b) **84**. (d) **85**. (b) **86**. (a) **87**. (b) **88**. (b) **89**. (c) **90**. (a)
91. (d) **92**. (b) **93**. (b) **94**. (a) **95**. (a) **96**. (a) **97**. (c) **98**. (d) **99**. (a) **100**. (d)

Brainteasers Objective Type Questions

101. (d) **102**. (b) **103**. (c) **104**. (a) **105**. (b) **106**. (c) **107**. (d) **108**. (c) **109**. (c) **110**. (d)
111. (b) **112**. (c) **113**. (d) **114**. (d) **115**. (c) **116**. (a) **117**. (d) **118**. (a) **119**. (b) **120**. (b)
121. (a) **122**. (c) **123**. (d) **124**. (c) **125**. (a) **126**. (d) **127**. (a) **128**. (b) **129**. (b) **130**. (a)
131. (a) **132**. (d) **133**. (b) **134**. (b) **135**. (d) **136**. (b) **137**. (d) **138**. (a) **139**. (d) **140**. (c)
141. (b) **142**. (a) **143**. (c) **144**. (d) **145**. (a) **146**. (c) **147**. (d) **148**. (a) **149**. (b) **150**. (c)
151. (c) **152**. (d) **153**. (c) **154**. (b)

Decisive Thinking Objective Type Questions

155. (a), (b) **156**. (a), (b), (d) **157**. (a), (b), (c), (d) **158**. (b), (c), (d) **159**. (a), (d)
160. (a), (b), (d) **161**. (c), (d) **162**. (a), (b), (d) **163.** (a), (b), (d) **164**. (a), (b), (d)

165. (a), (c), (d) **166**. (a), (b), (c) **167**. (a), (c), (d) **168**. (b), (d) **169**. (a), (b), (d)
170. (b), (c), (d) **171**. (a), (b), (d) **172**. (a), (c) **173**. (a), (b), (c) , (d) **174**. (a), (c)
175. (a), (c), (d) **176**. (a), (c) **177**. (a), (b), (c) **178**. (c), (d) **179**. (b), (c), (d)
180. (b), (c), (d).

Linked-Comprehension Type Questions

181. (c) **182**. (b) **183**. (b) **184**. (b) **185**. (d) **186**. (c) **187**. (b) **188**. (a) **189**. (d) **190**. (c)
191. (b) **192**. (c) **193**. (c) **194**. (c) **195**. (b)

Assertion-Reason Type Questions

196. (b) **197**. (c) **198**. (a) **199**. (c) **200**. (b) **201**. (d) **202**. (b) **203**. (b) **204**. (c) **205**. (b)
206. (c) **207**. (a) **208**. (c) **209**. (d) **210**. (b) **211**. (b) **212**. (a) **213**. (a) **214**. (a) **215**. (c)

Matrix-Match Type Questions

216. (a) - (t), (b) - (r, s), (c) - (q, r), (d) - (p)
217. (a) - (r), (b) - (s), (c) - (p), (d) - (q)
218. (a) - (q, r, t), (b) - (p), (c) - (s), (d) - (r)
219. (a) - (q, r), (b) - (p, r), (c) - (q, r), (d) - (r, s)
220. (a) - (p), (b) - (s), (c) - (r), (d) - (q)
221. (a) - (q), (b) - (p), (c) - (q), (d) - (s)
222. (a) - (q), (b) - q), (c) - (q), (d) - (r, s)
223. (a) - (q, r), (b) - (q, r, t), (c) - (p, s), (d) - (p)
224. (a) - (p), (b) - (q, r), (c) - (t), (d) - (s)
225. (a) - (p, r, s), (b) - (p, q, r, s), (c) - (p, q, r, s), (d) - (p, r, s)
226. (a) - (r), (b) - (s), (c) - (p), (d) - (q, t)

The IIT-JEE Corner

227. (c) **228**. (b) **229**. (c) **230**. (a) **231**. (c) **232**. (b) **233**. (d) **234**. (a) **235**. (a) **236**. (c)
237. (c)

HINTS AND EXPLANATIONS

Straight Objective Type Questions

1. Solubility increases as the branching increases. So t-butyl alcohol is most soluble in water.

2. $\underset{\text{acid}}{2C_2H_5OH} + \underset{\text{base}}{2Na} \rightarrow 2\,C_2H_5ONa + H_2$

3. Na reacts both with phenol and ethyl alcohol to evolve H_2 gas and hence cannot be used to distinguish phenol from ethyl alcohol. All the remaining reagents react only with phenol but not with ethyl alcohol and can be used for distinguishing phenol from ethyl alcohol.

4. In liebermann's nitroso reaction colour changes occur as follows:
Brown or Red → deep blue → green

7. Diethyl ether itself being a Lewis base is not attacked by nucleophiles that is, OH^- ions. And all others contains an electrophillic carbon and are readily attacked by nucleophiles.

8. Due to H-bonding, the boiling point of ethanol is much higher than that of the isomeric diethyl ether.

9. Solubility decreases as the length of carbon chain or hydrocarbon part increases. So $(CH_3)_3COH$ has the lowest solubility.

10. Ethyl alcohol forms stronger H-bonds than ethylamine or ammonia due to greater electronegativity of oxygen than nitrogen atom.

11. Among isomerism alcohols, the surface area decreases from $1^o \rightarrow 2^o \rightarrow 3^o$ alcohols and the boiling points decreases in the same order. The correct order is $1^o > 2^o > 3^o$

12. Because of the electron withdrawing effect of $–NO_2$ group, p-nitrophenol is most acidic.

13. phenoxide ion is stabilized through delocalization

14. Amongst isomeric alcohols, the alcohol with no branching has the highest boiling point.

17. p-nitrophenol (III) > phenol (I) > p-cresol (II).

18. Due to strong electron donating effect of the OH group, the electron density in phenol is much higher than that in toluene, benzene and chlorobenzene and phenol is readily attacked by the electrophile.

19. Magnesium first reacts with ethanol to form magnesium ethoxide which then reacts with water to regenerate C_2H_5OH along with $Mg(OH)_2$;

$$Mg + 2\,C_2H_5OH \rightarrow Mg(OC_2H_5)_2 + H_2$$

$$Mg(OC_2H_5)_2 + 2H_2O \rightarrow Mg(OH)_2 + 2C_2H_5OH$$

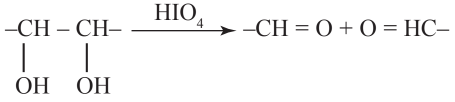
21. In acetylation, replacement of H of O–H occurs by CH_3CO- group.

$$–O – H + Cl\overset{\overset{O}{\|}}{C} – CH_3 \rightarrow –OCOCH_3 + HCl,$$

that is, H atom of mass 1 amu is lost and an acetyl group of mass 43 amu is added. Thus, there is a net gain of 43 – 1 = 42 amu for every acetyl group introduced. Mass of difference of final product and original compound is 190 – 106 = 84. Hence number of –OH groups = 84 / 42 = 2.

22. $CH_3CHOHCH_2CH_2OH$ has two OH groups and hence it undergoes maximum H-bonding.

25. Periodic acid (HIO_4) is specific for 1, 2-diol splitting.



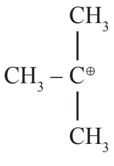
$$\underset{OH}{–\underset{|}{CH}} – \underset{OH}{\underset{|}{CH}–} \xrightarrow{HIO_4} –CH = O + O = HC–$$

27. Dehydration of alcohol is in order

$1^o < 2^o < 3^o$
so 3^o alcohol is dehydrated very easily.

28. Both o- and p-bromophenols are formed but p-bromophenol is the major product (= 82%) due to less strearic hinderance in case of p-substitution as compared to o-substitution.

29. This is because it will give the more stable tertiary carbonium ion.



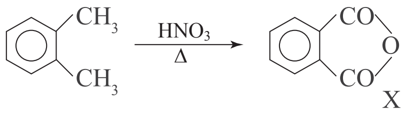
$$CH_3 – \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C^{\oplus}}}$$

30. Pyridinium chlorochromate oxidizes an alcoholic group selectively in the presence of carbon-carbon double bond.

32. $RCH{=}CH_2 \xrightarrow[\text{(ii) } H_2O_2/NaOH]{\text{(i) } B_2H_6} RCH_2CH_2OH$

33. Electron donating groups decreases while electron withdrawing groups increase the acidic character of phenols. Thus p-methylphenol is a weaker acid than phenol. Further, due to resonance stabilization of p-nitrophenoxide ion over m-nitrophenoxide ion, p-nitrophenol is stronger acid than m-nitrophenol. So the correct order is (B).

34.



$\xrightarrow[H_2SO_4]{\text{Phenol}}$ phenolphthalein (Y)

35. Phenol is more acidic than ethanol, methanol and p-methylphenol but is less acidic than o-nitrophenol.

36. $(CH_3)_3COH$ gives $(CH_3)_3C^+$ (tertiary) which is the most stable.

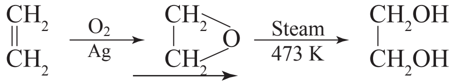
37. As compound Y reacts with I_2 and Na_2CO_3 to form triiodomethane, so Y must be a methyl ketone. As Y is obtained by oxidation of X with $K_2Cr_2O_7$, therefore, X must be a methylcarbinol. Thus X is $CH_3CHOHCH_3$.

38. $3CH_2 = CH_2 \xrightarrow{B_2H_6} (CH_3CH_2)B$
$\xrightarrow{H_2O_2/NaOH} 3CH_3CH_2OH$

39. Iodide ion attacks the smaller CH_3 group to give CH_3I and C_6H_5OH that is,

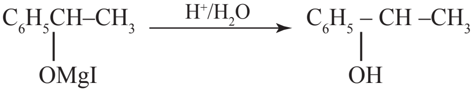
$$C_6H_5OCH_3 \boxed{\xrightarrow{HI}} C_6H_5OH + CH_3I$$

40.



41. $(C_2H_5)_2O + HI \rightarrow C_2H_5OH + C_2H_5I$

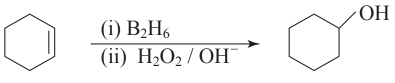
42. $CH_3I + Mg \overset{\text{ethers}}{\quad} CH_3MgI \xrightarrow{C_6H_5CHO}$



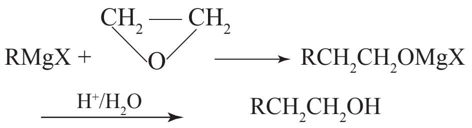
$$\underset{OMgI}{C_6H_5\underset{|}{CH}–CH_3} \xrightarrow{H^+/H_2O} \underset{OH}{C_6H_5 – \underset{|}{CH} –CH_3}$$

1-phenylethanol

43. Hydroboration–oxidation



44. Alcohols reactivity order is 1° alcohol < 2° alcohol < 3° alcohol
2-hydroxy-2-methyl propane is a 3° alcohol that is, more reactive.

45.


$$RMgX + \underset{O}{CH_2 — CH_2} \longrightarrow RCH_2CH_2OMgX \xrightarrow{H^+/H_2O} RCH_2CH_2OH$$

46. $\underset{A}{C_2H_5OH} \xrightarrow[-\frac{1}{2}H_2]{Na} \underset{B}{C_2H_5ONa}$

$2C_2H_5OH \xrightarrow[H_2O]{H_2SO_4} C_2H_5OC_2H_5$
Diethyl ether

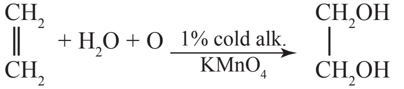
47. Due to greater electronegativity of sp^2 hybridized carbon atoms of the benzene rins. Diaryl ethers are not attacked by nucleophiles such as I^- ions and diaryl ethers are not cleaved by HI event at 525 K.

48. Dehydration of CH_3OH will give methylene which is unstable.

$CH_3OH \xrightarrow{H_2SO_4} \underset{(unstable)}{:CH_2} + H_2O$

49. $CH_3OH + (CH_3)_3Cl$

50. Due to greater electron withdrawing effect of NO_2 group or Cl-atom, nitrophenols are stronger acids than p-chlorophenol. Out of nitrophenols, p-nitrophenol is the strongest acid.

51.


$$\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + H_2O + O \xrightarrow[KMnO_4]{1\% \text{ cold alk.}} \begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix}$$

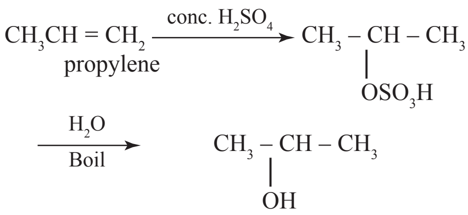
Ethylene ethylene glycol

52. $C_2H_5OH \xrightarrow{Cl_2} CCl_3CHO \xrightarrow{NaOH} CHCl_3$

53. 2-methylpropan-2-ol reacts fastest with the Lucas reagent as it generates the most stable tert-butyl carbocation.

54. $C_2H_5Br \xrightarrow{aq.\ NaOH} C_2H_5OH \xrightarrow{Na}$

$C_2H_5ONa \xrightarrow{CH_3I} C_2H_5 - O - CH_3 + NaI$
Ethyl methyl ether

55.


$$\underset{\text{propylene}}{CH_3CH = CH_2} \xrightarrow{\text{conc. } H_2SO_4} CH_3 - \underset{\underset{OSO_3H}{|}}{CH} - CH_3 \xrightarrow[Boil]{H_2O} CH_3 - \underset{\underset{OH}{|}}{CH} - CH_3$$

56. $(CH_3)_2C = O \xrightarrow[\text{(ii) } H^+/H_2O]{\text{(i) } CH_3MgBr} (CH_3)_3COH$

57. Esters react with Grignard reagents to form 3° alcohols.

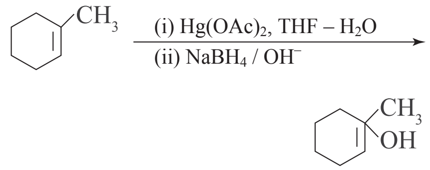
58. Grignard reagent react with formaldehyde to give 1° alcohols.

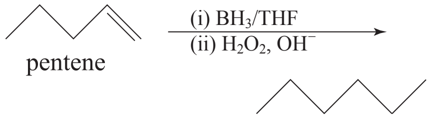
59. $CH_3CH_2OCH_2CH_3 \xrightarrow{Cl_2,\ hv} CCl_3CCl_2 - O - CCl_2CCl_3$
Perchlorodiethyl ether

60. $C_{12}H_{22}O_{11} + H_2O \xrightarrow[Yeast]{Invertase} C_6H_{12}O_6 + C_6H_{12}O_6$

$C_6H_{12}O_6 \xrightarrow[Yeast]{Zymase} 2C_2H_5OH + 2CO_2$

61. During oxymercuration-demercuration reactions products corresponding to Markownikoff's addition of H_2O are formed that is,



62.


pentene

1-pentanol

63. $(CH_3CH_2)_2O + (CH_3CO)_2O \xrightarrow{\text{anhyd. } AlCl_3} 2CH_3COOC_2H_5$

66. $\underset{\text{Lower ether}}{CH_3OCH_3} \xrightarrow{Cl_2,\ hv} CH_3OCH_2Cl$
α-chlorodimethyl ether
or methoxymethyl chloride

$CH_3OCH_2Cl + CH_3MgBr \xrightarrow{\text{dry ether}} CH_3OCH_2CH_3 + MgBrCl$
Ethyl methyl ether
(higher ether)

67. The alcohol is easily oxidized within two seconds. So it must be a primary alcohol

68. As a single alkyl halide is formed on treatment with HI, it must be a symmetrical ether, that is, ethoxyethane.
$C_2H_5OC_2H_5 + 2HI \rightarrow 2\ C_2H_5I + H_2O$

69. Only 2° alcohols on oxidation give ketones, so the compound is sec-Butyl alcohol.

70. Alcoholic iodine with NaOH gives iodoform

$$CH_3CH_2OH + 3I_2 + 4NaOH \rightarrow CHI_3 + CH_3\,COONa + 3NaI + 3H_2O$$

71. $\underset{(A)}{C_2H_5OH + PCl_5 \rightarrow C_2H_5Cl} + POCl_3 + HCl$

$C_2H_5Cl + AgNO_2 \rightarrow \underset{(B)}{C_2H_5NO_2} + AgCl.$

72. $\underset{(A)}{CH_3CHO} \xrightarrow[\text{(ii) }H^+/H_2O]{\text{(i) }CH_3MgI} \underset{\text{isopropyl alcohol }2^\circ\ (B)}{CH - CHOH - CH_3}$

$\xrightarrow{\text{victor Meyer' test}}$ Blue colour

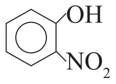
73. $C_2H_5OC_2H_5 \xrightarrow[\text{Cleavage of ethers}]{\text{Red P/HI}} 2C_2H_5I$

$\xrightarrow[\text{Reduction}]{\text{Red P/HI}} \underset{\text{ethane}}{2C_2H_6}$

74. Depending upon the rate of donation of proton the acidic nature decreases as follows:
RCOOH > HOH > ROH > HC ≡ CH

75. A + NaOH → alcohol + acid
Thus it is Cannizzaro reaction.
A is thus aldehyde without H at α-carbon. (as C_6H_5CHO, HCHO)

$$2C_6H_5CHO + NaOH \rightarrow C_6H_5CH_2OH + C_6H_5COONa$$

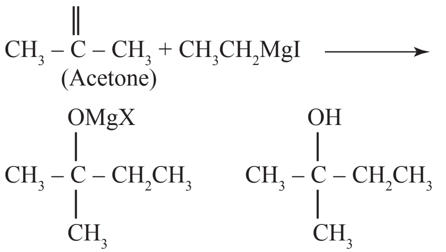
76. 

is most acidic since $-NO_2$ has strong –I, –R effects.

83. Phenol does not decompose sodium carbonate or sodium bicarbonate that is, CO_2 is not evolved, because phenol is a weaker acid than carbonic acid.

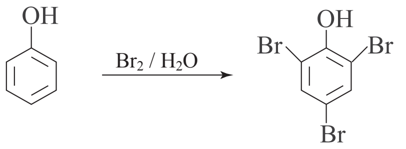
84. $\underset{\text{n-butanol}}{CH_3{-}CH_2{-}CH_2{-}CH_2OH} + SOCl_2 \xrightarrow{\text{pyridine}}$

$\underset{\text{1-chlorobutane}}{CH_3 - CH_2 - CH_2 - CH_2Cl}$

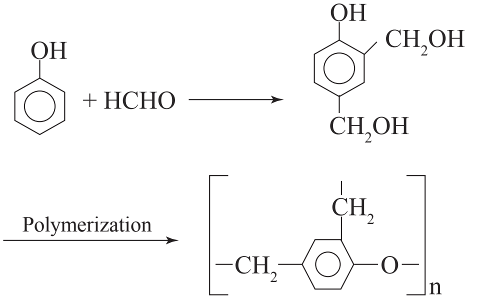
87. 

$$\underset{\text{(Acetone)}}{CH_3 - \overset{\overset{O}{\|}}{C} - CH_3} + CH_3CH_2MgI \longrightarrow CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{OMgX}{|}}{C}} - CH_2CH_3 \qquad CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}} - CH_2CH_3$$

2-methylbutan-2-ol

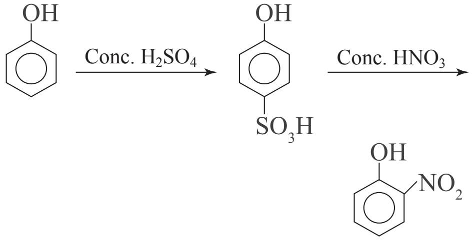
88. 

(-OH group is highly activating) 2,4,6-tribromophenol

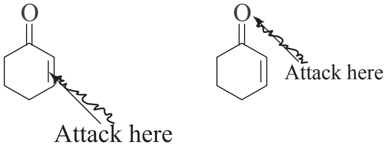
91. 

Bakelite
(Thermosetting plastic)

92. Here o-nitrophenol is formed as follows:

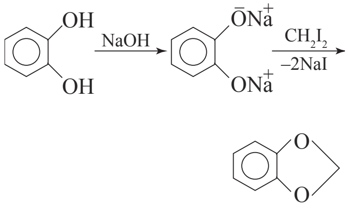


93. Here we have to decide if the nucleophile will undergo conjugate addition or direct addition. Nucleophiles that are relatively weak bases like CN^-, RNH_2 and X^- conjugate addition, while strong bases such as R-Li, R-MgX give direct addition.



Conjugate addition Direct addition

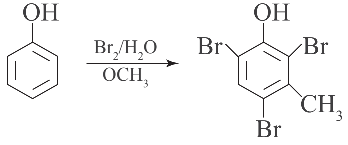
94. Catechol is most out of all dihydric phenols.



95. $RCH_2CH_2OH \xrightarrow{PBr_3} RCH_2CH_2Br \xrightarrow{KCN}$

$RCH_2CH_2COOH \xleftarrow{H_2O^+} RCH_2CH_2CN$

98. Compound (X) must be a phenolic compound as shown by various reactions. (X) on treatment with Br_2 water gives (Y) with 3 Br atoms, so the placement of OH and CH_3 must be such that they reinforce each other in electrophilic substitution. So, the compound (X) is m-cresol and (Y) is 2,4, 6-tribromo-3-methyl phenol



m –cresol 2,4,6-tribromo-3-methyl phenol

99. Acetaldehyde (ethanal) gives red ppt. with Fehiling solution.

$CH_3CHO + 2Cu(OH)_2 + 2NaOH \rightarrow$

$CH_3COONa + Cu_2O + 3H_2O$

Red ppt.

Ethanol also gives yellow ppt. with an alkaline solution of iodine (Iodoform test).

$CH_3CHO + 4NaOH + 3I_2 \rightarrow$

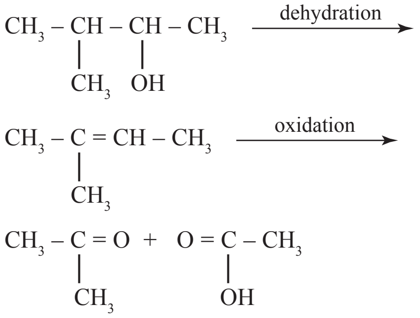
$CHI_3 + HCOONa + 3H_2O + 3NaI$

Yellow ppt.

101. As NO_2 group is electron attracting while CH_3 group is electron releasing group so NO_2 increases acidic nature while CH_3 decreases.

103. The facts that –I effect of the $–NO_2$ group and greater resonance stabilization of the p-nitrophenoxide

105.



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3 \xrightarrow{\text{dehydration}}$$

$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH-CH_3 \xrightarrow{\text{oxidation}}$$

$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=O \;+\; O=\underset{\displaystyle OH}{\underset{|}{C}}-CH_3$$

106. $R-OH \xrightarrow[NaOH]{C_6H_5COCl} RO-COC_6H_5$

In this reaction H is replaced by C_6H_5CO group. One unit molecular mass of alcohol is replaced by 105 unit (C_6H_5CO) molecular mass that is, there is an increase of 104 unit in molecular mass per –OH group.

$$\text{Number of –OH groups} = \frac{404-92}{104}$$

$$= \frac{312}{104} = 3$$

107. A and C gives yellow ppt. with 2, 4 DNP. B ($CH_2 = CH - CH_2OH$) reacts with metallic sodium. Thus D ($CH_2 = CH - OCH_3$) is the correct answer because it neither reacts with 2, 4-DNP nor with sodium.

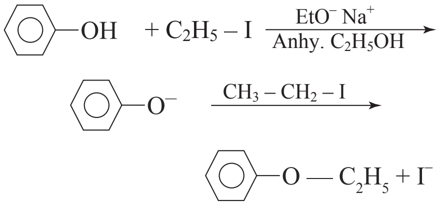
108. $\underset{94\ g}{C_6H_5OH} + \underset{3 \times 160\ g}{3Br_2} \rightarrow$ 2,4,6-tribromophenol

94 g of phenol require $Br_2 = 3 \times 160$ g

2 g of phenol will require Br_2

$$= \frac{3\times160}{94} \times 2 = 10.22 \text{ g}$$

110.

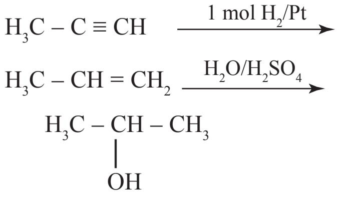


111. $RMgX + S \xrightarrow{\text{dry ether}} RSMgX \xrightarrow{H^+/H_2O}$

RSH

Mercaptan

112.



$$H_3C-C\equiv CH \xrightarrow{1\ mol\ H_2/Pt}$$

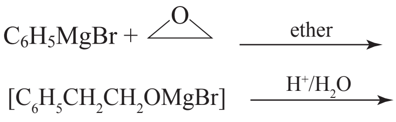
$$H_3C-CH=CH_2 \xrightarrow{H_2O/H_2SO_4}$$

$$H_3C-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$$

(Markowni koff's orientation)

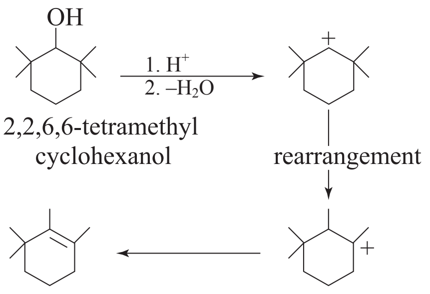
114. Here HBr attacks the oxygen of the cyclic structure, opens up to lead to $BrCH_2CH_2CH_2CH_2OH$. and the second HBr displaces the –OH group to give a dibromide

115.



$C_6H_5CH_2CH_2OH$
2-phenylethanol

117.



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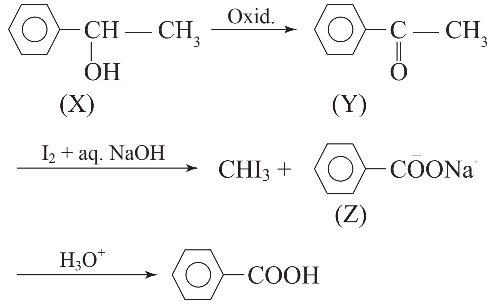

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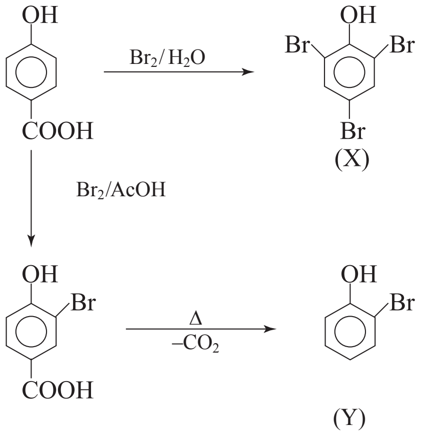

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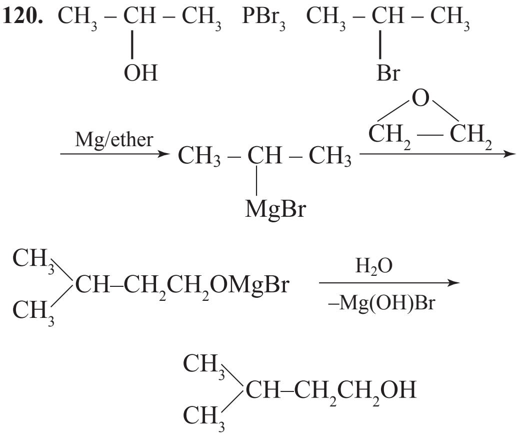


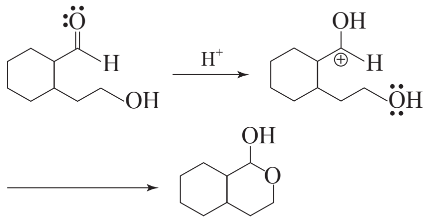
$$\underset{\underset{OH}{|}}{CH_3-CH-CH_3}\ \ PBr_3\ \ \underset{\underset{Br}{|}}{CH_3-CH-CH_3}$$

$$\xrightarrow{Mg/ether} \underset{\underset{MgBr}{|}}{CH_3-CH-CH_3} \xrightarrow{\overset{O}{CH_2—CH_2}}$$

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH–CH_2CH_2OMgBr \xrightarrow[-Mg(OH)Br]{H_2O}$$

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH–CH_2CH_2OH$$

122.



123. As the substrate is a neopentyl system, so a 1,2 migration of a methyl group occurs to form a more stable tertiary carbocation.

Now the bromide attaches itself to the tertiary carbon to form $(CH_3)_2C\ Br-CH_2CH_3$

124. CH_3MgI on reaction with active hydrogen containing compounds gives methane gas.

$ROH + CH_3MgI \rightarrow CH_4 + Mg(OR)I$

General molecular formula for saturated monohydric alcohol is $C_n\ H_{2n+2}\ O$ or $C_n\ H_{2n+1}\ OH$.

Moles of methane formed = Moles of active hydrogen = Moles of saturated monohydric alcohol reacted.

$$\frac{44.48}{22400} = \frac{0.12}{14n+18}.$$

On solving, we get

$n = 3$

Molecular formula of alcohol = C_3H_7OH.

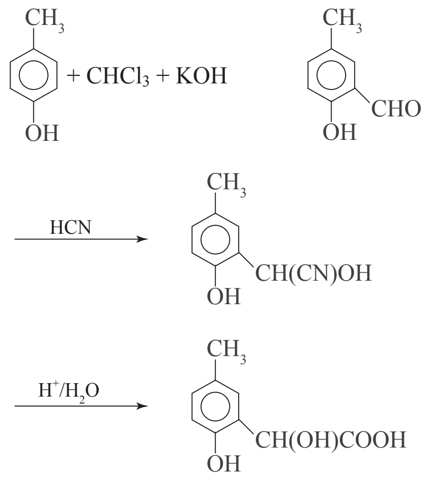
As it gives yellow precipitate of iodoform with I_2 and alkali so it will be $CH_3CH(OH)CH_3$.

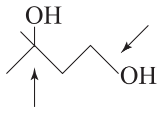
125. $CH_3CH = CH_2 \xrightarrow{B_2H_6} (CH_3CH_2CH_2)_3B$
Propene

$\xrightarrow{H_2O_2,\ OH^-} CH_3CH_2CH_2OH$
Propane-1-ol

It follows Anti Markowni Koff's rule.

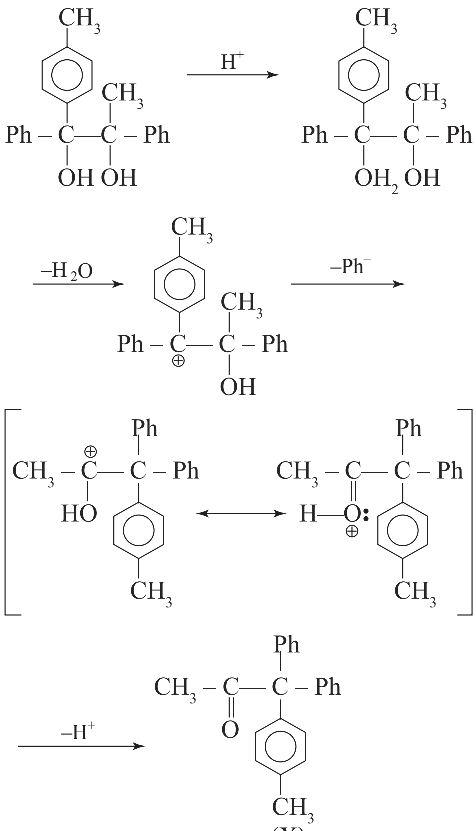
126.



133. 

1° alcohol, gives carboxylic acid on oxidation

3° alcohol not oxidized.

134. 

(X)

136. $$CH_3CH_2OH \xrightarrow{P+I_2} \underset{(A)}{CH_3CH_2I} \xrightarrow[Ether]{Mg}$$

$$\underset{(B)}{CH_3CH_2MgI} \xrightarrow{HCHO}$$

$$\underset{(C)}{CH_3-CH_2-CH_2OMgI} \xrightarrow{H_2O}$$

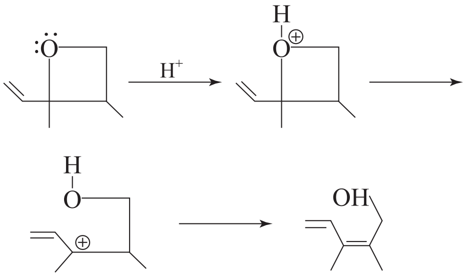
$$\underset{(D)}{CH_3CH_2CH_2OH + Mg(OH)I}$$

The compound D is n-propyl alcohol.

137. $$HC \equiv CH \xrightarrow[H_2SO_4]{HgSO_4} CH_3CHO$$

$$\xrightarrow{(i)\ CH_3MgBr\ (ii)\ H_2O} CH_3CHOHCH_3$$

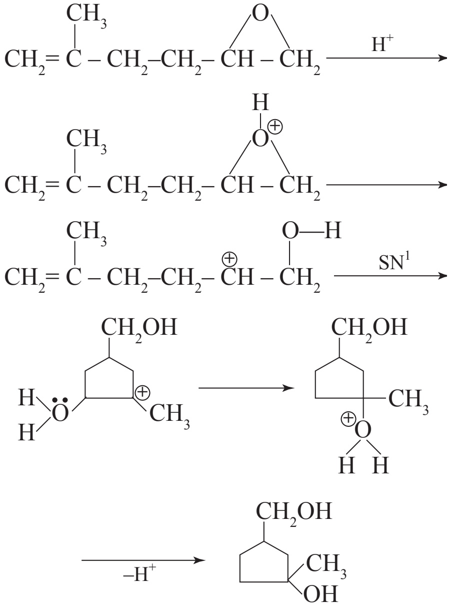
$$\xrightarrow{PBr_3} CH_3CHBrCH_3$$

139. 

141. $$C_2H_5OH \xrightarrow{PCl_5} C_2H_5Cl \xrightarrow{KCN} C_2H_5CN$$

$$\xrightarrow{H_3O^+} C_2H_5COOH + NH_3$$

Propanoic acid

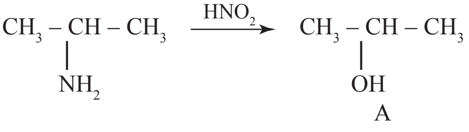
142. 

145. $CH_3CH_2OH + Cl_2 \rightarrow CH_3CHO$
Ethanol (from bleaching powder)

$CH_3CHO + Cl_2 \rightarrow CCl_3CHO + 3HCl$
Ethanal chloral

$2CCl_3CHO + Ca(OH)_2 \rightarrow$
(present in bleaching powder)

$2CHCl_3 + (HCOO)_2Ca$
chloroform calcium formate

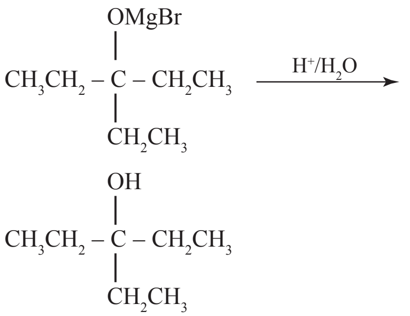
146. 

$$CH_3-\underset{\underset{NH_2}{|}}{CH}-CH_3 \xrightarrow{HNO_2} \underset{A}{CH_3-\underset{\underset{OH}{|}}{CH}-CH_3}$$

$$\xrightarrow{[O]} CH_3-CO-CH_3 \xrightarrow[(ii)\ H^+/H_2O]{(i)\ CH_3MgI}$$

$(CH_3)_3COH$
2-methylpropanol –2

148. $CH_3CH_2COCH_2CH_3 + CH_3CH_2MgBr \longrightarrow$



$$CH_3CH_2-\overset{\overset{\displaystyle OMgBr}{|}}{\underset{\underset{\displaystyle CH_2CH_3}{|}}{C}}-CH_2CH_3 \xrightarrow{H^+/H_2O}$$

$$CH_3CH_2-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle CH_2CH_3}{|}}{C}}-CH_2CH_3$$

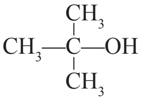
3-ethylpentan-3-ol

149. Higher homologoues of ethers can be prepared by Grignard reagents.

$$CH_3OCH_3 \xrightarrow{Cl_2,\ hv} CH_3OCH_2Cl$$

$$\xrightarrow{CH_3MgCl/ether} CH_3OCH_2CH_3 + MgCl_2$$

150. (1) Because the compound reacts with Na, it must be an alcohol. Therefore, the structure of $C_4H_{10}O$ is tert - butyl alcohol



$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-OH$$

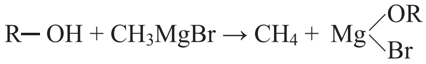
(2) A negative iodoform test would occur for the primary four - carbon alcohol, n- butyl alcohol:

$$CH_3CH_2CH_2CH_2OH$$

(3) In the Lucas test, the Lucas reagent with 1°, 2°, and 3° alcohols. the alcohol are distinguished by their reactivity with the Lucas reagent : 3° alcohol react immediately; 2° alcohols react within 5 minutes; and 1° alcohols react poorly at room temperature. Because the compound reacts with the reagent in 4 minutes, then the structure of $C_4H_{10}O$, a 2° alcohol, is sec -butyl alcohol

$$CH_3CH_2\underset{\underset{\displaystyle OH}{|}}{CH}CH_3$$

151. All the four options given are monohydric alcohols. When a monohydric alcohol is treated with CH_3MgBr. The number of CH_4 gas produced is equal to the number of mole s of alcohol.



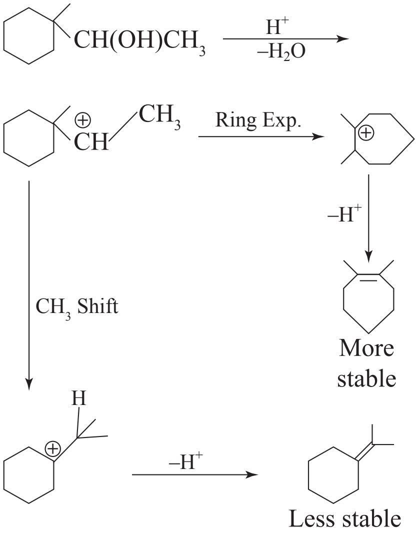
$$R-OH + CH_3MgBr \rightarrow CH_4 + Mg\begin{matrix} OR \\ Br \end{matrix}$$

Let M be the molecular weight of alcohol than

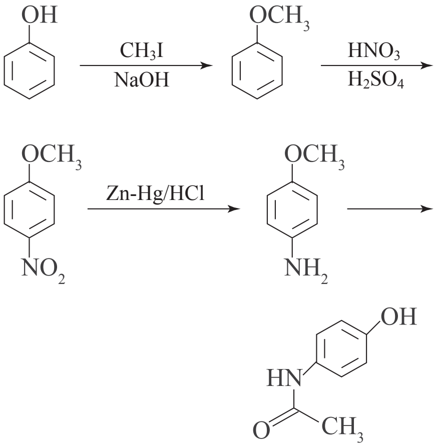
$$\frac{6.75}{M} = \frac{2.52}{22.4}$$

As on solving, M = 60. Hence the unknown alcohol is 1- propanol

152.

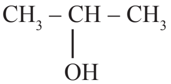


153.



Decisive Thinking Objective Type Questions

155. (1) $CH_2 = CH - CH_3 + H_2O \xrightarrow{H^+}$



$$CH_3-\underset{\underset{\displaystyle OH}{|}}{CH}-CH_3$$

(Markowni Koff's addition)

(2) $CH_3 - CH = O + CH_3MgI \longrightarrow$

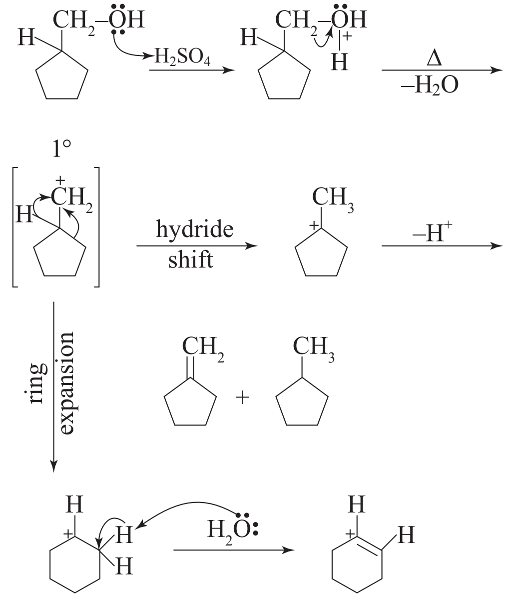
$(CH_3)_2\ CH - OMgI \xrightarrow{H_2O} (CH_3)_2CHOH$

159. In Reimer-Tiemann reaction intermediates are A and D.

162. As the reaction of CH_3MgI with phenol will give only methane but no anisole.

$C_6H_5OH + CH_3MgI \rightarrow CH_4 + C_6H_5OMgI$

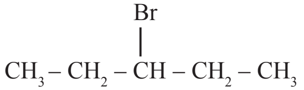
163.



165. $CH_3CH_2CH_2CH_2OH$ does not give iodoform test as it does not contain the grouping CH_3CHOH–.

166. 2,4,6-trinitrophenol, benzoic acid and benzenesulphonic acid are more acidic than carbonic acid and hence dissolve in $NaHCO_3$ solution. In contrast, o-nitrophenol is less acidic than carbonic acid and does not dissolve in $NaHCO_3$ solution.

170.



$CH_3-CH_2-\overset{\overset{\displaystyle Br}{|}}{CH}-CH_2-CH_3$

→ As 3-bromopentane is not chiral.

174. Ethers are readily attached by HI to give alcohols or phenols and halides.

$C_6H_5CH_2OC_6H_5 + HI \rightarrow C_6H_5OH + C_6H_5CH_2I$ Benzyl phenyl ether Phenol Benzyl iodine

However, when excess of HI is used , only iodide (alkyl or aryl) is obtained as major product.

175. As Tertiary alcohols such as $(CH_3)_3COH$ do not give Victor Meyer's test.

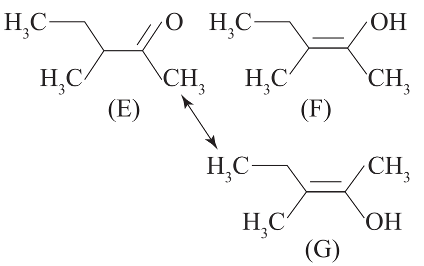
177. As with Cl_2, diethyl ether gives α-chlorodiethyl ether

$$CH_3CH_2OCH_2CH_2 \xrightarrow{Cl_2,\ hv} CH_3CHCl-O-CH_2CH_3$$

While all the remaining reactions give ethyl iodide/chloride.

179. As phenol does not react with heated Cu at 300°C.

180.

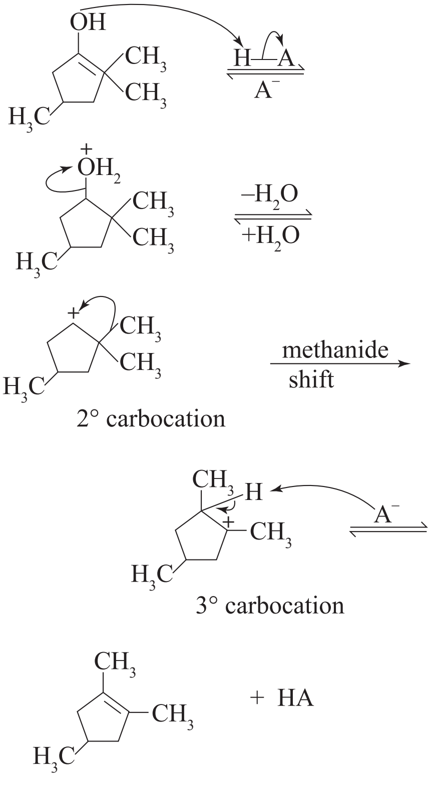


E – F & E- G are tautomers to each other.

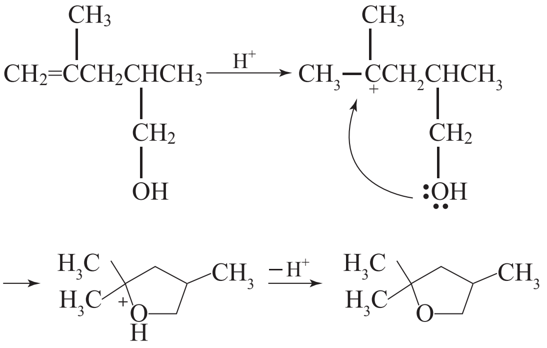
F and g are geometrical isomers as their methyl group can be cis and trans position to each other . Also all geometrical isomers are diastereomers to each other.

Linked-Comprehension Type Questions

181.



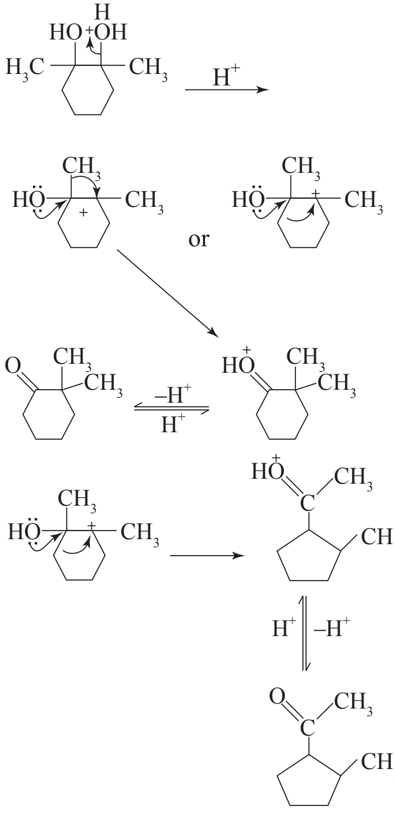
182. Addition of a proton to the double bond, following Markovnikov's rule, forms a carbocation intermediate. The alcohol group in the same molecule is the nucleophile that reacts with the carbocation.



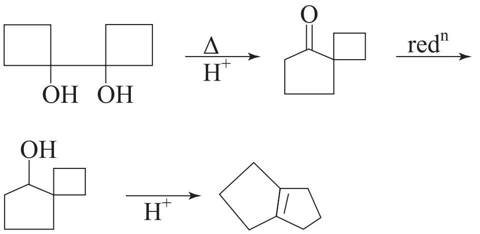
183. It is a case of intra molecular dehydration leading to formation of a cyclic ether.

184. Migration rate in effected by steric hindrance for example p- anisyl group can migrate nearly 1000 times more fast than o- anisyl group.

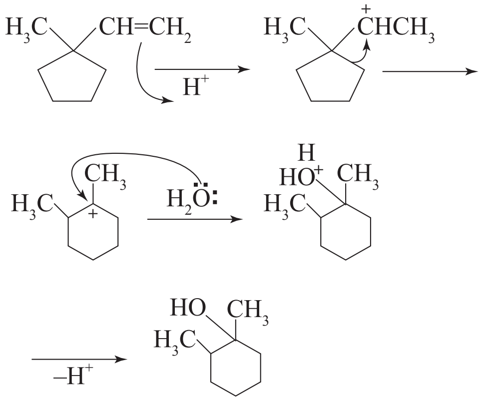
185.



186.

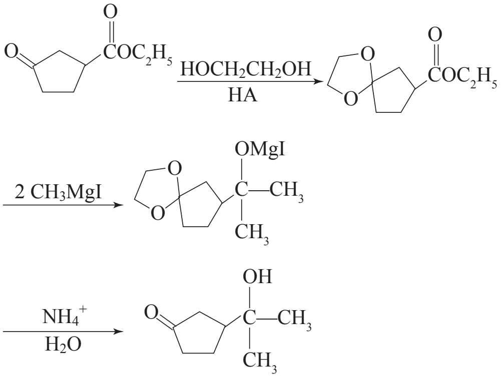


187. A proton adds to the alkene, forming a secondary carbocation, which undergoes ----- expansion rearrangement to form a more stable tertiary carbocation.

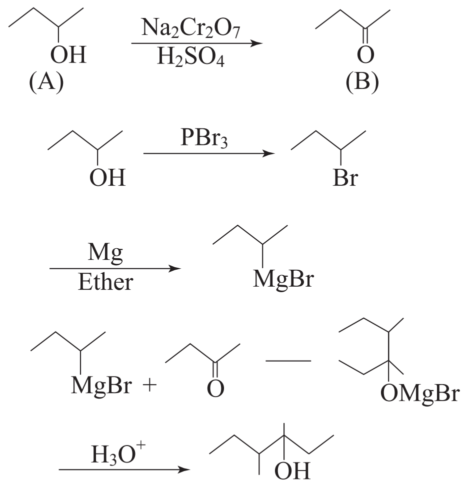


188. The reaction follow partly S_N1 and partly S_N2 mechanism in aqueous. In S_N1 mechanism, the 2° carbocation formed due to the loss of Cl^- undergoes rearrangement forming more stable benzylic carbocation $-OCH_3$ group at the p- position. Therefore, products (I) and (III) would be formed

189.



190.



193. $OH^{\ominus}$ (aq) + $CHCl_3 \rightleftharpoons {}^{\ominus}CCl_3 + H_2O$

$CCl_3^{\ominus} \rightarrow Cl^{\ominus} + :CCl_2$

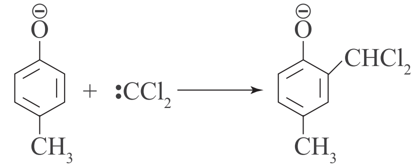
Dichlorocarbene
(intermediate)

194. $OH^{\ominus}$ (aq) + $CHCl_3 \rightleftharpoons {}^{\ominus}CCl_3 + H_2O$

$CCl_3^{\ominus} \rightarrow Cl^{\ominus} + :CCl_2$

Dichlorocarbene
(intermediate

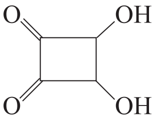
195.



Assertion-Reason Type Questions

199. The strong acid protonates the OH group thereby making it a good leaving group.

200.



is strong acid because it form more resonating structure. Both assertion and reason is correct but does not give correct explanation.

203. Phenols cannot be converted into esters by direct reaction with carboxylic acids since phenols are less nucleophillic than alcohols.

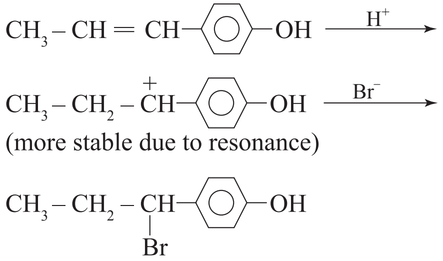
204. Benzoylation in phenols in usually carried out in the presence of aqueous NaOH because benzoyl chloride is not readily hydrolysed by alkalis.

208. Assertion is correct but reason is wrong as p-nitrophenolate ion is more acidic than phenolate ion.

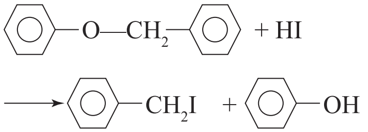
The IIT-JEE Corner

227. As the reactivity of alcohol is directly proportional to stability of Carbocation that is,
IV > III > II > I

228.



229.

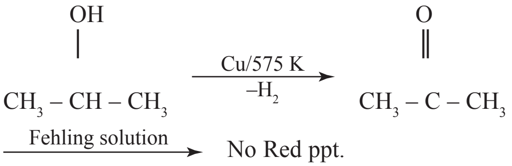


230. B-hydroxyaldehydes and β-hydroxyketones readily undergo dehydration to give α ,β-unsaturated aldehydes or ketones.

231. Here 'C' is correct answer as

$CH_3 - CH_2 - CH_2 - OH \xrightarrow[-H_2]{Cu/575\ K}$

$CH_3CH_2CHO \xrightarrow{\text{Fehling solution}}$ Red ppt.

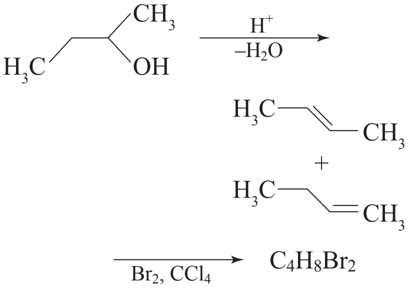


$CH_3 - \overset{OH}{\overset{|}{CH}} - CH_3 \xrightarrow[-H_2]{Cu/575\ K} CH_3 - \overset{O}{\overset{\|}{C}} - CH_3$

$\xrightarrow{\text{Fehling solution}}$ No Red ppt.

232. As stronger the H-bonding, more is the boiling point acids have stronger H-bond than alcohols while aldehydes do not show H-bonding. So the order of decreasing boiling point is III > I > II.

233.



235. $C_2H_5O^-$ will abstract proton from phenol converting it into phenoxide ion. This would then make nucleophilic attack on the methylene carbon of alkyl iodide. But $C_2H_5O^-$ is in excess. $C_2H_5O^-$ is better nucleophile than $C_6H_5O^-$ (phenoxide) ion since while in the former the negative charge is localized over oxygen in the latter it is delocalized over the whole molecular framework. So, it is $C_2H_5O^-$ ion that would make nucleophilic attack at ethyl iodide to give diethyl ether (Williamson synthesis).

$$C_2H_5O^- + CH_3 - CH_2 - I \rightarrow$$
$$C_2H_5 - O - CH_2CH_3 + I{:}^-$$

237. It is cumene hydroperoxide rearrangement reaction.

SUBJECTIVE SOLVED EXAMPLES

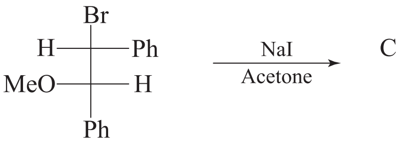
1. (i) Ethanol $\xrightarrow{I_2,\ NaOH}$

Solution

$$C_2H_5OH \xrightarrow[\text{[O]}]{I_2} CH_3CHO$$

$$CH_3CHO + 3I_2 + 4NaOH \xrightarrow{\text{haloform reaction}}$$
$$HCOONa + CHI_3 + 3H_2O + 3NaI$$

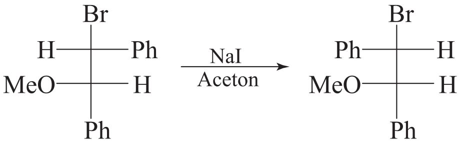
(ii) Predict the structure of the product in the following reaction:



[IIT 1996]

Solution

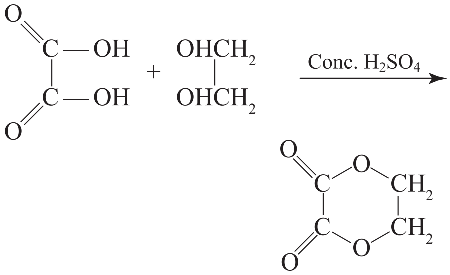
Br is replaced by I following SN² mechanism. There will be Walden inversion at the place of replacement.



(iii) $(COOH)_2 + (CH_2OH)_2 + \text{conc. } H_2SO_4 \longrightarrow (F)$

[IIT 1997]

Solution

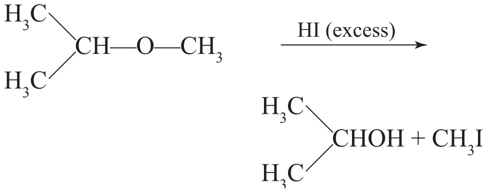


(iv) $(CH_3)_2CHOCH_3 \xrightarrow{\text{HI (excess), heat}}$

2 Products

[IIT 1998]

Solution



(v) 1-propanol from 2-propanol (in three steps)

Solution

$$\underset{\text{2-propanol}}{CH_3CH(OH)CH_3} \xrightarrow[-H_2O]{\text{conc. } H_2SO_4} CH_3CH = CH_2$$

$$\xrightarrow{HBr} CH_3CH_2CH_2Br \xrightarrow{\text{aq. NaOH}} \underset{\text{1-propanol}}{CH_3CH_2CH_2OH}$$

(vi) Ethyl alcohol to vinyl acetate (in mot more than 6 steps)

Solution

$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow{Al_2O_3,\ 350^\circ C} CH_2 = CH_2 \xrightarrow{Br_2}$$

$$BrCH_2.CH_2Br \xrightarrow{\text{alc. KOH}} CH \equiv CH$$

$$\xrightarrow{CH_3COOH} \underset{\text{Vinyl acetate}}{CH_2 = CHOCOCH_3}$$

(vii) Phenol to acetophenone

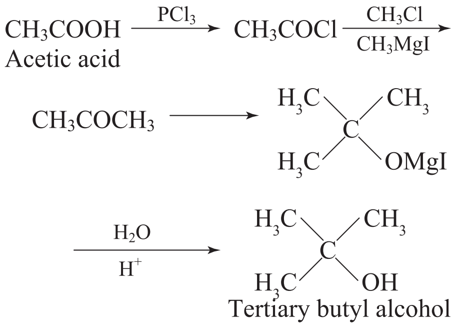
Solution

$$\underset{\text{Phenol}}{C_6H_5OH} \xrightarrow[\text{distillation}]{Zn} C_6H_6 \xrightarrow[\text{anhy. } AlCl_3]{CH_3COCl}$$

$$\underset{\text{Acetophenone}}{C_6H_5COCH_3}$$

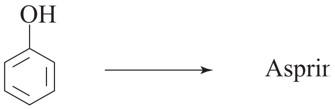
(viii) Acetic acid to tertiary butyl alcohol.

Solution



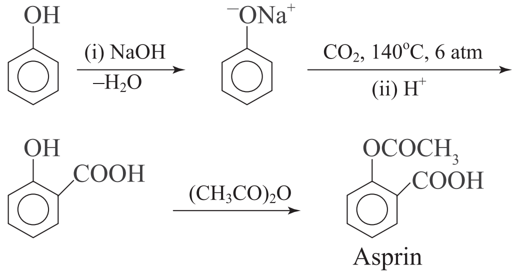
Tertiary butyl alcohol

(ix)



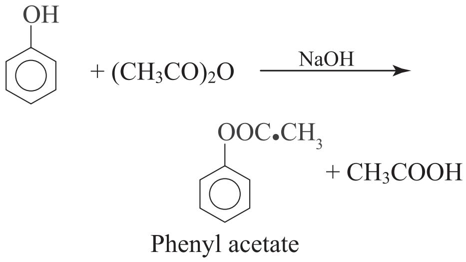
[IIT 2003]

Solution



2. State with balanced equations what happens when:
   (i) Acetic anhydride reacts with phenol in presence of a base.

Solution

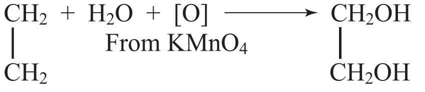


Phenyl acetate

(ii) Ethylene glycol is obtained by the reaction of ethylene with potassium permanganate.

[IIT 1991]

Solution



$$\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix} + H_2O + [O] \xrightarrow{} \begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix}$$

From $KMnO_4$

Ethylene glycol

3. State the conditions under which the following preparation are carried out. Give the necessary equations which need not to be balanced.
   (i) Ethanol from acetylene

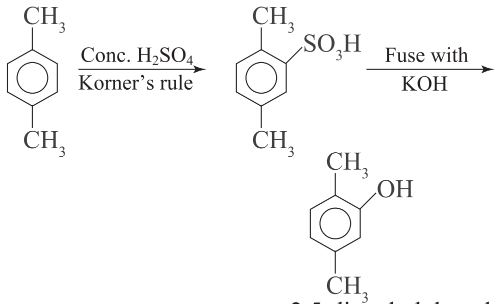
Solution

(i) $C_2H_2 \xrightarrow[Hg^{2+}]{H_2SO_4\text{ (dil.)}} CH_3CHO \xrightarrow[\text{reduction}]{H_2\text{ / cat.}}$

CH_3CH_2OH

4. What happens when p-xylene is reacted with concentrated sulphuric acid and the resultant product is fused with KOH?

Solution



2,5-dimethylphenol

5. Give a chemical test / suggest a reagent to distinguish between the following pairs of compounds:
   (i) Methanol and ethanol

Solution

Ethanol gives iodoform test while methanol does not.

$$C_2H_5OH + 4I_2 + 6NaOH \rightarrow CHI_3 \downarrow + 5NaI + HCOONa + 5H_2O$$

6. An unknown compound of carbon, hydrogen and oxygen contains 69.77% carbon and 11.63% hydrogen and has a molecular weight of 86. It does not reduce Fehling solution, but forms a disulphide addition compound and gives a positive iodoform test. What are the possible structures?

Solution

(i) Empirical formula:

Element	**%**	**Relative no. of atoms**	**Simplest ratio**
C	69.77	5.81	5
H	11.63	11.63	10
O	18.60	1.16	1

Empirical formula of compound is $C_5H_{10}O$ and empirical weight = 86.

Molecular weight = 86

So molecular formula of the compound is $C_5H_{10}O$.

7. An organic compound containing C. H and O exists in two isomeric forms A and B. An amount of 0.108 g of one of the isomers gives on combustion 0.308 g of CO_2 in 0.072 g of H_2O. A is insoluble in NaOH and $NaHCO_3$ while B is soluble in NaOH. A reacts with conc. HI to give compounds C and D. C can be separated from D by the ethanolic $AgNO_3$ solution and D is soluble in NaOH. B reacts readily with bromine water to give compound E of molecular formula, $C_7H_5OBr_3$. Identify, A, B, C, D and E with justification and give their structures.

[IIT 1991]

Solution

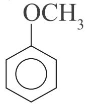
(i) For empirical formula of (A)

Element	**Percentage**	**Relative no. of atoms = %/ at. mass**	**Simplest ratio**
C	$\frac{12}{44}\times\frac{0.308}{0.108}\times100=77.77$	$\frac{77.77}{12}=6.46$	7
H	$\frac{2}{18}\times\frac{0.072}{0.108}\times100=7.40$	$\frac{7.40}{1}=7.40$	8
O	$100-(77.77+7.40)$ $=14.83$	$\frac{14.83}{16}=0.93$	1

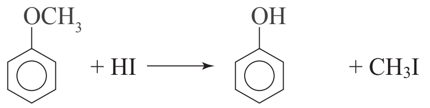
So the empirical formula of (A) = C_7H_8O

(ii) As (B) gives $C_7H_5OBr_3$ and (B) is isomer of (A). so molecular formula of (A) and (B) is C_7H_8O.

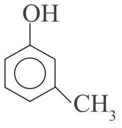
(iii) As (A) is insoluble in NaOH and $NaHCO_3$ so

(A) is 

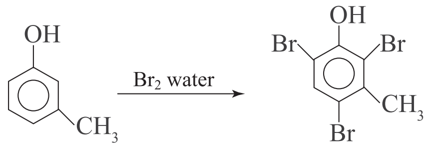
(iv) (A) is also confirmed by action with HI.



(A) (D) Soluble in (NaOH) (C) Soluble in $AgNO_3$

(v)  i.e., m-cresol since only.

(B) is soluble in NaOH and gives (E) ($C_7H_5OBr_3$) with Br_2 water, so (B) is



(B) (E)

2,4,6-tribromo m-cresol

meta-position can provide tribromo derivative.

8. Compound X (molecular formula, C_5H_8O) does not react appreciably with Lucas reagent at room temperature but gives a precipitate with ammonical silver nitrate. With excess of MeMgBr, 0.42 g of X gives 224 ml of CH_4 at STP. Treatment of X with H_2 in presence of Pt catalyst followed by boiling with excess HI, gives n-pentane. Suggest structure for X and write the equation involved.

[IIT 1992]

Solution

Compound 'X' $\xrightarrow{\text{Lucas reagent}}$ No reaction at room temperature

(Mol. formula C_5H_8O)

$\xrightarrow{\text{Ammonical AgNO}_3}$ Precipitates

$\xrightarrow{\text{Excess MeMgBr}}$ CH_4

$\xrightarrow[\text{(ii) Boil with excess HI}]{\text{(i) H}_2\text{ / Pt}}$ n-Pentane

Hence in compound X, five C-atoms are present in straight chain. It gives methane with excess GR, so in it acidic hydrogen is present. It gives precipitate with ammonical $AgNO_3$. Therefore, it must have acidic hydrogen in the form of alkynic group. It does not give any reaction with Lucas reagent therefore, it has p-alcoholic group.

So the basis of above properties, the possible structure of compound X is given as follows:

$HC \equiv C - CH_2 - CH_2 - CH_2OH$ (mol. formula C_5H_8O)

Reaction:

(i) $HC \equiv C–CH_2CH_2–CH_2OH \xrightarrow[\text{at room temp.}]{\text{Lucas reagent}}$ No reaction

(ii) $HC \equiv C–CH_2CH_2–CH_2OH + AgNO_3 + NH_4OH$
$\rightarrow AgC \equiv C - CH_2CH_2 - CH_2OH$
White ppt. $+ NH_4NO_3 + H_2O$

(iii) $HC \equiv C–CH_2CH_2–CH_2OH + 2MeMgBr \rightarrow$
$BrMg - C \equiv C - CH_2CH_2 - CH_2O - MgBr + 2CH_4$

(iv) $HC \equiv C–CH_2CH_2–CH_2OH + 2H_2 \xrightarrow{Pt}$
$CH_3 - CH_2 - CH_2 - CH_2 - CH_2OH$

$$\xrightarrow[(-I_2,\ -H_2O)]{\text{Boil HI}} CH_3-CH_2-CH_2-CH_2-CH_3$$
n-pentane

So the compound 'X' is $HC \equiv C - CH_2 - CH_2 - CH_2OH$

9. In the following reactions identify the compounds A, B, C and D?

$PCl_5 + SO_2 \rightarrow A + B$

$A + CH_3COOH \rightarrow C + SO_2 + HCl$

$2C + (CH_3)_2Cd \rightarrow 2D + CdCl_2$

[IIT 1994]

Solution

$$\underset{}{PCl_5} + SO_2 \rightarrow \underset{(A)}{SOCl_2} + \underset{(B)}{POCl_3}$$

$$SOCl_2 + CH_3COOH \rightarrow \underset{(C)}{CH_3COCl} + SO_2 + HCl$$

$$2CH_3COCl + (CH_3)_2Cd \rightarrow \underset{(D)}{2CH_3-CO-CH_3} + CdCl_2$$

10. When t-butanol and n-butanol are separately treated with a few drops of dilute $KMnO_4$, in one case only the purple colour disappears and a brown precipitate is formed. which of the two alcohols gives the above reaction and what is the brown precipitate?

[IIT 1994]

Solution

n-butanol gives the following reaction in which the purple colour of $KMnO_4$ changes to brown tertiary alcohols are not oxidisable easily, thus purple colour of $KMnO_4$ remains same.

$$\underset{\text{n-butanol}}{CH_3CH_2CH_2CH_2OH} + \underset{\text{Purple}}{KMnO_4} \longrightarrow$$

$$\underset{\text{Sol. in } H_2O}{CH_3CH_2CH_2COOK^+} + \underset{\text{Brown}}{MnO_2} + KOH$$

Here the brown coloured precipitate is of MnO_2.

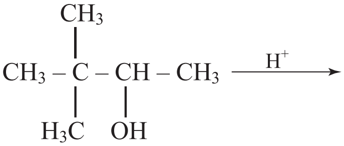
11. 3,3-Dimethylbutan-2-ol loses a molecule of water in the presence of concentrated sulphuric acid to give tetramethylethylene as a major product. Suggest a suitable mechanism.

[IIT 1996]

Solution

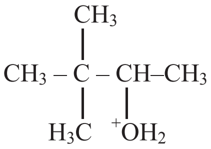
The mechanism is as follows:

(a) The protonation of hydroxyl group.



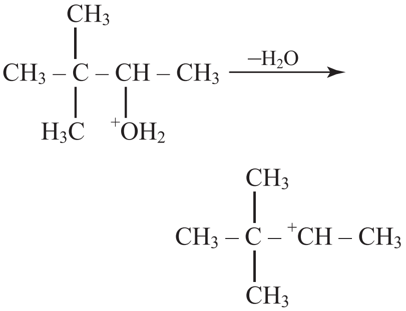
$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{H_3C}{|}}{C}}-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow{H^+}$$

3,3-Dimethylbutan-2-ol



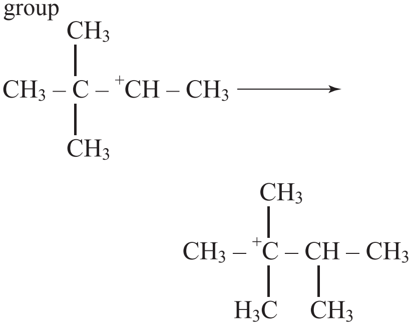
$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{H_3C}{|}}{C}}-\underset{\underset{^+OH_2}{|}}{CH}-CH_3$$

(b) The removal of H_2O to form a secondary (2°) carbonium ion



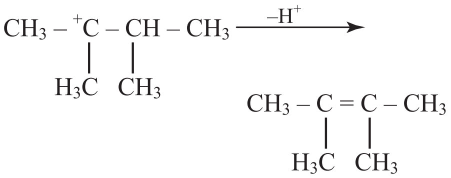
$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{H_3C}{|}}{C}}-\underset{\underset{^+OH_2}{|}}{CH}-CH_3 \xrightarrow{-H_2O} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-\overset{+}{C}H-CH_3$$

(c) The conversion of 2° carbonium to the more stable 3° carbonium ion by the shift of CH_3 group



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-\overset{+}{C}H-CH_3 \longrightarrow CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{H_3C}{|}}{\overset{+}{C}}}-\underset{\underset{CH_3}{|}}{CH}-CH_3$$

(d) The removal of H^+ to form a double bond



$$CH_3-\underset{\underset{H_3C}{|}}{\overset{+}{C}}-\underset{\underset{CH_3}{|}}{CH}-CH_3 \xrightarrow{-H^+} CH_3-\underset{\underset{H_3C}{|}}{C}=\underset{\underset{CH_3}{|}}{C}-CH_3$$

Tetramethyl ethylene

12. A compound D ($C_8H_{10}O$) upon treatment with alkaline solution of iodine gives a yellow precipitate. The filtrate on acidification gives a white solid E ($C_7H_6O_2$). Write the structures of D, E and explain the formation of E.

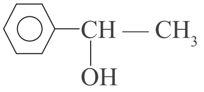
[IIT 1996]

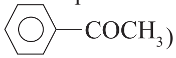
Solution:

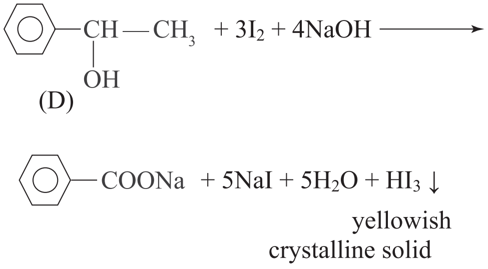
$$\text{Compound (D) } (C_8H_{10}O) \xrightarrow{I_2 + NaOH}$$

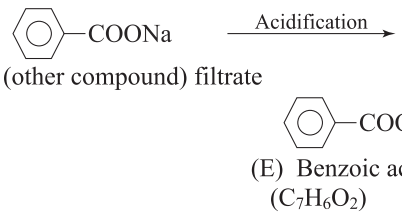
$$\underset{\text{Yellow ppt.}}{CHI_3\downarrow} + \underset{\text{(filterate)}}{\text{Compound}} \xrightarrow[(C_7H_6O_2)]{\text{Acid}} \text{Compound E}$$

This reaction indicates the presence of $-COCH_3$ group in given compound D or presence of $-CHOH-CH_3$ group in given compound D. On the basis molecular formula of compound D and above reaction, the possible structure is given below:



This compound gives iodoform test as in following reaction. (In it in first step this compound on oxidation with I_2 gives )





13. An optically active alcohol ($C_6H_{10}O$) absorbs two moles of hydrogen per mole of A upon catalytic hydrogenation and gives a product B. The compound B is resistant to oxidation by CrO_3 and does not show any optical activity. Deduce the structures of A and B.

[IIT 1996]

Solution:

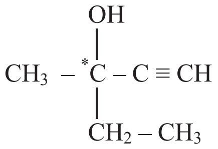
$$\underset{\substack{\text{Compound A}\\ \text{Optically active}}}{C_6H_{10}O} + 2H_2 \xrightarrow{\text{Catalyst}} \underset{\substack{\text{Compound B}\\ \text{optically inactive}}}{C_6H_{14}O}$$

$$\xrightarrow{CrO_3} \text{No reaction}$$

Compound A is unsaturated monohydric alcohol and it has either two C = C bonds or one triple bond.

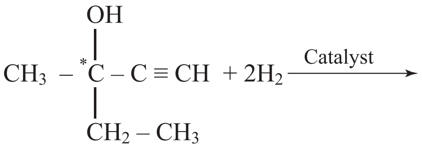
Compound A is optically active and after hydrogenation optically inactive compound 'B' is obtained which is not oxidized with CrO_3. So in it –OH group is attached with tertiary C-atom i.e., it is tertiary alcohol.

Thus, the possible structure of A is as follows:



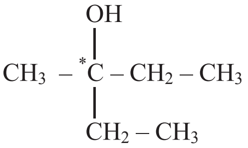
$$CH_3-{}^{*}\underset{\underset{CH_2-CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-C\equiv CH$$

${}^{*}C$ → Asymmetric C-atom and due to presence of it, it shows optically activity.



$$CH_3-{}^{*}\underset{\underset{CH_2-CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-C\equiv CH + 2H_2 \xrightarrow{\text{Catalyst}}$$

Compound A (optically active)



$$CH_3-{}^{*}\underset{\underset{CH_2-CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-CH_2-CH_3$$

Compound B
(Optically inactive)

14. Which of the following is the correct method for synthesizing methyl-t-butyl ether and why?

(i) $(CH_3)_3CBr + NaOMe \rightarrow$

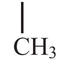
(ii) $CH_3Br + NaO\text{-}t\text{-}Bu \rightarrow$

[IIT 1997]

Solution

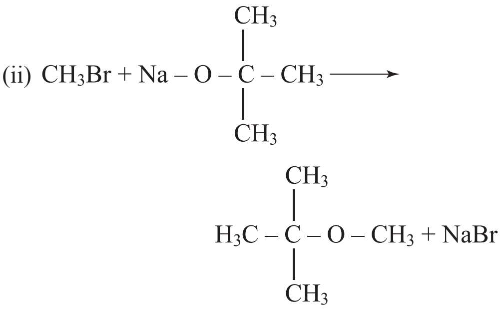
In these two methods, method (ii) is the correct method for the formation of ether because in method (i) alkene is formed in place of ether.

(i) $(CH_3)_3C-Br + Na-O-Me \rightarrow$



$$CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2 + NaBr + CH_3OH$$

Isobutene

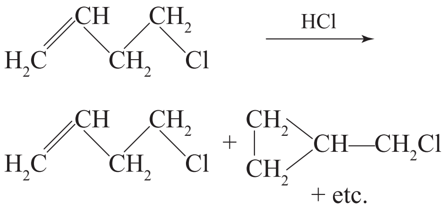


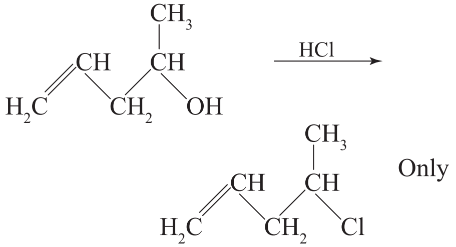
$$\text{(ii) } CH_3Br + Na-O-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 \longrightarrow$$

$$H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-O-CH_3 + NaBr$$

This reaction is known as Williamson's synthesis and it is based upon SN^2 reaction mechanism.

15. Explain briefly the formation of the products giving the structures of the intermediates.





[IIT 1999]

16. A biologically active compound, Bombykol ($C_{16}H_{30}O$) is obtained from a natural source. The structure of the compound is determined by the following reactions.

(i) On hydrogenation, Bombykol gives a compound A, $C_{16}H_{34}O$, which reacts with acetic anhydride to give an ester;

(ii) Bombykol also reacts with acetic anhydride to give another ester, which on oxidation ozonolysis (O_3 / H_2O_2) gives a mixture of butanoic acid, oxalic acid and 10-acetoxydecanoic acid.

Determine the number of double bonds in Bombykol. Write the structures of compound A and Bombykol. How many geometrical isomers are possible for Bombykol?

[IIT 2002]

Solution

$$\underset{\text{Bombykol}}{C_{16}H_{30}O} \xrightarrow{\text{Hydrogenation}} C_{16}H_{34}O$$

$$\xrightarrow{(CH_3CO)_2O} \text{Ester}$$

$$C_{16}H_{30}O \xrightarrow{(CH_3CO)_2O} \text{Ester} \xrightarrow[\text{ozonolysis}]{\text{Oxidative}}$$

$$\underset{\text{Butanoic acid}}{CH_3CH_2CH_2COOH} + \underset{\text{Oxalic acid}}{(COOH)_2}$$

$$+ \underset{\text{10-Acetoxydecanoic acid}}{AcOCH_2(CH_2)_8CH_2COOH}$$

(i) Hydrogenation of bombykol ($C_{16}H_{30}O$) to $C_{16}H_{34}O$ (A) shows the presence of two double bonds in bombykol.

(ii) Reaction of (A) with acetic anhydride to form ester shows the presence of an alcoholic group in (A) and also in bombykol.

(iii) Products of oxidative ozonolysis of bombykol ester suggests the structure of bombykol.

$$\underset{\text{Bombykol ester}}{CH_3CH_2CH_2CH{=}CH{-}CH{=}CH.(CH_2)_8CH_2OAc}$$

$$\Big\downarrow \text{Oxidative ozonolysis}$$

$$\underset{\text{Butanoic acid}}{CH_3CH_2CH_2COOH} + \underset{\text{Oxalic acid}}{HOOC.COOH}$$

$$+ \underset{\text{10-Acetoxydecanoic acid}}{HOOC.(CH_2)_8.CH_2OAc}$$

The structure of Bombykol ester indicates that Bombykol has the following structure:

$$\underset{\text{(Bombykol)}}{CH_3CH_2CH_2CH{=}CH\text{-}CH{=}CH\ (CH_2)_8\ CH_2OH}$$

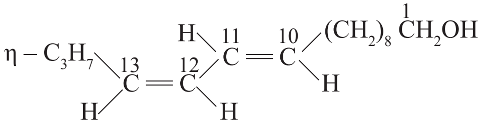
and structure of (A) is

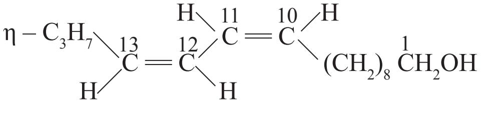
$$CH_3CH_2CH_2CH_2{-}CH_2\text{-}CH_2\text{-}CH_2(CH_2)_8.CH_2OH$$

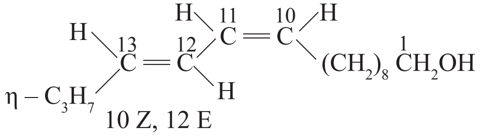
or

$$C_{16}H_{13}OH$$

Following four geometrical isomers are possible for this bombykol structure.


10 E, 12 Z


10 Z, 12 Z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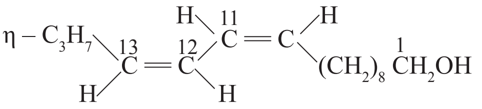
10 E, 12 E

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ORGANIC COMPOUNDS CONTAINING OXYGEN-2

(ALDEHYDE, KETONES)

CHAPTER 6

CHAPTER CONTENTS

Preparation, Properties of Carbonyl Compounds; Oxidation, Reduction, Oxime and Hydrazone Formation, Aldol condensation, Perkin Reaction, Cannizaro Reaction, Haloform Reaction and Nucleophilic Addition Reactions. Grignard Reagent and various levels of multiple-choice questions.

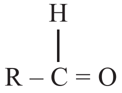
CARBONYL COMPOUNDS

(ALDEHYDE AND KETONE)

- These have >C = O group (Carbonyl group) with a general formula $C_n H_{2n} O$ so these are called carbonyl compounds.

  For example,

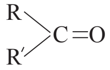
  Aldehyde

  $\overset{\displaystyle H}{\overset{|}{R - C = O}}$

  (where R = H or any alkyl or aryl group)

  Ketone

  $\begin{matrix} R \\ R' \end{matrix}\!\!>\!C = O$

  (where R and R' may be same or different alkyl or aryl groups).

- If R and R' represent the same alkyl or aryl groups, the ketone is a simple ketone.

  For example, Acetone (CH_3COCH_3), $C_6H_5 COC_6H_5$ (Benzophenone)

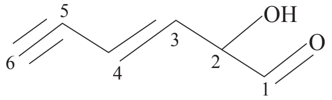
- If R and R' are different alkyl or aryl groups, the ketone is said to be a mixed ketone.

  For example, Acetophenone $CH_3COC_6H_5$

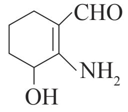
- **Nomenclature** Aldehydes are named as alkanal

For example, CH_3CHO Ethanal

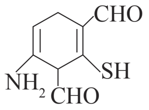
$CH_3CHClCH_2CHO$ 3-Chloro-butanal
$CHO – CH_2 – CH_2 – CHO$ Butan-1,4-dial



2- Hydroxy hex 3-en 5- yn 1 -al



2- Amino 3- hydroxy cylcohexene 1- carboxaldehyde

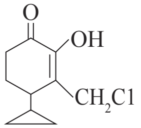


4- Amino 2- mercapto cyclohex 1,4 di -ene 1,4 di carboxaldehyde

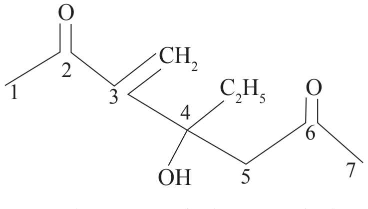
Ketones are named as alkanones.

For example, CH_3COCH_3 Propanone-2

$CH_3COCH_2COCH_3$ Penta-2,4-dione
$CH_2COCHBrCH_3$ 3-Bromo-butan-2-one



2- Hydroxy 2- chloromethyl 3- cyclo propyl cyclohex 2- en 1- one



4- Hydroxy 4- ethyl 3 - methylene hept 2,6 di- one

Isomerism Shown by Aldehydes and Ketones

- R – CHO can show functional isomerism and chain isomerism.
- R – CO – R can show functional isomerism and metamerism.

For example, C_4H_8O.

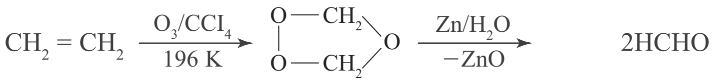
$CH_3CH_2CH_2CHO$ and $(CH_3)_2CHCHO$ are chain isomers.
$CH_3COCH_2CH_3$ is the functional isomer to both of these.

GENERAL METHODS OF PREPARATION FOR BOTH R – CHO AND R – CO – R

(1) From Alkenes

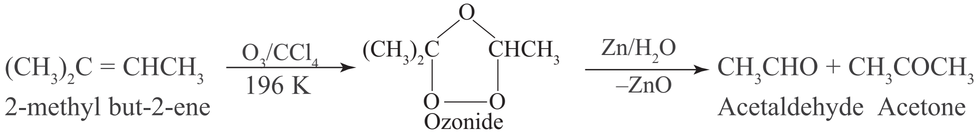
(i) By Ozonolysis of Alkenes Alkenes on ozonolysis followed by hydrolysis give aldehydes and ketones.

For example,



Formaldehyde

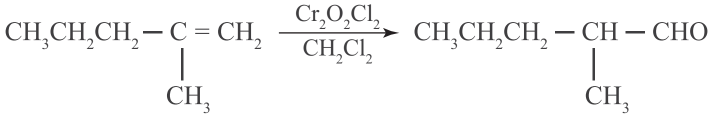
Ethylene ozonide



2-methyl but-2-ene Ozonide Acetaldehyde Acetone

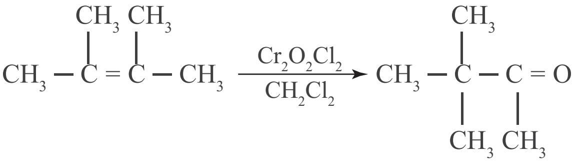
(ii) By Oxidation of Alkenes Alkenes can be oxidized to aldehydes and ketones by an oxidizing agent like CrO_2Cl_2 in CH_2Cl_2.

For example,



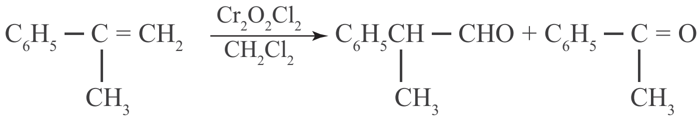
$$CH_3CH_2CH_2-\underset{\substack{|\\CH_3}}{C}=CH_2 \xrightarrow[CH_2Cl_2]{Cr_2O_2Cl_2} CH_3CH_2CH_2-\underset{\substack{|\\CH_3}}{CH}-CHO$$

2- Methyl pent -1- ene 2- Methyl pentanal



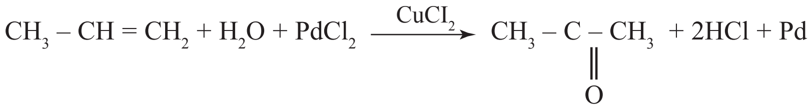
$$CH_3-\overset{\substack{CH_3\\|}}{C}=\overset{\substack{CH_3\\|}}{C}-CH_3 \xrightarrow[CH_2Cl_2]{Cr_2O_2Cl_2} CH_3-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_3}}{C}}-\underset{\substack{|\\CH_3}}{C}=O$$

2,3- Dimethyl but -2- ene 3,3- Dimethyl butan -2- one



$$C_6H_5-\underset{\substack{|\\CH_3}}{C}=CH_2 \xrightarrow[CH_2Cl_2]{Cr_2O_2Cl_2} C_6H_5\underset{\substack{|\\CH_3}}{CH}-CHO + C_6H_5-\underset{\substack{|\\CH_3}}{C}=O$$

(2) By Wacker Method



$$CH_3-CH=CH_2+H_2O+PdCl_2 \xrightarrow{CuCl_2} CH_3-\underset{\substack{\|\\O}}{C}-CH_3 + 2HCl + Pd$$

Acetone

(3) By the Hydration of Alkynes

$$RC \equiv CH + H_2O \xrightarrow[333\ K]{Hg^{2+},\ dil.\ H_2SO_4} RH = CHOH \xrightarrow{\text{Tautomerisation}} RCH_2CHO$$

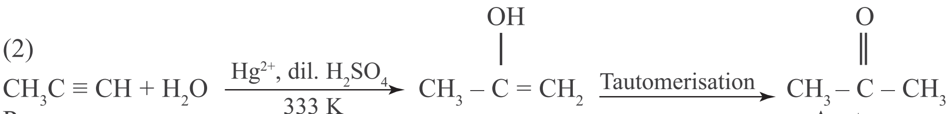
For example,

(1)

$$\underset{\text{Ethyne}}{HC \equiv CH + H_2O} \xrightarrow[333\ K]{Hg^{2+},\ dil.\ H_2SO_4} CH_2 = CHOH \xrightarrow{\text{Tautomerisation}} \underset{\text{Acetaldehyde}}{CH_3CHO}$$

For example,

(2)



$$\underset{\text{Propyne}}{CH_3C \equiv CH + H_2O} \xrightarrow[333\ K]{Hg^{2+},\ dil.\ H_2SO_4} CH_3 - \overset{\overset{OH}{|}}{C} = CH_2 \xrightarrow{\text{Tautomerisation}} \underset{\text{Acetone}}{CH_3 - \overset{\overset{O}{\|}}{C} - CH_3}$$

Propyne

Acetone

(4) By Hydrolysis of Gem Dihalides

$$RCHX_2 + 2KOH\ (aq) \xrightarrow[-2KX]{} RCH(OH)_2 \xrightarrow[-H_2O]{} RCHO$$

1,1-Dichloroalkane

For example, (1)

$$CH_3CHCl_2 + 2KOH\ (aq) \xrightarrow[-2KCI]{} CH_3CH(OH)_2 \xrightarrow[-H_2O]{} CH_3CHO$$

1,1-Dichloroethenae Acetaldehyde

For example,

(2)

$$(CH_3)_2C.Cl_2 + 2KOH\ (aq) \xrightarrow[-2KCI]{} (CH_3)_2C(OH)_2 \xrightarrow[-H_2O]{} CH_3 - CO - CH_3$$

2,2-Dichloroethenae Acetone

(5) By Dehydrogenation of Alcohols

Here the vapours of alcohols are passed over copper at 300°C as follows.

$$R - CH_2OH \xrightarrow{Cu/300^oC} R - CHO + H_2$$

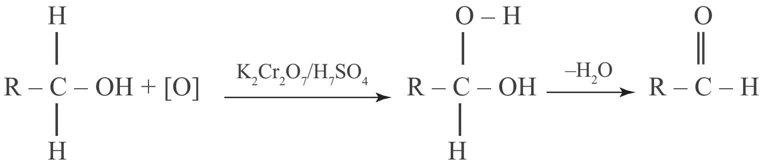
p°

$$(R)_2\ CHOH \xrightarrow{Cu/300^oC} R - CO - R + H_2$$

s°

(6) By the Oxidation of Alcohols

(a) Primary Alcohol A Primary alcohol gives aldehyde on oxidation by using acidic $K_2Cr_2O_7$ (Jones reagent), Pyridinium chlorochromate etc. This reaction can also be carried out by using CrO_3 – pyridine/ CH_2Cl_2. CrO_3 –Pyridine is called as Sarett's Reagent or Sarett-Collin's Reagent.

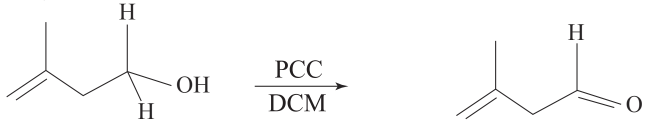


$$R - \underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}} - OH + [O] \xrightarrow{K_2Cr_2O_7/H_7SO_4} R - \underset{\underset{H}{|}}{\overset{\overset{O-H}{|}}{C}} - OH \xrightarrow{-H_2O} R - \overset{\overset{O}{\|}}{C} - H$$

1° alcohol Aldehyde

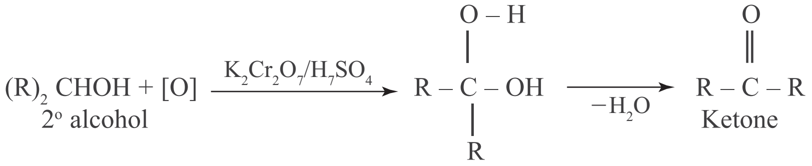
$$\underset{\text{Ethyl alcohol}}{H_3C - CH_2 - OH + [O]} \xrightarrow[CH_2Cl_2,\ -H_2O]{CrO_3-pyridine} \underset{\text{(Ethanal)}}{H_3C - CHO}$$

Ethyl alcohol (Ethanal)



Alcohol Aldehyde

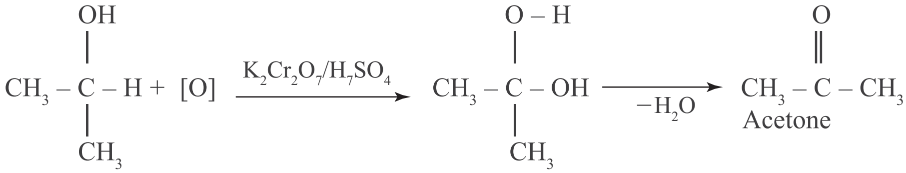
(b) Secondary Alcohol A secondary alcohol gives ketone on oxidation by using acidic $K_2Cr_2O_7$ under drastic conditions.



$$(R)_2\,CHOH + [O] \xrightarrow{K_2Cr_2O_7/H_7SO_4} R-\overset{O-H}{\underset{R}{C}}-OH \xrightarrow[-H_2O]{} R-\overset{O}{\overset{\|}{C}}-R$$

2° alcohol Ketone

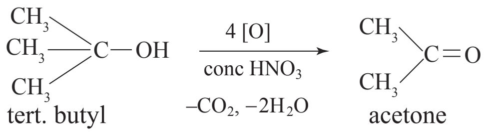
For example,



$$CH_3-\overset{OH}{\underset{CH_3}{C}}-H + [O] \xrightarrow{K_2Cr_2O_7/H_2SO_4} CH_3-\overset{O-H}{\underset{CH_3}{C}}-OH \xrightarrow[-H_2O]{} CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$

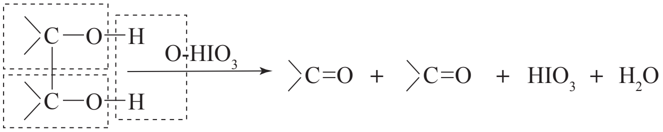
Isopropyl alcohol Acetone

(c) Tertiary Alcohol: A tertiary alcohol gives ketone on oxidation under drastic conditions only.

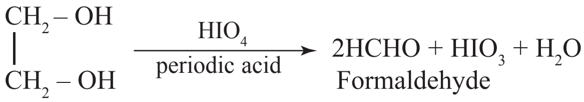


tert. butyl alcohol acetone

(7) From Diols Diols on reaction with periodic acid give carbonyl compound as follows:

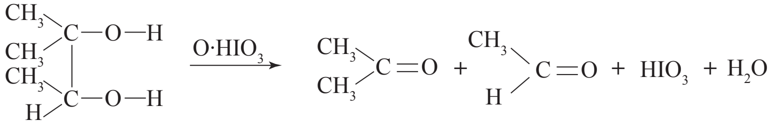


For example,



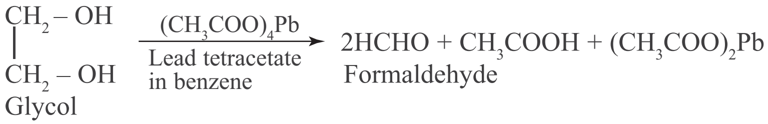
$$\begin{matrix}CH_2-OH\\ |\\ CH_2-OH\end{matrix} \xrightarrow[\text{periodic acid}]{HIO_4} 2HCHO + HIO_3 + H_2O$$

Glycol Formaldehyde



This reaction is called **Criegee's Reaction**.

Glycol on reaction with lead tetracetate also gives formaldehyde as follows



$$\underset{\text{Glycol}}{\begin{array}{l}CH_2-OH\\ |\\ CH_2-OH\end{array}} \xrightarrow[\text{Lead tetracetate in benzene}]{(CH_3COO)_4Pb} \underset{\text{Formaldehyde}}{2HCHO} + CH_3COOH + (CH_3COO)_2Pb$$

(8) From Amines

$$RCH_2NH_2 \xrightarrow[\text{Alk. } KMnO_4]{[O]} \underset{\text{Aldemine}}{R-CH=NH} \xrightarrow[H_2O]{} R-CHO + NH_3 + H_2O$$

$$(R)_2CHNH_2 \xrightarrow[\text{Alk. } KMnO_4]{[O]} \underset{\text{Ketemine}}{(R)_2\ C=NH} \xrightarrow[H_2O]{} R-CO-R + NH_3 + H_2O$$

(9) By Decarboxylation of Calcium Salts of Carboxylic Acids

$$\underset{\text{Calciucm Formate}}{(HCOO)_2\ Ca} \xrightarrow{\Delta} \underset{\text{Formaldehyde}}{HCHO} + \underset{\text{calcium carbonate}}{CaCO_3}$$

$$\underset{\text{calcium}}{(CH_3COO)_2\ Ca} \xrightarrow{\Delta} \underset{\text{acetone}}{CH_3-CO-CH_3} + \underset{\text{acetate}}{CaCO_3}$$

$$\underset{\text{calcium acetate}}{(CH_3COO)_2\ Ca} + \underset{\text{calcium formate}}{Ca(OOCH)_2} \xrightarrow{\Delta} 2CH_3CHO + 2CaCO_3$$

$$\begin{array}{c}(R-CO)_2\ Ca\\ +\\ (R^1-CO_2)_2\ Ca\end{array} \xrightarrow{\Delta} \begin{array}{c}R-COR'\\ +\\ R_2\ CO + R_2^1\ CO\end{array}$$

(10) By Catalytic Decomposition of Fatty Acids When vapours of fatty acids are passed over heated alumina or thoria or magnous oxide carbonyl compounds are formed.

$$RCOOH + HCOOH \xrightarrow[400^oC]{Al_2O_3} RCHO + H_2O + CO_2$$

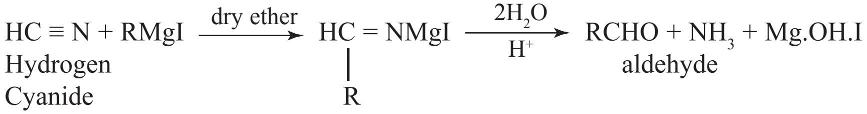
$$CH_3COOH + HCOOH \xrightarrow[400^oC]{Al_2O_3} CH_3CHO + CO_2 + H_2O$$

$$\underset{\text{acetic acid}}{2CH_3COOH} \xrightarrow[500^oC]{MnO} \underset{\text{Acetone}}{CH_3COCH_3} + H_2O + CO_2$$

Preparations for Aldehydes only

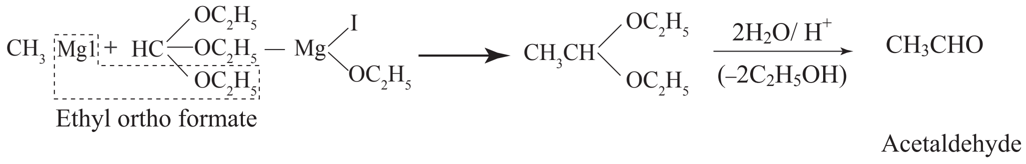
(11) From Grignard Reagent

(a) Grignard reagent gives aldehyde with HCN only as follows:



$$\underset{\text{Hydrogen Cyanide}}{HC\equiv N} + RMgI \xrightarrow{\text{dry ether}} \underset{\begin{array}{c}|\\ R\end{array}}{HC=NMgI} \xrightarrow[H^+]{2H_2O} \underset{\text{aldehyde}}{RCHO} + NH_3 + Mg.OH.I$$

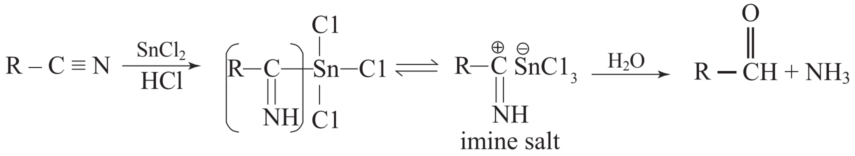
(b) On reaction with ortho ester (Ethyl orhto formate) Grignard reagent gives aldehyde.

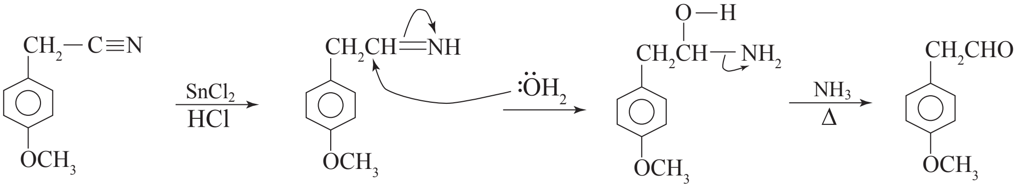


$$CH_3\,MgI + \underset{\text{Ethyl ortho formate}}{HC(OC_2H_5)_3} \longrightarrow CH_3CH(OC_2H_5)_2 + Mg\begin{array}{l}I\\ OC_2H_5\end{array} \xrightarrow[(-2C_2H_5OH)]{2H_2O/\ H^+} \underset{\text{Acetaldehyde}}{CH_3CHO}$$

(12) From Stephen's Reduction

$$\underset{\text{Alkane nitrile}}{R - C \equiv N + 2[H]} \xrightarrow{\text{Sn/HCl}} R - CH = NH \xrightarrow{H_2O/H^+} \underset{\text{Aldehyde}}{RCHO + NH_3}$$

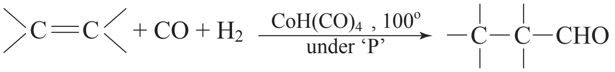




For example,

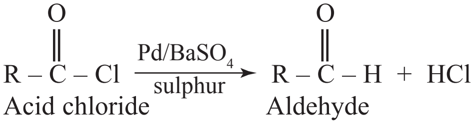
$$\underset{\text{Ethane nitrile}}{H_3C - C \equiv N + 2[H]} \xrightarrow{\text{Sn/HCl}} \underset{\text{Imine}}{H_3C - CH = NH} \xrightarrow{H_2O/H^+} \underset{\text{Acetaldehyde}}{CH_3CHO + NH_3}$$

(13) From Alkenes by Oxo Method



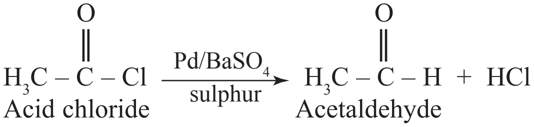
(14) Rosenmund's Reaction Aldehydes can be prepared by passing H_2 gas through a boiling solution of acid chloride in xylene in the presence of catalyst Pd supported by $BaSO_4$.

- Here the catalyst is poisoned by sulphur or quinoline to avoid further reduction of aldehydes into alcohols.

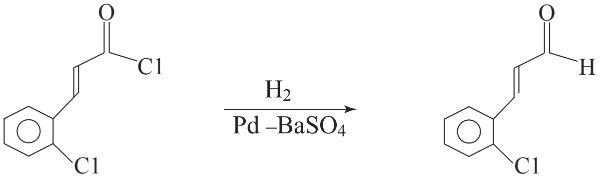


$$\underset{\text{Acid chloride}}{R - \overset{\overset{\displaystyle O}{\|}}{C} - Cl} \xrightarrow[\text{sulphur}]{Pd/BaSO_4} \underset{\text{Aldehyde}}{R - \overset{\overset{\displaystyle O}{\|}}{C} - H} + HCl$$

For example,



$$\underset{\text{Acid chloride}}{H_3C - \overset{\overset{\displaystyle O}{\|}}{C} - Cl} \xrightarrow[\text{sulphur}]{Pd/BaSO_4} \underset{\text{Acetaldehyde}}{H_3C - \overset{\overset{\displaystyle O}{\|}}{C} - H} + HCl$$



By Reduction of Esters and Cynides

Sodium aluminium hydride, $NaAlH_4$ or di-isobutyl aluminium hydrtide **(DIBAL- H)** can also reduces esters into aldehydes.

$$\underset{\text{Ester}}{R-CO-OR'} + H_2 \xrightarrow{NaAlH_4} \underset{\text{Aldehyde}}{R-CO-H} + R'OH$$

DIBAL-H can not reduces ethylenic double bonds and hence unsaturated nitriles can be reduced into the corresponding unsaturated aldehydes by using this reagent.

$$\underset{\text{Hex-4-en -1- nitrile}}{CH_3CH = CHCH_2CH_2CN} \xrightarrow[\text{(ii) } H_2O]{\text{(i) } AlH(i\text{-}Bu)_2} \underset{\text{Hex -4- en-1- al}}{CH_3CH = CHCH_2CH_2CHO}$$

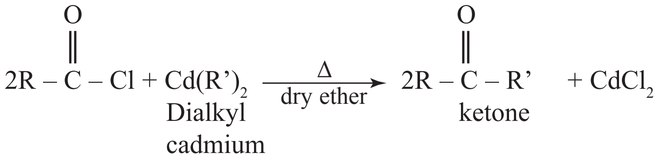
Similarly, esters can be reduced to aldehydes with DIBAL- H.

$$\underset{\text{Ethyl undecanoate}}{CH_3(CH_2)_9 - CO - OC_2H_5} \xrightarrow[\text{(ii) HOH}]{\text{(i) DIBAL–H}} \underset{\text{Undecanal}}{CH_3(CH_2)_9 - CHO}$$

Preparation for ketones only

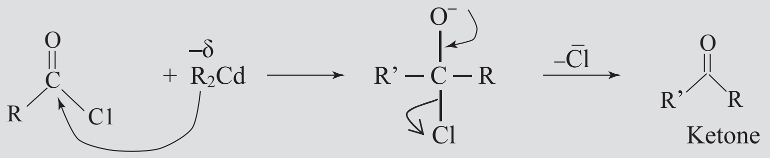
(15) From Organo Metallics Reaction of acid halides with organometallics readily give ketones.

(a) From Dialkyl Cadmium



$$2R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl + \underset{\text{Dialkyl cadmium}}{Cd(R')_2} \xrightarrow[\text{dry ether}]{\Delta} \underset{\text{ketone}}{2R-\overset{\overset{\displaystyle O}{\|}}{C}-R'} + CdCl_2$$

Mechanism



(b) From Grignard Reagent

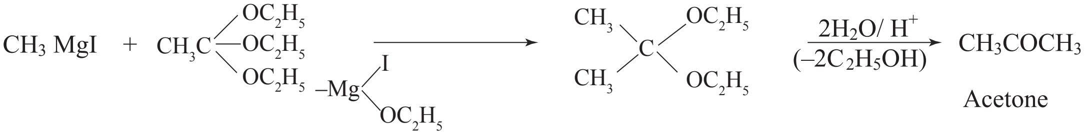
(i) From Grignard Reagent and Acid Chlorides

$R - CO - Cl + R'MgX \rightarrow R - CO - R + XMgCl$

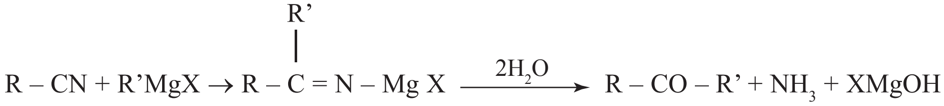
For example,

$CH_3 - CO - Cl + CH_3MgCl \rightarrow CH_3 - CO - CH_3 + MgCl_2$

Except ortho formic ester, all other ortho esters on reaction with Grignard reagent give ketones.

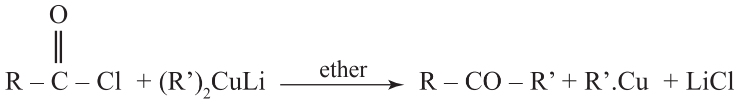


(ii) From Cyanide and Grignard Reagent



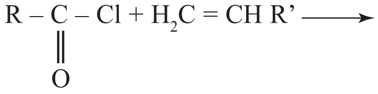
$$R - CN + R'MgX \rightarrow R - \overset{\overset{\displaystyle R'}{|}}{C} = N - Mg\,X \xrightarrow{2H_2O} R - CO - R' + NH_3 + XMgOH$$

(c) From Di alkyl Cuprates

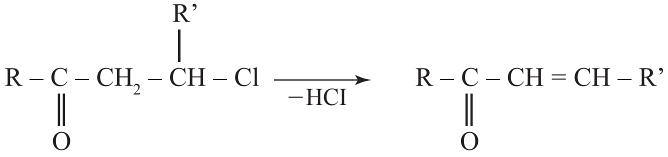


$$R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl + (R')_2CuLi \xrightarrow{\text{ether}} R-CO-R' + R'.Cu + LiCl$$

(16) By Acylation of Alkenes



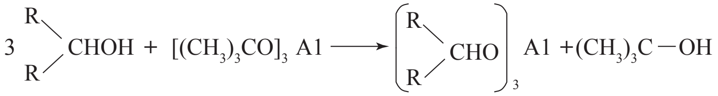
$$R-\underset{\underset{\displaystyle O}{\|}}{C}-Cl + H_2C=CH\,R' \longrightarrow$$

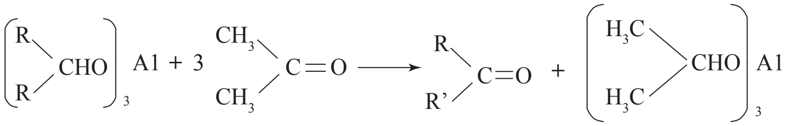


$$R-\underset{\underset{\displaystyle O}{\|}}{C}-CH_2-\overset{\overset{\displaystyle R'}{|}}{CH}-Cl \xrightarrow[-HCl]{} R-\underset{\underset{\displaystyle O}{\|}}{C}-CH=CH-R'$$

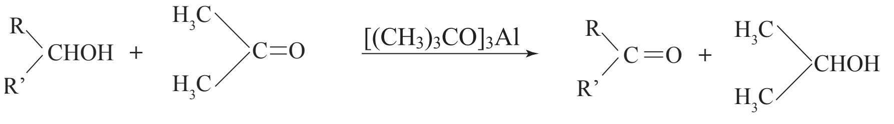
- It is an example of Markownikoff's addition initiated by $R-C^+=O$ [acylium cation].

(17) Oppenauer Oxidation Seconadry alcohols can be oxidised into ketones by using aluminium tert. butoxide, $[(CH_3)_3CO]_3$ Al. Here a secondary alcohol is refluxed with the reagent and then acetone (or cyclo hexanone, etc.) is added as follows





A Secondary alcohol oxidises to keotne while acetone reduces to isopropyl alcohol.



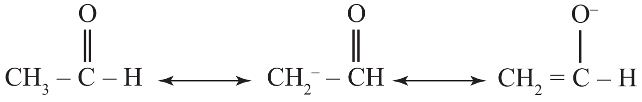
Sec.alcohol Acetone Ketone Isoprpyl alcohol

Cyclohex -2- en -1-ol Cyclohex -2- en -1- one

PHYSICAL PROPERTIES

- Formaldehyde is a gas while rest are colourless volatile liquids upto carbon number 10. Higher members are solids.
- Lower aldehydes have unpleasant smell while higher aldehydes and ketones have pleasant smell.
- The lower >C = O are soluble in water due to H-bonding but solubility decreases after 5 C-atom members.

- Ketones and aldehydes are polar compounds so they have more boiling points than non polar compounds with same molecular weight like alkanes, alkenes etc.
- These have lower boiling points than alcohols and acids due to lack of intermolecular Hydrogen bonding.
- **Acidic Nature** These are slightly acidic (as alcohols) due to the resonance of enolate ion.
  For example,

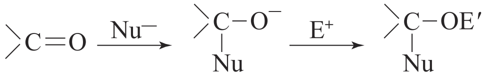


$$CH_3-\overset{\overset{O}{\|}}{C}-H \longleftrightarrow CH_2^{-}-\overset{\overset{O}{\|}}{C}H \longleftrightarrow CH_2=\overset{\overset{O^-}{|}}{C}-H$$

CHEMICAL PROPERTIES

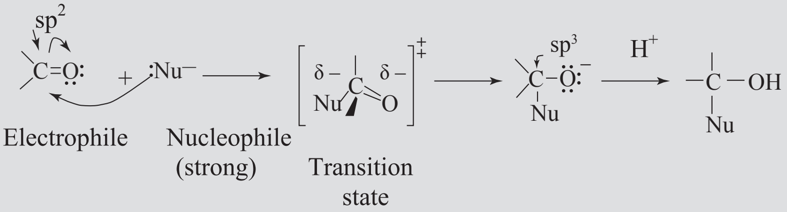
Reactions Due to Carbonyl Group

(1) Nucleophillic Addition Reaction Both aldehydes and ketones underogo nucleophilic addition reaction due to the presence of carbonyl group as follows

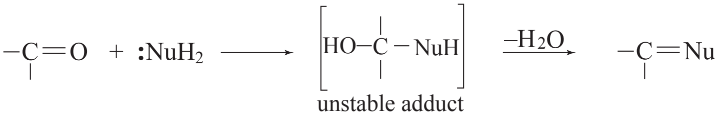


$$\rangle C=O \xrightarrow{Nu^-} \rangle\underset{Nu}{\underset{|}{C}}-O^- \xrightarrow{E^+} \rangle\underset{Nu}{\underset{|}{C}}-OE'$$

Mechanism



Here, $:Nu^-$ can be $:R'^-$ of R'MgX or :H- of $NaBH_4$. With $:NuH_2$, the adduct loses water to give -C= Nu. as follows

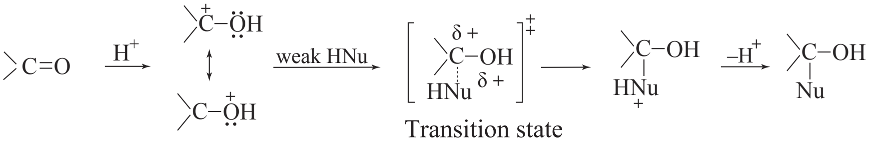


$$-\underset{|}{C}=O + :NuH_2 \longrightarrow \left[HO-\overset{|}{\underset{|}{C}}-NuH\right] \xrightarrow{-H_2O} -\underset{|}{C}=Nu$$

unstable adduct

$:NuH_2$ is most often a 1° amine, RNH_2, or one of its derivatives, such as $HONH_2$ (hydroxylamine).

Acid increases the rate of addition o weak nucleophiles by first protonating the O of $\rangle$C=O, thereby enhancing the electrophilicity of the C of $\rangle$C=O.



The reactivity of the carbonyl group decreases with increasing size of R's and with electron donation by R. Electron A, - attracting R's increase the reactivity of $\rangle$C=O.

- The reactivity for nucleophillic addition reaction of a carbonyl compound depends upon the magnitude of positive charge present on the carbon atom of carbonyl group that is, the reactivity is increased by electron attracting groups like $-NO_2$, $-CX_3$ etc. and decreased by electron releasing groups like methyl, alkoxy groups etc.

- Reactivity in decreasing order for nucleophillic addition reaction for carbonyl compounds decreases as follows:

  $HCHO > CH_3CHO > CH_3CH_2CHO > CH_3COCH_3 > CH_3COC_2H_5 > C_2H_5COC_2H_5 > \ldots$

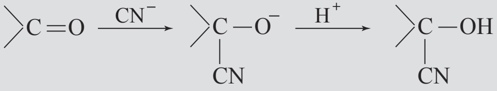
(i) With HCN

- Carbonyl compounds react with HCN or NaCN and dil. H_2SO_4 to give cyanohydrins which on hydrolysis give hydroxy acids.

Mechanism

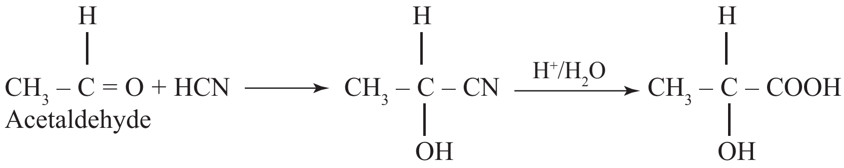
$NaCN + H_2SO_4 \rightarrow HCN + NaHSO_4$

$HCN + H_2O \leftrightarrow CN^- + H_3O^+$



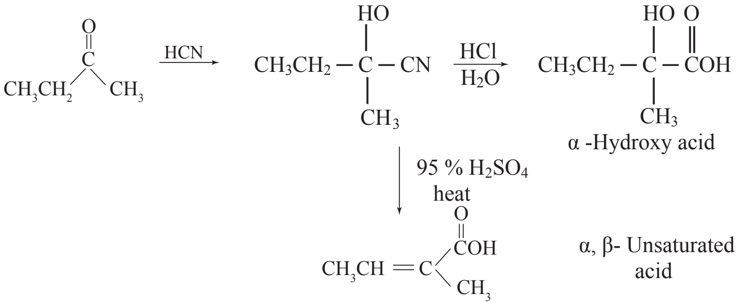
$$>C=O \xrightarrow{CN^-} >\underset{\displaystyle CN}{\underset{|}{C}}-O^- \xrightarrow{H^+} >\underset{\displaystyle CN}{\underset{|}{C}}-OH$$

For example,



$$\underset{\text{Acetaldehyde}}{CH_3-\overset{\displaystyle H}{\overset{|}{C}}=O} + HCN \longrightarrow CH_3-\overset{\displaystyle H}{\overset{|}{\underset{\displaystyle OH}{\underset{|}{C}}}}-CN \xrightarrow{H^+/H_2O} CH_3-\overset{\displaystyle H}{\overset{|}{\underset{\displaystyle OH}{\underset{|}{C}}}}-COOH$$

Acetaldehyde cyanohydrin Lactic acid



$$CH_3CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3 \xrightarrow{HCN} CH_3CH_2-\overset{\displaystyle HO}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CN \xrightarrow[H_2O]{HCl} CH_3CH_2-\overset{\displaystyle HO}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-\overset{\displaystyle O}{\overset{\|}{C}}OH$$

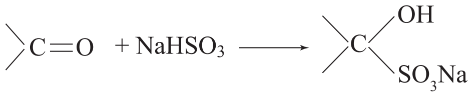
α -Hydroxy acid

$$\xrightarrow[\text{heat}]{95\ \%\ H_2SO_4} CH_3CH=C(CH_3)-\overset{\displaystyle O}{\overset{\|}{C}}OH$$

α, β- Unsaturated acid

(ii) Addition of Sodium Bi-Sulphite

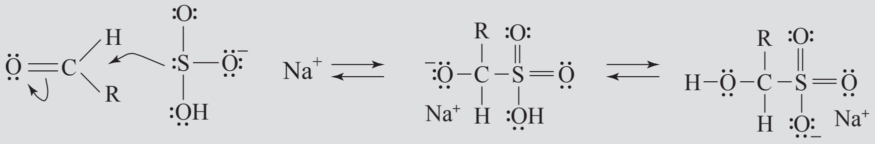
- Carbonyl compounds react with saturated aqueous solution of sodium bisulphite to give their solid crystaline bisulphite derivatives.



$$>C=O + NaHSO_3 \longrightarrow >C(OH)(SO_3Na)$$

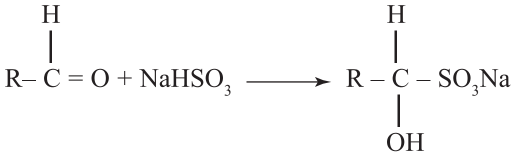
Bisulphite

Mechanism



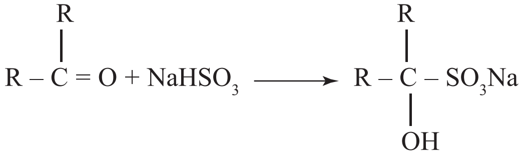
$$\ddot{O}=C(H)(R) + :\ddot{O}-\overset{\displaystyle :O:}{\overset{|}{\underset{\displaystyle :\ddot{O}H}{\underset{|}{S}}}}-\ddot{O}:^- \ Na^+ \rightleftharpoons {}^-:\ddot{O}-\overset{\displaystyle R}{\overset{|}{\underset{\displaystyle H}{\underset{|}{C}}}}-\overset{\displaystyle :O:}{\overset{\|}{\underset{\displaystyle :\ddot{O}H}{\underset{|}{S}}}}=\ddot{O}\ Na^+ \rightleftharpoons H-\ddot{O}-\overset{\displaystyle R}{\overset{|}{\underset{\displaystyle H}{\underset{|}{C}}}}-\overset{\displaystyle :O:}{\overset{\|}{\underset{\displaystyle :\ddot{O}:^-}{\underset{|}{S}}}}=\ddot{O}\ Na^+$$

For example,



$$R-\overset{\overset{H}{|}}{C}=O + NaHSO_3 \longrightarrow R-\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}}-SO_3Na$$

Sodium bisulphite salt

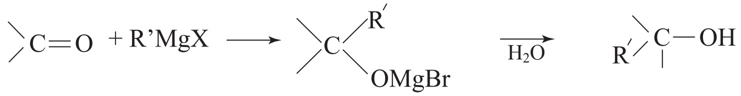


$$R-\overset{\overset{R}{|}}{C}=O + NaHSO_3 \longrightarrow R-\underset{\underset{OH}{|}}{\overset{\overset{R}{|}}{C}}-SO_3Na$$

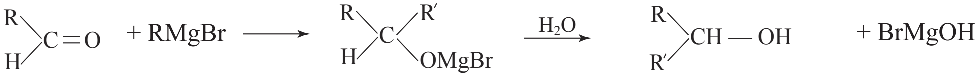
Sodium bisulphite salt

- In case of hindered ketones like $(CH_3)_3C-CO-C(CH_3)_3$ reaction is not possible due to the steric hindrance caused by bulky methyl groups.

(iii) Addition With Grignard Reagent Here alcohols are formed as follows.

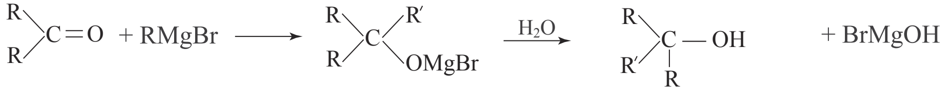


- Here all aldehydes give secondary alcohols except formaldehyde which gives primary alcohol.



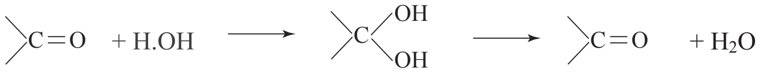
secondary alcohol

- All ketones give tertiary alcohols here.



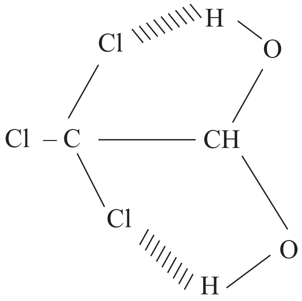
Tertiary alcohol

(iv) With H_2O

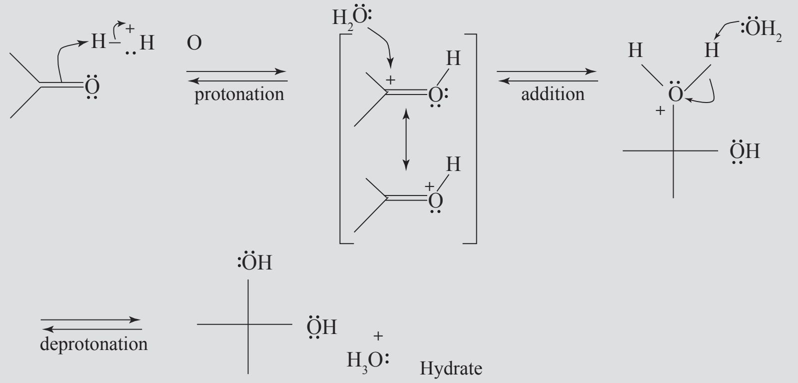


unstable products

- These products are unstable, however, chloral hydrate is stable due to intramolecular H-bonding in its butterfly like structure.

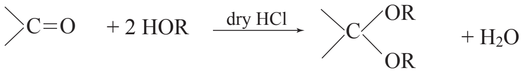


Mechanism



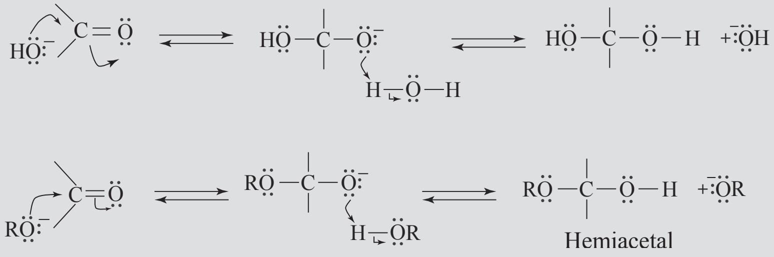
(v) Addition With Alcohols

Here, acetals and ketals are formed. Cyclic hemiacetals are often more stable than their open-chain.

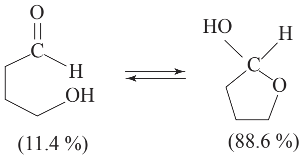


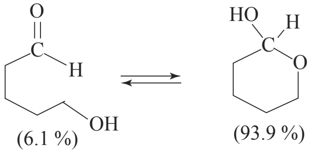
$$>C=O + 2\,HOR \xrightarrow{\text{dry HCl}} >C(OR)_2 + H_2O$$

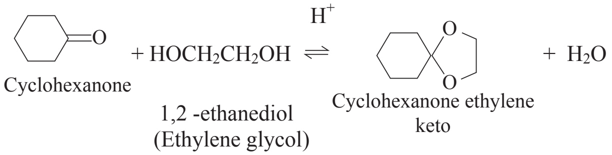
Mechanism



e.g.,





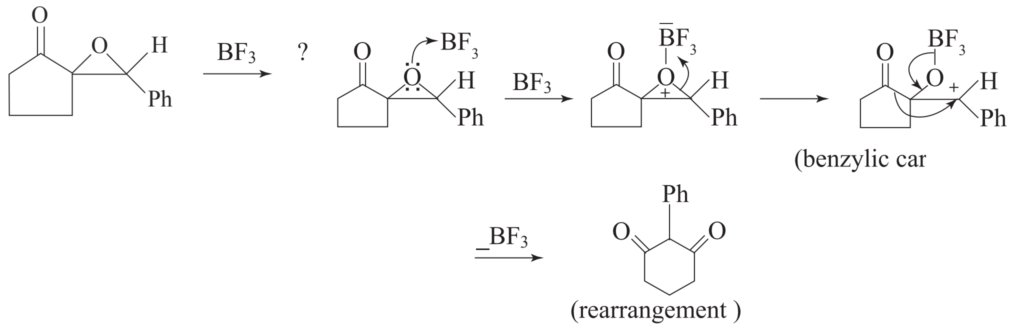


(vi) With Thiols (R –SH)

- Here, Thio acetal and Thio ketals are formed.

$$>C=O + 2H-S-R \longrightarrow >C(SR)_2$$

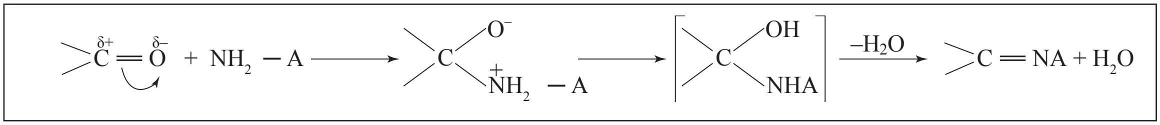
Thio Acetals or Ketals



(2) *Substitution Reactions*

In such reactions, the oxygen atom of carbonyl group is substituted by other groups. For example,

(i) *With NH_3 Derivatives*



- **Hydroxylamine (NH_2OH)** Here oximes are formed.

  $>C = O + H_2N - OH \rightarrow >C = N - OH + H_2O$

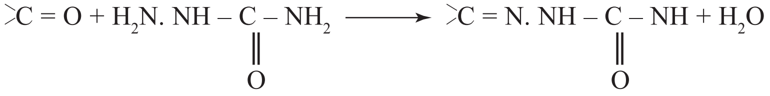
  Oximes

- **Hydrazine (NH_2NH_2)** Here hydrazones are formed.

  $>C = O + H_2N - NH_2 \rightarrow >C = N - NH_2 + H_2O$

  Hydrazone

- **With Semicarbazides ($H_2N.NH.CONH_2$)** Here semi carbazones are formed.



$$>C = O + H_2N.\,NH - \underset{\underset{O}{\|}}{C} - NH_2 \longrightarrow >C = N.\,NH - \underset{\underset{O}{\|}}{C} - NH + H_2O$$

Semicarbazones

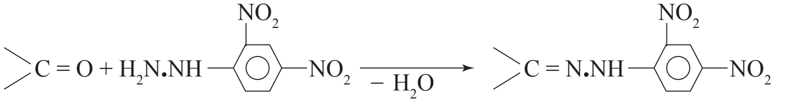
- **Phenyl Hydrazine ($NH_2.NH.C_6H_5$)** Here phenyl hydrazones are formed.

  $>C = O + H_2N.NH.C_6H_5 \rightarrow >C = N.NH.\,C_6H_5 + H_2O$

  Phenyl hydrazones

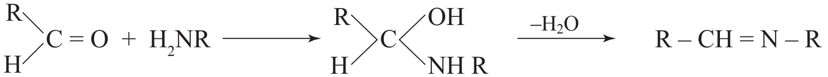
- **With 2, 4 Dinitro Phenyl Hydrazine (Brady's Reagent)**

  It gives bright orange or yellow precipitate so it is used to identify >C = O compounds.

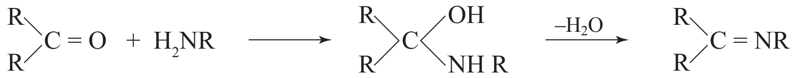


2, 4 Dinitro phenyl hydrazones
(Orange or yellow ppt.)

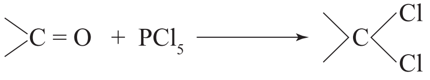
(ii) *With Primary Amines*



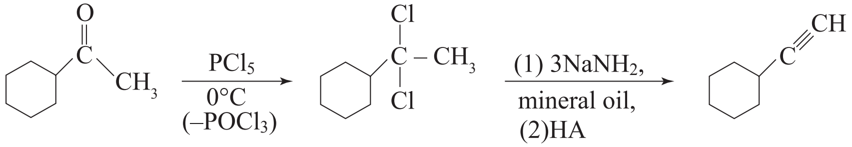
Aldimine (Schiff bases)


$$R_2C=O + H_2NR \longrightarrow R_2C(OH)(NHR) \xrightarrow{-H_2O} R_2C=NR$$

(iii) With PCl_5


$$>C=O + PCl_5 \longrightarrow >CCl_2$$

For example,



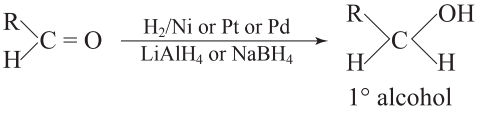
Cyclohexyl methyl ketone

A gem-dichloride (70 - 80%)

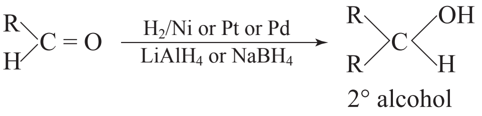
Cyclohexylacetylene (46 %)

(3) Reduction Reactions

- **Reduction into Alcohols**
  Carbonyl compounds on catalytic reduction and reduction with complex metal hydrides give alcohols as follows

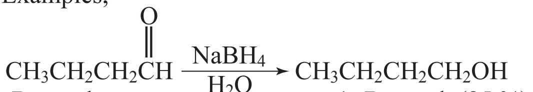

$$RHC=O \xrightarrow[LiAlH_4 \text{ or } NaBH_4]{H_2/Ni \text{ or } Pt \text{ or } Pd} RHC(OH)H$$

1° alcohol

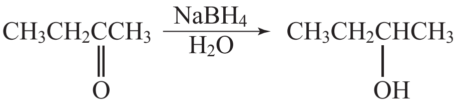

$$RHC=O \xrightarrow[LiAlH_4 \text{ or } NaBH_4]{H_2/Ni \text{ or } Pt \text{ or } Pd} R_2C(OH)H$$

2° alcohol

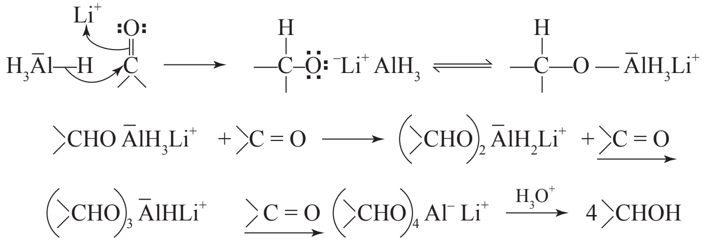
Examples,


$$CH_3CH_2CH_2CH{=}O \xrightarrow[H_2O]{NaBH_4} CH_3CH_2CH_2CH_2OH$$

Butanol 1- Butanol (85 %)


$$CH_3CH_2C(=O)CH_3 \xrightarrow[H_2O]{NaBH_4} CH_3CH_2CH(OH)CH_3$$

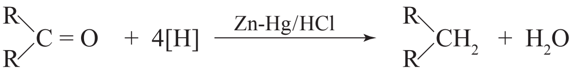
Butanone 2- Butanol (87 %)



- **Reduction into Alkanes** Carbonyl compounds on reduction by HI and red 'P' give alkanes.
  $$>C=O + 4\,HI \xrightarrow{\text{Red 'P'}} >CH_2 + 2I_2 + H_2O$$

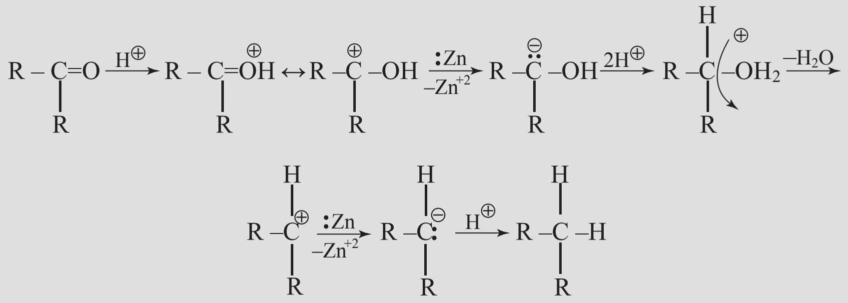
- **Clemmensen Reduction** It involves reduction of carbonyl compounds by zinc amalgam and conc. HCl into alkanes.

$$\mathrm{RCHO} + 4[\mathrm{H}] \xrightarrow{\text{Zn-Hg/HCl}} \underset{\text{Alkane}}{\mathrm{R-CH_3}} + \mathrm{H_2O}$$



$$\mathrm{R_2C=O} + 4[\mathrm{H}] \xrightarrow{\text{Zn-Hg/HCl}} \mathrm{R_2CH_2} + \mathrm{H_2O}$$

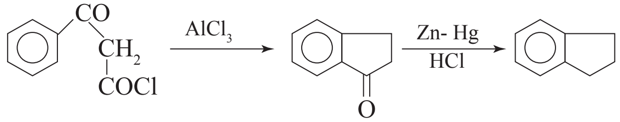
Mechanism



Examples

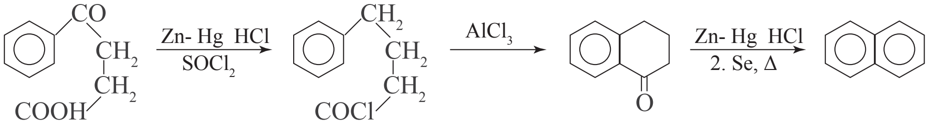
(i) Reduction of cyclic ketones

(a) In the synthesis of indane



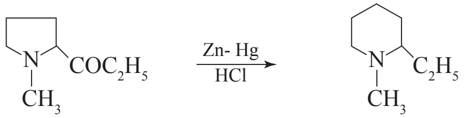
β- Phenyl propionyl chloride α- Hydrindone Indane

(b) In the synthesis of naphthalene



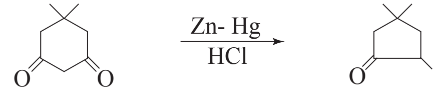
β- Benzoyl propoinic acid γ -Phenyl butanoyl chloride α - Tetralone Naphthalene

(ii) Reduction with ring expansion



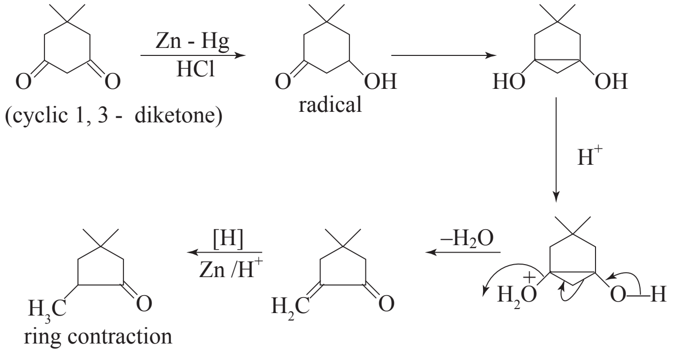
1, Methyl -2- propionyl pyrrolidine 2- Ethyl -1- methypiperidine

(iii) Reduction with ring contraction



5,5- Dimethyl cyclohexane -1,3-dione

2, 4, 4- Trimethyl cyclopentanone



(c) Wolff-Kishner Reduction It involves reduction of carbonyl compounds with hydrazine hydrate and KOH in ethylene glycol at 453 – 473 K or strong bases like $NaNH_2$, KNH_2 etc into alcohols.

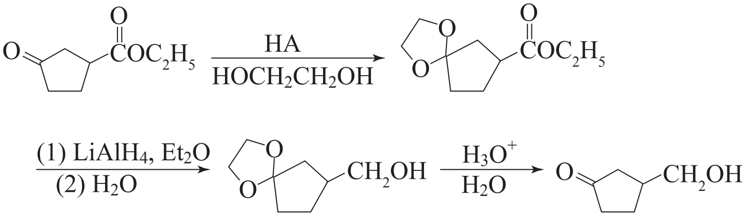
$$R-CH=O \xrightarrow[-H_2O]{NH_2.NH_2} \underset{\text{Hydrazone}}{R-CH=NNH_2} \xrightarrow[453-473\text{ K}]{\text{KOH, glycol}} R-CH_3 + N_2$$

$$R_2C=O \xrightarrow[-H_2O]{NH_2.NH_2} R_2C=NNH_2 \xrightarrow[453-473\text{ K}]{\text{KOH, glycol}} R-CH_2-R + N_2$$

Mechanism

$$R_2C=\ddot{N}-\ddot{N}H_2 \overset{\overset{\ominus}{O}H}{\rightleftharpoons} [\underset{(I)}{R_2C=\ddot{N}-\ddot{N}\overset{\ominus}{H}} \leftrightarrow R_2\overset{\ominus}{C}-\ddot{N}=\ddot{N}H] + H_2O \rightleftharpoons \underset{(II)}{R_2\overset{H}{C}-\ddot{N}=\ddot{N}H} + \overset{\ominus}{O}H$$

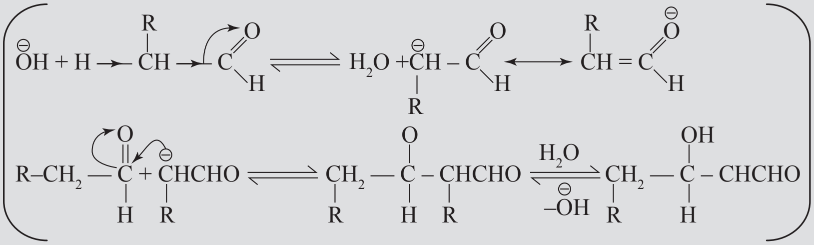
$$\longrightarrow R_2-\overset{H}{C}-\ddot{N}=\ddot{N}\!:\overset{\ominus}{} \rightarrow R_2CH \xrightarrow{-N_2} R_2\overset{\ominus}{C}H_2 \xrightarrow{HOH} R_2CH_2 + \overset{\ominus}{O}H$$



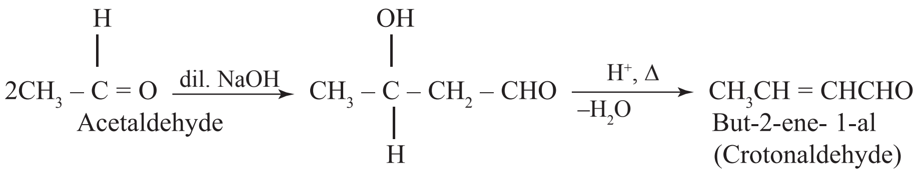
(4) Name Reactions

- **Aldol Condensation** It is given by those aldehydes and ketones which contain α-H-atoms in presence of dilute alkali like NaOH, $Ba(OH)_2$ etc. to give β-hydroxy carbonyl compounds (aldol or ketol) which on further heating give α, β-unsaturated carbonyl compounds.

Mechanism



For example,



$$2CH_3-\overset{\displaystyle H}{\overset{|}{C}}=O \xrightarrow{\text{dil. NaOH}} CH_3-\underset{\displaystyle H}{\underset{|}{\overset{\displaystyle OH}{\overset{|}{C}}}}-CH_2-CHO \xrightarrow[-H_2O]{H^+,\ \Delta} CH_3CH=CHCHO$$

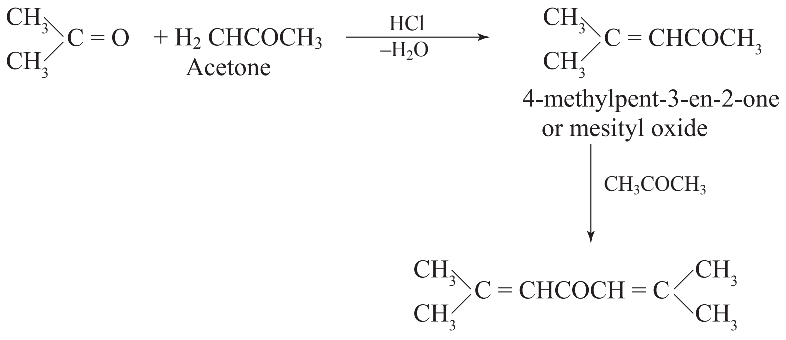
Acetaldehyde

3-hydroxybutanal (Aldol)

But-2-ene- 1-al
(Crotonaldehyde)

- Aldol condensation can also take place in presence of an acid.

For example,



$(CH_3)_2C=O + H_2\,CHCOCH_3 \xrightarrow[-H_2O]{HCl} (CH_3)_2C=CHCOCH_3$

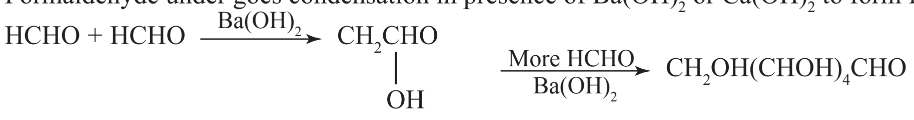
Acetone

4-methylpent-3-en-2-one
or mesityl oxide

$(CH_3)_2C=CHCOCH=C(CH_3)_2$

Phorone

- If the reaction is carried out in presence of $Ba(OH)_2$ the major product is mesityl oxide but with HCl it is phorone.
- Formaldehyde under goes condensation in presence of $Ba(OH)_2$ or $Ca(OH)_2$ to form formose.

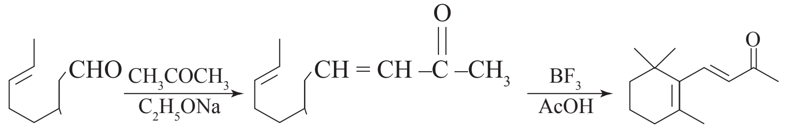


$$HCHO + HCHO \xrightarrow{Ba(OH)_2} \underset{\displaystyle OH}{\underset{|}{CH_2}}CHO \xrightarrow[Ba(OH)_2]{\text{More HCHO}} CH_2OH(CHOH)_4CHO$$

Formose

$3CH_2OHCHO \xrightarrow{NaOH} C_6H_{12}O_6$

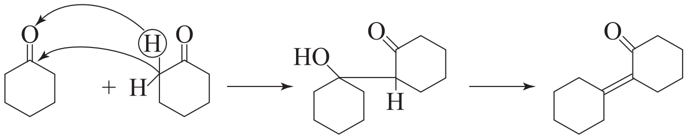
Glycolaldehyde formose



Citral

Ψ - Ionone

β - Ionone



$$2CH_3CH=O \xrightarrow[-H_2O]{OH^-} CH_3CH=CHCH=O \xrightarrow[OH^-]{CH_3CHO} CH_3CH=CHCH=CHCH=O$$

$$\Big\downarrow \text{ mild oxidation}$$

$$CH_3(CH=CH)_2COOH$$

- **Crossed Aldol Condensation** Aldol condensation between two different aldehydes or ketones or between one aldehyde and one ketone is called crossed aldol condensation.

For example, (I)

$$CH_3CHO + HCHO \xrightarrow[\Delta]{\text{dil. NaOH}} HOCH_2-CH_2-CHO \xrightarrow{H^+/H_2O} CH{=}CH_2-CHO$$

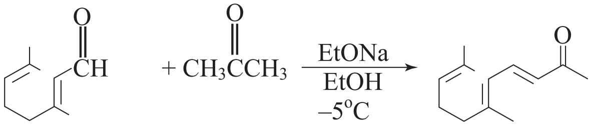
3-Hydroxypropanal Acrolein

(II) $C_6H_5CHO + CH_3COCH_3 \overset{OH^\ominus}{\rightleftharpoons} C_6H_5-CH=CH-CO-CH_3$
Benzyldihydeneactone

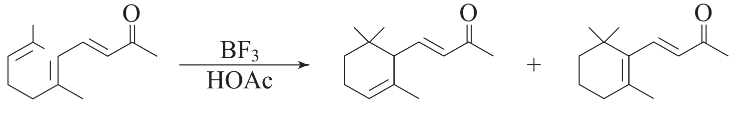
(III) $C_6H_5CHO + CH_3COC_6H_5 \xrightarrow{\overset{\ominus}{O}H} C_6H_5-CH=CH-CO-C_6H_5$
Benzyldihydeneactphenone

(IV) $CH_3COCH_3 + HCHO \xrightarrow{\overset{\ominus}{O}H} CH_3-CO-CH_2-CH_2OH$
4- Hydroxybutanone -2

(V)



Pseudoionone
(49 %)



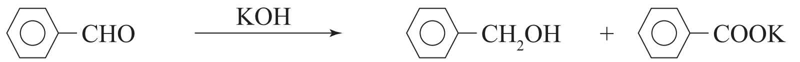
Pseudoionone α -Ionone β- Ionone

- **Cannizzaro Reaction** This reaction is given by only those aldehydes which do not contain α-H-atoms like formaldehyde, benzaldehyde, furfural, glyoxal etc. It is a Disproportionation Reaction in which such a aldehyde on reaction with strong base gives 1 molecule of alcohol and 1 molecule of acid salt. In this reaction, hydride shift is rate determining step.

For example,

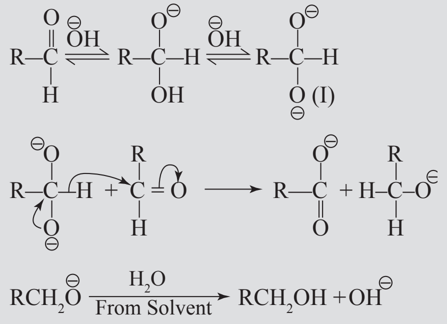
$$2H-\overset{\overset{\displaystyle O}{\|}}{C}-H + NaOH \longrightarrow CH_3OH + HCOONa$$

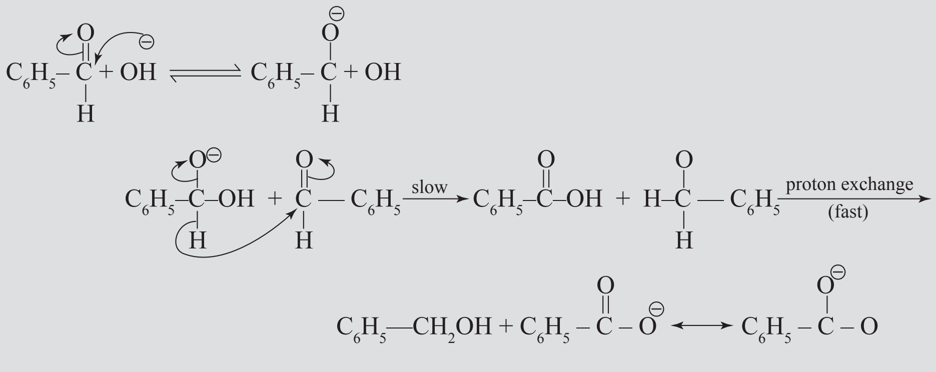
formaldehyde (50%) methyl alcohol sodium formate



Benzyl alcohol potassium benzoate

Mechanism





Crossed Cannizzaro Reaction It occurs between two different aldehydes. Here the smaller aldehyde get oxidized while the larger aldehyde get reduced into an alcohol.

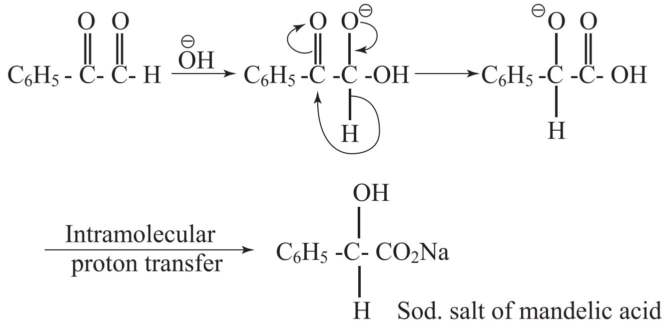
For example,

Benzyl alcohol Potassium formate

Intramolecular Cannizzaro Reaction Here disproportionation reaction occurs within the same molecule.

For example,

$$\underset{\text{Glyoxal}}{CHO - CHO} + NaOH \longrightarrow \begin{array}{c} CH_2OH \\ | \\ COONa \end{array}$$

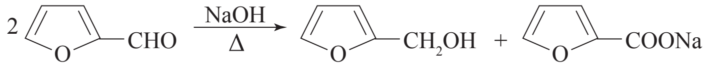


Synthesis of various types of alcohols and acids From Cannizaro Reaction

(i)

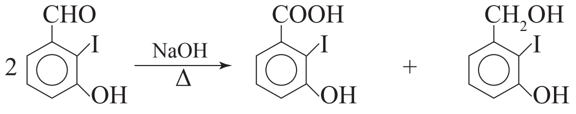
$$\underset{\text{Glycoxalic acid}}{2\begin{array}{l} CHO \\ | \\ COOH \end{array}} \xrightarrow[\Delta]{NaOH} \underset{\text{Sod.glycolate}}{\begin{array}{c} CH_2OH \\ | \\ COONa \end{array}} + \underset{\text{Sod. oxalate}}{\begin{array}{c} COONa \\ | \\ COONa \end{array}}$$

(ii)



Furfural Furfuryl Alcohol 2- Furoic acid (sod. salt)

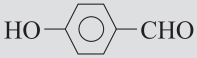
(iii)



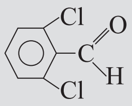
2- Iodo 3- hydroxy benzaldehyde 2- iodo 3- hydroxy benzoic acid 2- iodo 3- hydroxy benzyl alcohol

REMEMBER

- The order of reactivity of different aromatic aldehydes towards Cannizaro reaction is:

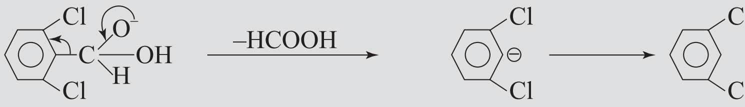
- 

does not contain any α - hydrogen but still fails to undergo Cannizzaro reaction because the corresponding hydroxide is strongly stabilised by -R - effect of CHO. Consequently , the electrophilicity of the carbonyl carbon reduced and the OH^- does not attack the carbonyl group.
- The inertness towards Cannizzaro reaction is also observed in some other aliphatic and aromatic aldehydes as well because of various reasons. For example,

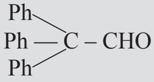


Fails to give Cannizzaro reaction

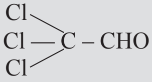
Because the intermediate formed due to attack of OH^- cleaves to give a stable anion. The stability of the anion is due the electron withdrawing Cl - atoms at ortho positions.



- Similarly, the following aldehydes also do not give Cannizzaro reaction although they are not enolisable .

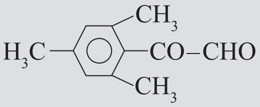


Ph_3C-CHO

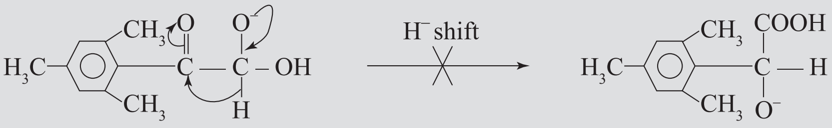


Cl_3C-CHO

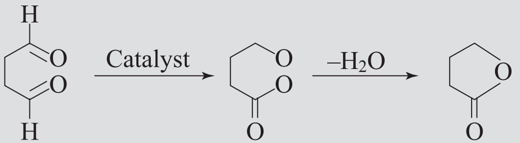
- The following dicabonyl compound does not give intramolecular Cannizzaro reaction.



It is due the fact that the tetrahedral intermediate likely to be formed after the hydride shift is severely crowded and therefore is not formed.



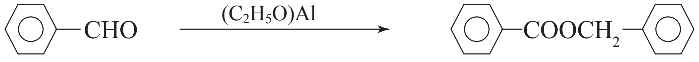
- Some molecules containing α -hydrogens also undergo Cannizaro reaction.



Lactone

- **Tischenko Reaction** It is the modified form of cannizzaro reaction as any aldehyde can take part in it. Here in the presence of aluminium ethoxide aldehydes form esters as follows.

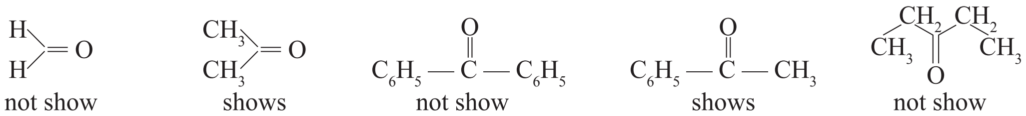
$$2CH_3CHO \xrightarrow{Al(OC_2H_5)_3} \underset{\text{Acetic acid}}{[CH_3COOH} + \underset{\text{Ethyl alcohol}}{CH_3CH_2OH]} \xrightarrow[H_2O]{} \underset{\text{Ethyl acetate}}{CH_3COOCH_2CH_3}$$



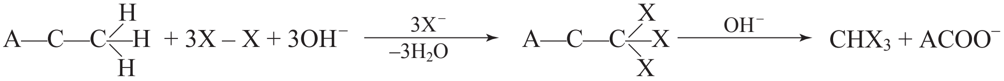
Benzyl benzoate

Haloform Reaction (A) It is given by >C = O having – $COCH_3$ group with X_2 and base like NaOH to give Haloform (CHX_3) and a salt of caboxylic acid.

For example,



- CH_3CHO is the only aldehyde to show the reaction.



Here A can be H, alkyl group, aryl group etc.

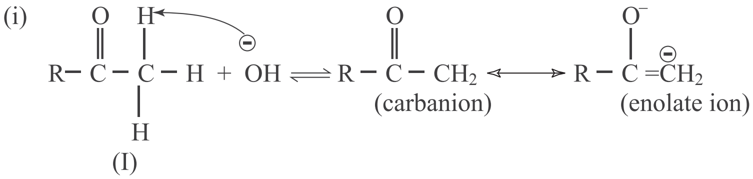
For example,

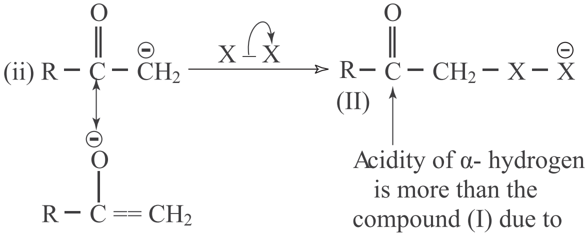
$$CH_3CHO + 3I_2 + 4NaOH \longrightarrow CHI_3\downarrow + HCOONa + 3NaX + 3H_2O$$

$$CH_3COCH_3 + 3I_2 + 4NaOH \longrightarrow CHI_3\downarrow + CH_3COONa + 3NaX + 3H_2O$$

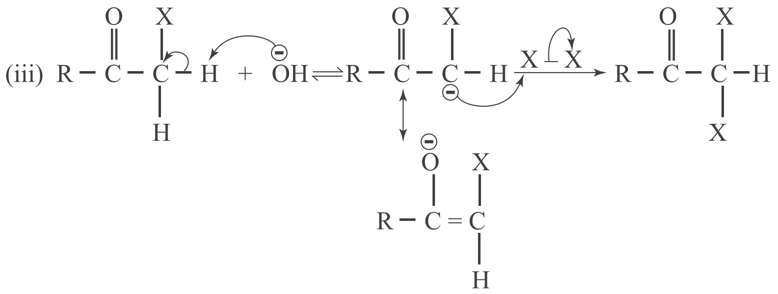
Mechanism of Haloform Reaction

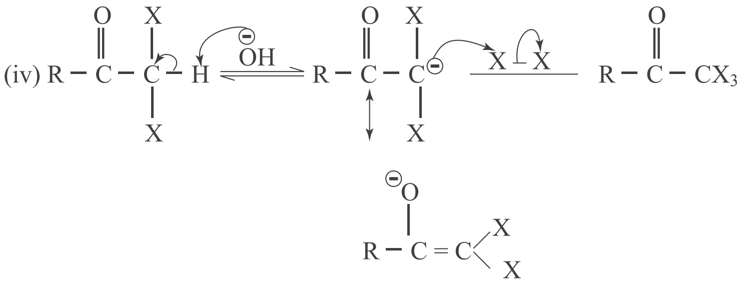
Step 1. α- Hydrogen of carbonyl compound is acidic in character and such a compound undergoes α- halogenation with $X_{2/}OH^-$ (that is, $X^{\oplus}$ in the presence of base, electrophilic substitution reaction).



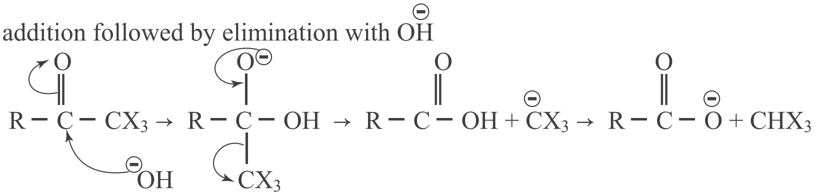


Acidity of α- hydrogen is more than the compound (I) due to the - I group (X)





Step II. Now α, α, α-Trihalocarbonyl compound obtained in the first step gives addition followed by elimination with $\overset{\ominus}{O}H$



REMEMBER

Alcohol having $CH_3 - \overset{|}{C}H - OH$ group shows haloform reaction.

For example, $CH_3 - CH_2 - OH + 4I_2 + 6NaOH \longrightarrow CHI_3 \downarrow + HCOONa + 5NaX$

Gem- dihalides having $R - \underset{X}{\underset{|}{\overset{X}{\overset{|}{C}}}} - CH_3$ can also give Haloform reaction

Compound having $R - \underset{X}{\underset{|}{CH}} - CH_3$ can also give Haloform reaction

REACTIONS SHOWN BY ALDEHYDES ONLY

- **Reducing Properties** Aldehydes differ from ketones in such properties as aldehydes show these properties but not ketones.
- **With Schiff's Reagent** Schiff's reagent is a dilute solution of rosaniline hydrochloride in water. The magenta or pink colour of this solution is discharged by passing SO_2 gas through it.

  R-CHO + Schiff's reagent → Pink colour
  (magenta or fuschine)

- Salicyldehyde fails to show this reaction due to chelation.
- **With Tollen's Reagent** Ammonical solution of silver nitrate is called Tollen's reagent.

  $AgNO_3 + NH_4OH \rightarrow NH_4NO_3 + AgOH$
  $AgOH + 2NH_4OH \rightarrow [Ag(NH_3)_2]^+ OH^- + 2H_2O$
  Tollen's reagent
  Diammine silver (I)
  Hydroxide

  $RCHO + 2[Ag(NH_3)_2]OH \rightarrow RCOOH + H_2O + 4NH_3 + 2Ag\downarrow$
  Aldehyde Tollen's reagent Carboxylic acid silver mirror
  Or
  $RCHO + Ag_2O \longrightarrow RCOOH + 2Ag\downarrow$

- It is also known as Silver mirror test for aldehydes and this test is also given by unsaturated aldehydes however double bond is not effected here.

  For example,

  $CH_2 = CH - CHO + Ag_2O \longrightarrow CH_2 = CH - COOH + 2Ag\downarrow$

- **With Fehling's Solution** Fehling's solution is copper sulphate solution or alkaline solution of sodium potassium tartrate (Rochelle salt).

  $CuSO_4 + 2NaOH \rightarrow Cu(OH)_2 + Na_2SO_4$
  $Cu(OH)_2 \xrightarrow{\Delta} CuO + H_2O$

  $RCHO + 2CuO \rightarrow Cu_2O\downarrow + RCOOH$
  Aldehyde cuprous oxide carboxylic
  (Red ppt.) acid
  or
  $RCHO + 2Cu^{+2} + 3OH^- \longrightarrow RCOO^- + 2Cu^+ + H_2O$
  Red ppt.

- This test is not shown by benzaldehyde as it is a weak reductant and can not reduce it.
- **With Benedict's Solution** It is a solution of $CuSO_4$, sodium citrate and Na_2CO_3. When heated with an aldehyde, a reddish brown ppt. of Cu_2O is formed,. This test is given by aliphatic aldehydes only.
- $RCHO + 2Cu^{+2} + 3OH^- \longrightarrow RCOO^- + 3H_2O + Cu_2O\downarrow$
  (red ppt.)

- **With Bromine Water** Aldehydes decolourise bromine water (red).

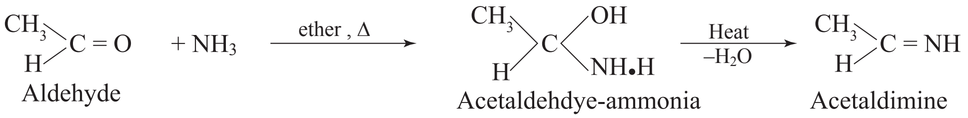
  $RCHO + Br_2 + H_2O \rightarrow RCOOH + 2HBr$

- **Reaction With Ammonia** Formaldehyde forms a stable complex with ammonia which is known as Urotropine.

  $6HCHO + 4NH_3 \rightarrow (CH_2)_6N_4 + 6H_2O$

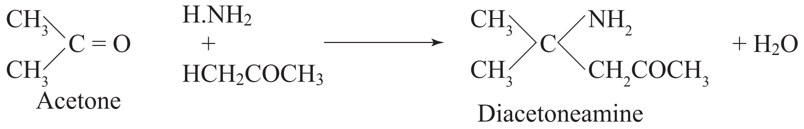
  Urotropine or
  Hexa methylene tetra amine

- It is very effective in urinary infections and arthritis.
- All other aldehydes react with ammonia in presence of ether to give adducts which upon heating give aldimines.



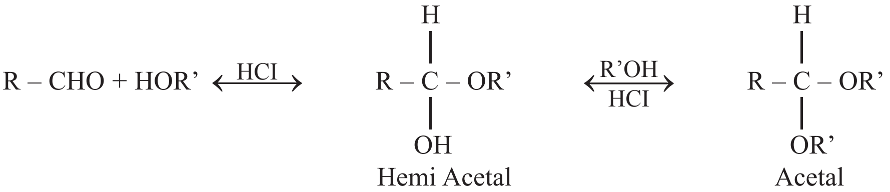
Aldehyde Acetaldehdye-ammonia Acetaldimine

- Aliphatic ketones also form complexes with ammonia called ketonic amines. For example, Acetone and ammonia give rise to diacetoneamine.



Acetone Diacetoneamine

- **Reaction With Alcohol**



$$R-CHO + HOR' \overset{HCl}{\rightleftarrows} R-\underset{OH}{\overset{H}{C}}-OR' \underset{HCl}{\overset{R'OH}{\rightleftarrows}} R-\underset{OR'}{\overset{H}{C}}-OR'$$

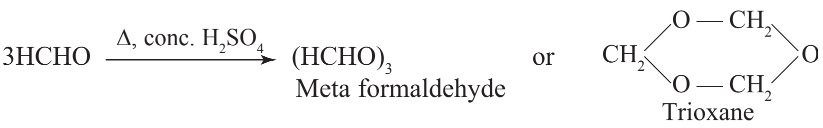
Hemi Acetal Acetal

- Acetals are only stable in basic medium but undergo hydrolysis in acidic medium to give original aldehydes again.

Polymerization of Aldehydes

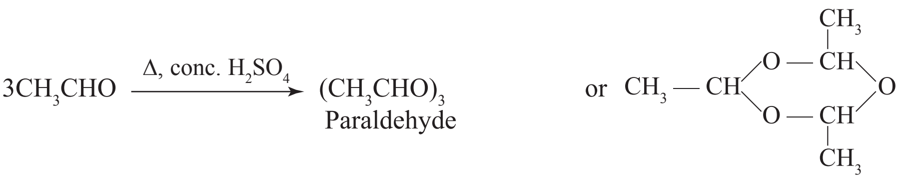
$$n\text{–}HCHO \xrightarrow{\Delta,\ conc.\ H_2SO_4} (CH_2O)n\ .H_2O$$

Aq. Solution Polyoxymethylene



$$3HCHO \xrightarrow{\Delta,\ conc.\ H_2SO_4} (HCHO)_3$$

Meta formaldehyde Trioxane



$$3CH_3CHO \xrightarrow{\Delta,\ conc.\ H_2SO_4} (CH_3CHO)_3$$

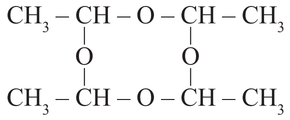
Paraldehyde

$4CH_3CHO \xrightarrow{\Delta,\ \text{conc. HCl}} (CH_3CHO)_4$

Metaldehyde

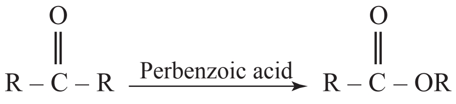
or

or



REACTIONS SHOWN BY KETONES ONLY

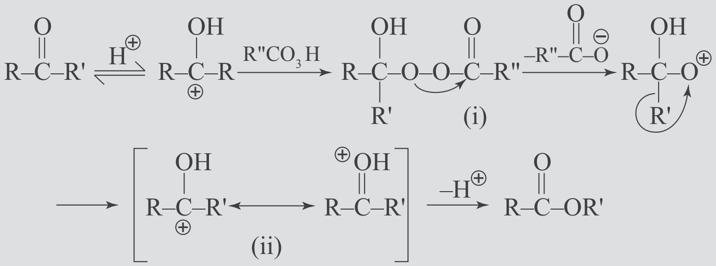
- **Baeyer-Villiger Oxidation** It involves the oxidation of aliphatic ketones into esters and that of cyclic ketones into esters by treatment with peroxyacids such as peracetic acid, perbenzoic acid, trifluoroperacetic acid.



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-R \xrightarrow{\text{Perbenzoic acid}} R-\overset{\overset{\displaystyle O}{\|}}{C}-OR$$

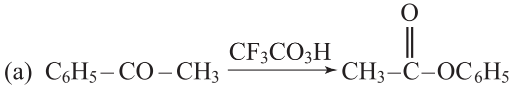
Ketone Ester

Mechanism



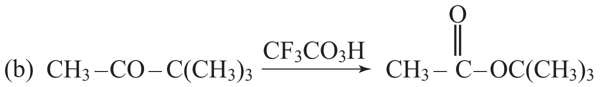
where R’ is equal to CH_3, C_6H_5, CF_3, etc.

Examples,



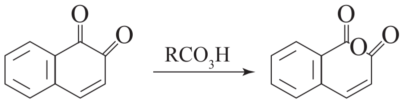
$$\text{(a)}\ C_6H_5-CO-CH_3 \xrightarrow{CF_3CO_3H} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OC_6H_5$$

Acetophenone Phenylacetate

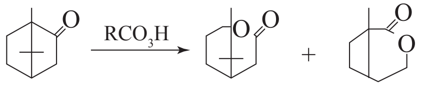


$$\text{(b)}\ CH_3-CO-C(CH_3)_3 \xrightarrow{CF_3CO_3H} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OC(CH_3)_3$$

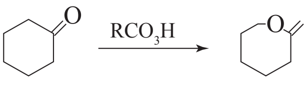
Pinacolone t- Butylacetate



α - Naphthaquinone

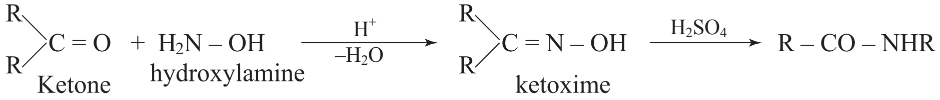


I (75%) II (25%)

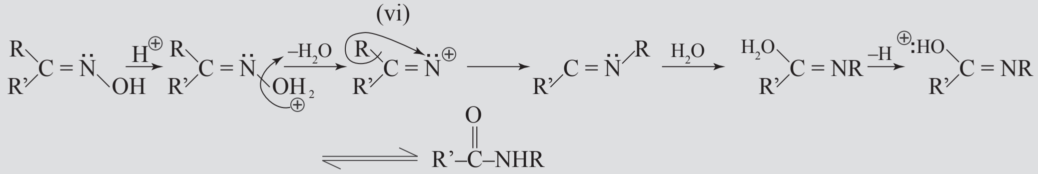


Cyclohexonone ε - Caprolactone

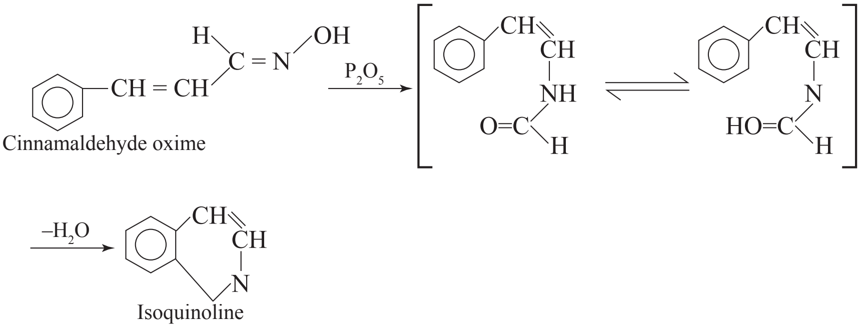
- **Beckmann's Rearranegent** Here ketoximes are converted into N-substituted amides with the help of H_2SO_4 , PCl_5 , $SOCl_2$ etc.

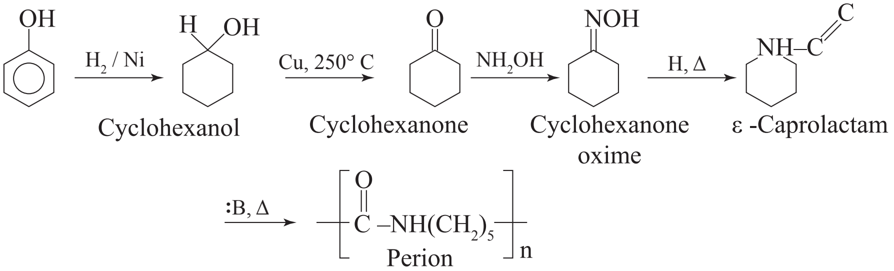


Mechanism

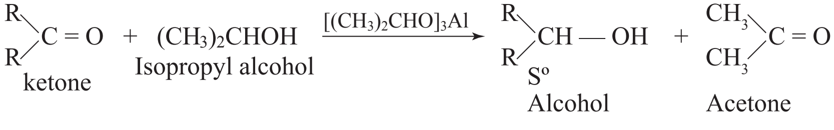


Examples of Synthesis of isoquinoline and lactams





- **Meerwein-Ponndorf-Verley Reduction (MPV Reduction)** Here ketones are reduced into secondary alcohols and it just opposite to Oppenauer oxidation.



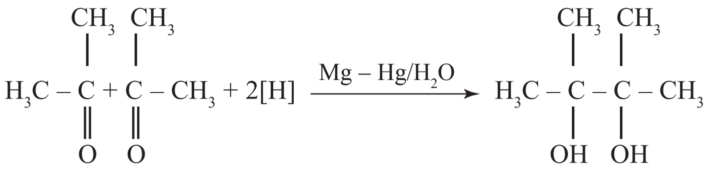
- **Oxidation of Ketone** During such oxidation reactions, the keto group stays with the smaller alkyl group (Popoff's rule).

  For example,

  $$\underset{\text{2-Pentanone}}{CH_3COCH_2CH_2CH_3} \xrightarrow{[O]} \underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Propionic acid}}{CH_3CH_2COOH}$$

- **Reduction of Ketone into Pinacol (Dicol)** When ketones are reduced by Mg/Hg in neutral or alkaline medium pinacols are formed.

  For example,



$$H_3C-\underset{\underset{O}{\|}}{\overset{\overset{CH_3}{|}}{C}}+\underset{\underset{O}{\|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3+2[H] \xrightarrow{Mg-Hg/H_2O} H_3C-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

  Acetone 2,3-Dimethylbutane-2, 3-diol (pinacol)

- **Reaction With Nitrous Acid** Here isonitroso derivatives are formed.

  For example,

  $$CH_3COCH_3 + HNO_2 \longrightarrow CH_3COCH=NOH + H_2O$$

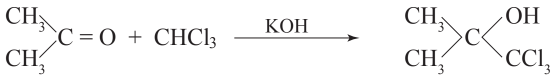
  Oximinoacetone or
  isonitroso acetone

- **Reaction With Sodamide** Here sodium derivatives are formed.

  For example,

  $$CH_3COCH_3 + NaNH_2 \xrightarrow{ether} CH_3COCH_2Na + NH_3$$

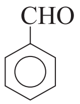
With Chloroform



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=O + CHCl_3 \xrightarrow{KOH} \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C<\!\!\begin{matrix}OH\\CCl_3\end{matrix}$$

Chloretone

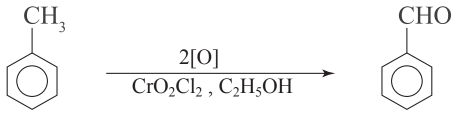
BENZALDEHYDE



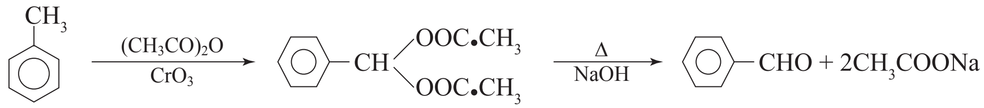
- In is present in bitter almonds in the form of its glycoside amygdalin so also known as oil of bitter almonds.

METHODS OF PREPARATION

- **From Toluene**
- **(a)** By Etard's Reaction or Oxidation by Chromyl Chloride

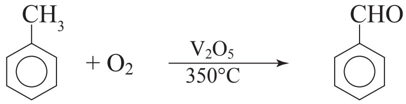


- **(b)** Toluene on oxidation by chromic oxide in acetic anhydride followed by hydrolysis gives benzaldehyde as follows



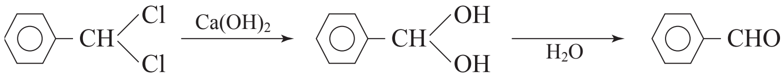
Intermediate benzal
Acetate

- **(c)** Toluene on oxidation by air in presence of V_2O_5 at 350°C gives benzaldehyde.



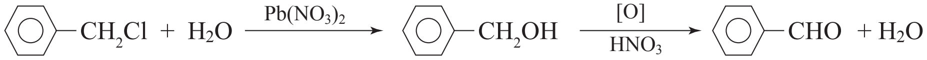
Here MnO_2, oxide of Zr, Mo can also be used as catalysts.

By the Hydrolysis of Benzal Chloride



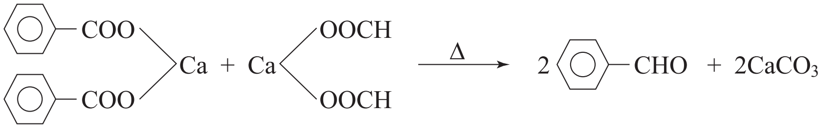
Benzal

From Benzyl Chloride



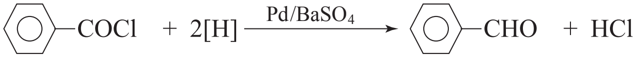
Benzyl chloride Benzyl alcohol

From distillation of Mixture of Calcium Benzoate and Calcium Formate



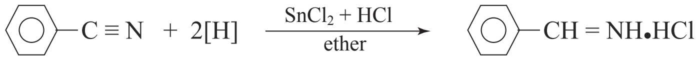
Calcium Benzoate Calcium Formate

By Rosenmund's Reduction

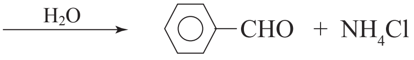


- Here $Pd/BaSO_4$ are poisoned by 'Sulphur or quinoline' to avoid further reduction.
- Here lithium tri tert. butoxy aluminium hydride can also be used at –78°C.

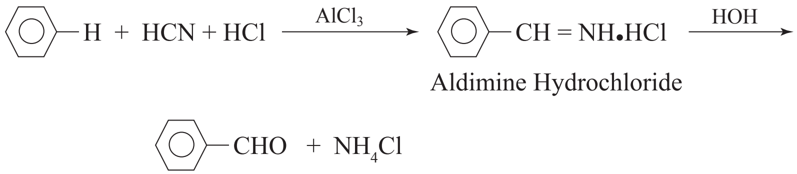
By Stephen's Reaction



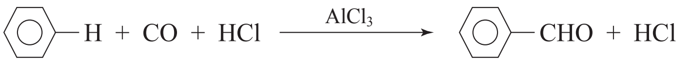
Aldimine Hydrochloride



Gatterman Aldehyde Reaction



- **By Gattermann Koch Reaction**



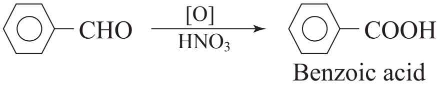
PHYSICAL PROPERTIES

- It is a colourless liquid with a boiling point of 179°C and have a smell like bitter almonds.
- It is insoluble in water but soluble in organic solvents.
- It is steam volatile and heavier than water.

CHEMICAL PROPERTIES

(a) Reactions Due to -CHO Group Here benzaldehyde shows similarities with aliphatic aldehydes.

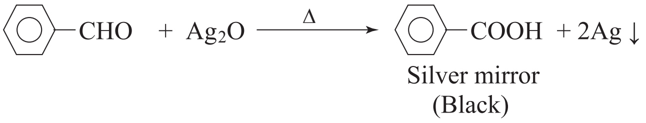
Oxidation by Acidic $KMnO_4$ or $K_2Cr_2O_7$



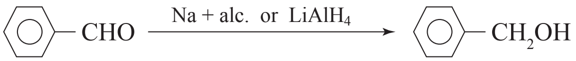
With Schiff's Reagent It gives pink colour with schiff's reagent. The pink colour disappears on passing SO_2.

With Fehling Solution No reaction with Fehling solution occurs here.

With Tollen's Reagent



Reduction



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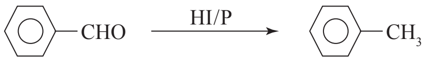

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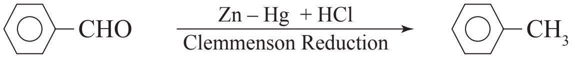
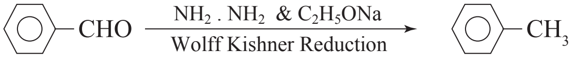


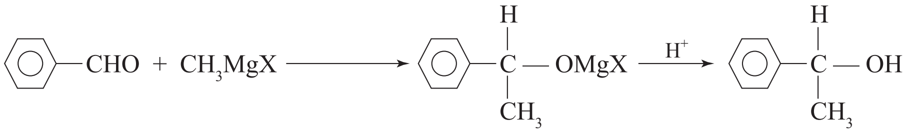


(b) Nucleophilic Addition Reactions

With HCN

Cyano hydrin of benzaldehyde
(Optically active)

With RMgX



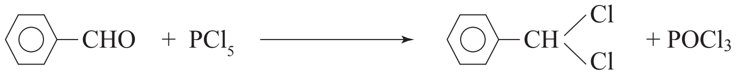
Phenyl ethanol

With NaHSO$_3$

Benzaldehyde sodium bisulphate
(A white solid)

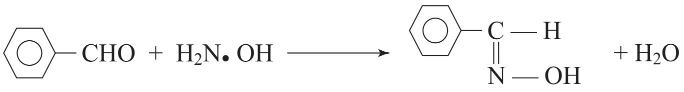
(c) Substitution Reactions

With PCl$_5$



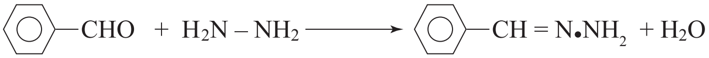
Benzal chloride

With Hydroxylamine



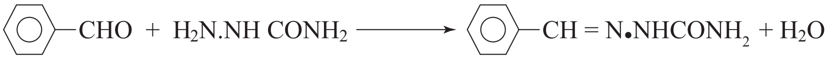
Hydroxylamine Benzaldoxime

With Hydrazine



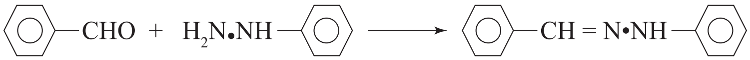
Hydrazine Benzene Hydrazone

With Semicarbazide



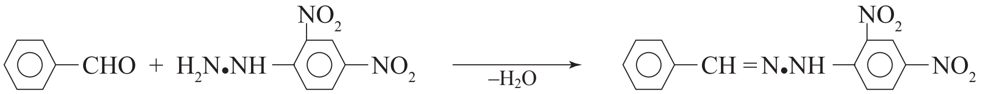
Semicarbazide Benzaldehyde semi Carbazone

With Phenyl Hydrazine



Phenyl Hydrazine Phenyl Hydrazone

With 2, 4 Dinitro Phenyl Hydrazine

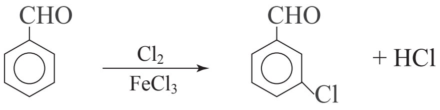


Benzaldehyde 2, 4 Dinitro phenyl hydrazones
orange or yellow ppt.

(d) Reaction Different From Aliphatic Aldehydes

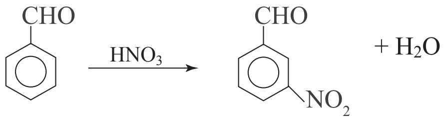
Electrophillic Substitution In benzaldehyde, –CHO group is ring deactivating, meta directing group so rate of electrophilic substitution will be slower than that of benzene.

Halogenation



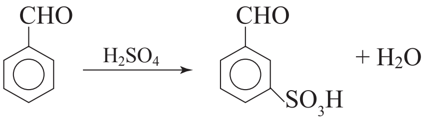
m-chlorobenzaldehyde

Nitration



m-nitrobenzaldehyde

Sulphonation

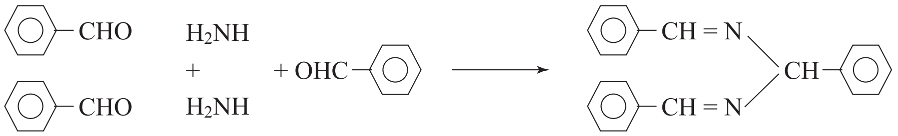


m-formyl benzene sulphonic acid

Reaction with Chlorine

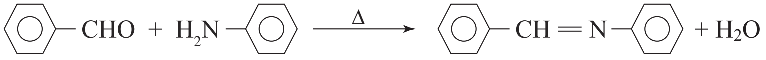
Benzoyl chloride

Reaction With Ammonia



Hydrobenzamide

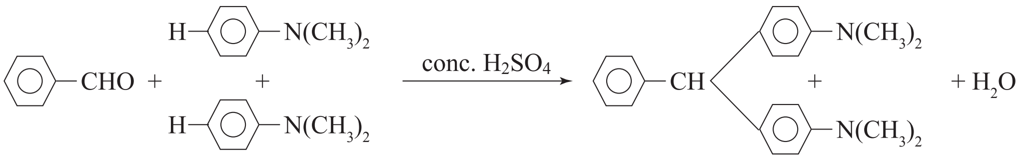
Condensation With Aniline



Schiff's base or
Benzilidine

Condensation With Dimethyl Aniline

Benzaldehyde reacts with N-N-dimethyl aniline in presence of conc. H_2SO_4 or $ZnCl_2$ to give malachite green.



Dimethyl aniline

Malachite green
(Tetramethyl diamino-triphenyl methane)

Perkin Condensation or Reaction Here aromatic aldehydes react with aliphatic acid anhydrides (having minimum two α-H-atoms) in presence of sodium salt of the same acid as base, to form condensation products which or upon hydrolysis give α, β-unsaturated acids. The reaction takes place through the formation of a carbanion and in the reaction α-H atoms of anhydride are involved.

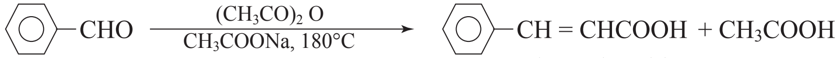
For example, $C_6H_5-CH=O + H_2\,CHCO-O-COCH_3$
Benzaldehyde Acetic anhydride

$$\xrightarrow[-H_2O]{CH_3COONa,\ 453\ K} [C_6H_5CH=CH-CO-O-COCH_3] \xrightarrow[\text{(hydrolysis)}]{H_2O,\ \text{boil}}$$

condensation product

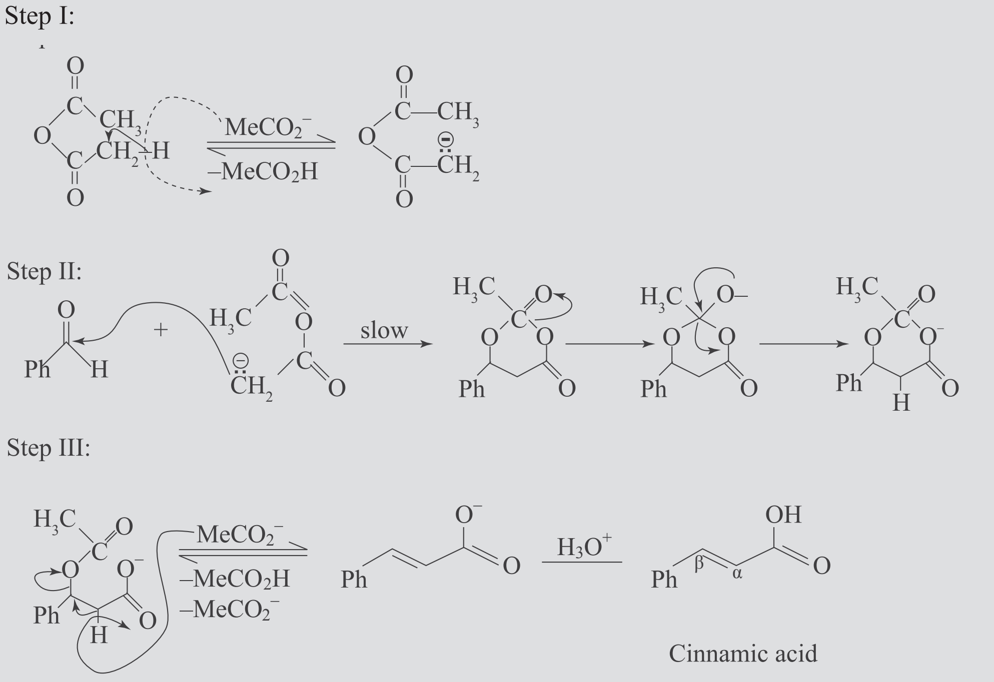
$C_6H_5CH=CHCOOH + CH_3COOH$
Cinnamic acid Acetic acid

Or



Cinnamic acid

Mechanism

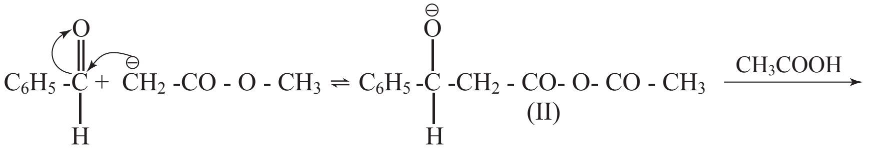


OR

$CH_3COONa \rightleftharpoons CH_3CO\overset{\ominus}{O} + \overset{\oplus}{Na}$

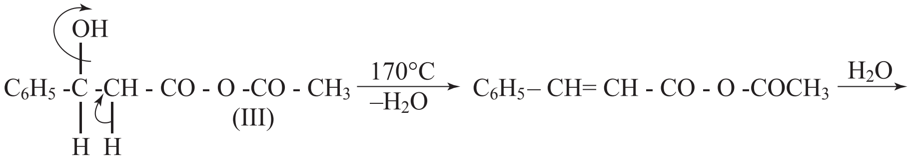
$CH_3CO\overset{\ominus}{O} + H\text{-}CH_2\text{-}CO\text{-}O\text{-}CO\text{-}CH_3 \rightleftharpoons CH_3COOH + \overset{\ominus}{C}H_2\text{-}CO\text{-}O\text{-}CO\text{-}CH_3$

Acetic anhydride (I)



$$C_6H_5\text{-}\underset{H}{\overset{O}{\overset{\|}{C}}} + \overset{\ominus}{C}H_2\text{-}CO\text{-}O\text{-}CH_3 \rightleftharpoons C_6H_5\text{-}\underset{H}{\overset{\overset{\ominus}{O}}{C}}\text{-}CH_2\text{-}CO\text{-}O\text{-}CO\text{-}CH_3 \xrightarrow{CH_3COOH}$$

(II)



$$C_6H_5\text{-}\underset{H}{\overset{OH}{C}}\text{-}\underset{H}{CH}\text{-}CO\text{-}O\text{-}CO\text{-}CH_3 \xrightarrow[-H_2O]{170°C} C_6H_5-CH=CH\text{-}CO\text{-}O\text{-}COCH_3 \xrightarrow{H_2O}$$

(III)

$C_6H_5CH=CH\text{-}COOH + CH_3\text{-}COOH$

(IV)

Examples,

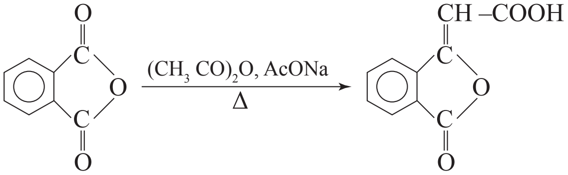
(a) $C_6H_5\text{ - CH = CH -CHO} \xrightarrow{(CH_3CO)_2\text{, AcONa}} C_6H_5\text{ -CH = CH- CH= CH- COOH}$

5- Phenyl -pent -2, 4- dienioc acid

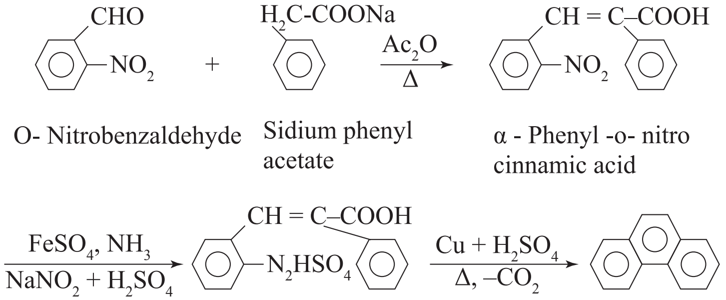
(b)

3 -(α -Furyl)- acrylic acid

(c)



Phthalylacetic acid



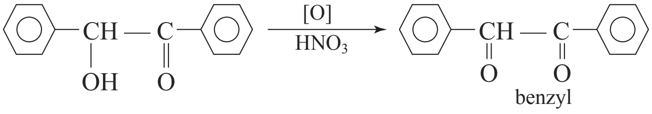
O- Nitrobenzaldehyde

Sidium phenyl acetate

α - Phenyl -o- nitro cinnamic acid

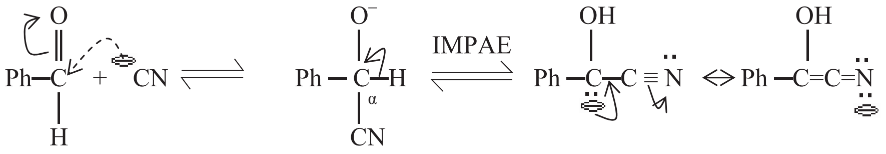
Phenanthrene

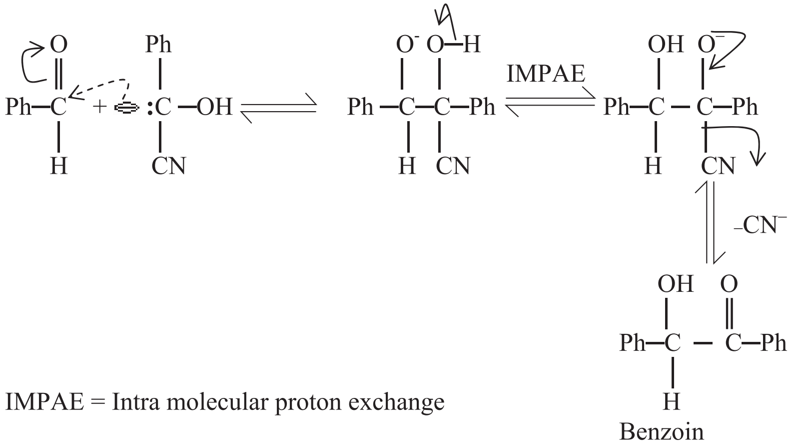
Benzoin Condensation Benzaldehyde on refluxing with aqueous alcoholic KCN forms benzoin as follows:



benzyl

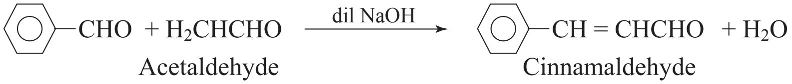
- Benzoin can be readily oxidized into benzyl.

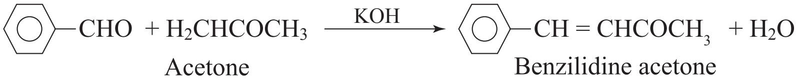


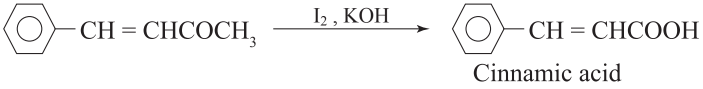


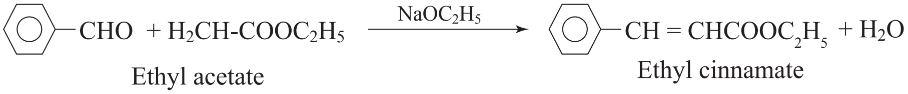
IMPAE = Intra molecular proton exchange

Claisen-Schmidt Reaction or Claisen Condensation Here benzaldehyde undergoes condensation with another compound having α-hydrogen atom in presence of alkali to form α, β-unsaturated compounds.

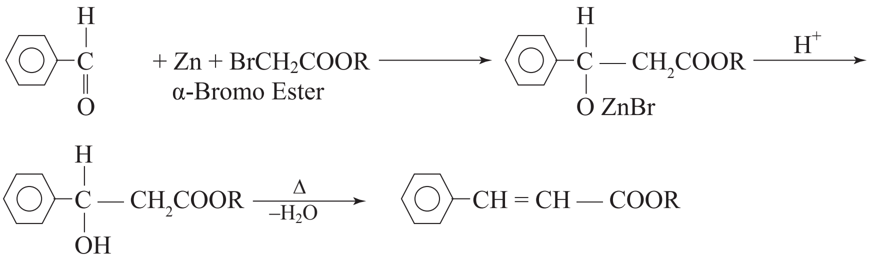




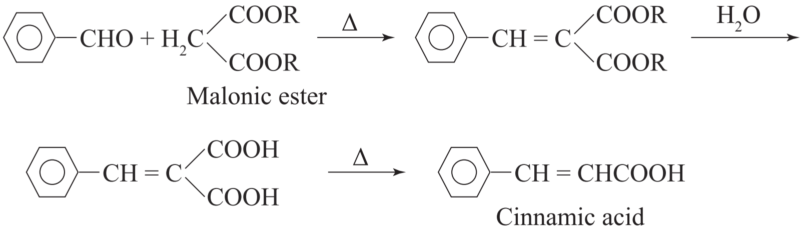




Reformatsky Reaction Here Benzaldehyde reacts with zinc and α-halogenated ester to give first β-hydroxy ester and then α, β-unsaturated ester.



Knoevenagle Reaction Here benzaldehyde reacts with malonic ester or malonic acid in presence of base like pyridine to give α, β-unsaturated acid that is, cinnamic acid.

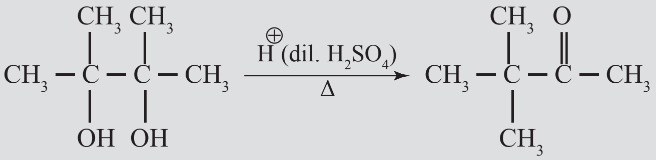


Malonic ester

Cinnamic acid

ENHANCE YOUR KNOWLEDGE

PINACOL-PINACOLONE REARRANGEMENT The acid catalysed rearrangement vicinail diols into carbonyl compound with elimination of water is called Pinacol-Pinacolone rearrangement. This rearrangement is also possible even with out elimination of water if we use drastic condition like 450°C Al_2O_3.

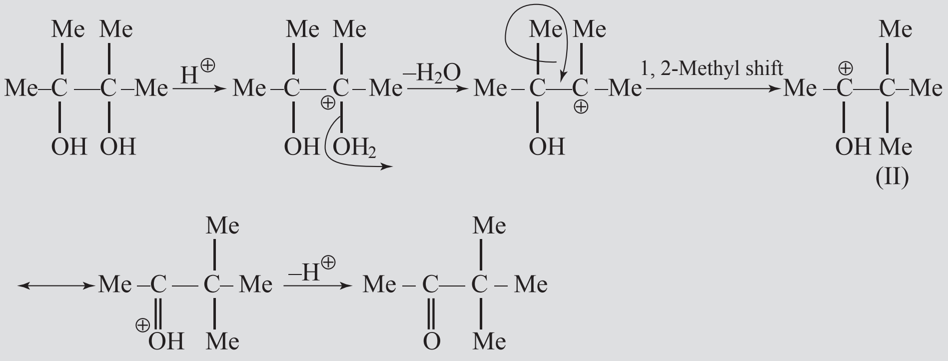


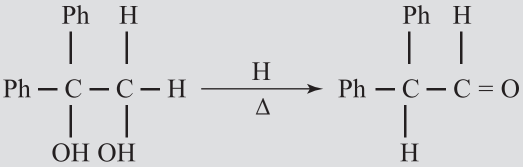
$$CH_3-\underset{OH}{\overset{CH_3}{C}}-\underset{OH}{\overset{CH_3}{C}}-CH_3 \xrightarrow[\Delta]{\overset{\oplus}{H}\,(\text{dil. } H_2SO_4)} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{O}{\overset{\|}{C}}-CH_3$$

Pinacol

pinacolone

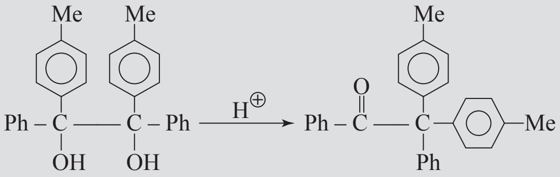
Mechanism

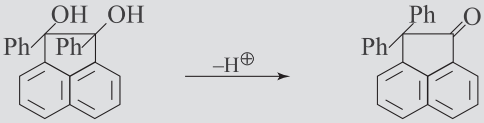




$$\mathrm{Ph-\underset{OH}{\overset{Ph}{C}}-\underset{OH}{\overset{H}{C}}-H \xrightarrow[\Delta]{H} Ph-\underset{H}{\overset{Ph}{C}}-\overset{H}{C}=O}$$

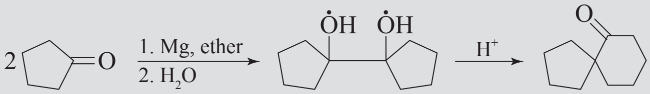
2,2- diphenyl -1,2-glycol 2,2- Diphenyl acetaldehyde



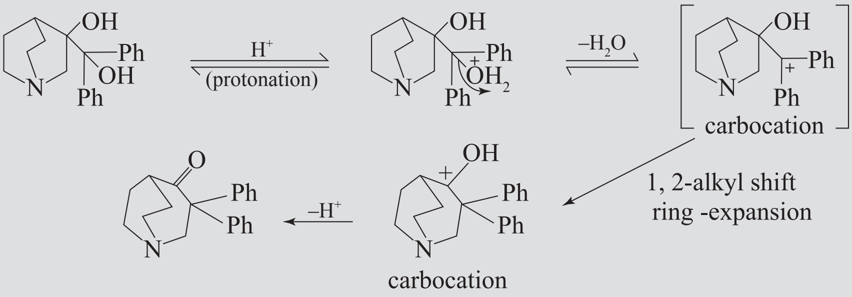


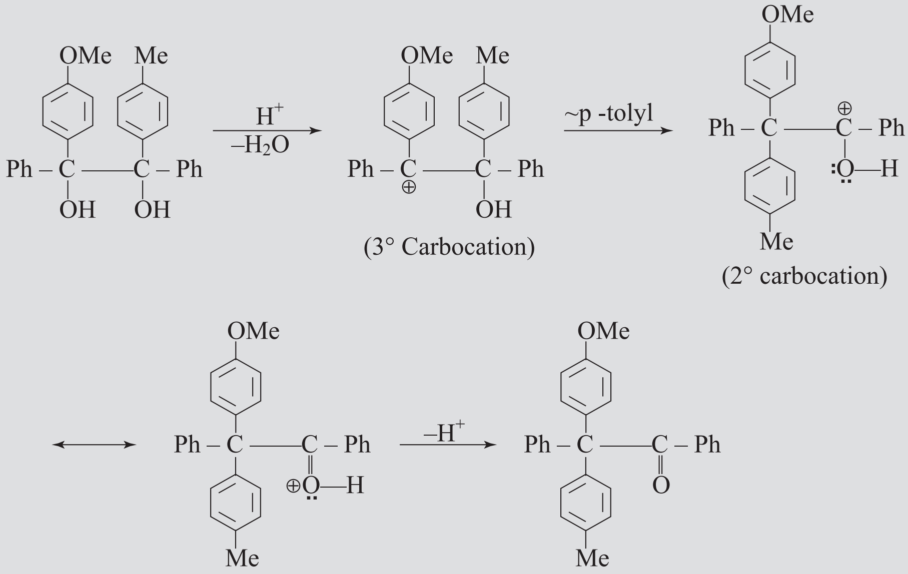
7, 8- Diphenyl acenaphthene -7, 8 diol

7- oxo -8, 8-diphenylacenaphthene

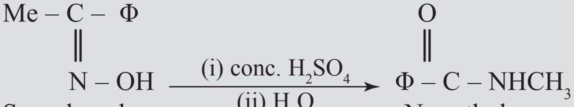


Cycloheptanone pinacol



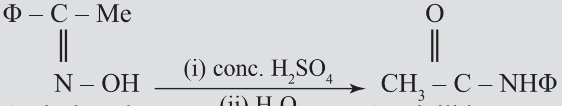


- **Brady's Reagent**: Aqueous solution of 2, 4-dinitrophenyl hydrazine (DNP) is known as Brady's reagent. It reacts with carbonyl compounds (aldehyde and ketone) to give coloured precipitate. These precipitates have sharp melting point. The melting points of the precipitates confirm the carbonyl compounds.
- **Beckmann Rearrangement**: Here oximes undergo rearrangement to form substituted amides on heating with conc. H_2SO_4/PCl_5 etc. as follows:



$$\text{Me}-\underset{\underset{\text{N}-\text{OH}}{\|}}{\text{C}}-\Phi \xrightarrow[\text{(ii) } H_2O]{\text{(i) conc. } H_2SO_4} \Phi-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{NHCH}_3$$

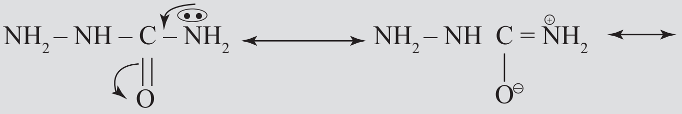
Syn-phenyl acetophenone oxime — N-methyl benzamide



$$\Phi-\underset{\underset{\text{N}-\text{OH}}{\|}}{\text{C}}-\text{Me} \xrightarrow[\text{(ii) } H_2O]{\text{(i) conc. } H_2SO_4} CH_3-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{NH}\Phi$$

Anti-phenyl acetophenone oxime — Acetinilide

In case of Semicarbazide the $-NH_2$ gp close to $\rangle C{=}O$ gp can not be used as it is deactivated due to resonance stabilization so terminal $-NH_2$ is used during the reaction.

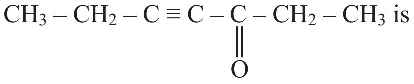


$$NH_2-NH-\underset{\underset{O}{\|}}{C}-\ddot{N}H_2 \longleftrightarrow NH_2-NH\ \underset{\underset{O^{\ominus}}{|}}{C}=\overset{\oplus}{N}H_2 \longleftrightarrow$$

MULTIPLE-CHOICE QUESTIONS

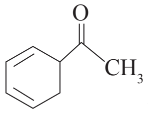
Straight Objective Type Questions (Single Choice only)

1. The IUPAC name of



$CH_3 - CH_2 - C \equiv C - \underset{\underset{O}{\|}}{C} - CH_2 - CH_3$ is

(a) 3-oxo-2-heptyne
(b) hept-3-yn-4-oxone
(c) hept-4-yn-3-one
(d) hept-3-yn-4-one

2. IUPAC name of  is

(a) 6-cyclohexa-1,3-dienylethanone
(b) Acetyl cyclohexadiene
(c) 1-cyclohexa-2,4-dienylethanone
(d) None of these

3. Which of the following compound is expected to be optically active?

(a) $(CH_3)_2CHCHO$
(b) $CH_3CH_2CH_2CHO$
(c) $CH_3CH_2CHBrCHO$
(d) $CH_3CH_2CBr_2CHO$

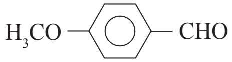
4. Which of the following correctly describes the bond angle and hybridizations present in formaldehyde?

(a) C, sp^3; O, sp^2; HCO, ~109.5°
(b) C, sp^2; O, sp^2; HCO, ~109.5°
(c) C, sp^2; O, sp^2; HCO, ~120°
(d) C, sp^2; O, sp^3; HCO, ~120°

5. Carbonyl compounds undergo nucleophillic addition because of

(a) more stable anion with negative charge on oxygen and less stable carbocation
(b) electromeric effect
(c) electronegativity difference of carbon and oxygen atoms
(d) none of these

6. When a nucleophile attacks a carbonyl compound, the one which is most reactive towards the nucleophile is

(a) $CH_3COCOC_2H_5$
(b) CH_3COCH_2Cl
(c) 
(d) $CH_3COCH_2CH_2Cl$

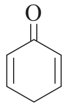
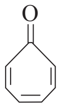
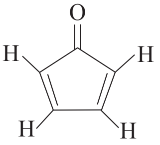
7. Polarization of acrolein as

(a) $\overset{+\delta}{C}H_2 = CH - \overset{-\delta}{C}HO$
(b) $\overset{-\delta}{C}H_2 = CH - \overset{+\delta}{C}HO$
(c) $\overset{-\delta}{C}H_2 = CH - \overset{+\delta}{C}HO$
(d) $\overset{+\delta}{C}H_2 = CH - \overset{-\delta}{C}HO$

8. The most reactive compound towards formation of cyanohydrin on treatment with KCN followed by acidification is

(a) p-nitrobenzaldehyde
(b) p-hydroxybenzaldehyde
(c) benzaldehyde
(d) phenylacetaldehyde

9. Which of the following carbonyl oxygen can form strongest hydrogen bond with H_2O molecule?

(a) 
(b) 
(c) 
(d) 

10. C_2H_5CHO and CH_3COCH_3 can be distinguished from one another by testing with:

(a) sodium bisulphate
(b) Fehling's solution
(c) phenylhydrazine
(d) 2, 4-dinitrophenyl hydrazine

11. The reagent with which both acetaldehyde and acetophenone react easily are

(a) Tollen's reagent
(b) 2, 4-Dinitrophenyl hydrazine
(c) Fehling's solution
(d) Schiff's reagent

12. The dipole moment is highest for:
(a) 1,3-dimethyl benzene
(b) trans-2-butene
(c) Ethanol
(d) Acetophenone

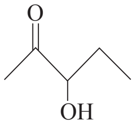
13. Which of the following represent the correct ranking in terms of increasing boiling point?
(a) n-pentane < diethyl ether < 2-butanone < 1-butanol
(b) n-pentane < diethyl ether < 1-butanol < 2-butanone
(c) 2-butanone < n-pentane < diethyl ether < 1-butanol
(d) n-pentane < 2-butanone < diethyl ether < 1-butanol

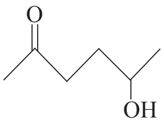
14. Among the following mixtures, dipole-dipole as the major interaction, is present in:
(a) benzene and ethanol
(b) acetonitrile and acetone
(c) KCl and water
(d) benzene and carbon tetrachloride

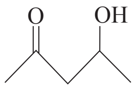
15. Which one of the following compounds is most reactive towards nucleophillic addition?
(a) CH_3CHO (b) $PhCOCH_3$
(c) CH_3COCH_3 (d) $PhCOPh$

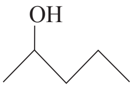
16. Carbonyl compounds fail to undergo nucleophilic substitution reactions because:
(a) Rearrangements are possible as side reactions.
(b) Nucleophiles used act as reducing agents.
(c) Strong nucleophiles like (H^-) or (R^-) which are difficult to replace have to be substituted by other nucleophiles.
(d) Carbonyl double bond (>C = O) is more active than a (>C = C<) olefinic double bond.

17. Which of the following will be most readily dehydrated in acidic conditions?

(a)


(b)


(c)


(d)


18. Hydrogenation of benzoyl chloride in the presence of Pd and $BaSO_4$ gives:
(a) benzyl alcohol (b) benzaldehyde
(c) benzoic acid (d) phenol

19. m-Chlorobenzaldehyde on reaction with conc. KOH at room temperature gives:
(a) potassium m-chlorobenzoate and m-hydroxybenzaldehyde
(b) m-hydroxybenzaldehyde and m-chlorobenzyl alcohol
(c) m-chlorobenzyl alcohol and m-hydroxybenzyl alcohol
(d) potassium m-chlorobenzoate and m-chlorobenzyl alcohol

20. Fomaldehyde when reacted with methyl magnesium bromide followed by hydrolysis gives:
(a) HCHO (b) CH_3COOH
(c) C_2H_5OH (d) CH_3CHO

21. Formaldehyde gives an additive product with methyl magnesium iodide which on aqueous hydrolysis gives:
(a) methyl alcohol (b) isopropyl alcohol
(c) propyl alcohol (d) ethyl alcohol

22. Which of the following compounds undergo aldol condensation?
(a) HCHO (b) CCl_3CHO
(c) $(CH_3)_3CHO$ (d) CH_3CHO

23. During reduction of carbonyl compounds by hydrazine and KOH, the first intermediate formed is
(a) $RCH = NH$ (b) $RCONH_2$
(c) $RCH = NNH_2$ (d) $RC \equiv N$

24. The reaction of benzaldehdye with alkali gives:
(a) benzene + benzyl alcohol
(b) phenol + benzene
(c) benzene + benzyl alcohol
(d) benzyl alcohol + sodium benzoate

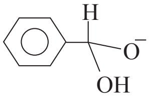
25. The cyanohydrin of a compound X on hydrolysis gives lactic acid; the X is
(a) $(CH_3)_2CO$
(b) CH_3CHO
(c) HCHO
(d) $C_6H_5CH_2CHO$

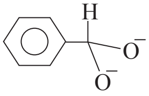
26. Which of the following products is formed when benzaldehyde is treated with CH_3MgBr and the addition product so obtained is subjected to acid hydrolysis?
(a) a primary alcohol (b) phenol
(c) secondary alcohol (d) tert-Butyl alcohol

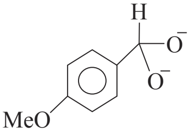
27. From which of the following tertiary butyl alcohol is obtained by the action of methyl magnesium iodide?
(a) CO_2 (b) HCHO
(c) CH_3CHO (d) CH_3COCH_3

28. A substance $C_4H_{10}O$ yields on oxidation a compound, C_4H_8O which gives an oxime and a positive iodoform test. The original substance on treatment with conc. H_2SO_4 gives C_4H_8. The structure of the compound is
(a) $(CH_3)_3COH$
(b) $CH_3CHOHCH_2CH_3$
(c) $CH_3CH_2CH_2CH_2OH$
(d) $CH_3CH_2 - O - CH_2CH_3$

29. In a Cannizzaro reaction, the intermediate that will be best hydride donor is

(a)


(b)


(c)


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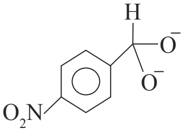


30. $(CH_3)_2CO \xrightarrow[(HCl)]{NaCN} A \xrightarrow{H_3O^+} B$

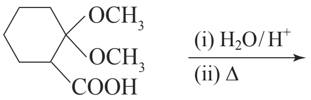
in the above sequence of reactions A and B are
(a) $(CH_3)_2C(OH)CN$, $(CH_3)_2CHCOOH$
(b) $(CH_3)_2C(OH)CN$, $(CH_3)_2C(OH)_2$
(c) $(CH_3)_2C(OH)CN$, $(CH_3)_2C(OH)COOH$
(d) $(CH_3)_2C(OH)CN$, $(CH_3)_2C = O$

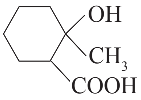
31. Ozonolysis of C_7H_{14} gave 2-methyl-3-pentanone. The alkene is
(a) 2-Methyl-2-ethyl-3-butene
(b) 2-Ethyl-3-methyl-1-butene
(c) 2-Methyl-3-ethyl-1-butene
(d) 2,5-Dimethyl-3, 4-diethylhex-3-ene

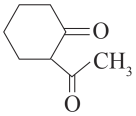
32. When 2-butyne is treated with dil. $H_2SO_4/HgSO_4$, the product formed is
(a) 2-Butanol (b) Acetone
(c) Butanol-1 (d) Butanone

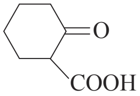
33. If 3-hexanone is reacted with $NaBH_4$ followed by hydrolysis with D_2O, the product will be
(a) $CH_3CH_2CD(OD)CH_2CH_2CH_3$
(b) $CH_3CH_2CH(OD)CH_2CH_2CH_3$
(c) $CH_3CH_2CD(OH)CH_2CH_2CH_3$
(d) $CH_3CH_2CH(OH)CH_2CH_2CH_3$

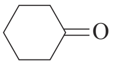
34. Identify (A) in the following reaction:



(a)


(b)


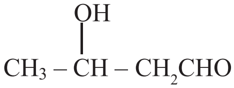
(c)


(d)


35. Which alkene is formed from the following yield carbonyl pair?
$CH_3CH_2CH_2CH = PPh_3$ + 2-butanone
(a) 1-methyl-5-methane
(b) 3-methyl-3-heptene
(c) 4-methyl-3-heptene
(d) 5-methyl-3-heptene

36. Predict the product 'B' in the sequence of reaction

$$HC \equiv CH \xrightarrow[HgSO_4]{30\ \%\ H_2SO_4} A \xrightarrow{NaOH} B$$

(a) CH_3CHO
(b) CH_3COOH
(c) CH_3COONa
(d)


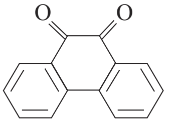
$CH_3 - CH(OH) - CH_2CHO$

37. The end product in the following sequence of reactions is

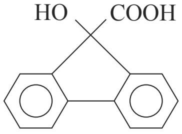
$$HC \equiv CH \xrightarrow[20\%\ H_2SO_4]{1\%\ HgSO_4} A \xrightarrow[H_2O]{CH_3MgX} B$$

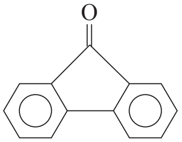
(a) ethanol
(b) acetone
(c) acetic acid
(d) isopropyl alcohol

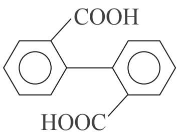
38. In the reaction

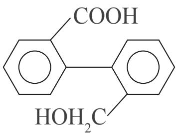


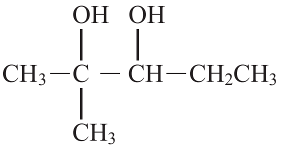
The product (P) is

(a)


(b)


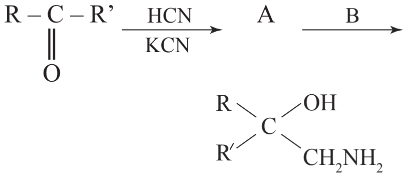
(c) 

(d) 

39. On vigorous oxidation by permanganate solution, $(CH_3)_2C = CH - CH_2 - CH_3$ gives:
(a) $(CH_3)_2CHOH + CH_3CH_2CH_2OH$
(b) $(CH_3)_2C = O + CH_3CH_2COOH$
(c) $(CH_3)_2CHCO_2H + CH_3CH_2COOH$
(d) 

$$CH_3-\underset{CH_3}{\overset{OH}{C}}-\overset{OH}{CH}-CH_2CH_3$$

40. A and B in the following reactions are



(a) A = RR'C(OH)(COOH) , B = NH_3
(b) A = $RR'CH_2CN$, B = NaOH
(c) A = RR'C(CN) (OH), B = $LiAlH_4$
(d) A = RR'C(CN)(OH), B = H_3O^+

41. Cinnamic acid is formed when C_6H_5CHO condensation with $(CH_3CO)_2O$ in presence of
(a) sodium metal (b) sodium acetate
(c) anhydrous $ZnCl_2$ (d) conc. H_2SO_4

42. A compound gives a yellow ppt. on warming with the aqueous solution of NaOH. Its vapour density is 29. The compound is
(a) CH_3CH_2CHO (b) CH_3COCH_3
(c) $CH_3CHOHCH_3$ (d) $CH_3CH_2CH_2OH$

43. CH_3CHCl_2, on hydrolysis will give:
(a) CH_3CHO (b) CH_3COOH
(c) $CHCl_3$ (d) CH_3CH_2OH

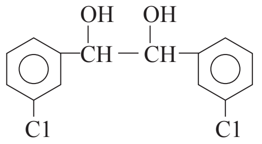
44. The compound that will not give iodoform on treatment with alkali and iodine is
(a) Acetone (b) Ethanol
(c) Diethyl ketone (d) isopropyl alcohol

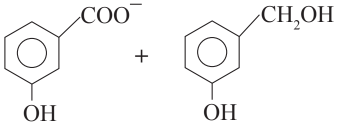
45. In the Cannizzaro reaction given below,

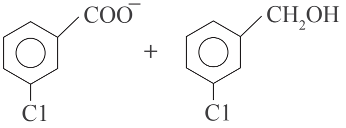
$$2\text{Ph-CHO} \xrightarrow{OH^-} \text{Ph} - \text{CH}_2\text{OH} + \text{PhCO}_2\text{-}$$

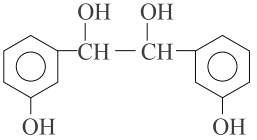
the slowest step is
(a) the attack of –OH at the carbonyl group
(b) the transfer of hydride ion to the carbonyl group
(c) the abstraction of proton from the carboxylic acid
(d) the deprotonation of Ph – CH_2OH.

46. When m-chlorobenzaldehyde is treated with 50% KOH solution, the product (s) obtained is (are):

(a) 

(b) 

(c) 

(d) 

47. In the reaction

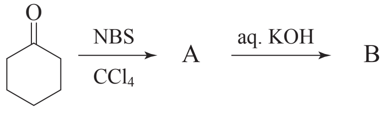
$$CH_3CH_2C \equiv CH \xrightarrow{H_2SO_4\text{ , }HgSO_4} [A]$$

The compound [A] is
(a) $CH_3 - CH_2 - CH_2 - COOH$
(b) $CH_3 - CH_2 - CH_2 - CHO$
(c) $CH_3 - CH_2 - CO - CH_3$
(d) none of these

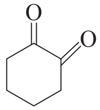
48. What is the product obtained when acetophenone is oxidized by selenium dioxide (in dioxane-acetic acid)?
(a) $C_6H_5 - CHO$
(b) $C_6H_5 - COOH$
(c) $C_6H_5 - CO - CHO$
(d) $C_6H_5 - CHO$

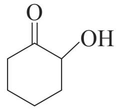
49. Acetyl bromide reacts with excess of CH_3MgI followed by treatment with a saturated solution of NH_4Cl gives:
(a) acetone
(b) acetamide
(c) 2-methyl-2-propanol
(d) acetyl iodide

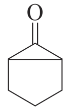
50. In the sequence of reactions

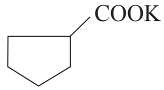


The final product B is

(a)


(b)


(c)


(d)


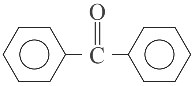
51. Which one of the following is reduced with zinc and hydrochloric acid to give the corresponding hydrocarbon?

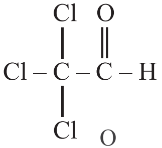
(a) ethyl acetate (b) acetic acid
(c) acetamide (d) butan-2-one

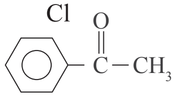
52. The best reagent to convert pent-3-en-2-ol into pent-3-en–2-one is

(a) acidic permanganate
(b) acidic dichromate
(c) chromic anhydride in glacial acetic acid
(d) pyridinium chloro-chromate

53. Which of the following is the correct reactivity order of various carbonyl compounds towards cyanohydrin formation?

(I)


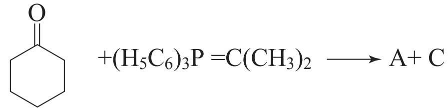
(II)

Cl_3C-CHO

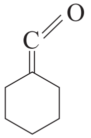
(III)


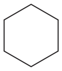
(IV) $CH_3-CO-CH_3$

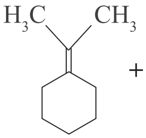
(a) III > I > II > IV
(b) II > III > I > IV
(c) II > IV > III > I
(d) IV > II > III > I

54. A and C in this reaction is



(a)

$+ (H_5C_6)_3P = O$

(b)

$+ C_6H_5CHO$

(c)

$+ (H_5C_6)_3P = O$

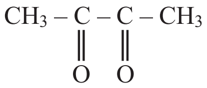
(d) none of these

55. Reaction of cyclohexanone with dimethylamine in the presence of catalytic amount of an acid forms a compound if water during the reaction is continuously removed. The compound formed is generally known as:

(a) a Schiff's base
(b) an enamine
(c) an imine
(d) an amine

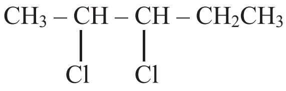
56. In the reaction,

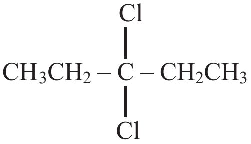
$$CH_3-C\equiv C-CH_3 \xrightarrow[\text{(ii) } H_2O/Zn]{\text{(i) X}}$$

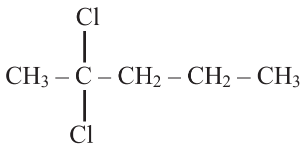

$$CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-CH_3$$

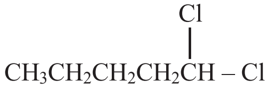
(a) O_2 (b) O_3
(c) $KMnO_4$ (d) HNO_3

57. A compound (A) $(C_5H_{10}Cl_2)$ on hydrolysis gives $C_5H_{10}O$ which reacts with NH_2OH, forms iodoform but does not give Fehling test. (A) is

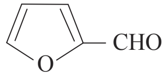
(a)

$$CH_3-\underset{\underset{Cl}{|}}{CH}-\underset{\underset{Cl}{|}}{CH}-CH_2CH_3$$

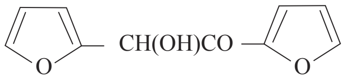
(b)

$$CH_3CH_2-\overset{\overset{Cl}{|}}{\underset{\underset{Cl}{|}}{C}}-CH_2CH_3$$

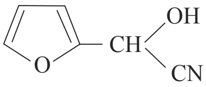
(c) 
$CH_3-CCl_2-CH_2-CH_2-CH_3$

(d) 
$CH_3CH_2CH_2CH_2CHCl-Cl$

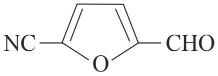
58. In which of the following reactions, carbon-carbon bond formation takes place?
(a) Reimer-Tiemann reaction
(b) Cannizaro reaction
(c) Schmidt reaction
(d) HVZ reaction

59. 
undergoes reaction in the presence of KCN to give:

(a) 

(b) 

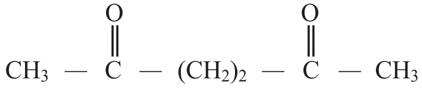
(c) 

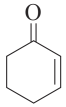
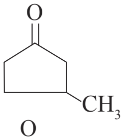
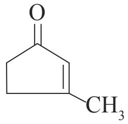
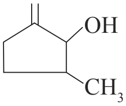
(d) 

60. Acetophenone on reaction with p-nitroperbenzoic acid gives:
(a) benzophenone (b) phenyl propionate
(c) phenyl acetate (d) methyl benzoate

61. Phenyl magnesium bromide reacts with methanol to give:
(a) a mixture of anisole and Mg(OH)Br
(b) a mixture of benzene and Mg(OMe)Br
(c) a mixture of toluene and Mg(OH)Br
(d) a mixture of phenol and Mg(Me)Br

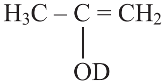
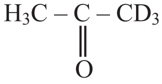
62. When compound X is oxidized by acidified potassium dichromate, compound Y is formed. Compound Y on reduction with $LiAlH_4$ gives X. X and Y respectively are
(a) C_2H_5OH, CH_3COOH
(b) CH_3COCH_3, CH_3COOH
(c) C_2H_5OH, CH_3COCH_3
(d) CH_3CHO, CH_3COCH_3

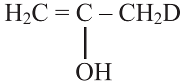
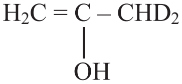
63. The diketone

$CH_3-C(=O)-(CH_2)_2-C(=O)-CH_3$
on intramolecular aldol condensation gives the final product:

(a) 
(b) 
(c) 
(d) 

64. Reaction of acetylene and propylene with $HgSO_4$ in presence of H_2SO_4 produces respectively
(a) acetone and acetaldehyde
(b) acetaldehyde and acetone
(c) propanaldehyde and acetone
(d) acetone and propanaldehyde

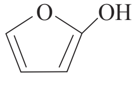
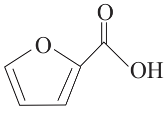
65. The enol form of acetone after treatment with D_2O gives:

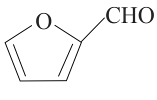
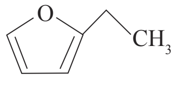
(a) 
$H_3C-C(OD)=CH_2$
(b) 
$H_3C-C(=O)-CD_3$

(c) 
$H_2C=C(OH)-CH_2D$
(d) 
$H_2C=C(OH)-CHD_2$

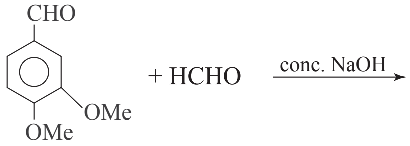
66. Nucleophillic addition reaction will be most favoured in:
(a) CH_3CH_2CHO
(b) CH_3CHO
(c) $CH_3 . CH_2 . CH_2COCH_3$
(d) $(CH_3)_2C = O$

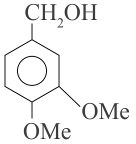
67. A compound on treatment with 50% aqueous NaOH gives 2-furoic acid and furfuryl alcohol. What is the structure of the parent compound?

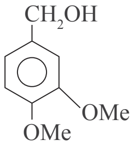
(a) 
(b) 

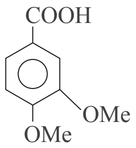
(c) 
(d) 

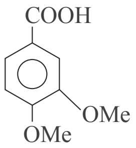
68. The following reaction gives:

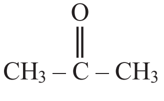


(a)  + CH_3OH

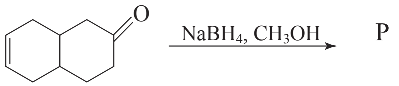
(b)  + HCOOH

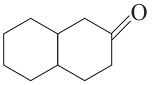
(c)  + HCOOH

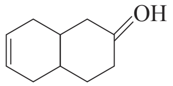
(d)  + CH_3OH

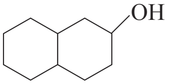
69. Which one of the following on treatment with 50 per cent aqueous sodium hydroxide yields the corresponding alcohol and acid?
(a) $C_6H_5CH_2CHO$
(b) C_6H_5CHO
(c) $CH_3CH_2CH_2CHO$
(d) 
$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$

70. The product P is



(a) 

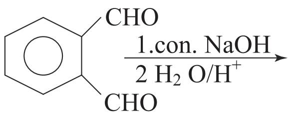
(b) 

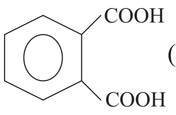
(c) 

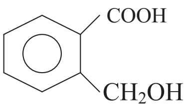
(d) none of these

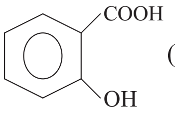
71. Pentan-3-ol on reaction with aluminium tertiary butoxide in presence of acetone gives:
(a) Pentan-3-one
(b) Pentanoic acid
(c) Pentane
(d) Pentanal

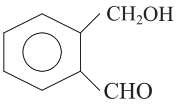
72. Identify the product in the following reaction:



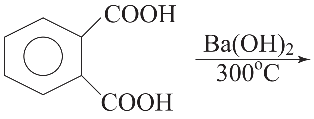
(a) 

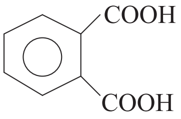
(b) 

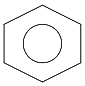
(c) 

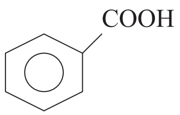
(d) 

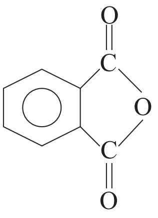
73. Identify the final product.



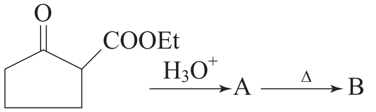
(a) 

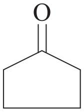
(b) 

(c) 

(d) 

74. The compound is



(a)


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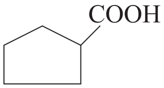

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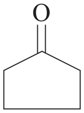

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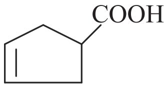
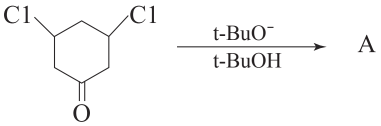
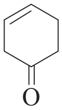
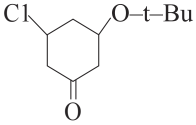


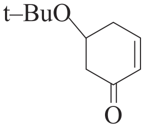
75.

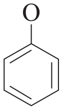


Here (A) can be?

(a)


(b)


(c)


(d)


Brainteasers Objective Type Questions (Single choice only)

76. Which one of the following pairs gives effervescence with aq. $NaHCO_3$?

CH_3COCl (I)
CH_3COCH_3 (II)
CH_3COOCH_3 (II)
$CH_3COOCOCH_3$ (IV)

(a) I & III
(b) I & IV
(c) II& III
(d) I & II

77. Consider the following substances:

1. HCHO
2. CH_3CHO
3. $CH_3CH_2COCH_3$
4. $CH_3CH_2COCH_2CH_3$

correct order of reactivity towards nucleophillic addition reaction is

(a) 1 > 4 > 2 > 3
(b) 1 > 2 > 4 > 3
(c) 1 > 3 > 2 > 4
(d) 1 > 2 > 3 > 4

78. The increasing order of the rate of HCN addition to compounds A – D is

(A) HCHO
(B) CH_3COCH_3
(C) $PhCOCH_3$
(D) PhCOPh

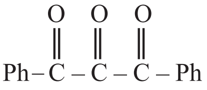
(a) A < B < C < D
(b) D < B < C < A
(c) D < C < B < A
(d) C < D < B < A

79. Consider the equilibrium of each of the carbonyl compounds with HCN to produce cyanohydrins. Which is the correct ranking of compounds in order of increasing Keq for this equilibrium?

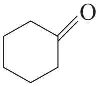
(a) 2-methylcyclohexanone < cyclohexanone < CH_3CHO < H_2CO
(b) Cyclohexanone < 2-methylcyclo hexanone < CH_3CHO < H_2CO
(c) Cyclohexanone < 2-methylcyclo hexanone < H_2CO < CH_3CHO
(d) 2-methylcyclohexanone < H_2CO < cyclohexanone < CH_3CHO

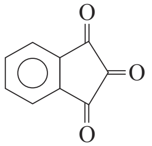
80. Which of the following does not form a stable hydrate by the addition of H_2O?

(a) CCl_3CHO

(b)


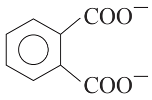
$$\text{Ph}-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle O}{\|}}{C}-\text{Ph}$$

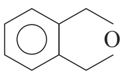
(c)


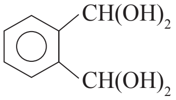
(d)


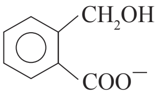
81. The reaction

Produces

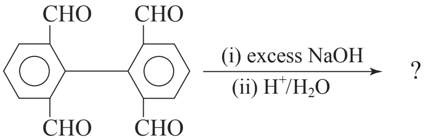
(a)


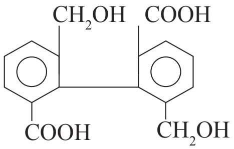
(b)


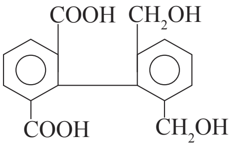
(c) 

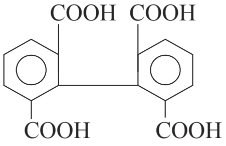
(d) 

82. Identify the product of the following reaction



(a) 

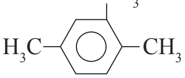
(b) 

(c) 

(d) Can be both A and C

83. A ketone reacted with C_2H_5MgBr reagent followed by hydrolysis gave a product which on dehydration gives an alkene. The alkene on ozonolysis gives
(a) diethyl ketone and acetaldehyde
(b) dimethyl ketone and formaldehyde
(c) ethyl methyl ketone and propionaldehyde
(d) none of these

84. Treatment of propionaldehyde with dil. NaOH solution gives
(a) $CH_3CH_2COCH_2CH_2CHO$
(b) $CH_3CH_2CHOHCH_2CH_2CHO$
(c) $CH_3CH_2CHOHCH(CH_3)CHO$
(d) $CH_3CH_2COOCH_2CH_2CH_3$

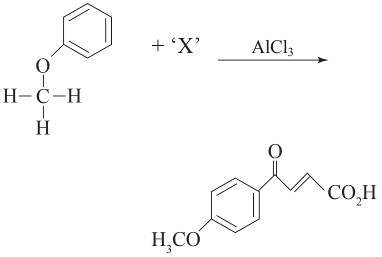
85. Acetone when distilled with conc. H_2SO_4 gives
(a) $(CH_3)_2C = CHCOCH_3$
(b) $(CH_3)_2C = CHCOCH = C(CH_3)_2$
(c) $(CH_3)_2C(OH)CH_2COCH_3$
(d) 

86. In the Cannizzaro reaction

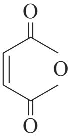
$$2PhCHO \xrightarrow{OH^-} PhCH_2OH + PhCOO^-$$

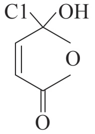
the slowest step is
(a) the abstraction of proton from the carboxylic acid
(b) the deprotonation of $PhCH_2OH$
(c) the transfer of hydride to the carbonyl group
(d) the attack of OH^- at the carboxyl group

87. The compound 'X' is



(a) $CH_2Cl.CO.CH = COOH$

(b) 

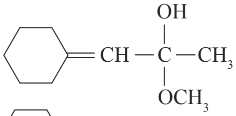
(c) 

(d) 

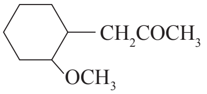
$$CH_3 - \underset{\underset{O}{\|}}{C} - CH = CH - COOH$$

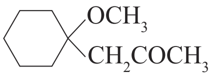
88. Consider the following reaction

The major product formed in the reaction is

(a) 

(b) 

(c) 

(d) 

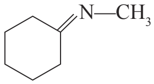
89. Identify the final product in the following sequence of reactions.

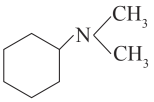
$CH_3CH_2MgBr \xrightarrow{H_2C–O–CH_2}$ (a) $\xrightarrow{H_3O^+}$

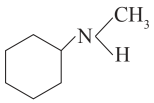
(b) $\xrightarrow{KMnO_4}$ (C)

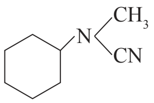
(a) $CH_3CH(CH_3)COOH$
(b) $CH_3CH_2CH_2CH_2OH$
(c) $CH_3CH_2CH_2COOH$
(d) CH_3CH_2COOH

90. Cyclohexanone is reacted with methyl amine and then with LiAlH$_4$, the final product formed is

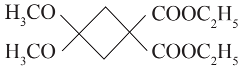
(a) 

(b) 

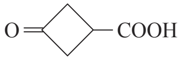
(c) 

(d) 

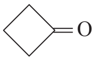
91. The final product on acid hydrolysis and decarboxylation of

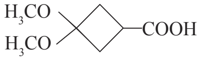


is

(a) 

(b) 

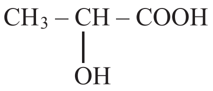
(c) 

(d) 

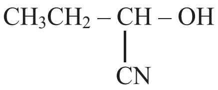
92. The structure of compound (B) is

$CH_3CHO + HCHO \xrightarrow{\text{dil. NaOH}, \Delta}$

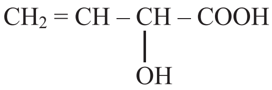
(A) $\xrightarrow{HCN, H_3O^+}$ (B)

(a) 

$CH_3-\underset{OH}{\underset{|}{CH}}-COOH$

(b) 

$CH_3CH_2-\underset{CN}{\underset{|}{CH}}-OH$

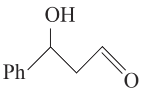
(c) 

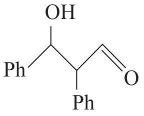
$CH_2=CH-\underset{OH}{\underset{|}{CH}}-COOH$

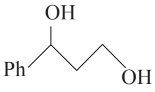
(d) 

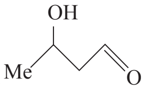
$CH_2=CH-\overset{CN}{\overset{|}{CH}}-OH$

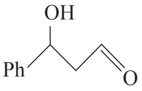
93. The product obtained by reaction of PhCHO and MeCHO are

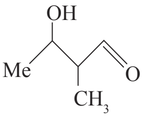
(a) 

and 

(b) 

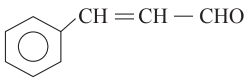
and 

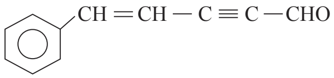
(c) 

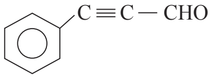
and 

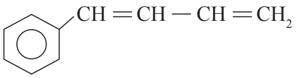
(d) none of these

94. An aldehyde, $C_{11}H_8O$ (P) which does not undergo self aldol condensation gives benzaldehyde and two moles of (Q) on ozonolysis. Compound (Q), on oxidation with silver ions gives oxalic acid. The structure of (P) is given as:

(a) 

(b) 

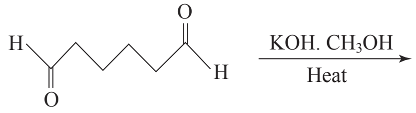
(c) 

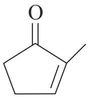
(d) 

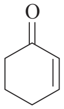
95. An organic compound 'A' has the molecular formula C_3H_6O. It undergoes iodoform test. When saturated with HCl it gives 'B' of molecular formula $C_9H_{14}O$. 'A' and 'B' respectively are

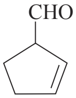
(a) Propanone and 2, 6-dimethyl-2, 5-heptadien-4-one
(b) propanone and mesitylene oxide
(c) propanal and mesitylene
(d) propanol and mesityl oxide

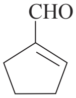
96. What is the product of the following intramolecular aldol condensation reaction?



(a) 

(b) 

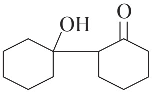
(c) 

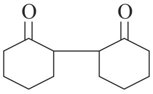
(d) 

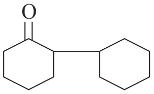
97. A compound $C_5H_{10}O$ (a) forms a phenylhydrazone and gives negative Tollen's test and a positive iodoform reaction. It gives n-pentane on reduction. The compound (a) is

(a) 3-pentanone
(b) pentanal
(c) 2-pentanone
(d) amyl alcohol

98. Cyclohexanone on reaction with sodium carbonate solution forms:

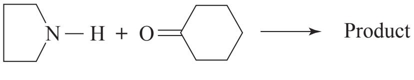
(a) 

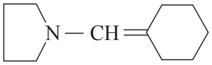
(b) 

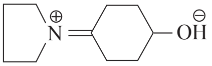
(c) 

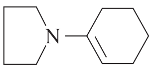
(d) Both A, and C

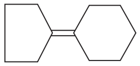
99. The structure of the product is



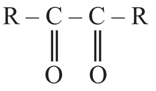
(a) 

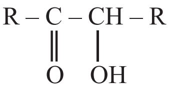
(b) 

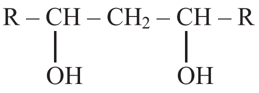
(c) 

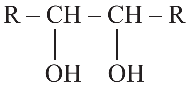
(d) 

100. Which of the following will be oxidized by HIO_4?

1. 
$R-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-R$

2. 
$R-\underset{\underset{O}{\|}}{C}-\underset{\underset{OH}{|}}{CH}-R$

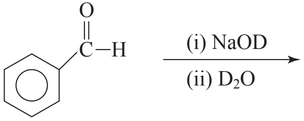
3. 
$R-\underset{\underset{OH}{|}}{CH}-CH_2-\underset{\underset{OH}{|}}{CH}-R$

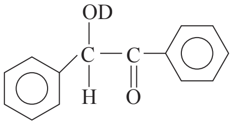
4. 
$R-\underset{\underset{OH}{|}}{CH}-\underset{\underset{OH}{|}}{CH}-R$

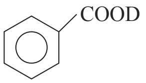
Select the correct answer using the codes below

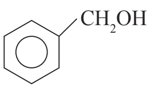
(a) 1, 2 and 4
(b) 1, 2 and 3
(c) 2, 3 and 4
(d) 1, 3 and 4

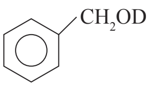
101. One of the products of the following reaction, is

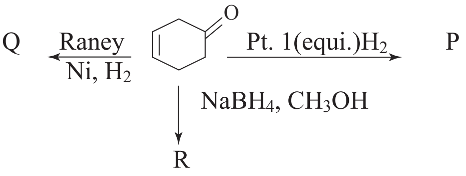


(a) 

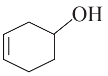
(b) 

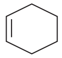
(c) 

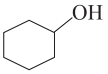
(d) 

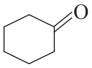
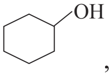
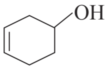
102. 

Here P , Q and R are

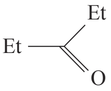
(a)  in all cases

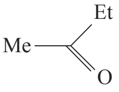
(b)  in all cases

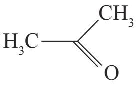
(c)  in all cases

(d) P:  , Q:  , R : 

103. A ketone A which undergoes a haloform reaction gives compound B on reduction. B on heating with H_2SO_4 gives compound C, which forms mono ozonide D. The compound D on hydrolysis in presence of zinc dust gives only acetaldehyde. A is

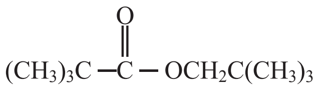
(a) 

(b) 

(c) 

(d) none

104. A carbonyl compound $C_5H_{10}O$ can show Cannizzaro's reaction. What can be its Tischenko's reaction product

(a) 
$(CH_3)_3C-\overset{\overset{\displaystyle O}{\|}}{C}-OCH_2C(CH_3)_3$

(b) $(CH_3)_3CCOO^-$

(c) $(CH_3)_3C\ CH_2OH$

(d) None of these

105. An optically active compound (P) gives haloform test and can also react with 2, 4- dinitro phenyl hydrazine. (P) can be

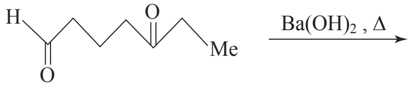
(a) $(CH_3)_2CHCOCH_3$

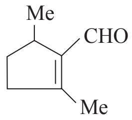
(b) $PhCH(CH_3)\ COCH_3$

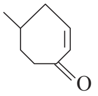
(c) $CH_3CH(OH)Et$

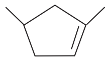
(d) $CH_3CH(Et)COCH_2CH_3$

106. Identify the major product (P) in the following reaction:



(a) 

(b) 

(c) 

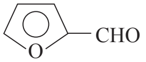
(d) None of these

107. Which of the following can undergo Cannizzaro reaction on heating with NaOH?

(I) C_6H_5CHO

(II) HCHO

(III) Cl_3C-CHO

(IV) 

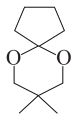
(a) I, II

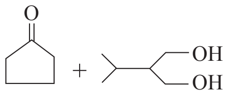
(b) I, II, III

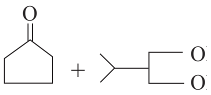
(c) I, II, IV

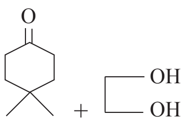
(d) I, II, III, IV

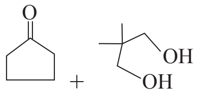
108. Which of these pair of reactants compounds may be used to make this given acetal?



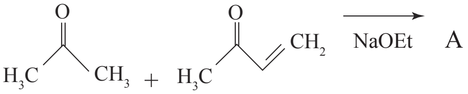
(a) 

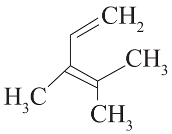
(b) 

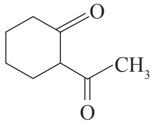
(c) 

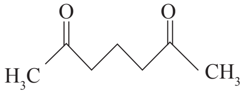
(d) 

109. In this reaction A is

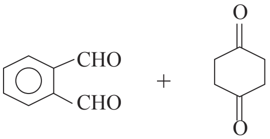


(a) 

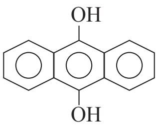
(b) 

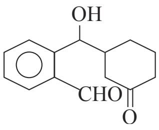
(c) 

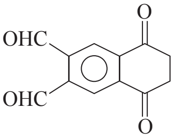
(d) EtOH

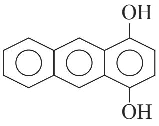
110.  OH⁻ (P),

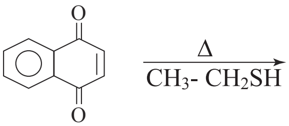
the most probable structure of (P) is

(a) 

(b) 

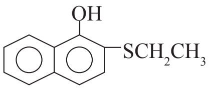
(c) 

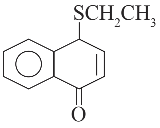
(d) 

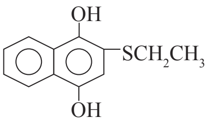
111. 

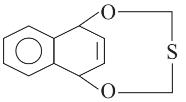
Product (P)

Here the product is given as?

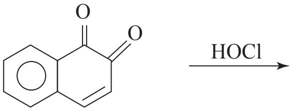
(a) 

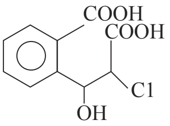
(b) 

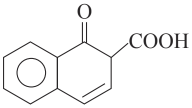
(c) 

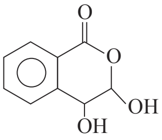
(d) 

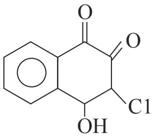
112. Product of this reaction is



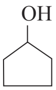
(a) 

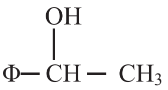
(b) 

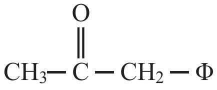
(c) 

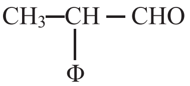
(d) 

113. Compound (P) C_4H_8O, can react with 2, 4- DNP derivative but give negative haloform test is

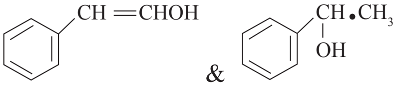
(a) 

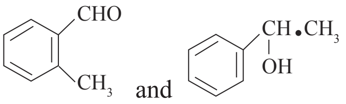
(b) 
$\Phi-\underset{}{\overset{\text{OH}}{\overset{|}{\text{CH}}}}-\text{CH}_3$

(c) 
$\text{CH}_3-\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{CH}_2-\Phi$

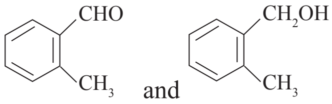
(d) 
$\text{CH}_3-\underset{\Phi}{\underset{|}{\text{CH}}}-\text{CHO}$

114. Two aromatic compound C_8H_8O (X) and $C_8H_{10}O$ (Y) are treated with sodium hypochlorite separately. The products that are formed can be distinguished by Tollen's reagent test. The compounds X and Y are

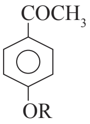
(a)


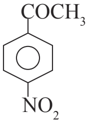
(b)


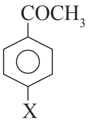
(c)

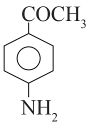

(d)


115. Which of the following shows the correct order of K_{eq} for the hydrate formation for following?

(I)


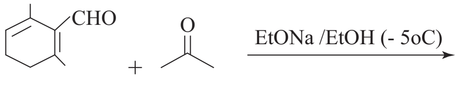
(II)


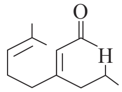
(III)


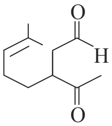
(IV)


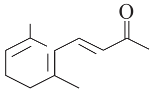
(a) I > IV > III > II
(b) II > III > IV > I
(c) III > II > I > IV
(d) II > III > I > IV

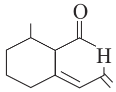
116. The structure of major product (pseudoionone) is ,

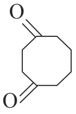


(a)


(b)


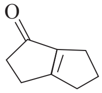
(c)


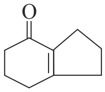
(d)


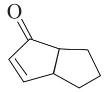
117.


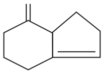
$\xrightarrow[H_2O]{H_2SO_4}$ (P),

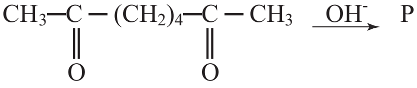
Here (P), product (P) is

(a)


(b)


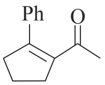
(c)


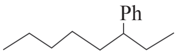
(d)


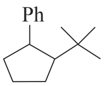
118.

$CH_3-\underset{\underset{O}{\|}}{C}-(CH_2)_4-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow{OH^-} P$

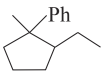
$\xrightarrow{\text{Ph -MgBr}}$ Q $\xrightarrow[\text{Conc. HCl}]{\text{Zn}-\text{Hg}}$ R

Here the product R is given as?

(a)


(b)


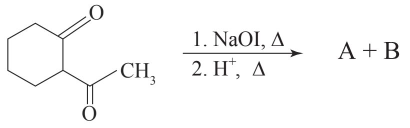
(c)


(d)


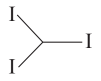
119. 'P is simplest saturated ketone which can not perform haloform reaction. 'P' on oxidation with hot $KMnO_4$ gives

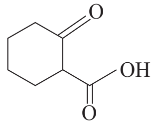
- (a) CH_3CH_2COOH only
- (b) HCOOH only
- (c) CH_3COOH and HCOOH
- (d) CH_3COOH and CH_3CH_2COOH

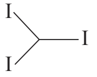
120. End products of the following sequence of reaction is

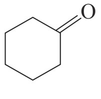


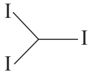
A and B are

(a)


and


(b)


and


(c)


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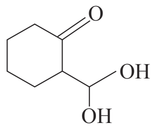
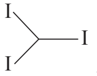


(d)


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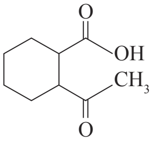
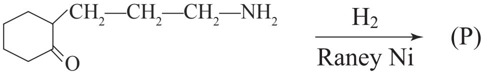
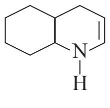


121.


Product (P) is

(a)


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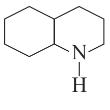
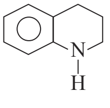
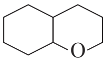
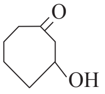
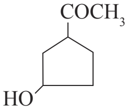


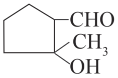
(c)


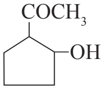
(d)


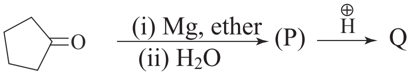
122. $CH_3COCH_2(CH_2)_2CH_2CHO$ undergoes intramolecular reaction in presence of OH^- to give

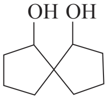
(a)


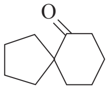
(b)


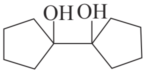
(c)


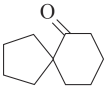
(d)


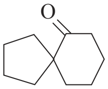
123.


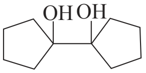
(a) P :


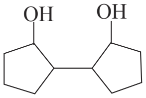
Q :


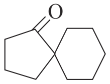
(b) P :


Q :


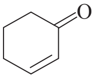
(c) P :


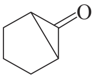
Q :


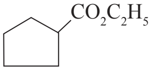
(d) P :


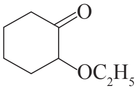
Q :


124. The major product in the reaction of 2-bromo cyclohexanone with potassium ethoxide is

(a)


(b)


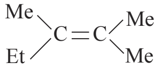
(c)


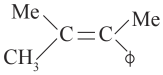
(d)


125. An aldehyde (P), ($C_{11}H_{10}O$) which does not undergo self aldol condensation gives benzaldehyde and two moles of compound (Q) on ozonolysis. Compound (Q) on oxidation with $[Ag(NH_3)_2]^+$ provides oxalic acid. The compound (P) is

- (a) 4-ene-5-phenyl-2-yne pentanal
- (b) 1-phenyl-1-ene-3-yne pentanal
- (c) 5-phenyl-2, 4-diene hexanal
- (d) 5-phenyl-2, 4-diene pentanal

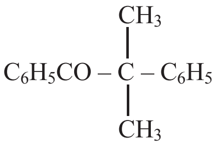
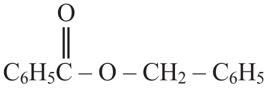
Decisive Thinking Objective Type Questions (One or more than one choice)

126. Which of the following alkene on ozonolysis can give acetone or aldehyde as one of the product
(a) Me_2C =CHMe
(b)


(c)


(d) $PhCH_2CH = CHCH_3$

127. Which one of the following pairs are correctly matched?
(a) $> C = O \rightarrow >CH_2$
Clemmensen reduction
(b) –COCl → –CHO
Rosenmund reduction
(c) $> C = O \rightarrow >CHOH$
Wolff –Kishner reduction
(d) $–C \equiv N \rightarrow$ -CHO
Stephen reduction

128. Keto-enol tautomerism is not observed in
(a) $C_6H_5COC_6H_5$
(b) $C_6H_5COCH_3$
(c)

$C_6H_5CO - C(CH_3)_2 - C_6H_5$
(d)

$C_6H_5C(=O) - O - CH_2 - C_6H_5$

129. Indicate the incorrect statement.
(a) 2- methyl propnal can show cannizaro reaction
(b) $C_6H_5 - CH = CH - CO - CH_3$ undergoes 1,4-addition with C_6H_5MgBr in preference to 1,2-addiiton with the same reagent
(c) oxidation of cyclic ketone by Caro's acid (H_2SO_5) to yield cyclic lactones is known as Riley's reaction
(d) disopropyl ketone is unreactive towards CH_3MgI because of steric blocking

130. Which of the following is/are correct?
(a) Fehling solution is used in detection of glucose.
(b) $NaHSO_3$ is used in detection of carbonyl compounds.
(c) $FeCl_3$ is used in detection of phenols.
(d) Tollen's reagent is used in detection of unsaturation.

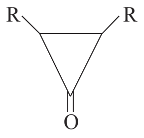
131. Which is true about acetophenone?
(a) reacts with I_2/NaOH to form iodoform
(b) reacts with Tollen's reagent to form silver mirror
(c) on oxidation with alkaline $KMnO_4$ followed by hydrolysis gives benzoic acid
(d) reacts to form 2, 4-dinitrophenyl-hydrazone

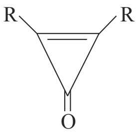
132. Which of the following statements regarding chemical properties of acetophenone are wrong?
(a) it is reduced to methylphenylcarbinol by sodium and ethanol
(b) it is oxidized to benzoic acid with acidified $KMnO_4$
(c) it does not undergo electrophillic substitution like nitration at meta position.
(d) it does not undergo iodoform reaction with iodine and alkali.

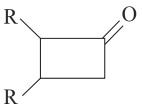
133. The compound which can be reduced by $LiAlH_4$ is
(a) 2-Methyl-butan 1-ol
(b) Cyclohexanone
(c) ω-capralactam
(d) Methyl benzoate

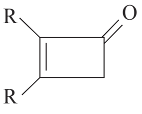
134. When the carbonyl group of a neutral ketone is protonated
(a) The resulting species has a positive charge.
(b) The resulting species is activated toward nucleophillic attack.
(c) Subsequent nucleophillic attack on the resulting species is said to occur under acid-catalysed conditions.
(d) Here rearrangement may take place in case of less stable carbocation.

135. Which of the following compounds does not give an aromatic salt on treatment with $HClO_4$?

(a)


(b)


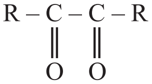
(c)


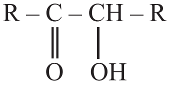
(d)


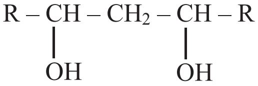
136. Which of following pairs can be differentiated by Tollen's reagent?
(a) Benzaldehyde and benzyl alcohol
(b) Pentanal and diethyl ether

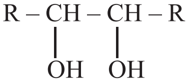
(c) 2- pentanol and 2- petnanone
(d) Pentanal and 2- petnanone

137. Which of the following will be oxidized by HIO_4?

(a) 
$R-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-R$

(b) 
$R-\underset{\underset{O}{\|}}{C}-\underset{\underset{OH}{|}}{CH}-R$

(c) 
$R-\underset{\underset{OH}{|}}{CH}-CH_2-\underset{\underset{OH}{|}}{CH}-R$

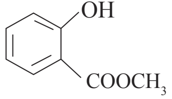
(d) 
$R-\underset{\underset{OH}{|}}{CH}-\underset{\underset{OH}{|}}{CH}-R$

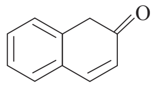
138. Acetophenone can be prepared by
(a) oxidation of 1-phenylethanol.
(b) reaction of benzaldehyde with methyl magnesium bromide.
(c) Friedal Crafts reaction of benzene with acetyl chloride.
(d) Distillation of calcium benzoate.

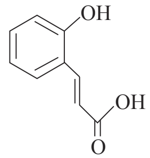
139. Which one of the following statements is/are correct? Benzaldehyde can be produced by the
(a) reduction of benzoyl chloride.
(b) oxidation of toluene.
(c) hydrolysis of benzal chloride.
(d) reduction of benzyl chloride.

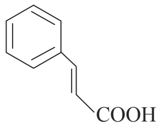
140. Which of the following can undergo aldol condensation?
(a) CCl_3-CHO
(b) $C_6H_5CH_2CHO$
(c) $ClCH_2CHO$
(d) $C_6H_5COC_6H_5$

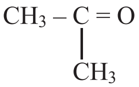
141. Which of the following are examples of aldol condensation?
(a) $2CH_3CHO \xrightarrow{\text{dil. NaOH}} CH_3CHOHCH_2CHO$
(b) $2CH_3COCH_3 \xrightarrow{\text{dil NaOH}} CH_3COH(CH_3)CH_2COCH_3$
(c) $2HCHO \xrightarrow{\text{dil. NaOH}} CH_3OH + HCOOH$
(d) $C_6H_5CHO + HCHO \xrightarrow{\text{dil NaOH}} C_6H_5CH_2OH$

142. When salicyldehdye is treated with anhydride in presence of sodium ethanoate
(a) the product formed is


(b) the product formed is


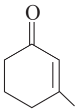
(c)  is formed as a intermediate to finally condense and form the product.

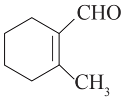
(d) the product is


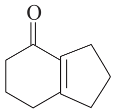
143. Which one of the following compound can undergo Aldol condensation?
(a) 
$CH_3-\underset{\underset{CH_3}{|}}{C}=O$

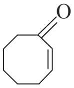
(b) CH_3-CHO
(c) $C_6H_5-CH_2-CHO$
(d) C_6H_5CHO

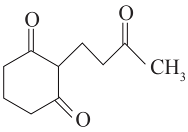
144. Which of the following compounds can be synthesized by intramolecular aldol condensation in very good yield (as a major product)?

(a) 

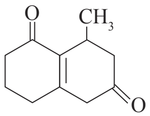
(b) 

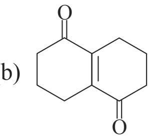
(c) 

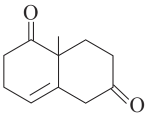
(d) 

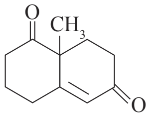
145. 

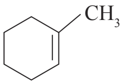
on aldol condensation followed by heating is not capable of giving:

(a) 

(b) 

(c) 

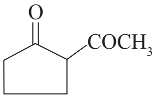
(d) 

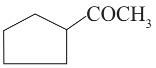
146. 

$$\begin{tikzcd} \xrightarrow{O_3 \text{ ozonolysis}} A \xrightarrow{\text{dil. } OH^-} B \xrightarrow{\text{oxidation}} C \arrow[r, "NaOEt"] & {} \arrow[r, "H_3O^+"] \arrow[d] & D \\ & E & \end{tikzcd}$$

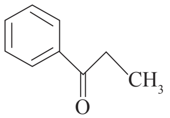
(a) D can be open chain structure while E a close ring structure

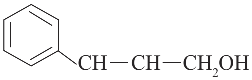
(b) A is 2 keto-heptanol

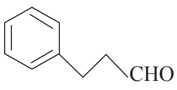
(c) is 

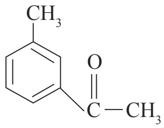
(d) B is 

147. Compound X having molecular formula $C_9H_{10}O$ is inert to Br_2 (CCl_4). Vigorous oxidation with hot alkaline $KMnO_4$ yields benzoic acid. X gives a precipitate with semicarbazide which is/are the possible structure of 'X'.

(a) 

(b) 

(c) 

(d) 

148. $3HCHO + CH_3CHO \xrightarrow{NaOH}$ Product (P)

P formed can:

(a) give Cannizzaro reaction

(b) reduce Tollen's reagent

(c) give green colour $Cr_2O_7^{-2}/H^+$

(d) react with Na

149. Which compound can give cannizzaro's reaction?

(a) trichloro acetaldehyde

(b) benzaldehyde

(c) formaldehyde

(d) acetaldehyde

150. Under Wolff-Kishner reduction conditions, the conversions which may be brought about are

(a) Benzophenone into diphenylmethane

(b) Benzaldehyde into benzyl alcohol

(c) Cyclohexanone into cyclohexane

(d) Cyclohexanone into cyclohexanol

151. Indicate among the following the correct formulation is/are

(a) $2R\text{-}CHO + H_2N - NH_2 \rightarrow R - CH = N - N = CH - R$

(b) acetophenone oxime $\xrightarrow{H_2SO_4\text{ , }100^\circ C}$ Acetanilide by rearrangement

(c) $2NH_3 + 3CH_2O \rightarrow CH_2 (N = CH_2)_2$

(d) $CH_3CHO + C_6H_5 - NH - NH_2 \rightarrow CH_3 - CH = NH - C_6H_5$

152. A compound X of molecule formula C_8H_8O is treated with two equivalents of Br_2 in ethane at 0^oC in presence of base to give a substituted product y (mol. formula $C_8H_6OBr_2$). Compound Y on treatment with alkali followed by HCl form α-hydroxy acid Z. (mol. formula CH_8O_3). 'X' forms oxime as well as give positive iodoform test.

(a) Y is $C_6H_5 - CBr_2 - CHO$

(b) X is $C_6H_5 - CO - CH_3$

(c) Z is $C_6H_5 - CHOH - COOH$

(d) Y must have undergone intermolecular cannizzaro reaction to form finally Z.

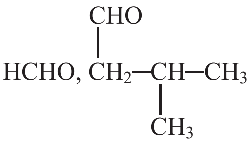
Linked-Comprehension Type Questions

Comprehension 1

An alkene (A) with a molecular formula C_5H_{10} on ozonolysis gives two molecules of carbonyl compounds (B, C). Both B and C are capable of showing Haloform reaction. When (b) is treated with dil. NaOH we got another unsaturated carbonyl compound (D). Compound C is unable to reduce. Tollen's reagent and on treatment with HCl gas at low temperature it gives a carbonyl compound (E) with two (= bonds) between C- atoms.

153. Here the alkenes (A) can be given as
- (a) Pent 2- ene
- (b) 2- methyl but -2- ene
- (c) 2- methyl but 1- ene
- (d) n- pentene

154. Here compound B and C are respectively.

(a) 

$$HCHO,\ \overset{\text{CHO}}{\overset{|}{CH_2}}-\underset{\underset{CH_3}{|}}{CH}-CH_3$$

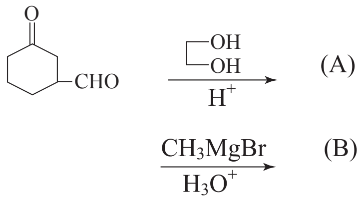
- (b) CH_3-CHO, CH_3-CH_2-CHO
- (c) CH_3CHO, CH_3COCH_3
- (d) CH_3COCH_3, CH_3CHO

155. Which statement is not correct here?
- (I) The I.U.P.A.C name of compound is but -2-en 1-al
- (II) The n I.U.P.A.C. name of compound (E) is 4-methyl pent -3- en -2- one
- (III) The n I.U.P.A.C. name of compound (E) is 2, 6dimethyl hepta -2, 5- di-en -4- one
- (IV) The compound (D) contains 3 sp^2 hybridised C- atoms and have 10 σ, 3π bonds.
- (a) I, III only
- (b) I, II, III
- (c) I, III ,IV
- (d) I, IV only

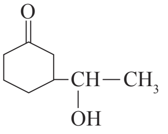
Comprehension 2

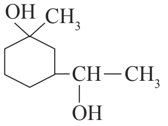
Grignard addition to carbonyl compounds is a specific case of nucleophillic addition reaction which leads to formation of all type of alcohols (p°, s°, t°). In this addition the strongly nucleophillic Grignard reagent uses its electron pair to form a bond with the C -atom of $>C=O$ group, where one e^- pair of $>C=O$ group. shifts out towards oxygen. It results in the formation of an intermediate species in which alkoxide ion associated with Mg^{2+} and X^-. Now addition of a aq. HX causes protonation of this species to give alcohol.

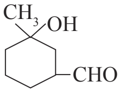
156.



Here the product (B) can be given as

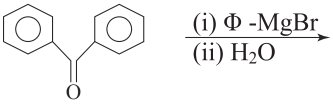
(a) 

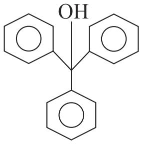
(b) 

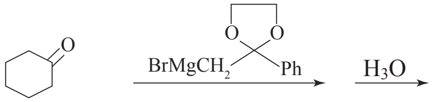
(c) 

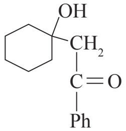
(d) all of these

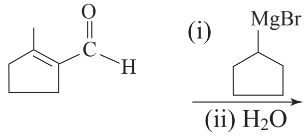
157. In which of the following reaction product formed is correctly given?

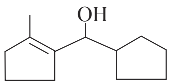


(I) 

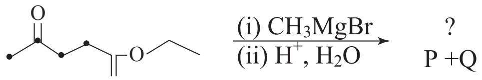


(II) 

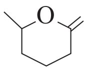


(III) 

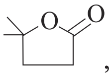
- (a) I, II
- (b) II, III
- (c) I, III
- (d) I, II, III

158. 

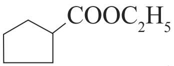
Here P and Q are respectively:

(a) 

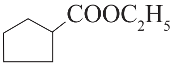
, CH_3-CH_2OH

(b) 

, C_2H_5OH

(c) 

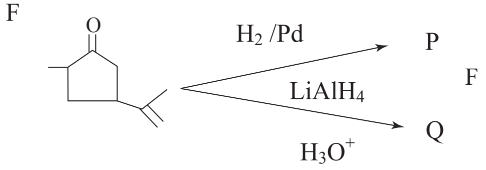
, C_2H_5OH

(d) 

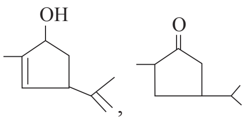
, CH_3OH

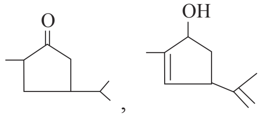
Comprehension 3

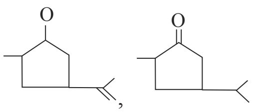
The reduction of carbonyl compounds into alcohols by hydrogen and a metal catalyst, Na/C_2H_5OH $LiAlH_4$, $NaBH_4$ is of great importance. The main step involve in the reduction of carbonyl compounds with $NaBH_4$ or $LiAlH_4$ is the transfer of a hydride ion from the metal to the carbonyl carbon. In this step the hydride ion behaves like a nucleophile. In presence of other functional groups like -COOH, -COOR etc. It is better to use $NaBH_4$.

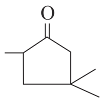
159. 

Here P and Q are respectively?

(a) 

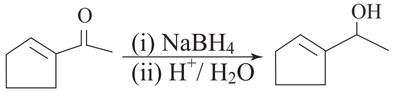
(b) 

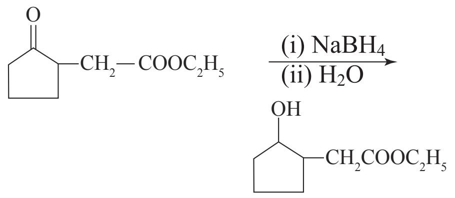
(c) 

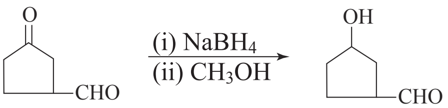
(d) 

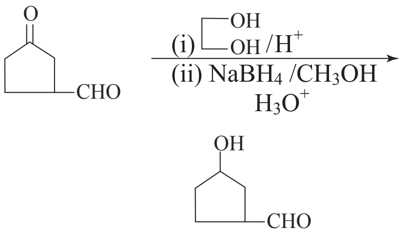
only A

160. Reactant Product

(I) 

(II) 

(III) 

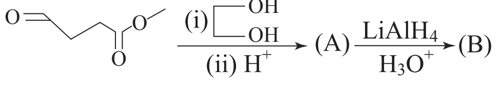
(IV) 

Which of the above reactions give correct product?

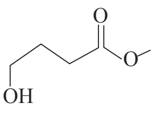
(a) I, II, III (b) I, II, IV

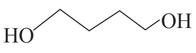
(c) II, III, IV (d) I, II only

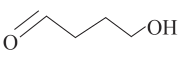
161. F

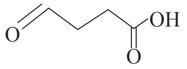


Here the compound (B) is?

(a) 

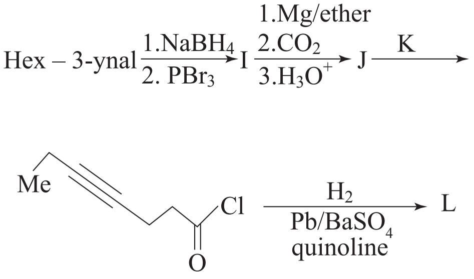
(b) 

(c) 

(d) 

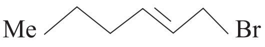
Comprehension 4

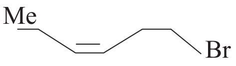
In the following reaction sequence products I, J and L are formed. K represents a reagent. **[I.I.T.-J.E.E. 2008]**



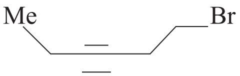
$$\text{Hex – 3-ynal} \xrightarrow[2.\ PBr_3]{1.NaBH_4} I \xrightarrow[3.H_3O^+]{1.Mg/ether \quad 2.CO_2} J \xrightarrow{K}$$

162. The structure of the product I is

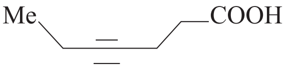
(a) 

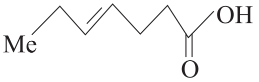
(b) 

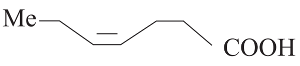
(c) 

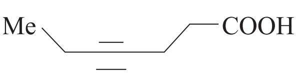
(d) 

163. The structures of compound J and K, respectively, are

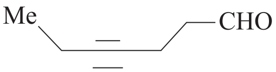
(a)  and $SOCl_2$

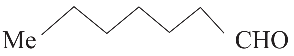
(b)  and SO_2Cl_2

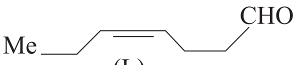
(c)  and $SOCl_2$

(d)  and CH_3SO_2Cl

164. The structure of product L is

(a) 

(b) 

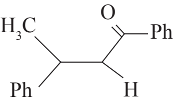
(c) 

(L)

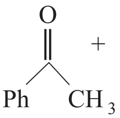
(d) 

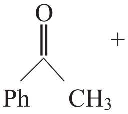
Comprehension 5

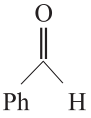
At tertiary alcohol H upon acid catalysed dehydration gives a product I. Ozonolysis of I leads to compounds J and K. Compound J upon reaction with KOH gives benzyl alcohol and s compound L, whereas K on reaction with KOH gives only M. **[I.I.T.-J.E.E. 2008]**

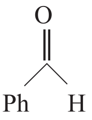
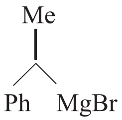
M = 

165. Compound H is formed by the reaction of

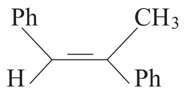
(a)  + PhMgbr

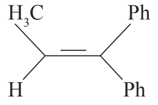
(b)  + $PhCH_2Mgbr$

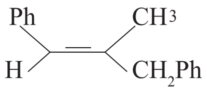
(c)  + Ph CH_2Mgbr

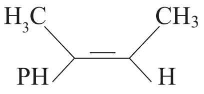
(d)  + 

166. The structure of compound I is

(a)


(b)


(c)


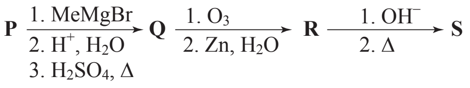
(d)


167. The structure of compound J, K and L, respectively

- (a) $PhCOCH_3$, $PhCH_2COCH_3$ and $PhC_2COO^-K^+$
- (b) $PhCHO$, $PhCH_2CHO$ and $PhCOO^-K^+$
- (c) $PhCOCH_3$, $PhCH_2CHO$ and $CH_3COO^-K^+$
- (d) $PhCHO$, $PhCOCH_3$ and $PhCOO^-K^+$

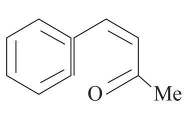
Comprehension 6

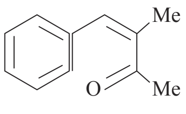
A carbonyl compound **P**, which gives positive iodoform test, undergoes reaction with MeMgBr followed by dehydration to give an olefin **Q**, Ozonolysis of **Q** leads to a dicarbonyl compound **R**, which undergoes intermolecular aldol reaction trop give predominantly **S**. **[IIT 2009]**

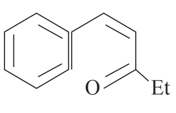


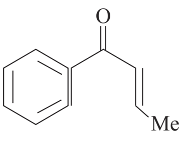
$$\mathbf{P} \xrightarrow[\substack{2.\ H^+,\ H_2O \\ 3.\ H_2SO_4,\ \Delta}]{1.\ MeMgBr} \mathbf{Q} \xrightarrow[2.\ Zn,\ H_2O]{1.\ O_3} \mathbf{R} \xrightarrow[2.\ \Delta]{1.\ OH^-} \mathbf{S}$$

168. The structure of the carbonyl compound P is

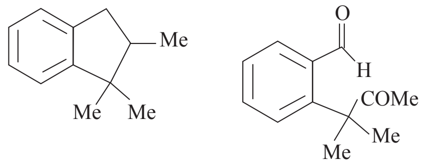
(a)


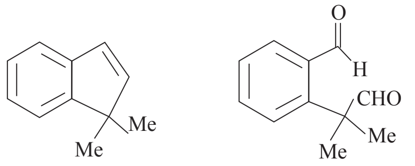
(b)


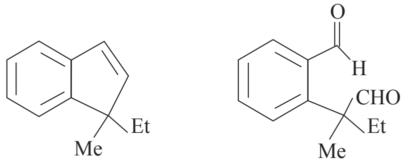
(c)


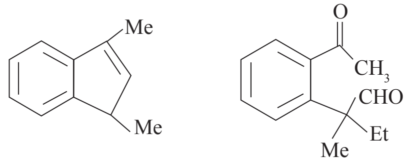
(d)


169. The structure of the product S, Q and R, respectively, are

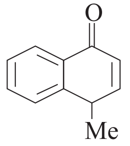
(a)


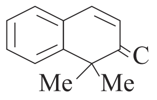
(b)


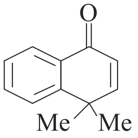
(c)


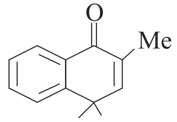
(d)


170. The structure of the product S is

(a)


(b)


(c)


(d)


Assertion-Reason Type Questions

In the following question two statements (Assertion) A and Reason (R) are given Mark.

- (a) if A and R both are correct and R is the correct explanation of A;
- (b) if A and R both are correct but R is not the correct explanation of A;
- (c) A is true but R is false;
- (d) A is false but R is true,

171. (A): In aldol condensation the final product is always α, β- unsaturated carbonyl compound.
(R): α, β-unsaturated carbonyl compounds are stabilized due to conjugation.

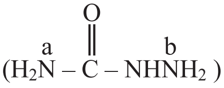
172. (A): Although ketones do not reduce Tollen's reagent and Fehling's solution but α –hydroxyketones give positive test.
(R): Secondary alcoholic group of α-hydroxy ketones gets oxidized to ketonic group.

173. (A): Benzaldehyde does not give Fehling's test.
(R): Benzaldehyde is a weak reducing agent.

174. (A): Crossed aldol condension between two different ketones is quite rare
(R): In ketones reactivity of $>C=O$ gp. is poar due to it effect and space crowding

175. (A): In the addition of Grignard reagent to carbonyl compound, the R group of RMgX attacks carbonyl carbon.
(R): The carbon magnesium bond of the Grignard reagent is highly polar, carbon being negative relative to electropositive magnesium.

176. (A): Cyanohydrin obtained from reaction of HCN in dilute alkaline medium with acetaldehyde is racemic mixture.
(R): Cyanohydrin obtained above is formed by attack of CN^- on planar $>C=O$ group.

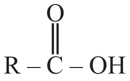
177. (A): Semicarbazide 
$(\overset{a}{H_2N} - \overset{O}{\overset{\|}{C}} - \overset{b}{NHNH_2})$
attacks in carbonyl group through nitrogen atom labeled as 'a'.
(R): Nitrogen labeled 'b' is having more nucleophilicity.

178. (A): Methyl n-propyl ketone and diethyl ketone can be distinguished by haloform test.
(R): Methyl ketones give haloform reaction.

179. (A): 4,4-Dimethyl-2-pentanone cannot be easily prepared from aceto acetic ester.
(R): $(CH_3)_3$ CBr is a tertiary alkyl halide which due to steric effect, prefers elimination rather than substitution.

180. (A): When chloral is heated with conc. potassium hydroxide, it yields
$[CCl_3 - COO^-$ and $CCl_3CH_2OH]$
(R): In the cannizaro's reaction hydride transfer is the slowest step.

181. (A): Unlike the $>C=O$ group of aldehdye and ketones, the $>C=O$ group of


$R - \overset{O}{\overset{\|}{C}} - OH$

Does not undergo nucleophillic addition reactions.
(R): Carboxylic acids exists as dimmers due to intermolecular hydrogen bonding.

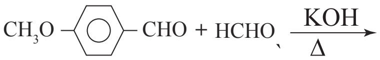
182. (A): 2,2-dimethylpropanal undergoes Cannizzaro reaction with concentrated NaOH.
(R): Cannizzaro is a disproportionation reaction.

183. (A): Acetaldehyde undergoes aldol condensation with dilute NaOH.
(R): Aldehydes which do not contain α-hydrogen undergo aldol condensation.

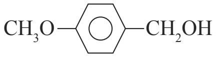
184. (A): Ketones are less reactive than aldehydes.
(R): Ketones go not give Schiff's test.

185. (A): Presence of acids and bases activates carbonyl compounds for reaction.
(R): Carbonyl compound possess positive and negative centres and provide seat for electrophillic and nucleophilic attack.

186.

(A): 

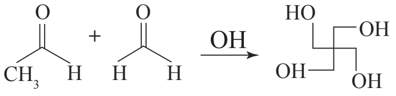
Expected major product from the above reaction is and $HCOO^-K^+$



(R): With increase in electrophilicity on $> C = O$ group, rate of attack of nucleophile increases.

187. (A): Benzaldehyde gives a positive test with Benedict's and Fehling solution.

(R): Benzaldehyde forms black precipitate or silver mirror with Tollen's reagent.

188. (A): 

(R): Intramolecular aldol forms in presence of dil. alkali.

189. (A): Palladium chloride and cupric chloride are used as catalysis in oxo process.
(R): Oxo process is also called hydroformylation reaction.

190. (A): p-dimethylamino-benzaldehyde does not undergo benzoin condensation.
(R): The aldehydic-(-CHO) group is meta directing.

191. **(A):** PhCHO upon reaction by 2 mole in presence of Al $(OEt)_3$ gives an ester

(R): In presence of $Al(OEt)_3$ intramolecular hydride shift takes place

Matrix-Match Type Questions

192. Match the following:

Column I (Compound)

(a) Bakelite
(b) Urotropine
(c) Chloretone
(d) Benzoin

Column II (Possible component)

(p) Benzaldehyde
(q) Acetaldehyde
(r) Acetone
(s) Formaldehyde

193. Match the following:

Column I

(a) $RCHO + 2R'OH \xrightarrow{\text{dry HCl gas}}$

(b) $R_2C = O + R'NH_2 \longrightarrow$

(c) $RCH = O$ (or $R_2C = O$) + Phenyl hydrazine $\xrightarrow{H^+}$

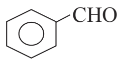
(d) $PhCHO + NH_2OH \xrightarrow{H^+}$

Column II

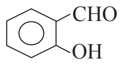
(p) Benzaldehyde oxime
(q) A phenyl hydrazone
(r) A Schiff's base
(s) An acetal

194. Match the following:

Column I

(a) 

(b) CH_3COCH_3
(c) HCHO

(d) 

Column II

(p) Fehling solution
(q) Schiff base
(r) Tollen's reagent
(s) Iodoform test
(t) 2, 4- dinitrophenyl hybridizing test

195. Match the following:

Column I

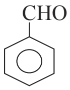
(a) CH_3COCHO
(b) 1, 2-cyclohexanedione
(c) PhCH(OH)CHO
(d) $CH_3CH_2CH(OH)COCH_3$

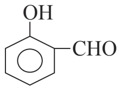
Column II

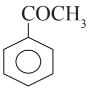
(p) $PhCH = O + HCOOH$
(q) $CH_3CH_2CHO + HOOCCH_3$
(r) $HOOC(CH_2)_4COOH$
(s) $CH_3COOH + HCOOH$

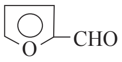
196. Match the following:

Column I

(a) 

(b) 

(c) 

(d) 

Column II

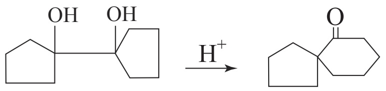
(p) Perkin reaction
(q) Cannizaro's reaction
(r) Aldol condensation
(s) Haloform reaction

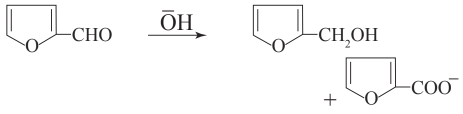
197. Match the following:

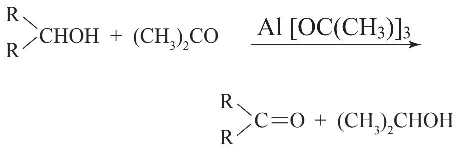
Column I

(a) Rosen mond's reaction
(b) Cannizaro's reaction
(c) Oppenauer oxidation
(d) Pinacole-pinacolone rearrangement

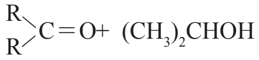
Column II

(p) 

(q) 

(r) 

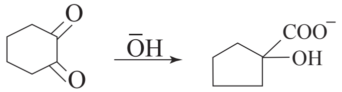
$$\begin{matrix}R\\R\end{matrix}\!\!>CHOH + (CH_3)_2CO \xrightarrow{Al[OC(CH_3)_3]_3} \begin{matrix}R\\R\end{matrix}\!\!>C{=}O + (CH_3)_2CHOH$$



$R_2C=O + (CH_3)_2CHOH$

(s) $R-COCl \xrightarrow[\text{Pd/BaSO}_4\text{ quinoline}]{H_2} R-CHO + HCl$

(t)



198. Match the following:

Column I

(a) Formalin

(b) Trioxane

(c) Ketene

(d) Metaldehyde

Column II

(p) Trimer of HCHO

(q) Compounds of the general formula, $R_2C = C = O$

(r) A tetramer of acetaldehyde

(s) 40 % aqueous solution of HCHO

199. Match the following:

Column I

(a) Aldol condensation

(b) Cannizaro reaction

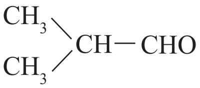
(c) Beckmann's rearrangement

(d) Tischenko reaction

Column II

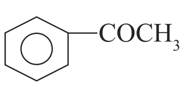
(p) CH_3CHO

(q)

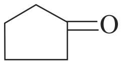


$(CH_3)_2CH-CHO$

(r)



(s)



200. Match the following:

Column I

(a) Hyponone

(b) Pyrene

(c) Urotropine

(d) Salol

Column II

(p) Insecticide

(q) Internal antiseptic

(r) Urinary problem

(s) Perfumery

(t) Fire extinguisher

201. Match the following:

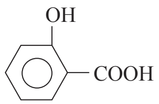
Column I (reaction)

(a) $C_6H_5CHO + NaOH \longrightarrow C_6H_5COOH + C_6H_5CH_2OH$

(b) $C_6H_6 + CH_3Cl \xrightarrow{\text{Anhyd. AlCl}_3} C_6H_5CH_3$

(c) $RCOCl + H_2 \xrightarrow{Pd / BaSO_4} RCHO$

(d) $C_6H_5OH + NaOH + CO_2 \xrightarrow{1.\ heat,\ 2.\ H^+}$



Column II (name of reactions)

(p) Rosenmund reduction

(q) Kolbe's reaction

(r) Claisen reaction

(s) Cannizzaro reaction

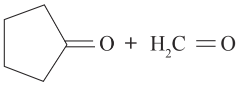
(t) Friedal-Craft's reaction

202. Match the following:

Column I

(a) $PhCH = O + CH_3COCH_3$

(b)



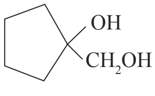
(c) $2H_2C = O + HCOOH$

(d) $O = CH(CH_2)_3CH = O$

Column II

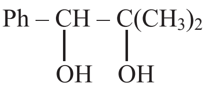
(p) Cyclopentane-1,2-diol

(q)



(r) Glycerol

(s)

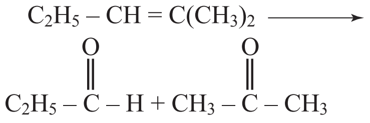


$Ph-CH(OH)-C(OH)(CH_3)_2$

203. Match the following:

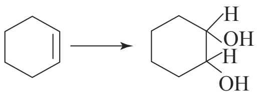
Column I

(a)

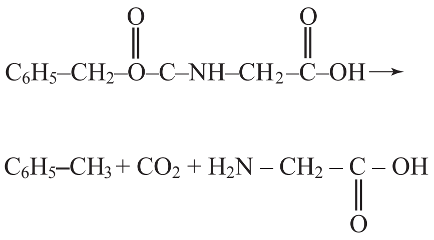


$C_2H_5-CH=C(CH_3)_2 \longrightarrow C_2H_5-\overset{\overset{O}{\|}}{C}-H+CH_3-\overset{\overset{O}{\|}}{C}-CH_3$

(b)

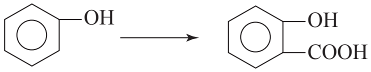


(c)



$C_6H_5-CH_2-O-\overset{\overset{O}{\|}}{C}-NH-CH_2-\overset{\overset{O}{\|}}{C}-OH \longrightarrow C_6H_5-CH_3+CO_2+H_2N-CH_2-\underset{\underset{O}{\|}}{C}-OH$

(d)



Column II

(p) $KMnO_4$

(q) $CHCl_3$ + aq. NaOH

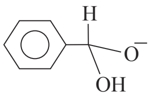
(r) O_3 .Zn + H_2O

(s) H_2/Pd – C

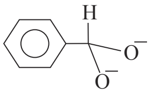
The IIT-JEE Corner

204. In a Cannizzaro reaction, the intermediate that will be best hydride donor is

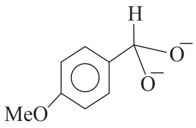
(a)



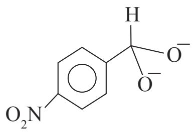
(b)



(c)



(d)



[IIT 1997]

205. Which of the following will give yellow precipitate with I_2/NaOH?

1. $ICH_2COCH_2CH_3$	2. $CH_3COOCOCH_3$
3. CH_3CONH_2	4. $CH_3CH(OH)CH_2CH_3$
(a) 1, 3	(b) 3, 4
(c) 1, 2	(d) 1, 4

[IIT 1997]

206. Which of the following undergoes aldol condensation?

1. Acetaldehyde
2. Propionaldehyde
3. Benzaldehyde
4. Trideuteroacetaldehyde.

(a) 1, 2	(b) 1, 2, 3
(c) 1, 2, 4	(d) 2, 4

[IIT 1998]

207. A new carbon-carbon bond formation is possible in

1 Cannizzro reaction
2 Feirdel-Craft's reaction
3 Clemmensen reduction
4 Reimer – Teimann reaction

(a) 2, 4	(b) 1, 2
(c) 2, 3	(d) 1, 2, 4

[IIT 1998]

208. Which of the following will react with water:

(a) $CHCl_3$	(b) Cl_3CCHO
(c) CCl_4	(d) $ClCH_2CH_2Cl$

[IIT 1998]

209. Which of the following reagents converts C_6H_5CO-CHO to $C_6H_5CH(OH)COOH$?

(a) aq. NaOH	(b) Acidic Na_2SO_3
(c) Na_2CrO_4/H_2SO_4	(d) $NaNO_2$/HCl

[IIT 1998]

210. The product (s) obtained via oxymercuration ($HgSO_4$ + H_2SO_4) of But-1-yne would be

(a) $CH_3CH_2COCH_3$

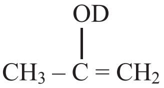
(b) $CH_3CH_2CH_2CHO$

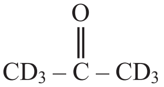
(c) CH_3CH_2CHO + HCHO

(d) CH_3CH_2COOH + HCOOH

[IIT 1999]

211. The enol form of acetone, after treatment with D_2O, gives:

(a) 
$CH_3-\overset{\overset{\displaystyle OD}{|}}{C}=CH_2$

(b) 
$CD_3-\overset{\overset{\displaystyle O}{\|}}{C}-CD_3$

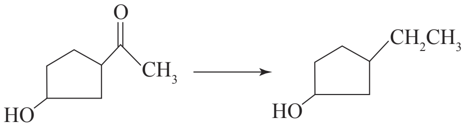
(c) $CH_2=C-CH_2D$
(d) $CD_2=C-CH_2D$

[IIT 1999]

212. Which of the following has the most acidic hydrogen?
(a) 3-Hexanone
(b) 2, 4-Hexanedione
(c) 2, 5-Hexanedione
(d) 2, 3-Hexanedione

[IIT 2000]

213. The appropriate reagent for the transformation



(a) Zn(Hg), HCl	(b) NH_2NH_2, OH^-
(c) H_2/Ni	(d) $NaBH_4$

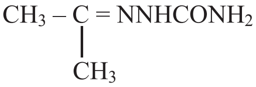
[IIT 2000]

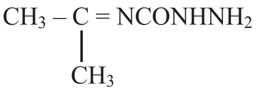
214. A mixture of benzaldehyde and formaldehyde on heating with aqueous NaOH solution gives
(a) Benzyl alcohol and sodium formate
(b) sodium benzoate and methyl alcohol
(c) sodium benzoate and sodium formate
(d) benzyl alcohol and methyl alcohol.

[IIT 2001]

215. Compound 'A' (molecular formula C_3H_8O) is treated with acidified potassium dichromate to form a product 'B' (molecular formula C_3H_6O). 'B' forms a shining silver mirror on warming with ammonical silver nitrate. 'B' when treated with an aqueous solution of $H_2NCONHNH_2$ HCl and sodium acetate gives a product 'C'. Identify the structure of 'C'.

(a) $CH_3CH_2CH=NNHCONH_2$

(b) 
$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{C}=NNHCONH_2$

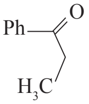
(c) 
$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{C}=NCONHNH_2$

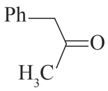
(d) $CH_3CH_2CH=NCONHNH_2$.

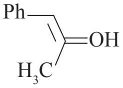
[IIT 2002]

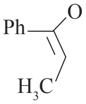
216. Ph —C≡ C—CH_3 $\xrightarrow{Hg^{2+}/H^+}$ A, A is

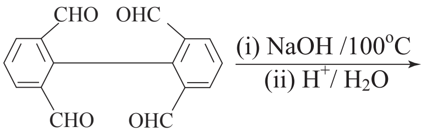
[2003]

(a) 

(b) 

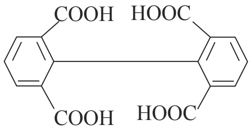
(c) 

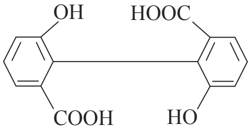
(d) 

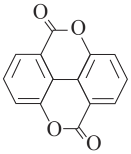
217. 

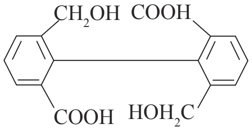
Major product is:

[2003]

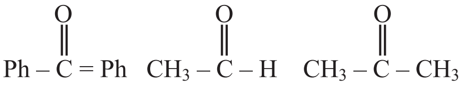
(a) 

(b) 

(c) 

(d) 

218. The correct order of reactivity of PhMgBr with



$$Ph-\overset{\overset{O}{\|}}{C}=Ph \quad CH_3-\overset{\overset{O}{\|}}{C}-H \quad CH_3-\overset{\overset{O}{\|}}{C}-CH_3$$

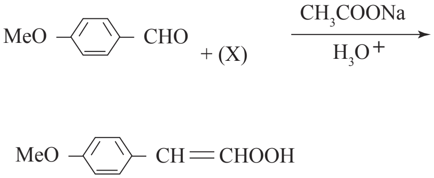
(I) (II) (III)

is

(a) I > II > III (b) III > II > I
(c) II > III > I (d) I > III > II

[IIT 2004]

219.



[2005]

the compound (X) is:

(a) CH_3 — COOH
(b) $BrCH_2$ —COOH
(c) $(CH_3CO)_2O$
(d) CHO — COOH

220. How will you convert butan -2 -one to propanoic acid? [2005]

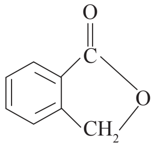
(a) Tollen's reagent (b) Fehling solution
(c) NaOH/I_2/H^+ (d) NaOH/NaI/H^+

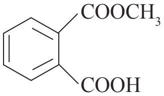
221. The smallest ketone and its next homologue are reacted with NH_2OH to form oxime.

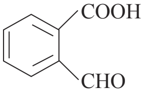
(a) two different oximes are formed
(b) three different oximes are fomed
(c) two oximes are optically active
(d) all oximes are optically active

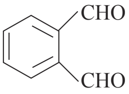
[IIT 2006]

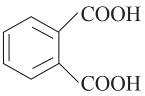
222. Which of the following reactants on reaction with conc. NaOH followed by acidification gives the following lactone as the only product?



(a)


(b)


(c)


(d)


[IIT 2006]

ANSWERS

Straight Objective Type Questions

1. (c) **2.** (c) **3.** (c) **4.** (c) **5.** (a) **6.** (a) **7.** (d) **8.** (a) **9.** (a) **10.** (b) **11.** (b) **12.** (d)
13. (a) **14.** (b) **15.** (a) **16.** (c) **17.** (c) **18.** (b) **19.** (d) **20.** (c) **21.** (d) **22.** (d) **23.** (c) **24.** (d)
25. (b) **26.** (c) **27.** (d) **28.** (b) **29.** (d) **30.** (c) **31.** (b) **32.** (d) **33.** (b) **34.** (d) **35.** (b) **36.** (d)
37. (b) **38.** (a) **39.** (b) **40.** (c) **41.** (b) **42.** (a) **43.** (a) **44.** (c) **45.** (b) **46.** (c) **47.** (c) **48.** (c)
49. (c) **50.** (d) **51.** (d) **52.** (d) **53.** (c) **54.** (c) **55.** (b) **56.** (b) **57.** (c) **58.** (a) **59.** (a) **60.** (d)
61. (b) **62.** (a) **63.** (c) **64.** (b) **65.** (a) **66.** (b) **67.** (c) **68.** (b) **69.** (b) **70.** (b) **71.** (a) **72.** (b)
73. (c) **74.** (a) **75.** (d)

Brainteasers Objective Type Questions

76. (b) **77.** (d) **78.** (c) **79.** (a) **80.** (c) **81.** (d) **82.** (a) **83.** (a) **84.** (c) **85.** (d)
86. (c) **87.** (b) **88.** (d) **89.** (c) **90.** (c) **91.** (a) **92.** (d) **93.** (d) **94.** (b) **95.** (a)
96. (d) **97.** (c) **98.** (a) **99.** (c) **100.** (a) **101.** (d) **102.** (d) **103.** (b) **104.** (a) **105.** (b)
106. (b) **107.** (c) **108.** (d) **109.** (c) **110.** (d) **111.** (c) **112.** (d) **113.** (d) **114.** (b) **115.** (b)
116. (c) **117.** (a) **118.** (d) **119.** (d) **120.** (b) **121.** (b) **122.** (d) **123.** (b) **124.** (c) **125.** (d)

Decisive Thinking Objective Type Questions

126. (a), (c), (d) **127.** (a), (b), (d) **128.** (a), (c), (d) **129.** (b), (c), (d) **130.** (a), (b), (c)
131. (a), (c), (d) **132.** (c), (d) **133.** (b), (c), (d) **134.** (a), (b), (c) **135.** (a), (b)
136. (a), (b), (d) **137.** (a), (b), (d) **138.** (a), (c) **139.** (a), (b), (c) **140.** (b), (c)
141. (a), (b) **142.** (b), (c) **143.** (a), (b), (c) **144.** (a), (c) **145.** (b), (c), (d)
146. (a), (b), (d) **147.** (a), (b), (c) **148.** (a), (b), (d) **149.** (a), (b), (c) **150.** (a), (c)
151. (a), (b), (d) **152.** (a), (b), (c)

Linked-Comprehension Type Questions

153. (b) **154.** (c) **155.** (c) **156.** (c) **157.** (d) **158.** (b) **159.** (b) **160.** (b) **161.** (c) **162.** (d) **163.** (a) **164.** (c)
165. (b) **166.** (a) **167.** (d) **168.** (b) **169.** (a) **170.** (b)

Assertion-Reason Type Questions

171. (a) **172.** (a) **173.** (a) **174.** (a) **175.** (a) **176.** (a) **177.** (d) **178.** (a) **179.** (a) **180.** (d) **181.** (b) **182.** (b)
183. (c) **184.** (b) **185.** (b) **186.** (a) **187.** (d) **188.** (c) **189.** (a) **190.** (b) **191.** (a)

Matrix-Match Type Questions

192. (a) - (s), (b) - (s), (c) - (r), (d) - (p)
193. (a) - (s), (b) - (r), (c) - (q), (d) - (p)
194. (a) - (r, t), (b) - (s, t), (c) - (p, q, r, t), (d) - (r, t)
195. (a) - (s), (b) - (r), (c) - (p), (d) - (q)
196. (a) - (p, q), (b) - (p, q), (c) - (r, s), (d) - (p, q)
197. (a) - (s), (b) - (q, t), (c) - (r), (d) - (p)
198. (a) - (s), (b) - (p), (c) - (q), (d) - (r)
199. (a) - (p, r, s), (b) - (q), (c) - (s), (d) - (p, q)
200. (a) - (s), (b) - (t), (c) - (r), (d) - (q)
201. (a) - (s), (b) - (t), (c) - (p), (d) - (q)
202. (a) - (s), (b) - (q), (c) - (p), (d) - (r)
203. (a) - (r), (b) - (p), (c) - (s), (d) - (q)

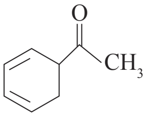
The IIT-JEE Corner

204. (d) **205.** (d) **206.** (c) **207.** (a) **208.** (b) **209.** (a) **210.** (a) **211.** (b) **212.** (b) **213.** (b)
214. (a) **215.** (a) **216.** (a) **217.** (d) **218.** (c) **219.** (c) **220.** (c) **221.** (b) **222.** (c)

HINTS AND EXPLANATIONS

Straight Objective Type Questions

2.



IUPAC name of this compound is 1-cyclohexa-2,4-dienylethanone.

5. Carbocation with sexlet of electrons can easily take up a nucleophile.

6. As the nucleophillic attack on a carbonyl carbon atom depends on the electrophilicity of the carbon. atom. Here a strong electron withdrawing $\underset{|}{-\mathrm{CO}}$ group is attached next to the carbonyl carbon atom so the electrophilicity of this carbon is considerably increased.

7. In acrolein oxygen is more electronegative, so 'O' possess partial negative charge and 'C' posses partial positive charge.

8. Due to electron withdrawing nature of NO_2 group, the partial positive charge on the carbon atom of the C = O group in p-nitrobenzaldehyde increases and becomes more susceptible to nucleophilic attack by the CN^- ion.

10. Fehling solution test is given by aldehyde only, where as all other tests are given by aldehydes as well as ketones.

11. The reagent with which both acetaldehyde and acetophenone react easily are 2,4-dinitrophenyl hydrazine.

12. Dipole moment is maximum for acetophenone (3 Debye) as it has strong electron withdrawing group.

14. Both these molecules are polar and possess dipole.

15. This is due to the + R effect of the benzene ring. From the above nucleophillic addition reaction in the following compound will be

$PhCOPh < PhCOCH_3 < CH_3COCH_3 < CH_3CHO$

16. Nucleophillic substitution reactions are not observed in carbonyl compounds because the leaving nucleophiles like H^-, CH_3^- or R^- are very strong bases and poor leaving groups, compared to common nucleophiles like the derivatives of ammonia, hydrazine or 2,4-DNP, hydroxylamine etc.

18. $_6H_5COCl + H - H \xrightarrow[-KCl]{Pd\text{-}BaSO_4}$

C_6H_5CHO
Benzaldehyde

21. $CH_2O + CH_3MgI \longrightarrow CH_3CH_2\,OMgI$

$\xrightarrow{HOH} CH_3CH_2OH + Mg.OH.I$
Ethyl alcohol

22. Carbonyl compounds which contain atleast one α-hydrogen undergo into aldol condensation.

23. $>C = O \xrightarrow[-H_2O]{NH_2NH_2} \underset{\text{hydrazone}}{>C = NNH_2} \xrightarrow[\Delta]{KOH}$

$>CH_2 + N_2$

24. $C_6H_5CHO \xrightarrow[\text{Cannizzaro reaction}]{NaOH}$

$C_6H_5CH_2OH + C_6H_5CO_2Na$

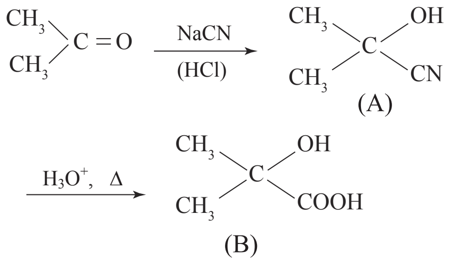
25. $\underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{HCN} CH_3(OH)CN \xrightarrow{H^+/H_2O}$

$CH_3CHOHCOOH$
Lactic acid

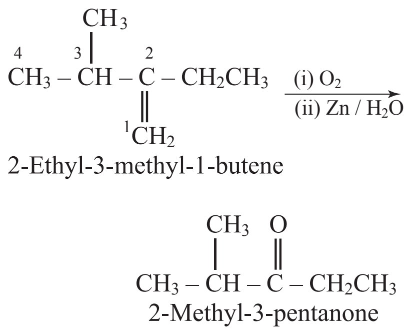
26. $C_6H_5CHO \xrightarrow[(ii)\ H^+ / H_2O]{(i)\ CH_3MgBr} \underset{2^o\ \text{alcohol}}{C_6H_5CH(OH)CH_3}$

27. $CH_3COCH_3 \xrightarrow[(ii)\ H^+/H_2O]{(i)\ CH_3MgI} \underset{\text{tert-butyl alcohol}}{(CH_3)_3COH}$

30.



31.



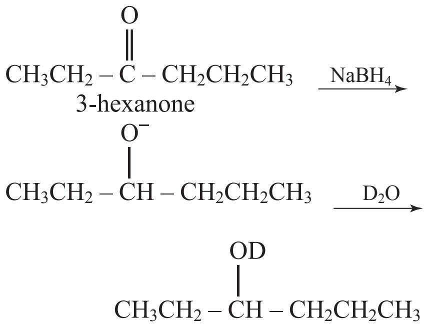
$$\overset{4}{CH_3}-\overset{CH_3}{\overset{3\,|}{CH}}-\overset{2}{\underset{\underset{^{1}CH_2}{\|}}{C}}-CH_2CH_3 \xrightarrow[\text{(ii) Zn / H}_2\text{O}]{\text{(i) O}_2}$$

2-Ethyl-3-methyl-1-butene

$$CH_3-\overset{CH_3}{\overset{|}{CH}}-\overset{O}{\overset{\|}{C}}-CH_2CH_3$$

2-Methyl-3-pentanone

33.



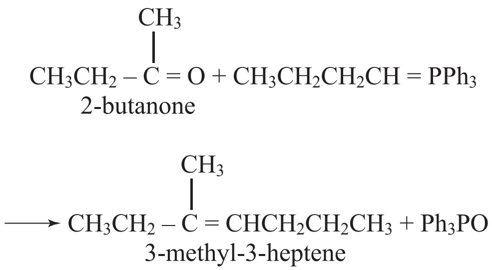
$$CH_3CH_2-\overset{O}{\overset{\|}{C}}-CH_2CH_2CH_3 \xrightarrow{NaBH_4}$$

3-hexanone

$$CH_3CH_2-\overset{O^-}{\overset{|}{CH}}-CH_2CH_2CH_3 \xrightarrow{D_2O}$$

$$CH_3CH_2-\overset{OD}{\overset{|}{CH}}-CH_2CH_2CH_3$$

35.



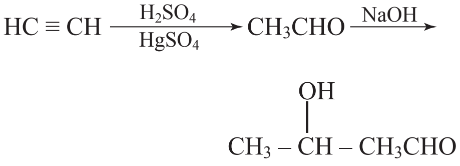
$$CH_3CH_2-\overset{CH_3}{\overset{|}{C}}=O+CH_3CH_2CH_2CH=PPh_3$$

2-butanone

$$\longrightarrow CH_3CH_2-\overset{CH_3}{\overset{|}{C}}=CHCH_2CH_2CH_3+Ph_3PO$$

3-methyl-3-heptene

36.



$$HC\equiv CH \xrightarrow[HgSO_4]{H_2SO_4} CH_3CHO \xrightarrow{NaOH}$$

$$CH_3-\overset{OH}{\overset{|}{CH}}-CH_3CHO$$

37. $HC\equiv CH \xrightarrow[20\%\ H_2SO_4]{1\%\ HgSO_4} \underset{(A)}{CH_3CHO} \xrightarrow[H_2O]{CH_3MgX}$

$\underset{(B)}{CH_3-CHOH-CH_3} \xrightarrow{[O]} CH_3COCH_3$

39. $(CH_3)_2C=CHCH_2CH_3 \xrightarrow{KMnO_4}$

$(CH_3)_2C=O+HOOCCH_2CH_3$

41. $\underset{\text{Benzaldehyde}}{C_6H_5CHO}+\underset{\text{acetic anhydride}}{H_2CHCO-O-COCH_3}$

$\xrightarrow[\text{Perkin condensation}]{CH_3COONa} C_6H_5CH=CHCO\text{-}O\text{-}COCH_3$

$\xrightarrow{H_3O^+,\ \text{boil}} \underset{\text{Cinnamic acid}}{C_6H_5CH{=}CHCOOH}+CH_3COOH$

42. Mol. Wt. = 2 x vapour density
= 2 x 29 = 58

Two compounds CH_3COCH_3 and CH_3CH_2CHO show molecular weight 58. CH_3COCH_3 do not produce yellow ppt. on warming with aq. Solution of NaOH. Hence CH_3CH_2CHO is the compound.

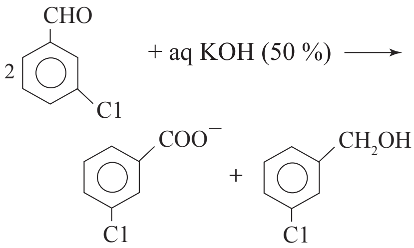
43. $CH_3CHCl_2 \xrightarrow[-3HCl]{2H.OH} CH_3-CH(OH)_2$

$\xrightarrow[-H_2O]{} \underset{\text{Acetaldehyde}}{CH_3CHO}$

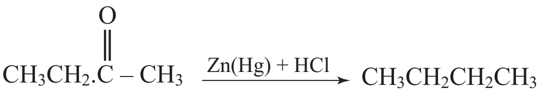
44. As it does not have CH_3CO- group so it can not give the reaction

45. In cannizaro reaction the slowest step is transfer of hydride ion to the carbonyl group.

46. It is a case of Cannizaro's reaction



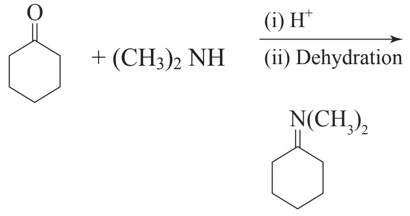
51. Carbonyl compounds are reduced to corresponding alkanes with (Zn + conc HCl). It is called Clemmensen reduction.



$$CH_3CH_2.\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{Zn(Hg)+HCl} CH_3CH_2CH_2CH_3$$

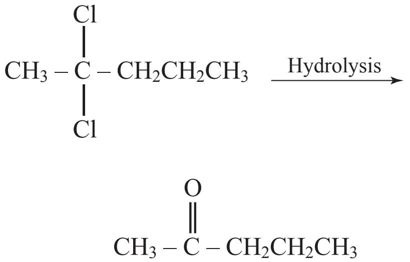
52. Pyridinium chlorochromate oxidizes an alcoholic group selectively in the presence of carbon-carbon double bond.

55.



enamine

57.



$$CH_3-\overset{\overset{Cl}{|}}{\underset{\underset{Cl}{|}}{C}}-CH_2CH_2CH_3 \xrightarrow{\text{Hydrolysis}}$$

$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2CH_2CH_3$$

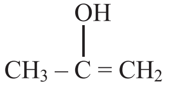
(A) Methyl ketone

61. $C_6H_5MgBr + HOCH_3 \rightarrow C_6H_6 + Mg(Br)OCH_3$

64. $CH \equiv CH + H_2O \xrightarrow{H_2SO_4,\ HgSO_4}$
Acetylene
$[CH_2 = CHOH] \rightarrow$ CH CHO
Acetaldehyde

$CH_3C \equiv CH + H_2O \xrightarrow{H_2SO_4,\ HgSO_4}$
Propylene
$[CH_3C(OH) = CH_2] + CH_3COCH_3$
Acetone

65. The enol form of acetone is

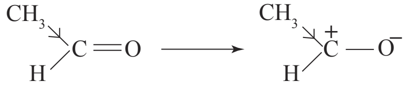


$CH_3-\overset{\overset{OH}{|}}{C}=CH_2$

When it reacts with D_2O, the H-atom of the OH group will be substituted by D atom.

$$CH_3-\overset{\overset{OH}{|}}{C}=CH_2 \quad D_2O \quad CH_3-\overset{\overset{OD}{|}}{C}=CH_2$$

66. Nucleophillic addition reaction will be most favoured in CH_3CHO.



67. The formation of one alcohol and the corresponding acid in presence of conc. NaOH shows that it is a Cannizaro reaction.

69. As it has no α-hydrogen-atom so it can give cannizaro reaction.

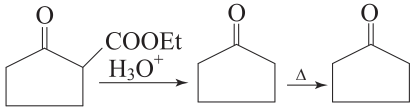
$$C_6H_5CHO \xrightarrow{O^-H} C_6H_5CH_2OH + C_6H_5COO^-$$

71. Pentan-3-ol on reaction with aluminium tertiary butoxide in presence of acetone gives pentan-3-one.

72. This is an example of intermolecular Cannizzaro reaction.

73. In presence of $Ba(OH)_2$ when heated phthalic acid undergoes decarboxylation.

74.

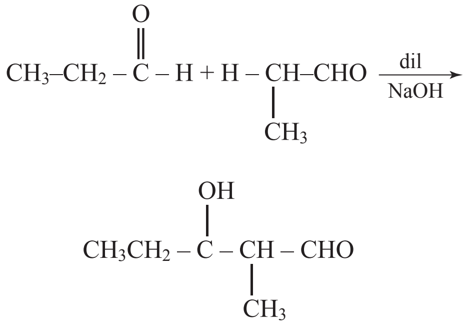


β-keto acid undergoes decarboxylation when heated.

Brainteasers Objective Type Questions

76. Acid chloride and acid anhydride are extremely reactive out of acid derivatives. They react independently with water even in the absence of catalyst to give carboxylic acid, which will ultimately reacts with $NaHCO_3$ to give sodium salt of acid and CO_2. Ester reacts with water in presence of acid catalyst to produce acid. Acetone in inert toward $NaHCO_3$ solution.

84. This is aldol condensation.

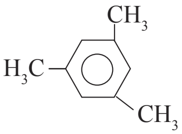


$$CH_3\text{–}CH_2-\overset{\overset{O}{\|}}{C}-H + H-\underset{\underset{CH_3}{|}}{CH}\text{–}CHO \xrightarrow[NaOH]{dil}$$

$$CH_3CH_2-\overset{\overset{OH}{|}}{C}-\underset{\underset{CH_3}{|}}{CH}-CHO$$

(β-hydroxy aldehyde)

85. $3(CH_3)_2CO \xrightarrow{H_2SO_4}$

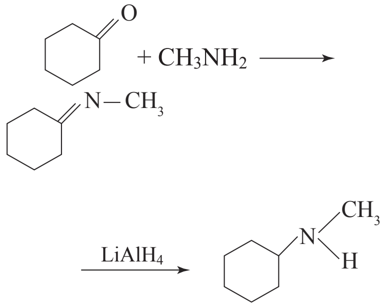


$+ 3H_2O$

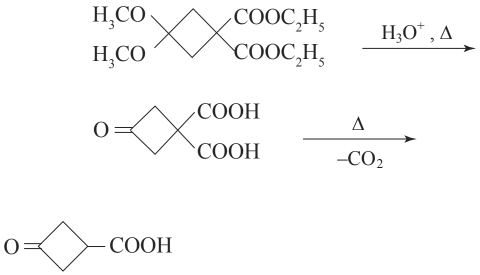
87. The presence of a carbonyl group attached to an aromatic ring, specifically in an activated position para to a methoxy group suggests a Friedal-Crafts acylation reaction.

89. In this reaction
$[A] = CH_3CH_2CH_2CH_2O^-MgBr^+$
$[B] = CH_3CH_2CH_2CH_2OH$
$[C] = CH_3CH_2CH_2COOH$

90.



91.

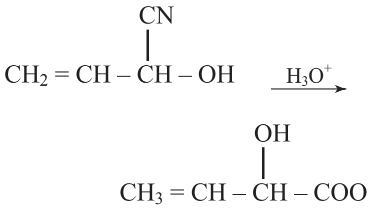


92.

$CH_3CHO + HCHO \xrightarrow[\text{(Cross aldol condensation)}]{\text{dil. NaOH}}$

$HOCH_2 - CH_2CHO \xrightarrow[-H_2O]{\text{Heat}}$
3-Hydroxypropanal

$CH_2 = CH - CHO \xrightarrow[\text{1,2-addition}]{HCN}$
Prop-2-enal (A)



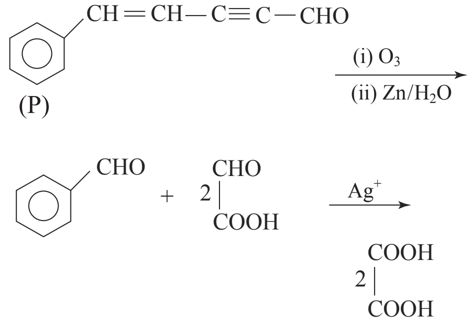
$CH_2 = CH - \underset{}{\overset{CN}{\overset{|}{C}}}H - OH \xrightarrow{H_3O^+}$

$CH_3 = CH - \overset{OH}{\overset{|}{C}}H - COOH$

2-Hydroxybut-3-enoic acid (B)

94. As compound (Q), on oxidation with Ag^+ ions (a mild oxidizing agent) gives oxalic acid, so (Q) is HOOC – COOH. Compound

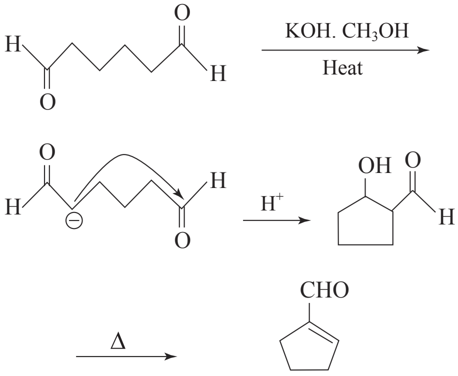
(P) gives two moles of (Q) and benzaldehyde, hence (P) is



95. $3CH_3COCH_3 \xrightarrow[-2H_2O]{HCl}$
propanone (A)

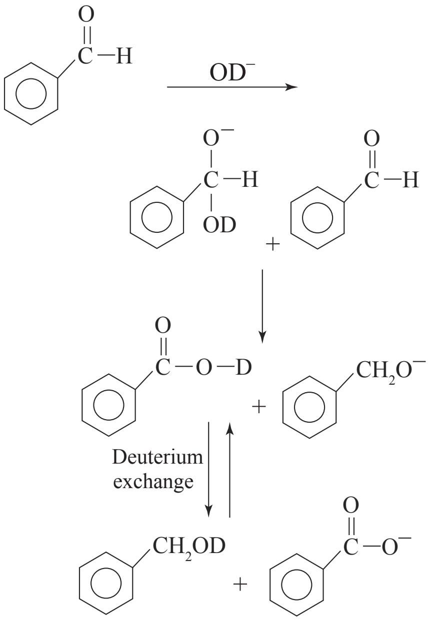
$(CH_3)_2C = CHCOCH = C(CH_3)_2$
2, 6-dimethyl-2, 5-heptadien-4-one (B)

96.

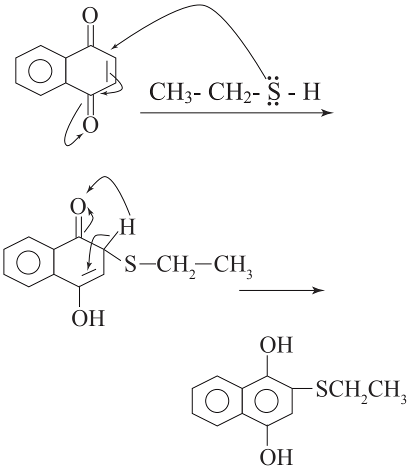


99. The product formed is an enamine. When a secondary amine reacts with a ketone as shown, it results in a stable product known as enamine.

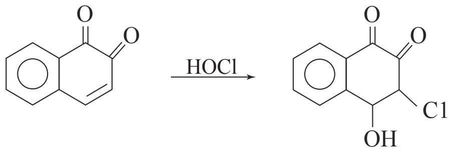
101.



111.

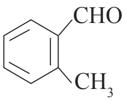


112.



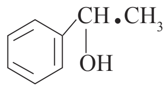
114. It is haloform reaction.

X is



No reaction with sodium hypochlorite as it does not consists $-COCH_3$ or $-CHCH_3$. But it gives +ve Tollen's reagent test.

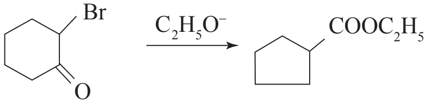
Y is



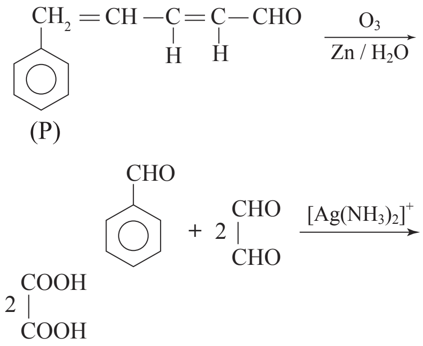
With sodium hypochlorite, it is converted to C_6H_5. COOH, which gives –ve Tollen's reagent test.

115. As greater the electron withdrawing ability of the para substituent , the greater is the Keq for hydrate formation.

124. The transformation of α-haloketones to esters with rearranged carbon skeleton by the treatment with alkoxide ions is called Favorskii rearrangement.

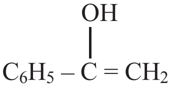


125.



Decisive Thinking Objective Type Questions

128. For keto-enol tautomerism to occur, there should be a hydrogen, on the carbon adjacent to the carbonyl group, which can enolize in the presence of a base. Such a hydrogen is available in acetophenone. The enol forms of acetophenone can be represented as



$$C_6H_5-\overset{\overset{\displaystyle OH}{|}}{C}=CH_2$$

130. Tollen's reagent is not used in the detection of unsaturation but is used for distinction of (i) aldehydes from ketones (ii) terminal alkynes from non-terminal alkynes.

131. As Acetophenone being a ketone does not react with Tollen's reagent to give silver mirror.

132. It undergoes electrophilic substitution.

138. $\underset{\text{1-Phenylethanol}}{C_6H_5-CHOH-CH_3} \xrightarrow{[O]} \underset{\text{acetophenone}}{C_6H_5-COCH_3}$

$C_6H_6 + CH_3COCl \xrightarrow[\text{reaction}]{\text{F.C.}} C_6H_5COCH_3 + HCl$

tion at m-position and also give iodoform test.

139. As $C_6H_5CH_2Cl \xrightarrow{\text{reduction}} C_6H_5CH_3$.

141. Aldol condensation is given by those carbonyl compounds which have α-hydrogen atom.


in $CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H$ and $CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$

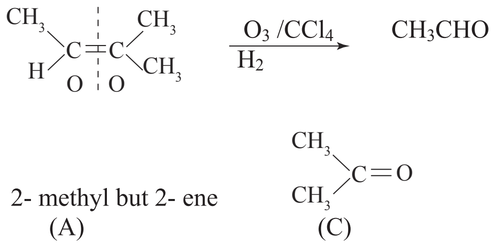
α-hydrogen is present.

143. Aldol condensation is seen in case of carbonyl compounds containing α-hydrogen
Benzaldehyde does not undergo Aldol condensation as it does not contain α-hydrogen.

150. In Wolff-Kishner reduction, carbonyl group (>C = O) is converted to >CH_2 group.

Linked-Comprehension Type Questions

154. As B can reduce Tollen's reagent while (C) can not reduce it so (B) and (C) are ethanal and acetone respectively.



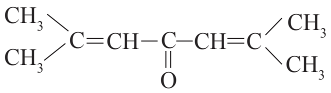
2- methyl but 2- ene
(A)

(C)

155. Here compound (D) is crotonaldehyde

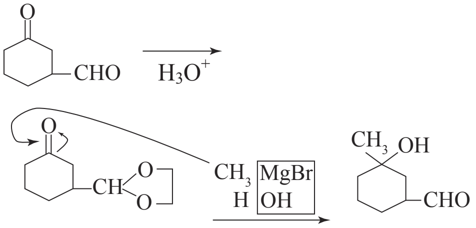
$CH_3-\overset{sp^2}{CH}=\overset{sp^2}{CH}-\overset{sp^2}{CHO}$

but 2- en 1- al
It has 10 σ, 3π bonds.
Compound (E) is Phorone

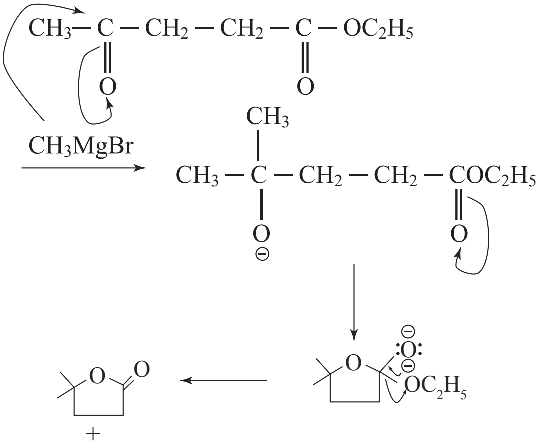

$(CH_3)_2C=CH-\underset{\underset{\displaystyle O}{\|}}{C}-CH=C(CH_3)_2$

2, 6 dimethyl hepta -2, 5-di -en -4-one

156.

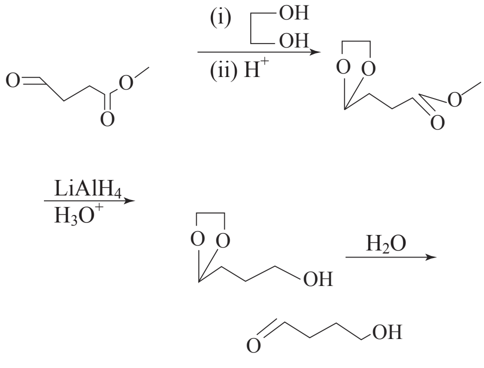


158.



$C_2H_5O^- \xrightarrow{H^+} C_2H_5OH$

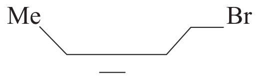
161.



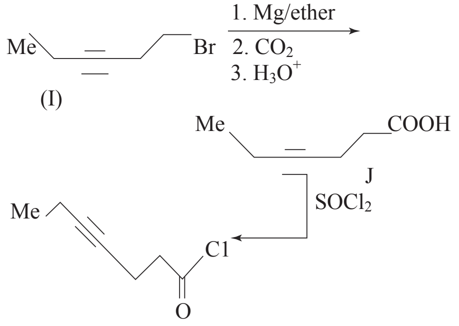
162. $\underset{\text{Hex -3- ynal}}{CH_3-CH_2-C\equiv C\text{-}CH_2-CHO} \xrightarrow[\text{2. PBr}_3]{\text{1.NaBH}_4}$

$\underset{\text{I}}{CH_3-CH_2-C\equiv C-CH_2\text{ - }CH_2Br}$

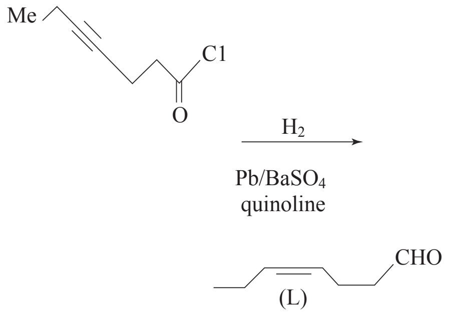
Or



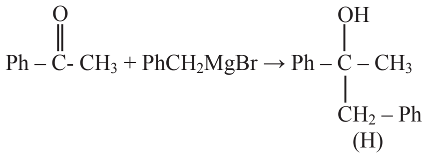
163.



164.



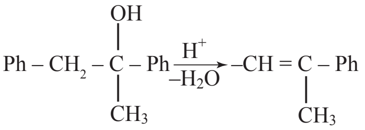
165.



$$\mathrm{Ph-\overset{\overset{O}{\|}}{C}-CH_3 + PhCH_2MgBr \rightarrow Ph-\underset{\underset{CH_2-Ph}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3}$$

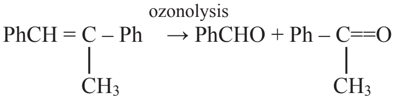
(H)

166.



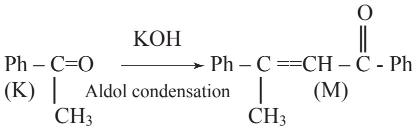
$$\mathrm{Ph-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-Ph \xrightarrow[-H_2O]{H^+} -CH=\underset{\underset{CH_3}{|}}{C}-Ph}$$

167.



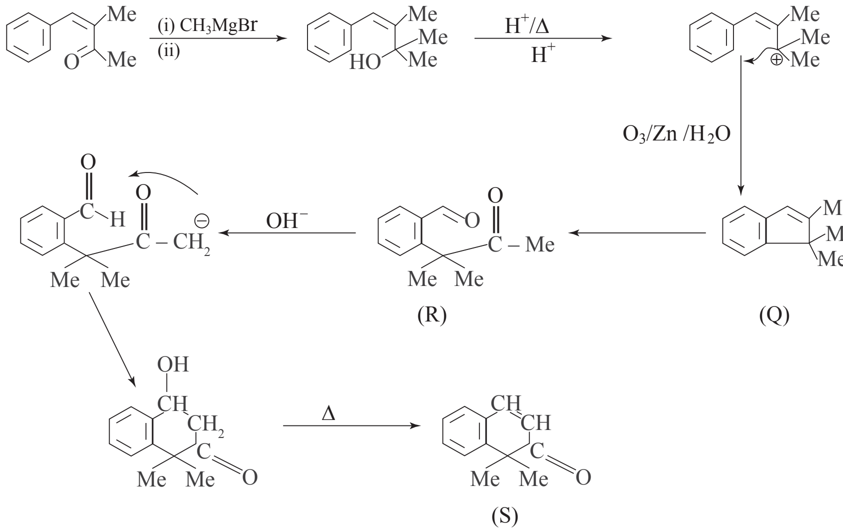
$$\mathrm{PhCH=\underset{\underset{CH_3}{|}}{C}-Ph \xrightarrow{\text{ozonolysis}} PhCHO + Ph-\underset{\underset{CH_3}{|}}{C}{=}O}$$

$$\mathrm{Ph-CHO \xrightarrow[\text{cannizzaro reaction}]{KOH} Ph-CH_2-OH + Ph-COO^-K^+}$$



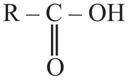
$$\mathrm{\underset{(K)}{Ph-\underset{\underset{CH_3}{|}}{C}=O} \xrightarrow[\text{Aldol condensation}]{KOH} Ph-\underset{\underset{CH_3}{|}}{C}=CH-\overset{\overset{O}{\|}}{C}-Ph \quad (M)}$$

Comprehension 6



Assertion-Reason Type Questions

181. Both are correct but does not give correct explanation,



$R-\underset{\underset{\displaystyle O}{\|}}{C}-OH$

and not undergo nucleophillic addition due to presence of –OH.

183. Aldehydes which contain α-hydrogen undergo aldol condensation.

184. The positive inductive effect of two alkyl groups in ketones makes the carbon atom less positive and makes it less reactive in comparison to aldehdyes.

189. Oxo process is used for preparing aldehydes. At high temperature and pressure , an alkene reacts with CO and H_2 (water gas) in presence of cobalt carbonyl which acts as catalyst.

The IIT-JEE Corner

204. The electron withdrawing nitro group facilitates the release of hydride ion.

205. As they fulfill the condition. See text part

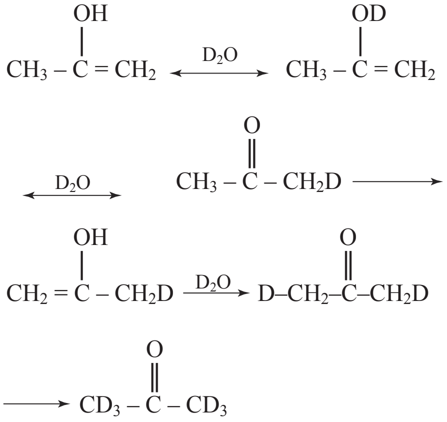
206. Here benzaldehyde has no α-hydrogen so it does not give aldol condensation.

207. Cannizzaro reaction involves H-transfer. Clemmensen reduction involves the formation of new C – H bond. Friedel craft and Reimer-Tiemann reaction involves the formation of new C – C bonds.

208. Cl_3CCHO (chloral) reacts with water to form chloral hydrate.

209. This is an example of intramolecular cannizzaro reaction.

211. As the enol form of acetone on treatment with D_2O undergoes repeated enolization and deuteration give CD_3COCD_3 finally.



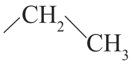
$$CH_3-\overset{\overset{\displaystyle OH}{|}}{C}=CH_2 \xleftrightarrow{D_2O} CH_3-\overset{\overset{\displaystyle OD}{|}}{C}=CH_2$$

$$\xleftrightarrow{D_2O} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2D \longrightarrow$$

$$CH_2=\overset{\overset{\displaystyle OH}{|}}{C}-CH_2D \xrightarrow{D_2O} D-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2D$$

$$\longrightarrow CD_3-\overset{\overset{\displaystyle O}{\|}}{C}-CD_3$$

212. 1, 3-diketones (e.g., 2, 4-hexanedione) has the most acidic hydrogen as the carbanion formed after the removal of a proton that is, resonance stabilized.

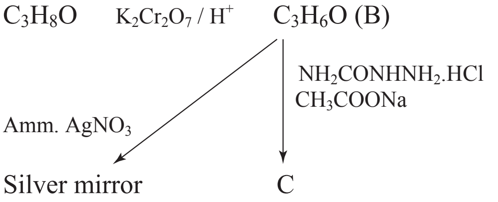
213. Both Zn(Hg), HCl (Clemmenson's reduction) and NH_2NH_2, OH^- (Wollf-Kishner reduction) can reduce $-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$ to  group but as HCl may also bring about the dehydration of alcohol to give an alkene. So the most appropriate reagent will be NH_2NH, OH.

214. It is cross-cannizzaro reaction

$$C_6H_5CHO + HCHO \xrightarrow{NaOH}$$

$$C_6H_5CH_2OH + HCONa$$

215.

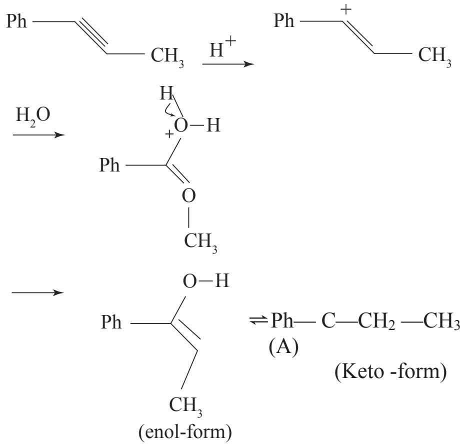


Here B is an aldehyde as it gives silver mirror test with ammonical $AgNO_3$ solution. Tollen's reagent B is formed by oxidation of A, so A must be 1° alcohol ($CH_3CH_2CH_2$ – OH)

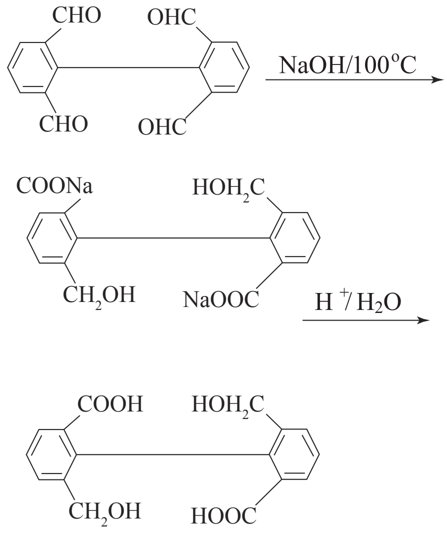
$$\underset{(B)}{CH_3CH_2-CH=O} + H_2NCONHNH_2.HCl$$

$$\xrightarrow[-HCl,\,-H_2O]{\text{sod. Acetate}} CH_3–CH_2–CH=N.NHCONH_2$$

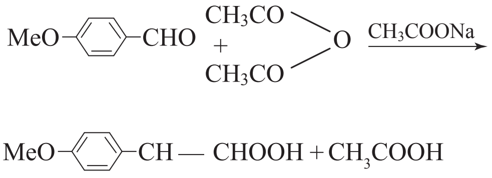
216.



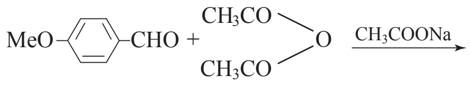
217.

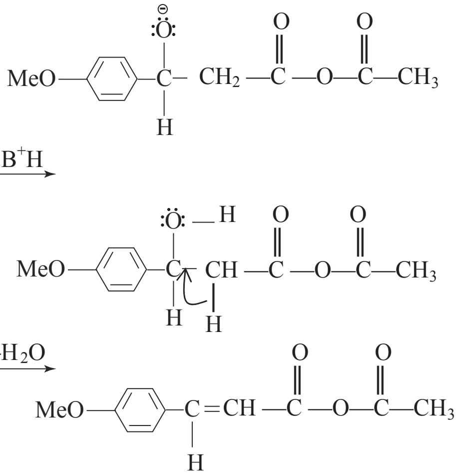


219. This reaction in an example of Perkin's reaction because in it α, β- unsaturated acid is obtained with aromatic aldehydes. Therefore (X) is acetic anhydride that is, $(CH_3CO_2)O$.

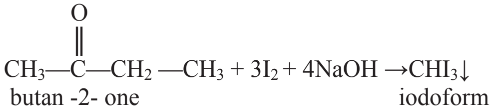


Machanism of this reaction is prepared as follows





220. Tollen's reagent, Fehling solution and NaOH/NaI/ H^+ are not able to change butan -2- one (keton) into propanoic acid because these are mild oxidizing agents, so $NaOH/I^2$ firstly form iodoform along with C_2H_5CONa with butan -2- one (ethyl methyl keton). In these C_2H_5COONa reacts with acid (H^+) to give C_2H_5COOH (proponoic acid)



$$\underset{\text{butan -2- one}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_3} + 3I_2 + 4NaOH \rightarrow \underset{\text{iodoform}}{CHI_3\downarrow}$$

$$C_2H_5COONa + H^+ \rightarrow C_2H_5COOH + Na^+$$

Propanoic acid

SUBJECTIVE SOLVED EXAMPLES

1. Arrange the following in increasing order of expected enol content:

CH_3COCH_2CHO , CH_3COCH_3 , CH_3CHO, $CH_3COCH_2COCH_3$

[IIT 1992]

Solution

$CH_3CHO < CH_3COCH_3 < CH_3COCH_2CHO < CH_3COCH_2COCH_3$

2. Write the structural formula of the main organic product formed when:

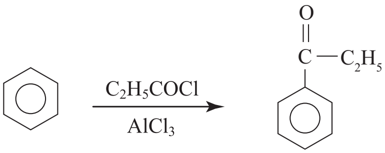
(i) Methanal reacts with ammonia

(ii) Ethyl acetate is treated with double the molar quantity of ethyl magnesium bromide and the reaction mixture poured into water.

(iii) Benzene $\xrightarrow{CH_3CH_2COCl\ /\ AlCl_3}$

Solution

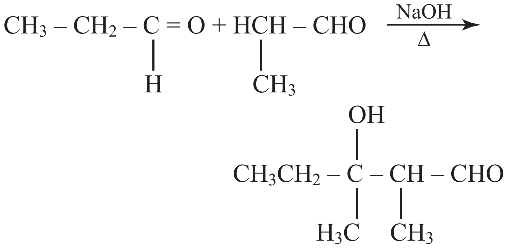
(i) and (ii) see text part

(iii)


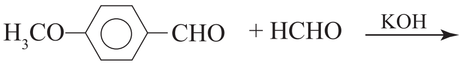
Phenyl ethyl ketone

(iv) Propanal $\xrightarrow{\text{NaOH, heat}}$

Solution

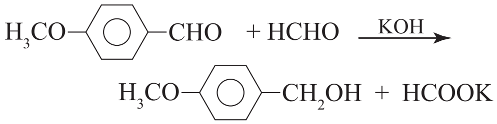


$$CH_3-CH_2-\underset{H}{\underset{|}{C}}=O + H\underset{CH_3}{\underset{|}{C}}H-CHO \xrightarrow[\Delta]{NaOH} CH_3CH_2-\overset{OH}{\overset{|}{\underset{H_3C}{\underset{|}{C}}}}-\underset{CH_3}{\underset{|}{CH}}-CHO$$

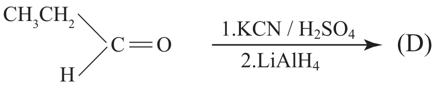
(v)


[IIT 1992]

Solution

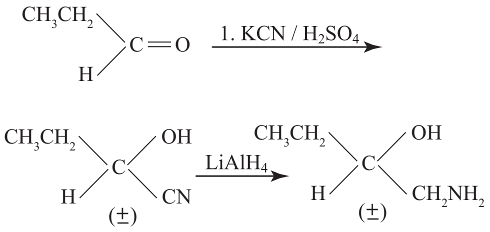


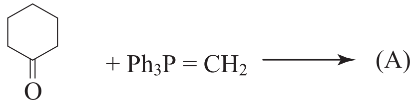
(vi) Complete the following reaction with appropriate structure.



[IIT 1996]

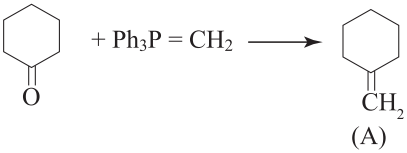
Solution

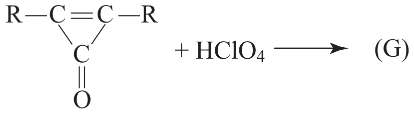


(vii)


[IIT 1997]

Solution

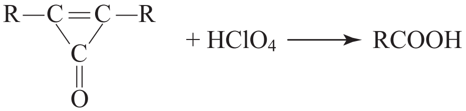


(viii)


(Here R = n-Pr)

[IIT 1997]

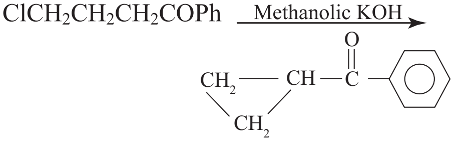
Solution

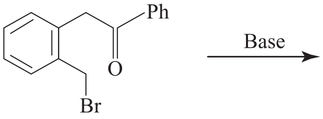


(ix) $ClCH_2CH_2CH_2COPh + KOH + MeOH \longrightarrow (I)$

[IIT 1997]

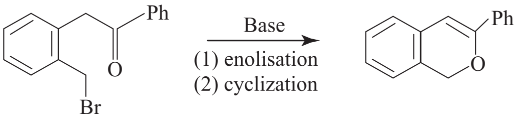
Solution



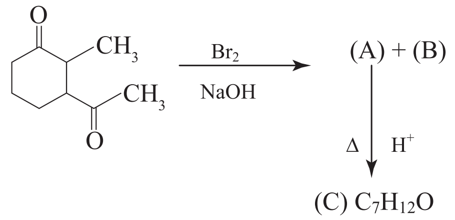
(x)


[IIT 2000]

Solution

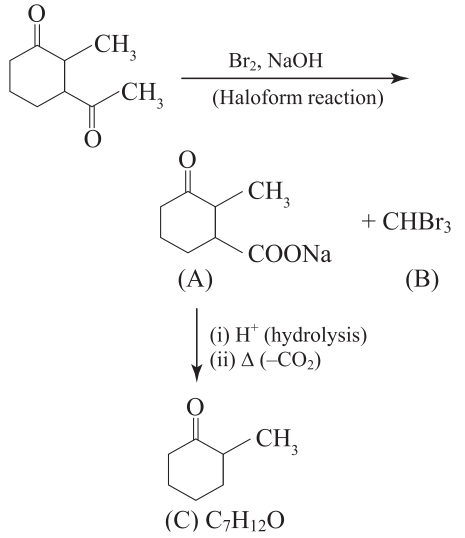


(xi) Identify A, B, C and give their structures.

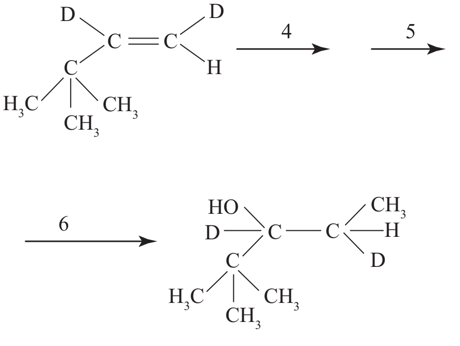


[IIT 2000]

Solution

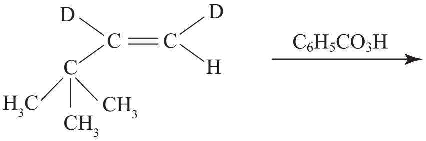


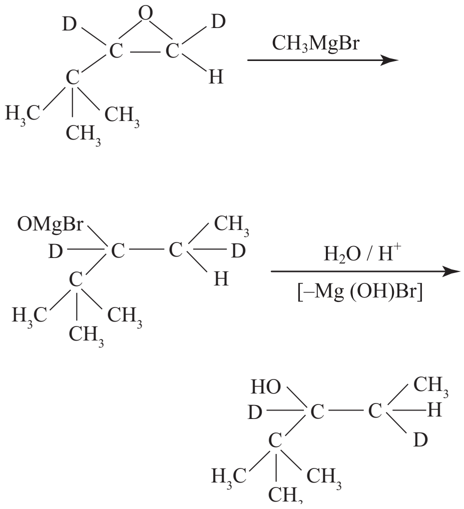
3. Complete the following reaction with appropriate reagents:



[IIT 1999]

Solution





4. (i) Outline the reaction sequence for the conversion of methanal to ethanal (the number of steps should not be more than three).

Solution

$$HCHO \xrightarrow{[O]} HCOOH \xrightarrow{Ca(OH)_2}$$

$$(HCOO)_2Ca \xrightarrow[\text{Heat}]{(CH_3COO)_2Ca} 2CH_3CHO$$

(ii) Acetylene to acetone

Solution

$$\underset{\text{Acetylene}}{CH \equiv CH} \xrightarrow[Hg^{2+}]{H_2SO_4} CH_3CHO \xrightarrow[\text{oxidation}]{KMnO_4}$$

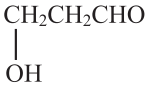
$$CH_3COOH \xrightarrow{Ca(OH)_2} (CH_3COO)_2Ca$$

$$\xrightarrow{\text{distillation}} \underset{\text{Acetone}}{(CH_3)_2CO}$$

(iii) Ethanal to 2-hydroxy-3-butenoic acid

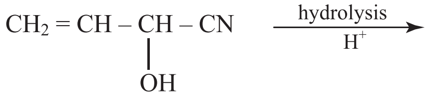
[IIT 1990]

Solution



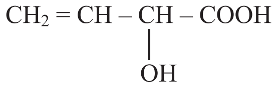
$$\underset{\text{Ethanal}}{CH_3CHO} \xrightarrow{+HCHO\,/\,NaOH} \underset{OH}{CH_2}CH_2CHO$$

$$\xrightarrow[\text{Heat}]{\text{Dehydration}} CH_2 = CHCHO \xrightarrow{HCN}$$



$$\underset{\text{OH}}{CH_2 = CH - \overset{|}{C}H - CN} \xrightarrow[H^+]{\text{hydrolysis}}$$

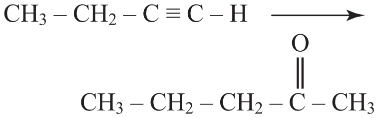
Propanal cyanohydrin



$$CH_2 = CH - \underset{\text{OH}}{\underset{|}{C}H} - COOH$$

2-hydroxy butenoic acid

(iv) Carry out the following transformation in not more than three steps.



$$CH_3 - CH_2 - C \equiv C - H \longrightarrow CH_3 - CH_2 - CH_2 - \overset{\overset{\text{O}}{\|}}{C} - CH_3$$

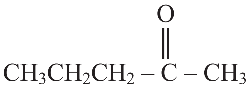
[IIT 1999]

Solution

$CH_3CH_2 - C \equiv CH + Na^+ NH_2^- \longrightarrow$

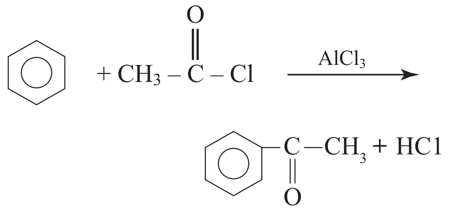
$CH_3CH_2 - C \equiv C^- :Na^+ \xrightarrow{CH_3I}$

$CH_3CH_2 - C \equiv C - CH_3 \xrightarrow[H_2SO_4]{HgSO_4}$



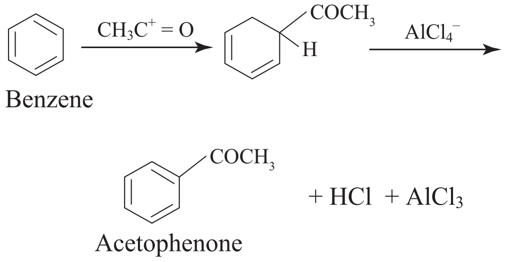
$$CH_3CH_2CH_2 - \overset{\overset{\text{O}}{\|}}{C} - CH_3$$

5. Outline the accepted mechanism of the following reaction. Show the various steps including the charged intermediates.



Solution

$CH_3COCl + AlCl_3 \rightarrow CH_3C^+ = O + AlCl_4^-$



6. Give a chemical test/suggest a reagent to distinguish between the following pairs of compounds:

(ii) Acetaldehyde from acetone

Solution

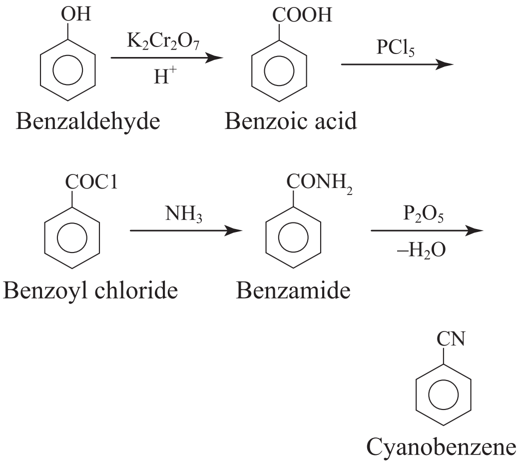
Acetaldehyde can be distinguished from acetone by using Tollen's reagent or Fehling solution or Schiff's reagent. Aldehydes respond to all these tests.

$$CH_3CHO + \underset{\text{Tollen's reagent}}{[Ag(NH_3)_2]^+ OH^-} \rightarrow RCOOH + \underset{\substack{\text{Silver}\\ \text{mirror}}}{Ag\downarrow}$$

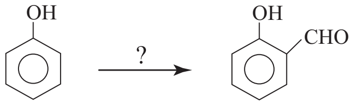
7. How may the following transformation be carried out (in not more than six steps)?

"Benzaldehyde to cyanobenzene"

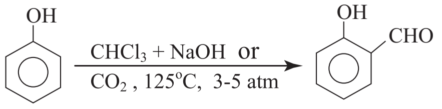
Solution



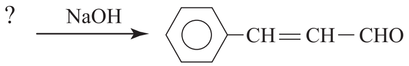
8. (i)



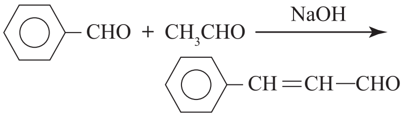
Solution

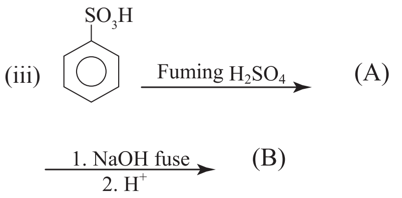


(ii)



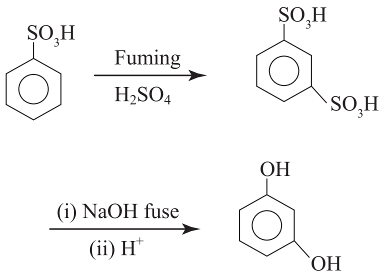
Solution



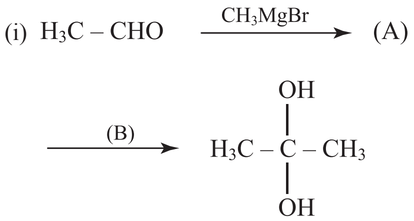
(iii)


[IIT 1992]

Solution

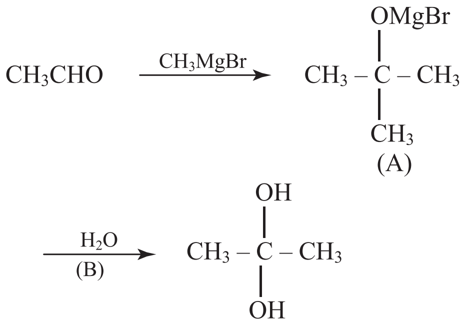


9. Complete the following reactions:



(i) $H_3C-CHO \xrightarrow{CH_3MgBr} (A) \xrightarrow{(B)} H_3C-\underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3$

Solution



$$CH_3CHO \xrightarrow{CH_3MgBr} \underset{(A)}{CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{OMgBr}{|}}{C}}-CH_3}$$

$$\xrightarrow[(B)]{H_2O} CH_3-\underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3$$

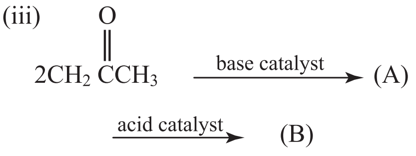
(ii) $CH_3COOH \xrightarrow{(A)} ClCH_2COOH$

$\xrightarrow{\text{excess ammonia}} (B)$

Solution

$CH_3COOH \xrightarrow{P/Cl_2\ (A)} ClCH_2COOH$

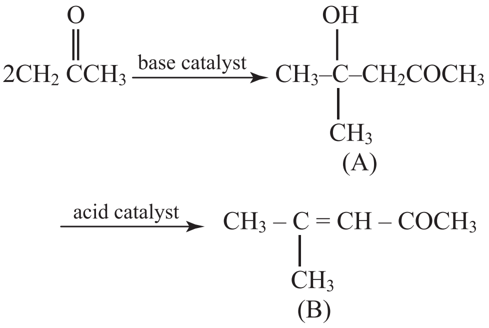
$\xrightarrow{\text{excess ammonia}} NH_2CH_2COONH_4$



(iii) $2CH_3\overset{\overset{O}{||}}{C}CH_3 \xrightarrow{\text{base catalyst}} (A)$

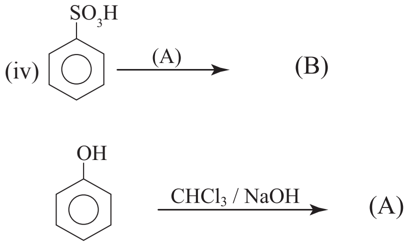
$\xrightarrow{\text{acid catalyst}} (B)$

Solution



$$2CH_3\overset{\overset{O}{||}}{C}CH_3 \xrightarrow{\text{base catalyst}} \underset{(A)}{CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-CH_2COCH_3}$$

$$\xrightarrow{\text{acid catalyst}} \underset{(B)}{CH_3-\underset{\underset{CH_3}{|}}{C}=CH-COCH_3}$$

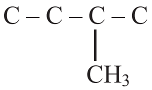
(iv)


10. A hydrocarbon A (molecular formula C_5H_{10}) yields 2-methyl butane on catalytic hydrogenation. A adds HBr (in accordance with Markowni Koff's rule) to form a compound B which on reaction with silver hydroxide forms an alcohol C, $C_5H_{12}O$. Alcohol C on oxidation gives a ketone D. Deduce the structures of A, B, C and D and show the reactions involved.

Solution

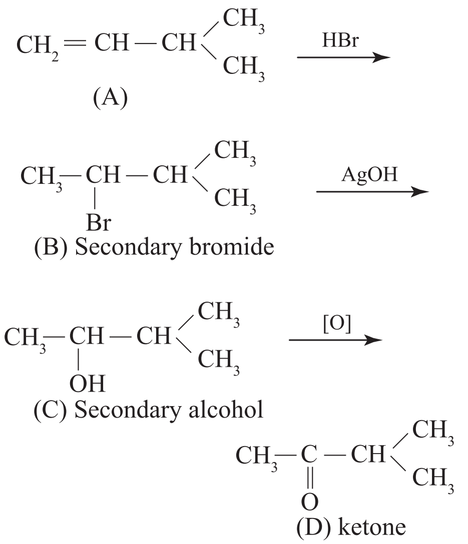
(i) (A) adds HBr and its molecular formula C_5H_{10} suggests it to be an alkene.

(ii) (A) on hydrogenation gives 2-methylbutane, so it has the chain of



$C-C-\underset{\underset{CH_3}{|}}{C}-C$

(iii) Addition of HBr on (A) gives (B), which on treating with AgOH forms an alcohol (C), which on oxidation forms a ketone (D). Thus, (C) is secondary alcohol and (B) is secondary bromide which can be formed only when (A) is



11. Compound A ($C_6H_{12}O_2$) on reduction with $LiAlH_4$ yielded two compounds B and C. The compound B on oxidation gave D, which on treatment with aqueous alkali and subsequent heating furnished E. The later on catalytic hydrogenation gave C. The compound D was oxidized further to give F which was found to be a monobasic acid (molecular formula weight = 60.0 g). Deduce the structures of A, B, C, D and E.

[IIT 1990]

Solution

(i) Compound A ($C_6H_{12}O_2$) on reduction with $LiAlH_4$ gives two compound B and C, so it should be an ester RCOOR'.

(ii) $$\underset{(A)}{RCOOR'} \xrightarrow{\text{Reduction}} \underset{(B)}{RCH_2OH} + \underset{(C)}{R'OH}$$

(iii) (F) is monobasic acid of molecular weight 60, so (F) is CH_3COOH.

(As RCOOH = 60 so R = 15 i.e., CH_3)

(iv) (F) is obtained by oxidation of (D) and (D) is obtained by oxidation of (B), therefore (D) is CH_3CHO and (B) is CH_3CH_2OH.

$$\underset{\text{Acetaldehyde (D)}}{CH_3CHO} \xrightarrow{[O]} \underset{\text{Acetic acid (F)}}{CH_3-COOH}$$

$$\underset{\text{Ethyl alcohol (B)}}{CH_3CH_2OH} \xrightarrow{[O]} \underset{\text{Acetaldehyde (D)}}{CH_3CHO}$$

(v) An ester of six C-atoms giving two alcohols, one of 2-carbon atoms, the other alcohol, must be of four carbon atoms, so ester (A) is

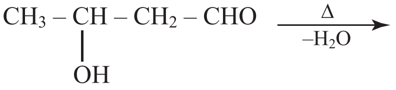
$$\underset{(A)}{CH_3-CH_2-CH_2-COO-CH_2-CH_3}$$
$$\Big\downarrow \text{Reduction}$$
$$\underset{(C)}{CH_3-CH_2-CH_2-CH_2OH} + \underset{(B)}{CH_3CH_2OH}$$
$$\Big\downarrow [O]$$
$$CH_3CHO\ (D)$$
$$\Big\downarrow [O]$$
$$CH_3COOH\ (F)$$

OR

$$\underset{(A)}{CH_3-COO-CH_2-CH_2-CH_2-CH_3}$$
$$\Big\downarrow \text{Reduction}$$
$$\underset{(B)}{CH_3-CH_2OH} + \underset{(C)}{CH_3-CH_2-CH_2-CH_2OH}$$

(vi) (D) on treating with alkali and subsequent heating gives (E) which on catalytic hydrogenation gives (C).

$$\underset{(D)}{2CH_3CHO} \xrightarrow[\text{Aldol condensation}]{\text{NaOH (aq)}}$$



$$CH_3-\underset{OH}{\underset{|}{CH}}-CH_2-CHO \xrightarrow[-H_2O]{\Delta}$$

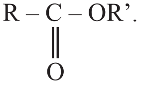
$$\underset{\text{Crotonaldehyde (E)}}{CH_3-CH=CH-CHO} \xrightarrow{\text{Reduction}}$$

$$\underset{\text{(C) Butanol-1}}{CH_3-CH_2-CH_2-CH_2OH}$$

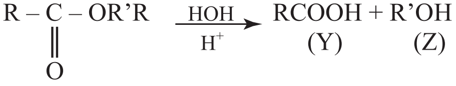
12. A liquid (X), having a molecular formula $C_6H_{12}O_2$ is hydrolysed with water in the presence of an acid to give a carboxylic acid (Y) and an alcohol (Z). Oxidation of (Z) with chromic acid gives (Y). What are the structures of (X), (Y) and (Z)?

Solution

(X) is hydrolysed to give an acid (Y) and an alcohol (Z), therefore (X) is ester



$$R-\underset{O}{\underset{\|}{C}}-OR'.$$



$$R-\underset{O}{\underset{\|}{C}}-OR'R \xrightarrow[H^+]{HOH} \underset{(Y)}{RCOOH} + \underset{(Z)}{R'OH}$$

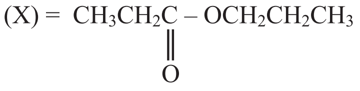
Oxidation of alcohol (Z) gives acid (Y).

$$\underset{(Z)}{R'OH} \xrightarrow{\text{oxidation}} RCOOH$$

$$RCH_2OH \longrightarrow RCOOH$$

(As R' is R-CH_2)

Here



$$(X) = CH_3CH_2\overset{}{\underset{\underset{O}{\|}}{C}} - OCH_2CH_2CH_3$$

(Propyl propanoate)

(Y) = CH_3CH_2COOH
(Propanoic acid)

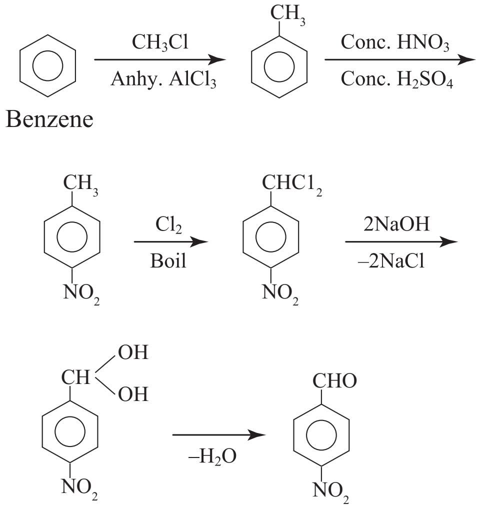
(Z) is $CH_3CH_2CH_2OH$
(Propan-1-ol)

13. How will you bring about the following conversions?

"4-nitrobenzaldehyde from benzene"

[IIT 1994]

Solution



14. An organic compound A, C_8H_6, on treatment with dilute sulphuric acid containing mercuric sulphate gives a compound B, which can also be obtained from a reaction of benzene with an acid chloride in the presence of anhydrous aluminium chloride. The compound B, when treated with iodine in aqueous KOH, yields C and a yellow compound D. Identify A, B, C and D with justification. Show how B is formed from A.

[IIT 1994]

Solution

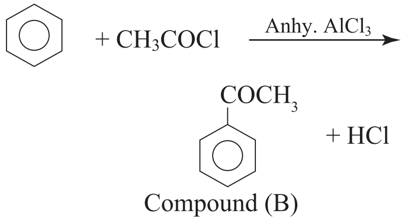
$$C_8H_6 \xrightarrow{\text{dil. } H_2SO_4 + HgSO_4} \text{Compound (B)}$$

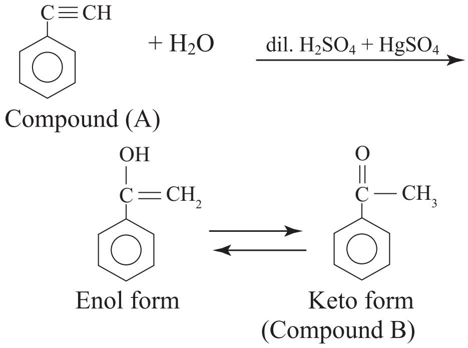
$$\xleftarrow{C_6H_6\text{ , anhy. } AlCl_3} \text{Acid chloride}$$

$$\text{Compound (B)} \xrightarrow{I_2 + KOH} \text{Compound (D)} + \text{Compound (C)}$$

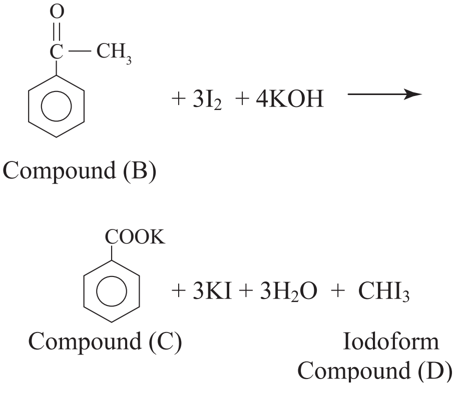
(Yellow colour)

Compound (D) is iodoform which is produced with compound (B) by the reaction of I_2 in presence of KOH (i.e., iodoform reaction). So compound (B) must have CH_3CO– group.

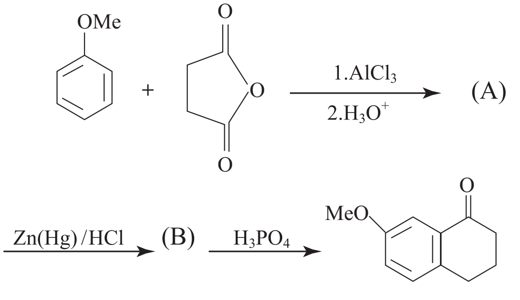




Compound (B) gives iodoform test.

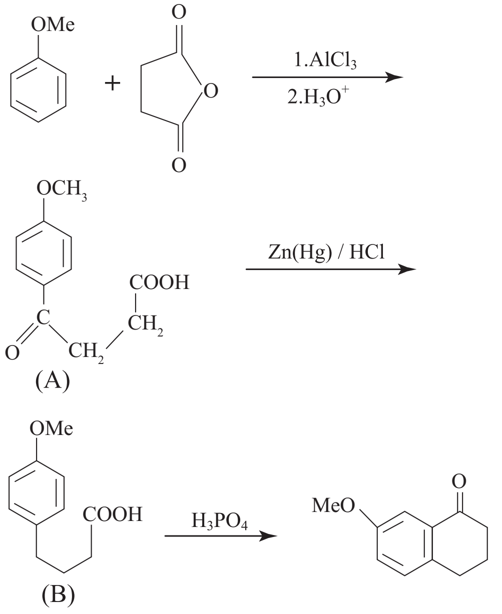


15. Predict the structures of the intermediates/products in the following reaction sequence:



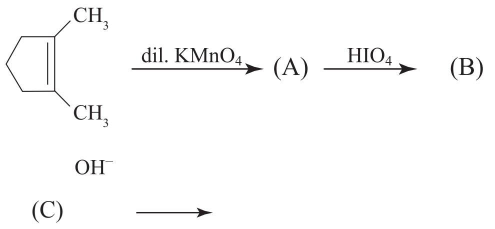
[IIT 1996]

Solution



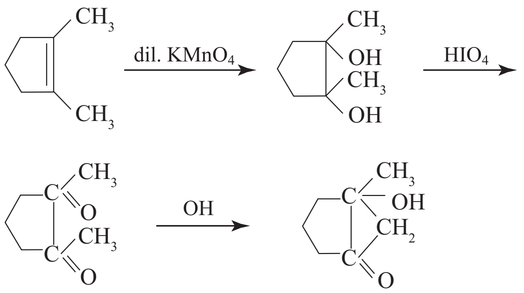
16. Suggest appropriate structures for the missing compounds.

(The number of carbon atoms remains the same throughout the reactions.)



[IIT 1996]

Solution

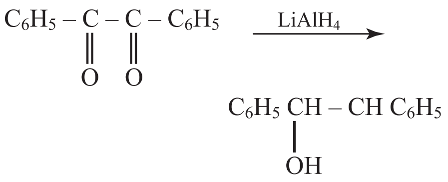


Here the last step is intramolecular aldol condensation.

17. How many asymmetric carbon atoms are created during the complete reduction of benzol (PhCO – COPh) with $LiAlH_4$? Also write the number of possible stereo-isomers in the product.

[IIT 1997]

Solution



$$C_6H_5-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-C_6H_5 \xrightarrow{LiAlH_4} C_6H_5\,\underset{\underset{OH}{|}}{CH}-CH\,C_6H_5$$

The molecule after reduction possesses two asymmetric carbon with symmetry in molecule.

So $a = 2^{n-1} = 2^{2-1} = 2$

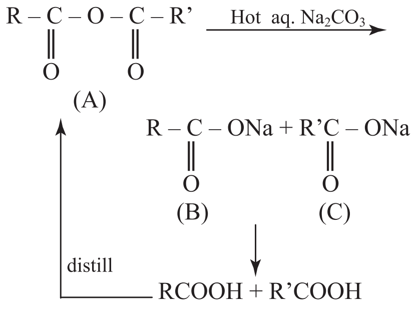
$m = 2^{n/2-1} = 2^0 = 1$

Thus number of stereoisomers = 2 + 1 = 3

18. A liquid A is reacted with hot aqueous sodium carbonate solution. A mixture of two salts B and C are produced in the solution. The mixture on acidification with sulphuric acid and distillation produces the liquid A again. Identify A, B and C and write the equations involved.

[IIT 1997]

Solution



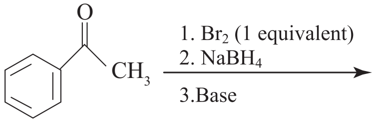
$$\underset{(A)}{R-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-R'} \xrightarrow{\text{Hot aq. } Na_2CO_3} \underset{(B)}{R-\underset{\underset{O}{\|}}{C}-ONa} + \underset{(C)}{R'\underset{\underset{O}{\|}}{C}-ONa}$$

$$\downarrow$$

$$RCOOH + R'COOH \xrightarrow{\text{distill}} (A)$$

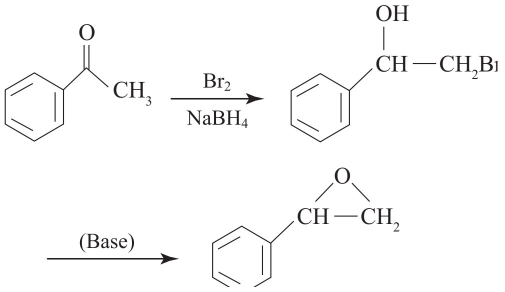
19. Predict the major product in each of the following reactions:

(1)



[IIT 1997]

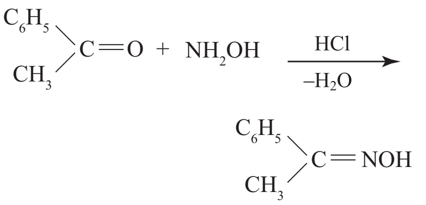
Solution



20. Acetophenone on reaction with hydroxyl amine hydrochloride can produce two isomeric oximes. Write structures of the oxime.

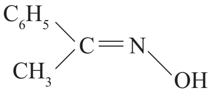
[IIT 1997]

Solution

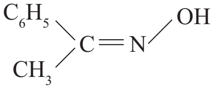


Acetophenoxime

It shows two isomers which are geometrical isomers to each other and represented as follows:

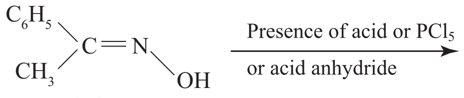
(i) 

Sym-methyl anti-Sym phenyl-ketoxime

(ii) 

Sym-phenyl anti-Sym methyl ketoxime

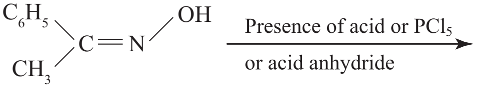
Their configuration may be identified with the help of Beckmann's rearrangement



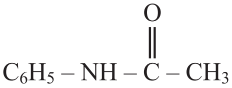
(i) isomer

$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-NH-C_6H_5$$

N-phenyl acetamide



(ii) isomer



$$C_6H_5-NH-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

N-phenyl acetamide

As both isomers give different products, so they are different in arrangement/properties.

21. An ester A ($C_4H_8O_2$), on treatment with excess methyl magnesium chloride followed by acidification, gives an alcohol B as the sole organic product. Alcohol B, on oxidation with NaOCl followed by acidification, gives acetic acid. Deduce the structures of A and B. Show the reactions involved.

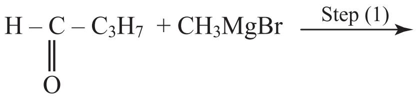
[IIT 1998]

Solution

$$\text{Ester A } (C_4H_8O_2) \xrightarrow[\text{(ii) Acidification}]{\text{(i) } CH_3MgBr \text{ (excess)}}$$

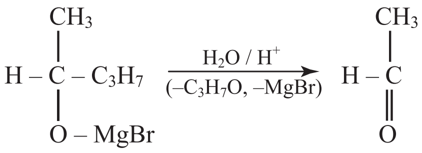
$$\text{Alcohol (B)} \xrightarrow{NaOCl} CH_3COOH$$

Here compound B is secondary alcohol as it gives CH_3COOH which contains lesser number of C-atom with respect to alcohol. So compound A is formate ester (as other esters with excess GR give t-alcohol).

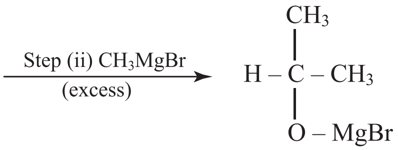


$$H-\underset{\underset{\displaystyle O}{\|}}{C}-C_3H_7 + CH_3MgBr \xrightarrow{\text{Step (1)}}$$

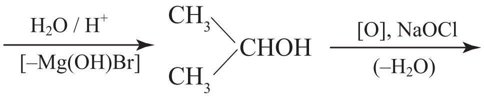
(A)



$$H-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle O-MgBr}{|}}{C}}-C_3H_7 \xrightarrow[(-C_3H_7O,\ -MgBr)]{H_2O/H^+} H-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle O}{\|}}{C}}$$

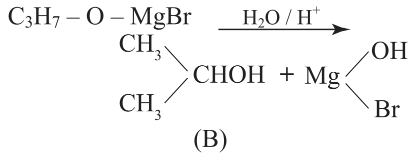


$$\xrightarrow[\text{(excess)}]{\text{Step (ii) } CH_3MgBr} H-\underset{\underset{O-MgBr}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$



$$\xrightarrow[\text{[}-Mg(OH)Br\text{]}]{H_2O / H^+} (CH_3)_2CHOH \xrightarrow[(-H_2O)]{[O],\ NaOCl}$$

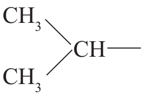
$$CH_3COCH_3 \xrightarrow[-H_2O]{4[O]} CH_3COOH + CO_2$$



$$C_3H_7-O-MgBr \xrightarrow{H_2O / H^+} (CH_3)_2CHOH + Mg(OH)Br$$

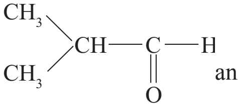
(B)

Therefore C_3H_7 group is



$$(CH_3)_2CH-$$

Compound A is



$$(CH_3)_2CH-\underset{\underset{O}{\|}}{C}-H$$

and compound B is $CH_3-CHOH-CH_3$.

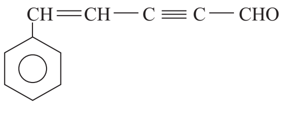
22. An aldehyde A ($C_{11}H_8O$), which does not undergo self aldol condensation, gives benzaldehyde and two moles of B on ozonolysis. Compound B, on oxidation with silver ion gives oxalic acid. Identify the compounds A and B.

[IIT 1998]

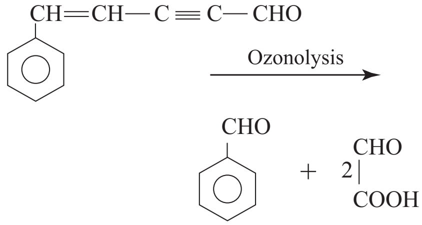
Solution

Aldehydes does not have α-hydrogen atoms but ozonolysis to give two moles of compound (B) and benzaldehyde. Compound B on oxidation with Ag^+ (Tollen's reagent) to give oxalic acid.

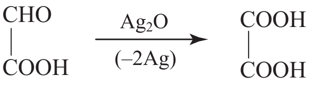
So aldehyde A may be



This aldehyde on ozonolysis gives following product:



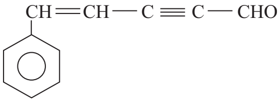
(On ozonolysis –CH = CH – gives aldehyde and group –C ≡ C – gives acidic group)



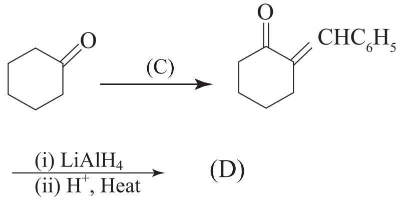
$$\underset{COOH}{\overset{CHO}{|}} \xrightarrow[(-2Ag)]{Ag_2O} \underset{COOH}{\overset{COOH}{|}}$$

Oxalic acid

So the compound A is

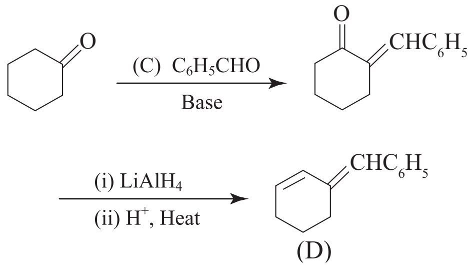


23. Complete the following reaction with appropriate structures of products/reagents:



[IIT 1998]

Solution

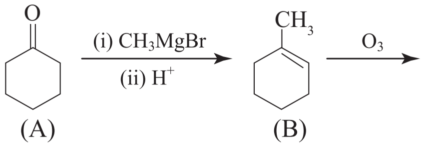


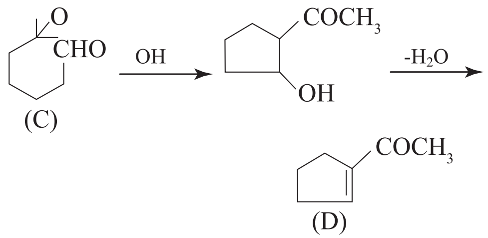
$LiAlH_4$ reduces only ketonic group to 2° alcoholic group without affecting double bond.

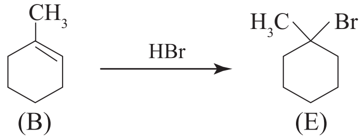
24 An organic compound A, $C_6H_{10}O$ on reaction with CH_3MgBr followed by acid treatment gives compound B. The compound B on ozonolysis gives compound C, which in presence of a base gives 1- acetyl cyclopentene D. The compound B on reaction with HBr gives compound E. Write the structures of A, B, C and E. Show how D is formed from C.

[IIT 2000]

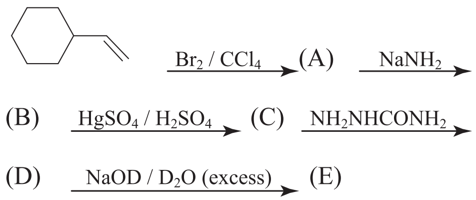
Solution





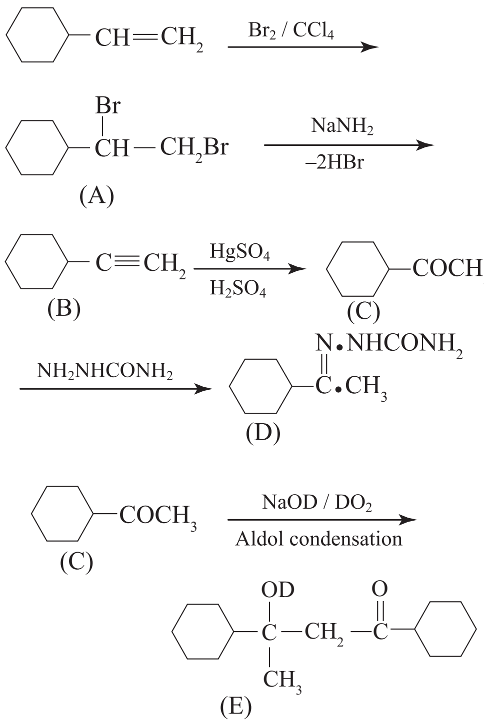


25. Identify (A), (B), (C), (D) and (E) in the following schemes and write their structures:



[IIT 2001]

Solution



26. An alkene (A) $C_{16}H_{16}$ on ozonolysis gives only one product (B) C_8H_8O. Compound (B) on reaction with NaOH/I_2 yields sodium benzoate. Compound (B) reacts with KOH/NH_2NH_2 yielding a hydrocarbon (C) C_8H_{10}. Write the structures of compounds (B) and (C). Based on this information two isomeric structures can be proposed for alkene (A). Write their structures and identify the isomer which on catalytic hydrogenation (H_2/Pd-C) gives a racemic mixture.

[IIT 2001]

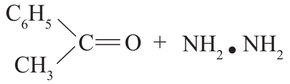
Solution

Alkene (A) is symmetric because it gives a carbonyl compound (C_8H_8O) on ozonolysis.

$$\underset{\text{Compound (B)}}{C_8H_8O} \xrightarrow{NaOH + I_2} C_6H_5COONa$$

As, it gives iodoform test with a mixture of NaOH and I_2, so it must have $CH_3CO–$ group. Thus the possible structure of compound (B) is $C_6H_5 – CO – CH_3$.

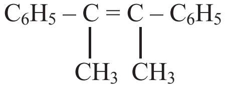
$$C_6H_5COCH_3 + 4NaOH + 3I_2 \rightarrow \underset{\text{Iodoform}}{CHI_3} \downarrow + C_6H_5COONa + 3H_2O + 3NaI$$



$$\underset{\text{Compound (B)}}{(C_6H_5)(CH_3)C{=}O} + \underset{\text{Hydrazine}}{NH_2 \bullet NH_2}$$

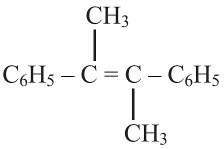
$$\xrightarrow[\substack{\text{Wolff-Kishner reduction}\\(-N_2, -H_2O)}]{KOH} \underset{(C_8H_{10})\ (C)}{C_6H_5 – CH_2 – CH_3}$$

According to the structure of compound (B), the compound (A) is



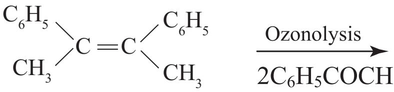
$$\underset{\text{cis}}{C_6H_5 – \underset{CH_3}{C} = \underset{CH_3}{C} – C_6H_5}$$

Or

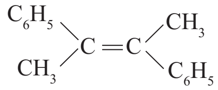


$$\underset{\text{trans}}{C_6H_5 – \overset{CH_3}{C} = \underset{CH_3}{C} – C_6H_5}$$

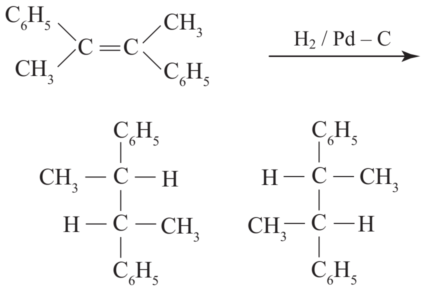
So



or



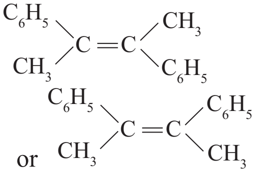
Symmetric alkenes show the properties of geometrical isomerism. So its cis and trans isomers are possible. In these isomers trans isomer gives racemic mixture on hydrogenation (H_2/Pd – C).



Racemic mixture

Hence, compounds

(A) =



(B) = $C_6H_5COCH_3$

(C) = $C_6H_5 - CH_2 - CH_3$

27. Identify (X), (Y) and (Z) in the following synthetic scheme and write their structures. Explain the formation of labeled formaldehyde (H_2C^*O) as one of the products when compound (Z) is treated with HBr and subsequently ozonolysed. Mark the C* carbon in the entire scheme.

$BaC^*O_3 + H_2SO_4 \rightarrow$ (X) gas
(Here C* denotes C^{14})

$CH_2 = CH - Br \xrightarrow{(i)\ Mg / ether,\ (ii)\ X\ (iii)\ H_3O}$

(Y) $\xrightarrow{LiAlH_4}$ (Z)

[IIT 2001]

Solution

$$BaCO_3 + H_2SO_4 \rightarrow \underset{(X)}{C^*O_2} \uparrow$$

$$CH_2 = CHBr \xrightarrow{(i)\ Mg / ether} CH_2 = CHMgBr$$

$$\xrightarrow[(iii)\ H_3O^+]{(ii)\ C^*O_2\ (X)} \underset{(Y)}{CH_2 = CHC^*OOH} \xrightarrow{LiAlH_4}$$

Formation of C^*H_2O from (Z)

$$CH_2 = CH.C^*H_2OH \xrightarrow{H^+} CH_2 = CH_{+}.C^*H_2$$

$$\longleftrightarrow C^+H_2 - CH = C^*H_2 \xrightarrow{Br^-}$$

$$BrCH_2.CH = C^*H_2 \xrightarrow{O_3} C^*H_2 = O$$

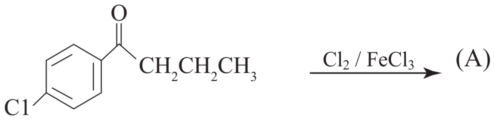
28. Five isomeric para-disubstituted aromatic compounds A to E with molecular formula $C_8H_8O_2$ were given for identification. Based on the following observations, give structures of the compounds.

(1) Both (A) and (B) form a silver mirror with Tollen's reagent; also (B) gives a positive test with $FeCl_3$ solution.
(2) (C) gives positive iodoform test.
(3) (D) is readily extracted in aqueous $NaHCO_3$ solution.
(4) (E) on acid hydrolysis gives 1,4-Dihydroxybenzene.

[IIT 2002]

29. Write structures of the products A, B, C, D and E in the following scheme:

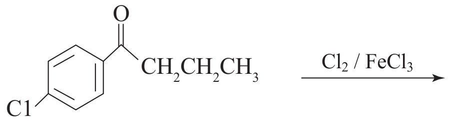
Solution

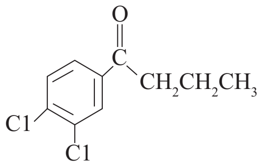


$\xrightarrow{Na\text{-}Hg / HCl}$ (B) $\xrightarrow{HNO_3 / H_2SO_4}$ (C)

$\xrightarrow{CH_2 = CHCH_2O^-Na^+}$ (D) $\xrightarrow{H_2 / Pd/C}$ (E)

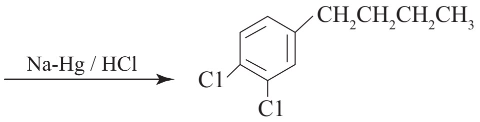
Solution



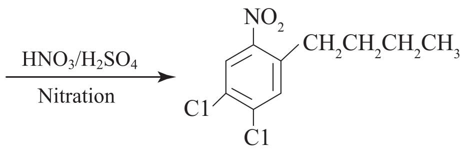


Compound (A)

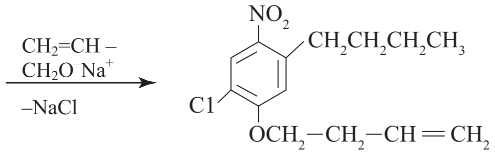
[In this substitution reaction further substitution takes place according to –Cl (o / p directive)]



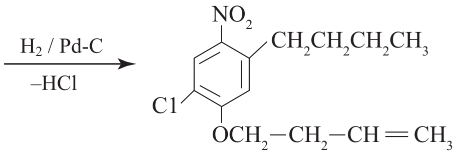
Compound (B)



Compound (C)



Compound (D)

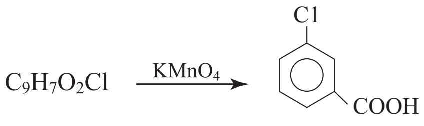


Compound (E)

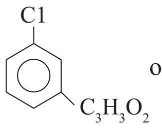
30. Compound (A) of molecular formula $C_9H_7O_2Cl$ exists in ketoform and predominantly in enolic form (B). On oxidation with $KMnO_4$, (A) gives m-chlorobenzoic acid. Identify (A) and (B).

[IIT 2003]

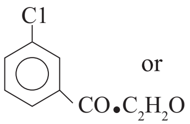
Solution



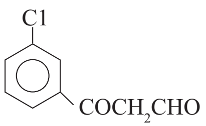
Hence compound should have following part structure.



or

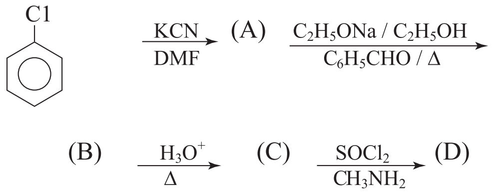


or



As it exists mainly in enolic form

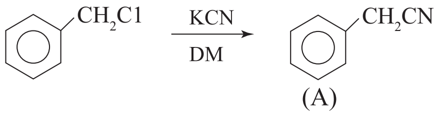
31.

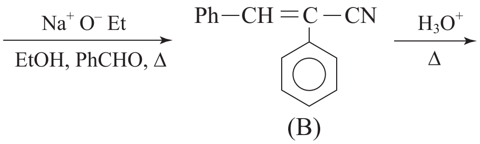


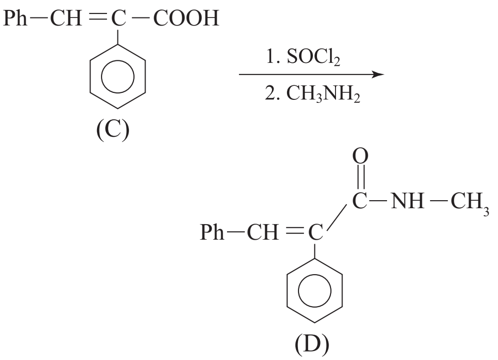
Identify A to D.

[IIT 2004]

Solution

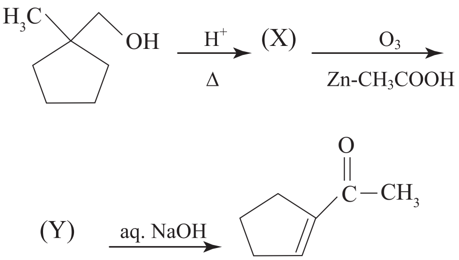






Questions For Self Assesments

32. Identify (X) and (Y) in the following reaction sequence.



33. A compound (X) containing C, H and O is unreactive towards sodium. It does not add bromine. It also does not react with Schiff's reagent. On refluxing with an excess of hydroiodic acid, (X) yields only one organic product (Y). On hydrolysis, (Y) yields a new compound (Z) which can be converted into (Y) by reaction with red phosphorous and iodine. The compound (Z) on oxidation with potassium permanganate gives a carboxylic acid. The equivalent weight of this acid is 60. What are the compound (X), (Y) and (Z)? Write chemical equations leading to the conversion of (X) to (Y).

34. An alkene (A) on ozonolysis yields acetone and an aldehyde. The aldehyde is easily oxidized to an acid (B). When (B) is treated with bromine in presence of phosphorous, it yields a compound (C) which on hydrolysis gives a hydroxy acid (D). This acid can also be obtained from acetone by the reaction with hydrogen cyanide followed by hydrolysis. Identify the compounds A, B, C and D.

35. An alcohol A, when heated with conc. H_2SO_4 gives an alkene B. When B is bubbled through bromine water and the product obtained is dehydro-halogenated with excess of sodamide, a new compound C is obtained. The compound C gives D when treated with warm dilute H_2SO_4 in presence of $HgSO_4$. D can also be obtained either by oxidizing A with $KMnO_4$ or from acetic acid through its calcium salt. Identify A, B, C and D.

ACIDS AND ACID DERIVATIVES

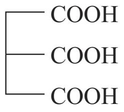
CHAPTER 7

CHAPTER CONTENT

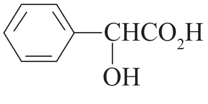
Preparations and Properties of Acids and Acid Derivatives
Carboxylic Acids: Formation of Esters, Acid Chlorides and Amides. Hydrolysis of Esters and various level of multiple-choice questions.

- Organic compounds having carboxylic group (– COOH) are called carboxylic acids. The general formula of monocarboxylic acid is $CnH_2n\ O_2$.
- The name carboxyl is derived from carbonyl (>C = O) and hydroxyl (–OH).
- Monocarboxylic acids of aliphatic series are commonly known as fatty acids.
- These are known as alkanoic acids. For example, CH_3COOH Ethanoic acid.

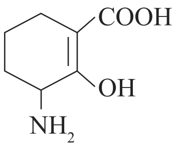
$CH_3CH_2CH_2COOH$ Butanoic acid
$(CH_3)_2CHCOOH$ 2-Methyl propanoic acid
$CH_3 – CH_2 – CH = CH – COOH$
Pent-2-ene-1-oic acid or 2-Pentenoic acid
$(COOH)_2$ Ethan-1,2-dioic acid



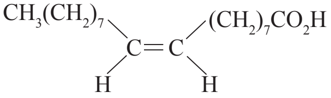
Propan 1,23 tri
Carboxylic acid



2- hydroxyl -2- Phenylethanoic acid
(Mandelic acid)



3 Amino 2 - hydroxy
Cyclohex line 1-carboxylic acid



(Z) -9- Octadecenoic acid
(Oleic acid)

- Some acids are given common names from the sources from which they are obtained.

  For example, HCOOH formic acid {source is formica (red ant)}

  C_3H_7COOH butyric acid {source is butyrum that is, butter, Citric acid from citrous plant.

ISOMERISM SHOWN BY ACIDS

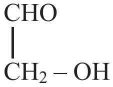
Acids may show chain isomerism and functional isomerism with esters, hydroxy carbonyl compounds and hydroxy oxiranes or cyclic ethers.

For example, $\mathbf{C_2H_4O_2}$:

(1) $CH_3 - COOH$

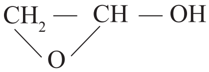
(2) $HCOOCH_3$

(3)

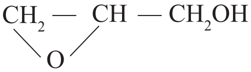


$\begin{array}{l} CHO \\ | \\ CH_2 - OH \end{array}$

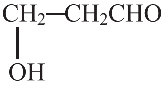
(4)



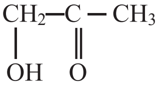
($C_3H_6O_2$): CH_3CH_2COOH;



Propionic acid
2,3 Epoxypropan -1-ol
$HCOOC_2H_5$;
CH_3COOCH_3
Ethyl formate
Methyl acetate



$\begin{array}{l} CH_2-CH_2CHO \\ | \\ OH \end{array}$;



$\begin{array}{l} CH_2-C-CH_3 \\ |\quad\ \ \| \\ OH\ \ O \end{array}$

3- Hydroxy propanal 1- Hydroxy propan -2- one
and
1- Positional isomere (2- hydroxyl propanal)

SOME VALUABLE FACTS

- R –COOH + $NaHCO_3$ → Efferences of CO_2 [Test of RCOOH]
  Aq

- B.P. of R-COOH > R –OH or R –CHO or R – COOR'

  As acids have more extent of Hydrogen bonding.

$$\begin{tikzcd} HCOOH \arrow[r] \arrow[d, "\text{Liquid phase}"] & \text{Dimer in vapour or gas phase} \\ \text{Polymer} & \end{tikzcd}$$

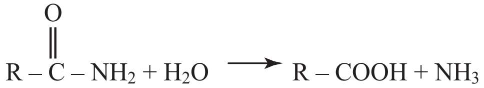
- HCOOH is a very powerful reducing agent and it reduces Tollen's reagent, Fehling solution and $HgCl_2$.
- Polymer $\xleftarrow[\text{Phase}]{\text{liquid}}$ CH_3COOH $\xrightarrow[\text{benzene}]{\text{Dry}}$ Dimer

GENERAL METHODS OF PREPARATION

By the Hydrolysis of Acid Derivatives Acid derivatives can be easily hydrolysed into acids by using dilute acids or dilute alkalines as follows:

$$R-\overset{\overset{O}{\|}}{C}-Cl + H_2O \longrightarrow R-COOH + HCl$$

Acid chloride

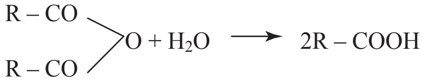


$$R-\overset{\overset{O}{\|}}{C}-NH_2 + H_2O \longrightarrow R-COOH + NH_3$$

Amide

$$R-\overset{\overset{O}{\|}}{C}-OR' + H_2O \longrightarrow R-COOH + R'-OH$$

Ester



$$(R-CO)_2O + H_2O \longrightarrow 2R-COOH$$

Acid anhydride

By the Hydrolysis of Cyanides (R – CN) Cyanides on hydrolysis by dilute HCl give acids as follows:

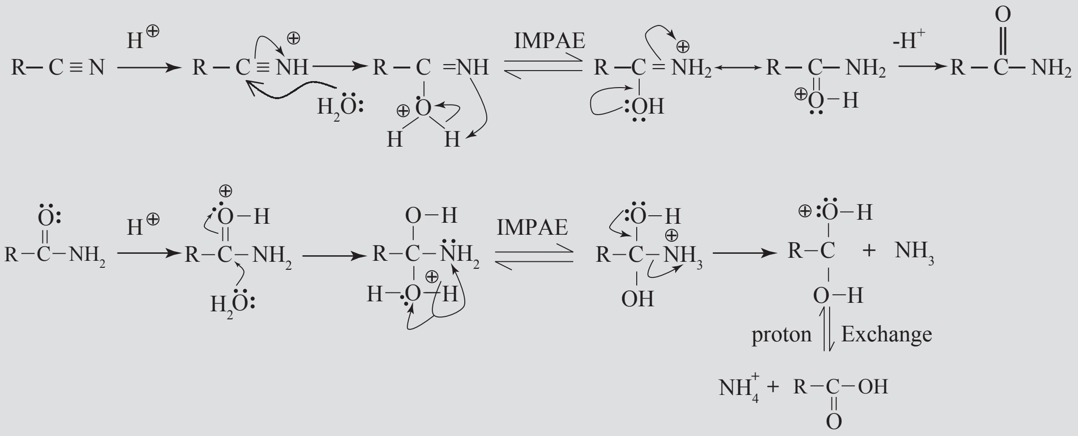
$$R-C\equiv N + 2H_2O \rightarrow R-COOH + NH_3\uparrow$$

For example,

$$CH_3-C\equiv N + 2H_2O \xrightarrow{HCl} CH_3COOH + NH_3\uparrow$$

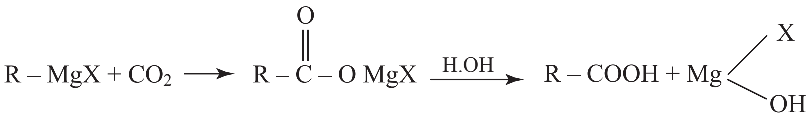
- If hydrolysis is done by H_2O_2 Amide is the final product.

Mechanism

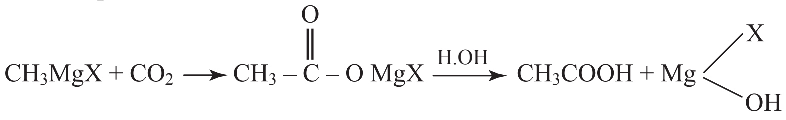


From Grignard Reagent and Carbon Dioxide

Grignard reagent on reaction with carbon dioxide followed by hydrolysis gives acids as follows:

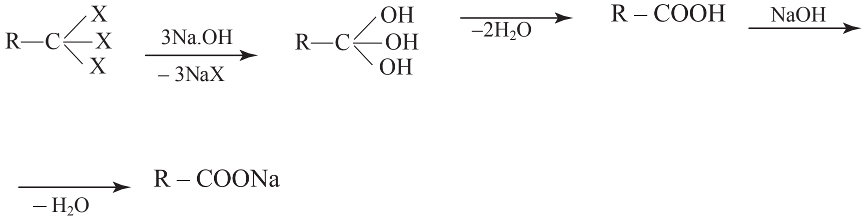


For example,



From the Hydrolysis of Haloforms

Haloforms undergo hydrolysis to give acids as follows:



- Here in place of NaOH, KOH can also be used.

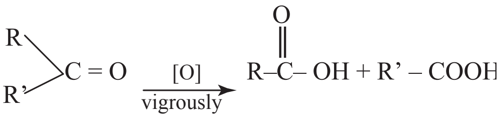
By the Oxidation of Carbonyl Compounds

Carbonyl compounds undergo oxidation into acids by using oxidizing agent like acidic $K_2Cr_2O_7$ or $KMnO_4$ etc., as follows:

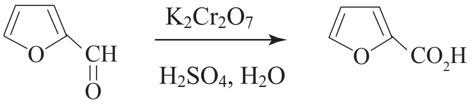
$R-CHO + [O] \rightarrow R-COOH$

For example,

(I) $CH_3CHO + [O] \rightarrow CH_3COOH$

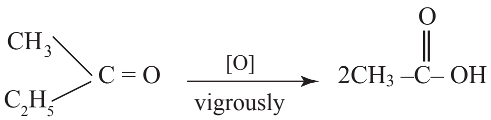


(II)

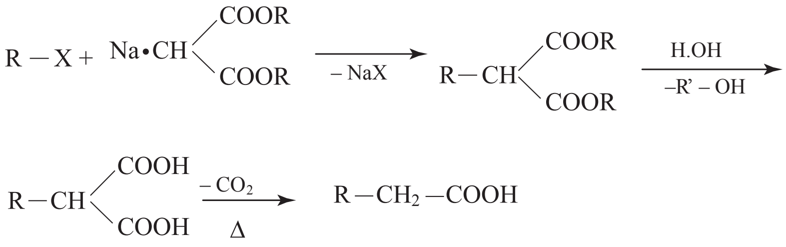


- During oxidation of ketones the carobnyl group goes with smaller alkyl group according to Popoff 's rule.

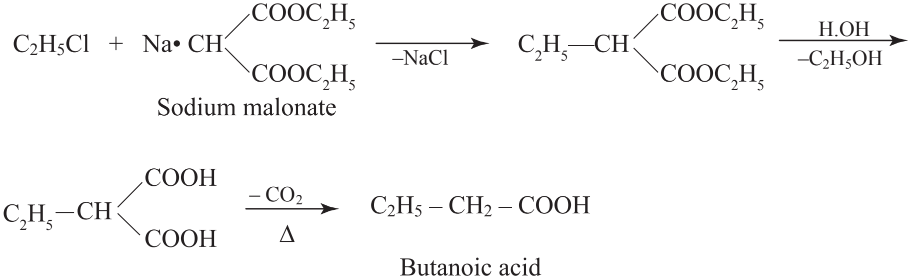
For example,



FROM DICARBOXYLIC ACID OR ESTERS



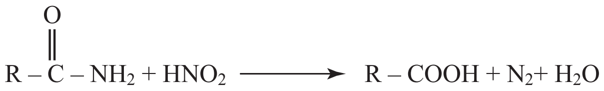
For Example,



Sodium malonate

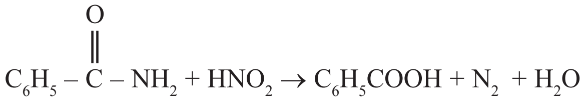
Butanoic acid

FROM AMIDE (R – CONH$_2$) Amides on reaction with nitrous acid give acids as follows:



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 + HNO_2 \longrightarrow R-COOH + N_2 + H_2O$$

For example,



$$C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 + HNO_2 \rightarrow C_6H_5COOH + N_2 + H_2O$$

BY KOCH REACTION Here alkenes are heated with carbon monoxide and water at high temperature and pressure to give acids.

$$R-CH=CH_2 + CO + H_2O \xrightarrow[350^\circ C]{H_3PO_4} R-CH_2-CH_2-COOH$$

For example,

$$CH_3-CH=CH_2 + CO + H_2O \xrightarrow[350^\circ C]{H_3PO_4} \underset{\text{Butanoic acid}}{CH_3-CH_2-CH_2-COOH} + \underset{\text{2-Methyl propanoic acid}}{(CH_3)_2CHCOOH}$$

FROM R – ONA WITH CO

Sodium alkoxide on reaction with carbon monoxide followed by reaction with HCl gives acids.

$$R-ONa + CO \xrightarrow[NaOH]{\Delta} R-COONa \xrightarrow{HCl} R-COOH$$

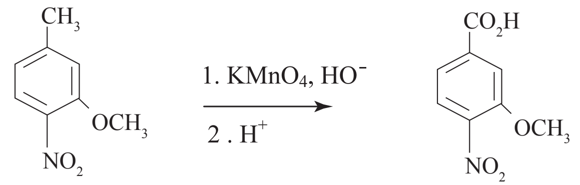
For Example, $\underset{\text{Sod. ethoxide}}{C_2H_5ONa + CO} \xrightarrow[\text{NaOH}]{\Delta} C_2H_5COONa \xrightarrow{\text{HCl}} C_2H_5COOH$

From Higher Alkanes

Higher alkanes like hexane, heptane etc undergo oxidation to give acids as follows:

$$2R-CH_3 + 3O_2 \xrightarrow[\text{Mn acetate or stearate}]{\Delta,\ 120^{\circ}C} 2R-COOH + 2H_2O$$

For example, $\underset{\text{Normal heptane}}{2C_6H_{13}-CH_3} + 3O_2 \xrightarrow[\text{Mn acetate or stearate}]{\Delta,\ 120^{\circ}C} \underset{\text{Heptanoic acid}}{2C_6H_{13}-COOH + 2H_2O}$



3- Methoxy -4- nitrotoluene

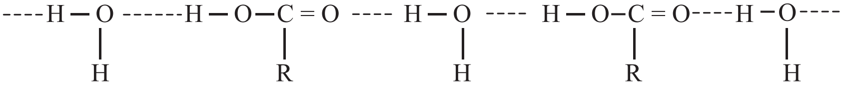
3- Methoxy -4- nitrobenzoic acid (100 %)

PHYSICAL PROPERTIES

Physical State Acids with $C_1 - C_3$ carbon atoms are pungent smelling colourless liquid and with $C_4 - C_9$ are rotten butter smelling colourless liquids.

Solubility Lower acids with C_1 to C_4 carbon atom are completely soluble in H_2O due to intermolecular hydrogen bonding with water however solubility decreases with the increase of molecular weight.

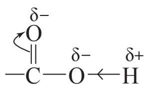
For example, $HCOOH > CH_3COOH > C_2H_5COOH > C_3H_7COOH$



$$\text{----}H-\underset{H}{\underset{|}{O}}\text{------}H-O-\underset{R}{\underset{|}{C}}=O\text{ ---- }H-\underset{H}{\underset{|}{O}}\text{ ---- }H-O-\underset{R}{\underset{|}{C}}=O\text{----}H-\underset{H}{\underset{|}{O}}\text{----}$$

Boiling Point The boiling points of acids are comparably more than the corresponding alcohols, carbonyl compounds or acid derivatives. It indicates that strength of H- bonds in carboxylic acid is even more than alcohols. It is explained as follows:

—O—H bond is more polarized due to adjacent electron withdrawing carbonyl group, in carboxylic acids.

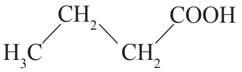


$$-\overset{\overset{\delta-}{O}}{\overset{\|}{C}}-\overset{\delta-}{O}\leftarrow\overset{\delta+}{H}$$

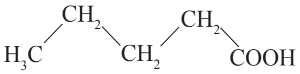
Boiling point of acids α Molecular weight

For example, $HCOOH < CH_3COOH < C_2H_5COOH < C_3H_7COOH <$

Melting Point The melting point of carboxylic acids show alternation effect or oscillation effect, that is, melting point of even number acid is always higher than the next lower and higher odd number acid. This is because even number acids are more symmetrical and fits well into the crystal lattice as –COOH group and alkyl group lie on opposite sides to provide more close packing in any lattice and more energy is required to break them.

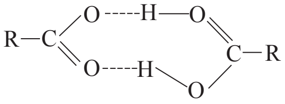


Butanoic acid



Pentanoic acid

- Acids get dimerise that is, exits as cyclic dimmers due to hydrogen bonding



For example,

Acetic acid is a dimer in benzene

CHEMICAL PROPERTIES

Reactions Due to –COOH Group

- **Salt Formation**

  Acid reacts with sodium, sodium hydroxide, sodium bicarbonate, sodium carbonate etc to form acid salts.

$$R-COOH \xrightarrow[\text{NaOH , NaHCO}_3 \text{ or Na}_2\text{CO}_3]{\text{Na}} R-COONa$$

For example,

$$CH_3COOH \xrightarrow[\text{NaOH}]{\text{Na}} CH_3COONa$$

- **With PCl_5 or $SOCl_2$**

$$R-COOH + PCl_5 \longrightarrow R-COCl + HCl + POCl_3$$

For example,

$$CH_3COOH + PCl_5 \longrightarrow CH_3COCl + HCl + POCl_3$$

$$R-COOH + SOCl_2 \xrightarrow{\text{Pyridine}} R-COCl + SO_2 + HCl$$

For example,

$$CH_3COOH + SOCl_2 \xrightarrow{\text{Pyridine}} CH_3COCl + SO_2 + HCl$$

Ester Formation or Esterification

Acid on reaction with alcohols or diazomethane in presence of dilute acid or base gives esters as follows:

$$R - COOH + HOR \xrightarrow[\text{Acid}]{\text{Dil.}} R - COOR' + H_2O$$

For example, $$CH_3COOH + HOC_2H_5 \xrightarrow[\text{Acid}]{\text{Dil.}} \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5 + H_2O}$$

$$R\text{–}COOH + CH_2.N_2 \xrightarrow[\text{HCl}]{\text{Dil}} R\text{–}COOCH_3 + NH_3$$

For example, $$C_2H_5COOH + CH_2.N_2 \xrightarrow{\text{dil HCl}} \underset{\text{Methyl propanoate}}{C_2H_5COOCH_3 + NH_3}$$

REMEMBER

- For ester formation reactivity decreases as follows
  For alcohols: primary > secondary > tertiary alcohol
- For acids: $HCOOH > CH_3COOH > C_2H_5COOH >$

With NH_3

Acid reacts with ammonia to give ammonium salt which on heating gives amide as follows:

$$R\text{–} COOH \xrightarrow{NH_3} RCOONH_4 \xrightarrow[-H_2O]{\Delta} R\text{–}CONH_2$$

For example,

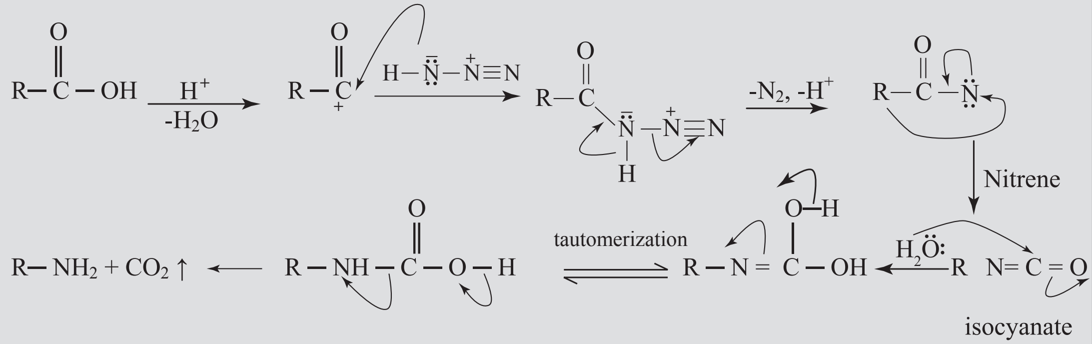
$$CH_3COOH \xrightarrow{NH_3} CH_3COONH_4 \xrightarrow[-H_2O]{\Delta} \underset{\text{Acetamide}}{CH_3CONH_2}$$

Schmidt Reaction

Acid reacts with hydrazoic acid in presence of conc. H_2SO_4 to give a primary amine.

$$R - COOH + \underset{\text{Hydrazoic Acid}}{N_3H} \xrightarrow[\text{conc. } H_2SO_4]{\Delta} R - NH_2 + N_2 + CO_2$$

Mechanism



For example,

$$\underset{\text{Hydrazoic Acid}}{C_2H_5COOH + N_3H} \xrightarrow[\text{conc. } H_2SO_4]{\Delta} \underset{\text{Ethyl amine}}{C_2H_5NH_2} + N_2 + CO_2$$

- **Decarboxylation** Acids undergo decarboxylation with soda lime to give alkane.

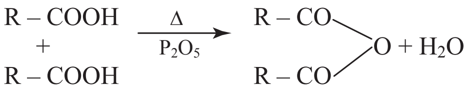
$$R-COOH \xrightarrow[-H_2O]{NaOH} R-COONa \xrightarrow[+NaOH]{\Delta\ CaO} R-H + Na_2CO_3$$

For example,

$$CH_3COOH \xrightarrow[-H_2O]{NaOH} CH_3COONa \xrightarrow[+NaOH]{\Delta\ CaO} CH_4 + Na_2CO_3$$

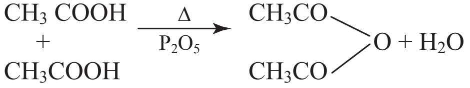
$$HCOONa + NaOH \xrightarrow{CaO,\Delta} Na_2CO_3 + H_2$$

- **Dehydration** Acids undergo dehydration with P_2O_5 to give acid anhydrides.



$$\begin{matrix} R-COOH \\ + \\ R-COOH \end{matrix} \xrightarrow[P_2O_5]{\Delta} \begin{matrix} R-CO \\ R-CO \end{matrix}\!\!>\!O + H_2O$$

For Example,



$$\begin{matrix} CH_3\ COOH \\ + \\ CH_3COOH \end{matrix} \xrightarrow[P_2O_5]{\Delta} \begin{matrix} CH_3CO \\ CH_3CO \end{matrix}\!\!>\!O + H_2O$$

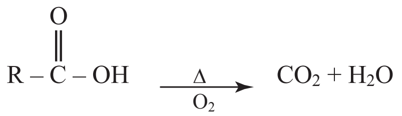
Acetic anhydride

- **Reduction** Acids can be reduced into alcohols with the help of $LiAlH_4$.

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH + 4[H] \xrightarrow{LiAlH_4} R-CH_2OH + H_2O$$

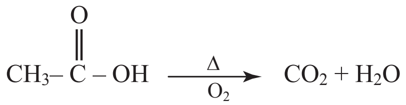
- **Oxidation or Burning**

Except formic acid all other mono carboxylic acids are highly resistant to oxidation so they can be oxidized only by prolong heating using strong oxidizing agents into CO_2 and H_2O.



$$R-\overset{\overset{O}{\|}}{C}-OH \xrightarrow[O_2]{\Delta} CO_2 + H_2O$$

For example,



$$CH_3-\overset{\overset{O}{\|}}{C}-OH \xrightarrow[O_2]{\Delta} CO_2 + H_2O$$

- **With Urea**

Acid reacts with urea to give amides.

$$R-COOH + NH_2CONH_2 \longrightarrow R-CONH_2 + NH_3 + CO_2$$

For example,

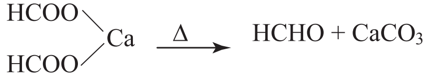
$$CH_3COOH + NH_2CONH_2 \longrightarrow CH_3CONH_2 + NH_3 + CO_2$$

- **Heating Effect of Acid Salts**

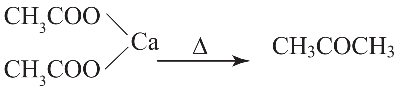
When calcium salts of acids are heated ketones are formed while when calcium formate is taken an aldehyde is formed.

$$(R-COO)_2Ca + (R'COO)_2Ca \xrightarrow{\Delta} R-CO-R + R'-CO-R' + R\text{-}COR'$$

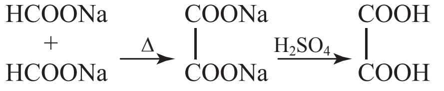
For Example,



calcium formate



calcium acetate

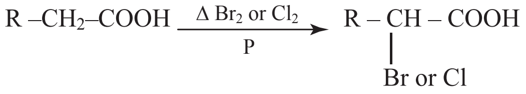


$$\begin{matrix}HCOONa\\+\\HCOONa\end{matrix} \xrightarrow{\Delta} \begin{matrix}COONa\\|\\COONa\end{matrix} \xrightarrow{H_2SO_4} \begin{matrix}COOH\\|\\COOH\end{matrix}$$

Oxalic acid

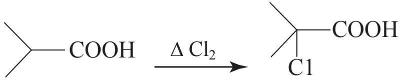
- **Hell–Volhard Zelinsky Reaction**

Carboxylic acids having α-hydrogen atoms react with chlorine or bromine in presence of catalysts like red phosphorous, iron etc., to give α-chloro or bromo substituted acids.



$$R{-}CH_2{-}COOH \xrightarrow[P]{\Delta\ Br_2 \text{ or } Cl_2} R-\underset{\text{Br or Cl}}{\underset{|}{CH}}-COOH$$

For Example,



$$CH_3COOH \xrightarrow{Cl_2/\ P} \underset{\text{Chloroacetic acid}}{Cl-CH_2COOH} \xrightarrow{NaOH} \underset{\text{Sodium chloroacetate}}{Cl-CH_2CO\overset{-}{O}\overset{+}{Na}} \xrightarrow{CN^-}$$

$$\underset{\text{Sodium cyanoacetate}}{N\equiv C-CH_2CO\overset{-}{O}\overset{+}{Na}} \xrightarrow{H_3O^+} HOOC-CH_2-COOH + NH_4^+$$

Reducing Properties of HCOOH

Formic acid shows reducing properties and reduces Tollen's reagent, Fehling's solution, mercuric chloride and $KMnO_4$ etc.

$$HCOOH \xrightarrow[\text{Tollen reagent}]{Ag_2O} H_2O + CO_2 + \underset{\text{silver mirror}}{2Ag\downarrow}$$

$$HCOOH \xrightarrow[\text{Fehling solution}]{2CuO} H_2O + CO_2 + \underset{\text{Red ppt.}}{Cu_2O\downarrow}$$

$$HCOOH \xrightarrow{2HgCl_2} 2HCl + CO_2 + Hg_2Cl_2\downarrow$$

$$HCOOH \xrightarrow{Hg_2Cl_2} 2HCl + CO_2 + \underset{\text{Black}}{2Hg\downarrow}$$

$$2KMnO_4 + 3H_2SO_4 + 5CH_2O \longrightarrow K_2SO_4 + 3MnSO_4 + 5CO_2 + 8H_2O$$

With Organo Metallics

Acids react with organo metallics to give alkanes.

$$R' - CH_2MgX + R - COOH \longrightarrow R' - CH_3 + R - COOMgX$$

For example,

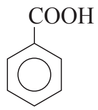
$$CH_3CH_2MgX + CH_3COOH \longrightarrow CH_3 - CH_3 + CH_3COOMgX$$

$$R - COOH + RLi \longrightarrow R' - H + R\text{-}\ COOLi$$

For example,

$$CH_3\ COOH + C_2H_5Li \longrightarrow C_2H_6 + CH_3COOLi$$

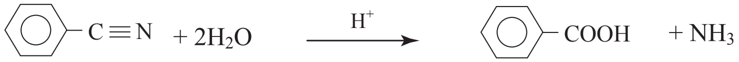
BENZOIC ACID



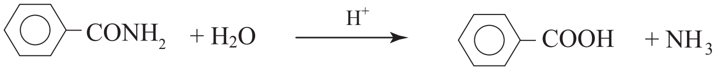
- It is present in nature in combined state as esters in Balsam and in the urine of horse as benzoyl glycine (Hippuric acid).

METHODS OF PREPARATION

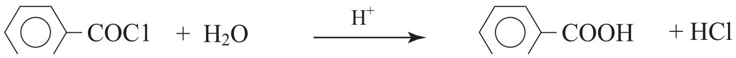
- **By the Hydrolysis of Cyanobenzene**



- **By the Hydrolysis of Benzamide**

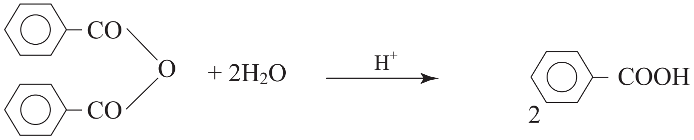


- **By the Hydrolysis of Benzoyl Chloride**

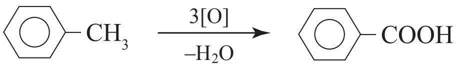


- **By the Hydrolysis of Ethyl Benzoate**

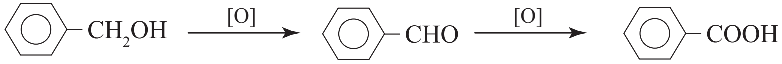
- **By the Hydrolysis of Benzoic Anhydride**



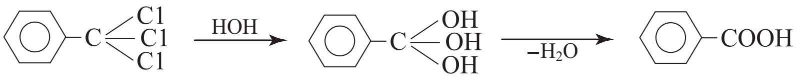
- **By Oxidation Reactions**
- Toluene on oxidation by alkaline $KMnO_4$ or CrO_3 gives benzoic acid.



- Benzyl alcohol on oxidation by acidic or alkaline $KMnO_4$ gives benzoic acid.



- **By the Hydrolysis of Benzo Trichloride**



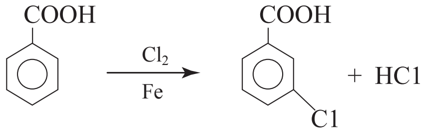
Benzo trichloride

- **From Grignard Reagent**

CHEMICAL PROPERTIES

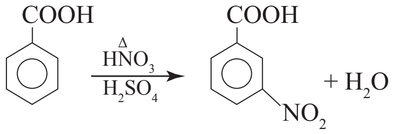
Electrophilic Substitution In benzoic acid –COOH group is ring deactivating and meta directing so rate of electrophilic substitution will be slower than in benzene.

- **Halogenation**



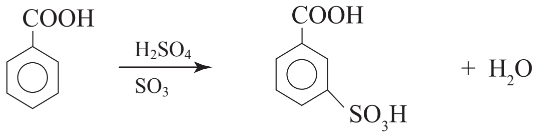
m-chlorobenzoic acid

- **Nitration**

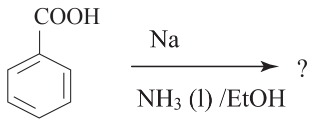


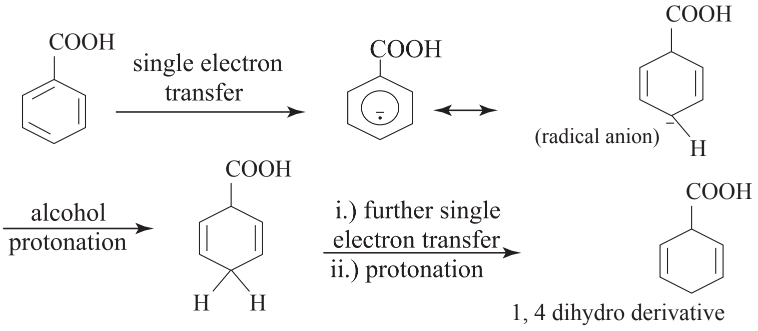
m-nitrobenzoic acid

- **Sulphonation**



m- sulphonic benzoic acid

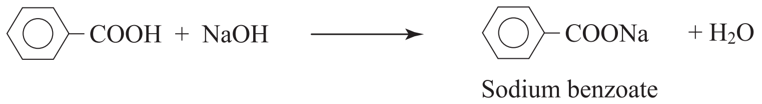




(Birch reduction)

Reactions Due to – COOH Groups

- ***Salt Formation***



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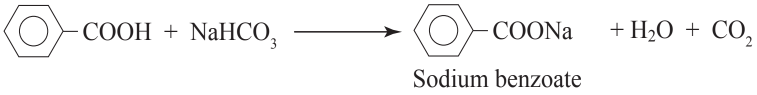
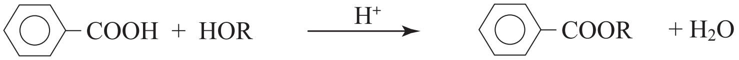
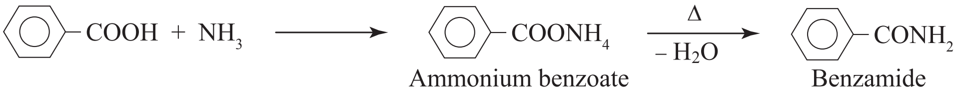


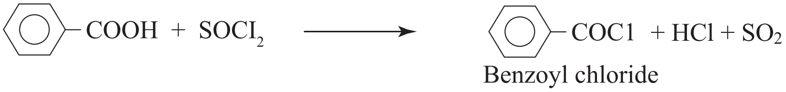
- ***Ester Formation***

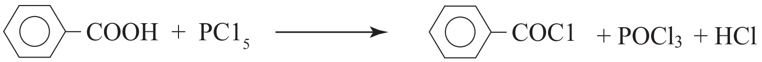


- ***From NH_3***

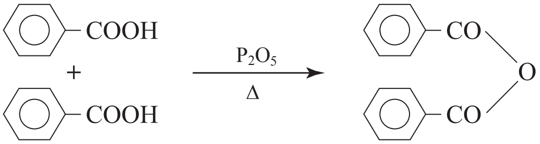


- ***With $SOCl_2$ or PCl_5***

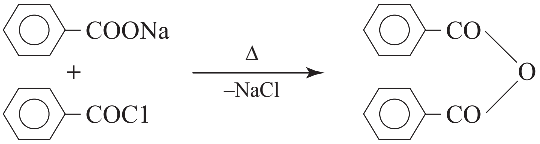


- 

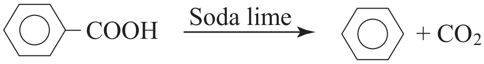
- ***Anhydride Formation or Dehydration***



Benzoic anchydride

- 

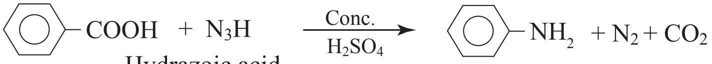
- ***Dicarboxylation***



- ***With Diazomethane***

Diazomethane Methyl benzoate

- ***Schmidt Reaction***

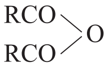


Hydrazoic acid

- ***Reduction***

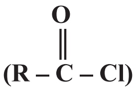
ACID DERIVATIVES

Acid derivatives are as follows:

- Acid halide
  RCOCl
  For example, CH_3COCl
- Acid anhydride 
  $\left.\begin{matrix}RCO\\RCO\end{matrix}\right>O$
  For example, $(CH_3CO)_2O$, $(C_6H_5CO)_2O$ (Benzoic anhydride)
- Acid ester
  ROOR'
  For example, $CH_3COOC_2H_5$, $CH_3COOC_6H_5$, (Phenyl ethanoate)
- Acid amide
  $RCONH_2$,
  For example, CH_3CONH_2 $C_6H_5CONH_2$ (Benzamide)

> ***REMEMBER***
>
> - Acid halide > acid anhydride > acid ester > acid amide.
> - It is the decreasing order of reactivity.
> - It is the decreasing order of reactivity towards hydrolysis.
> - It is the decreasing order of reactivity towards nucleophillic substitution.

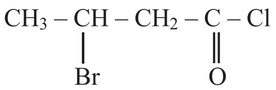
ACID HALIDES



$$(R-\overset{\displaystyle O}{\overset{\|}{C}}-Cl)$$

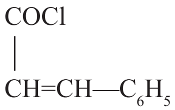
- These are named as alkanoyl chlorides.

  For example, CH_3COCl Ethanoyl chloride



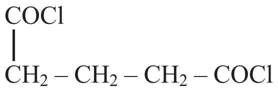
$CH_3-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_2-\underset{\displaystyle O}{\underset{\|}{C}}-Cl$

3-Bromo butanoyl chloride



$\overset{\displaystyle COCl}{\overset{|}{CH}}=CH—C_6H_5$

3-Phenyl prop 2-enoylchloride



$\overset{\displaystyle COCl}{\overset{|}{CH_2}}-CH_2-CH_2-COCl$

Pent-1,4-dioyl chloride

METHODS OF PREPARATION

- **From Acids** Acids on heating with PCl_5 or PCl_3 or $SnCl_2$ give acid chlorides as follows:

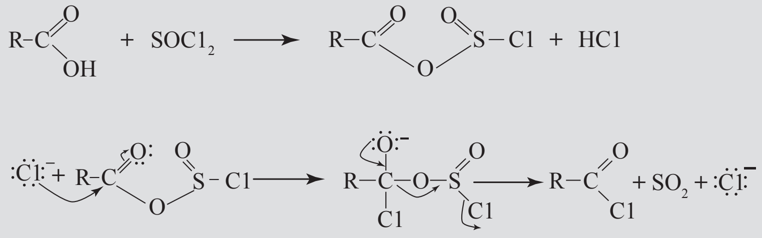
$$RCOOH + PCl_5 \xrightarrow{\Delta} RCOCl + POCl_3 + HCl$$

$$3RCOOH + PCl_3 \xrightarrow{\Delta} 3RCOCl + H_3PO_3$$

$$RCOOH + SOCl_2 \xrightarrow{\Delta} RCOCl + SO_2 + HCl$$

- Here $SOCl_2$ that is thionyl chloride is the best reagent as the gaseous by-products are easily separated by pyridine.

Mechanism

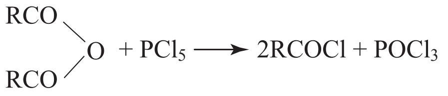


- **From Ester**

$$RCOOR' + PCl_5 \longrightarrow RCOCl + POCl_3 + R'Cl$$

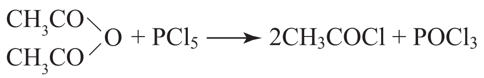
For example, $CH_3COOC_2H_5 + PCl_5 \longrightarrow CH_3COCl + POCl_3 + C_2H_5Cl$
Ethyl acetate

- **From Acid Anhydride**



$$(RCO)_2O + PCl_5 \longrightarrow 2RCOCl + POCl_3$$

For example,



$$(CH_3CO)_2O + PCl_5 \longrightarrow 2CH_3COCl + POCl_3$$

- **Industrial Method** Acid chlorides are prepared on large scale as follows:

$$3RCOONa \xrightarrow[\Delta]{PCl_3} 3RCOCl + Na_3PO_3$$

For example,

$$3CH_3COONa \xrightarrow[\Delta]{PCl_3} 3CH_3COCl + Na_3PO_3$$

- $2RCOONa \xrightarrow[\Delta]{POCl_3} 3RCOCl + NaPO_3 + NaCl$

For example,

$$2CH_3COONa \xrightarrow[\Delta]{POCl_3} 3CH_3COCl + NaPO_3 + NaCl$$

- $(RCOO)_2Ca + SO_2Cl_2 \xrightarrow{\Delta} 2RCOCl + CaSO_4$

For example,

$$(CH_3COO)_2Ca + SO_2Cl_2 \xrightarrow{\Delta} 2CH_3COCl + CaSO_4$$

PHYSICAL PROPERTIES

- These are mostly colourless liquids.
  For example, Acetyl chloride is a colourless liquid with a pungent smell.
- Acetyl chloride has a boiling point of 325 K.
- Acetyl chloride is insoluble in water but soluble in organic solvents like acetone, ether etc.
- Acetyl chloride fumes in moist air as HCl is formed.

CHEMICAL PROPERTIES

- Acid chlorides are most reactive among the acid derivative as Cl^- is highly electronegative that is it reduces electron density greatly at $-C^+-O^-$ so it is very easily attacked by a nucleophile.
- **Hydrolysis**

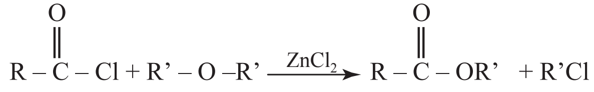
  $$RCOCl + H_2O \longrightarrow RCOOH + HCl$$

  For example, $CH_3COCl + H_2O \longrightarrow CH_3COOH + HCl$
- **With Alcohol** Acid chlorides react with alcohols to form esters. The reaction is called alcoholysis.

  $$RCOCl + HOR' \longrightarrow RCOOR' + HCl$$

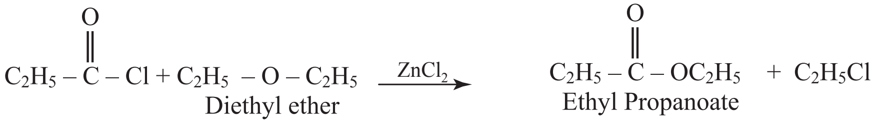
  For example,

  $$CH_3COCl + HOC_2H_5 \longrightarrow CH_3COOC_2H_5 + HCl$$
- **Formation of Ester** Acid chlorides react with ethers to give esters as follows:



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl + R'-O-R' \xrightarrow{ZnCl_2} R-\overset{\overset{\displaystyle O}{\|}}{C}-OR' + R'Cl$$

For example,



$$\underset{}{C_2H_5-\overset{\overset{\displaystyle O}{\|}}{C}-Cl} + \underset{\text{Diethyl ether}}{C_2H_5-O-C_2H_5} \xrightarrow{ZnCl_2} \underset{\text{Ethyl Propanoate}}{C_2H_5-\overset{\overset{\displaystyle O}{\|}}{C}-OC_2H_5} + C_2H_5Cl$$

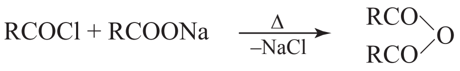
- **With Ammonia** Acid chlorides react with ammonia to form amides.

$$RCOCl + NH_3 \longrightarrow RCONH_2 + HCl$$

For example,

$$CH_3COCl + NH_3 \longrightarrow CH_3CONH_2 + HCl$$

- **With Acid Salts or Formation of Acid Anhydride** Acid chlorides react with acid salts to give acid anhydrides

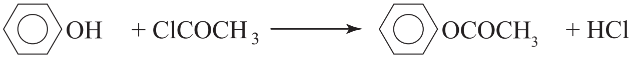

$$RCOCl + RCOONa \xrightarrow[-NaCl]{\Delta} \begin{matrix} RCO \\ RCO \end{matrix} \rangle O$$

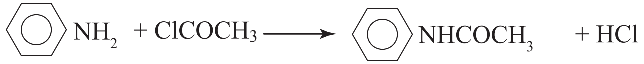
For Example,

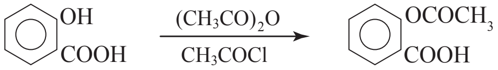

$$\underset{\text{Sodium acetate}}{CH_3COCl + CH_3COONa} \xrightarrow[-NaCl]{\Delta} \begin{matrix} CH_3CO \\ CH_3CO \end{matrix} \rangle O$$

Acetic anhydride

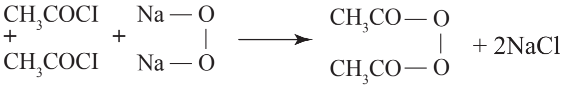
- **Acetylation** CH_3COCl is used for the acetylation of –OH group, $–NH_2$ group etc to find their number and location.


Phenol
Phenyl acetate


Aniline
Acetanilide


Salicylic acid
Acetyl salicylic acid
Aspirin [Pain killer]

- **With Sodium Peroxide**


$$\begin{matrix} CH_3COCl \\ + \\ CH_3COCl \end{matrix} + \begin{matrix} Na-O \\ | \\ Na-O \end{matrix} \longrightarrow \begin{matrix} CH_3CO-O \\ | \\ CH_3CO-O \end{matrix} + 2NaCl$$

Acetyl peroxide

Reduction Reactions

- ***Rosenmund's Reduction*** Acid chlorides are reduced by palladium/$BaSO_4$ poisoned by sulphur or quinoline to avoid further reduction of carbonyl compounds (aldehyde) into alcohols.

$$RCOCl + 2H \xrightarrow{Pd/BaSO_4} RCHO + HCl$$

For example,

$$CH_3COCl \xrightarrow[Pd/BaSO_4]{H_2} CH_3CHO + HCl$$

- ***With $LiAlH_4$*** Here alcohols are formed.

$$RCOCl \xrightarrow[LiAlH_4]{4[H]} R - CH_2 - OH$$

For example,

$$CH_3COCl \xrightarrow[LiAlH_4]{4[H]} CH_3 - CH_2 - OH$$

- **Reaction With Amines** Acid chlorides react with primary and secondary amines to give substituted amides.

- ***With Primary Amine***

$$RCOCl + H.NH.R \longrightarrow R - CO - NHR$$

For example,

$$CH_3COCl + H.NH.CH_3 \longrightarrow CH_3 - CO - NHCH_3$$

N-methyl acetamide

- ***With Secondary Amine***

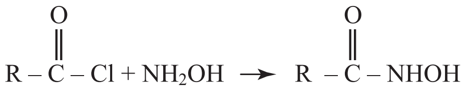
$$RCOCl + H.N.R_2 \longrightarrow R - CO - NR_2$$

For example,

$$CH_3COCl + H.N(CH_3)_2 \longrightarrow CH_3 - CO - N(CH_3)_2$$

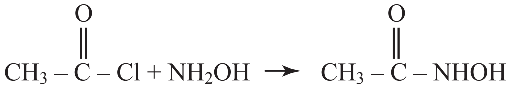
N, N-dimethyl acetamide

- ***With Hydrazine and Hydroxyl Amine***



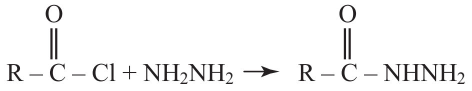
$$R - \overset{\overset{\displaystyle O}{\|}}{C} - Cl + NH_2OH \rightarrow R - \overset{\overset{\displaystyle O}{\|}}{C} - NHOH$$

For example,



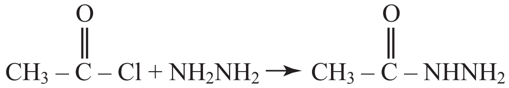
$$CH_3 - \overset{\overset{\displaystyle O}{\|}}{C} - Cl + NH_2OH \rightarrow CH_3 - \overset{\overset{\displaystyle O}{\|}}{C} - NHOH$$

Acetyl hydroxyl amine
(Hydro oxamic acid)



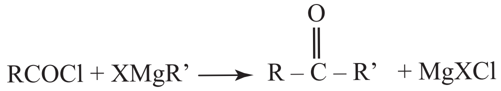
$$R-\overset{O}{\overset{\|}{C}}-Cl + NH_2NH_2 \rightarrow R-\overset{O}{\overset{\|}{C}}-NHNH_2$$

For example,



$$CH_3-\overset{O}{\overset{\|}{C}}-Cl + NH_2NH_2 \rightarrow CH_3-\overset{O}{\overset{\|}{C}}-NHNH_2$$

- ***With Grignard Reagent*** Acid chlorides react with grignard reagent to give ketones which further react with grignard reagent to give tertiary alcohols.



$$RCOCl + XMgR' \longrightarrow R-\overset{O}{\overset{\|}{C}}-R' + MgXCl$$

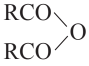
$$RCOCl \xrightarrow[-KCl]{KCN} RCOCN \xrightarrow[-NH_3]{2H_2O} R-\overset{O}{\overset{\|}{C}}-COOH$$

For example,

$$CH_3COCl \xrightarrow[-KCl]{KCN} CH_3COCN \xrightarrow[-NH_3]{2H_2O} CH_3-\overset{O}{\overset{\|}{C}}-COOH$$

Pyruvic acid (2 - oxo propunoic acid)

ACID ANHYDRIDE



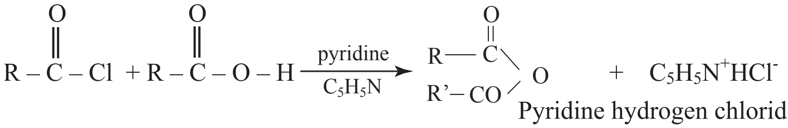
- These are named as alkanoic anhydrides.

  For example, $(CH_3CO)_2O$ Ethanoic anhydride

  $(C_2H_5CO)_2O$ Propanoic anhydride, $(C_6H_5CO)_2O$ BenOic Anhydride

METHODS OF PREPARATION

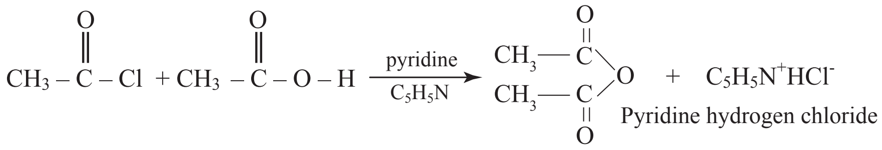
- **Lab Method**



$$R-\overset{O}{\overset{\|}{C}}-Cl + R-\overset{O}{\overset{\|}{C}}-O-H \xrightarrow[C_5H_5N]{\text{pyridine}} (RCO)(R'CO)O + C_5H_5N^+HCl^-$$

Pyridine hydrogen chloride

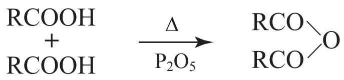
For Example



$$CH_3-\overset{O}{\overset{\|}{C}}-Cl + CH_3-\overset{O}{\overset{\|}{C}}-O-H \xrightarrow[C_5H_5N]{\text{pyridine}} (CH_3CO)_2O + C_5H_5N^+HCl^-$$

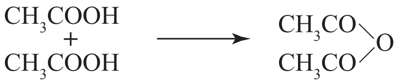
Pyridine hydrogen chloride

By the Dehydration of Alcohols



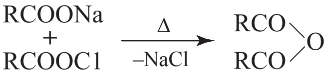
$$\begin{array}{c}RCOOH\\+\\RCOOH\end{array} \xrightarrow[P_2O_5]{\Delta} \begin{array}{c}RCO\\RCO\end{array}\!\!>O$$

For Example,



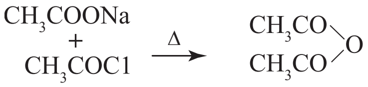
$$\begin{array}{c}CH_3COOH\\+\\CH_3COOH\end{array} \longrightarrow \begin{array}{c}CH_3CO\\CH_3CO\end{array}\!\!>O$$

Manufacture



$$\begin{array}{c}RCOONa\\+\\RCOOC1\end{array} \xrightarrow[-NaCl]{\Delta} \begin{array}{c}RCO\\RCO\end{array}\!\!>O$$

For example,



$$\begin{array}{c}CH_3COONa\\+\\CH_3COC1\end{array} \xrightarrow{\Delta} \begin{array}{c}CH_3CO\\CH_3CO\end{array}\!\!>O$$

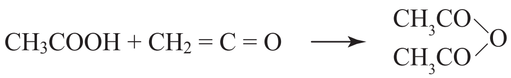
From Acetaldehyde Acetaldehyde is converted into acetic anhydride by air oxidation at 50 – 70°C in presence of catalysts like cobalt acetate–copper acetate.

$$CH_3CHO \xrightarrow[\text{Catalyst}]{\Delta O_2} CH_3CO_3H \xrightarrow{CH_3CHO} (CH_3CO)_2O + H_2O$$

With Acetone and Acetic Acid In this reaction first ketene is formed which then reacts with acetone to give acetic anhydride as follows:

$$CH_3COOH \xrightarrow[AlPO_4/\,700^{o}C]{\text{aluminium phosphate}} \underset{\text{Ketene}}{CH_2=C=O} + H_2O$$

$$CH_3COCH_3 \xrightarrow{\Delta} CH_2=C=O + CH_4$$

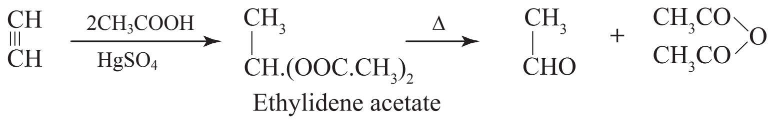


$$CH_3COOH + CH_2=C=O \longrightarrow \begin{array}{c}CH_3CO\\CH_3CO\end{array}\!\!>O$$

- **From Sodium Acetate and Sulphur Dichloride**

$$8CH_3COONa + SCl_2 + 2Cl_2 \longrightarrow 4(CH_3CO)_2O + 6NaCl + Na_2SO_4$$

From Acetylene: When acetylene is passed through glacial acetic acid in presence of mercuric sulphate followed by distillation acetic anhydride is formed as follows.



$$\begin{matrix}CH\\ \|\!|\\ CH\end{matrix} \xrightarrow[HgSO_4]{2CH_3COOH} \begin{matrix}CH_3\\ |\\ CH.(OOC.CH_3)_2\end{matrix} \xrightarrow{\Delta} \begin{matrix}CH_3\\ |\\ CHO\end{matrix} + \left.\begin{matrix}CH_3CO\\ CH_3CO\end{matrix}\right\rangle O$$

Ethylidene acetate

PHYSICAL PROPERTIES

- Acetic anhydride is a colourless liquid having a pungent smell.
- Acetic anhydride has a boiling point of 139.5°C.
- Acetic anhydride is partially soluble in water but readily soluble in solvents like ether, alcohol etc.

CHEMICAL PROPERTIES

- **Hydrolysis**

$$\left.\begin{matrix}RCO\\ RCO\end{matrix}\right\rangle O + H_2O \longrightarrow 2RCOOH$$

$$\left.\begin{matrix}RCO\\ RCO\end{matrix}\right\rangle O + NaOH \longrightarrow RCOOH + RCOONa$$

$$\left.\begin{matrix}RCO\\ RCO\end{matrix}\right\rangle O \xrightarrow{\text{Dry HCl}} RCOCl + RCOOH$$

- **With Alcohol or Alcoholysis** Acid anhydrides on reaction with alcohols give esters as follows:

$$\left.\begin{matrix}RCO\\ RCO\end{matrix}\right\rangle O + R'OH \longrightarrow RCOOR' + RCOOH$$

For example,

$$\left.\begin{matrix}CH_3CO\\ CH_3CO\end{matrix}\right\rangle O + C_2H_5OH \longrightarrow \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + CH_3COOH$$

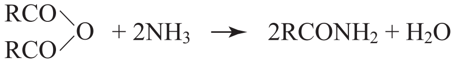
- **With PCl_5**

$$\left.\begin{matrix}RCO\\ RCO\end{matrix}\right\rangle O + PCl_5 \longrightarrow 2RCOCl + POCl_3$$

For example,

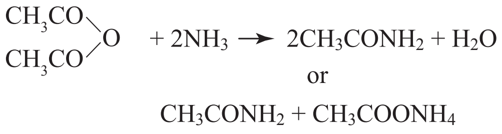
$$(CH_3CO)_2O + PCl_5 \longrightarrow 2CH_3COCl + POCl_3$$

- **With Ammonia**



$$\left.\begin{matrix}RCO\\RCO\end{matrix}\right\rangle O + 2NH_3 \rightarrow 2RCONH_2 + H_2O$$

For example,

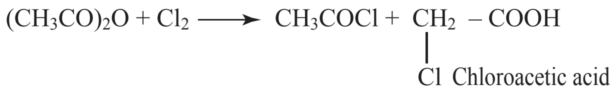


$$\left.\begin{matrix}CH_3CO\\CH_3CO\end{matrix}\right\rangle O + 2NH_3 \rightarrow 2CH_3CONH_2 + H_2O$$

or

$$CH_3CONH_2 + CH_3COONH_4$$

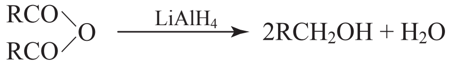
- **With Chlorine**



$$(CH_3CO)_2O + Cl_2 \longrightarrow CH_3COCl + \underset{\substack{|\\ Cl}}{CH_2} - COOH$$

Chloroacetic acid

- **Reduction** An acid anhydride on reduction by $LiAlH_4$ gives alcohol.



$$\left.\begin{matrix}RCO\\RCO\end{matrix}\right\rangle O \xrightarrow{LiAlH_4} 2RCH_2OH + H_2O$$

For example,

$$(CH_3CO)_2O \xrightarrow[Ether]{LiAlH_4} C_2H_5OH$$

- **Acetylation** It reacts with compounds having active hydrogen atom like aniline, phenol etc and here the active hydrogen atom is substituted by $CH_3 - CO-$ group. This reaction conforms the number of –OH or $-NH_2$ groups.

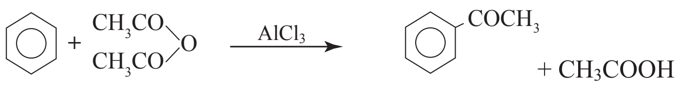
For example, in glycerol after acetylation glycerol triacetate is formed that is, glycerol has 3 –OH groups on different carbon atoms.

For example,

$$\underset{\text{Phenol}}{C_6H_5OH} + (CH_3CO)_2O \longrightarrow \underset{\text{Phenyl acetate}}{C_6H_5OCOCH_3} + CH_3COOH$$

- $$\underset{\text{Aniline}}{C_6H_5NH_2} + (CH_3CO)_2O \longrightarrow \underset{\text{Acetanilide}}{C_6H_5NHCOCH_3} + CH_3COOH$$

- **Freidal Craft Reaction** Benzene when treated with acetic anhydride in presence of anhydrous $AlCl_3$ acetophenone is obtained.

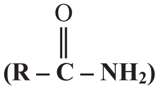


Acetophenone

- **With Acetaldehyde** Acetic anhydride reacts with acetaldehyde to give Ethylidene diacetate.

$$(CH_3CO)_2O + CH_3CHO \longrightarrow \underset{\text{Ethylidene diacetate}}{CH_3 - CH.(OOC.CH_3)_2}$$

AMIDES

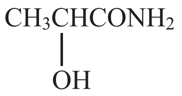


$$(R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2)$$

- Amides are named as Alkanamides.

  For example,

  (i) CH_3CONH_2 Ethanamide

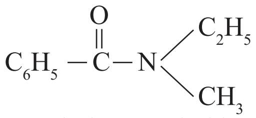
  (ii) 

  $\underset{\underset{\displaystyle OH}{|}}{CH_3CH}CONH_2$ 2-Hydroxy propanamide

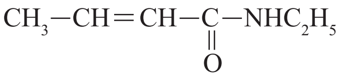
  (iii) 

  $\underset{\underset{\displaystyle CN}{|}}{CH_3CH}CONHCH_3$

  3-Cyano N-methyl propanamide

  (iv) 

  N-Ethyl. N-methyl benzanamide

  (v) 

  $CH_3-CH=CH-\underset{\underset{\displaystyle O}{\|}}{C}-NHC_2H_5$

  N-Ethyl but 2-enamide

METHODS OF PREPARATION

- **By Partial Hydrolysis of Cyanides** Cyanides on partial hydrolysis by alkaline H_2O_2 give amides:

  $$R-CN + H_2O \xrightarrow[\text{Alk.}]{H_2O_2 + NaOH} RCONH_2$$

  For example,

  $$CH_3CH_2CN + H_2O \xrightarrow[\text{Alk.}]{H_2O_2 + NaOH} \underset{\text{Propanamide}}{CH_3CH_2CONH_2}$$

- **From Acids** Acids react with ammonia to give acid amides as follows:

  $$RCOOH + NH_3 \longrightarrow RCOONH_4 \xrightarrow{\Delta} RCONH_2 + H_2O$$

  For example,

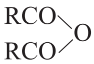
  $$CH_3COOH + NH_3 \longrightarrow CH_3COONH_4 \xrightarrow{\Delta} \underset{\text{Acetamide}}{CH_3CONH_2} + H_2O$$

- **From Acid Derivatives**

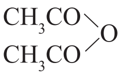
  $RCOCl + NH_3 \rightarrow RCONH_2 + HCl$

  For example,

  $CH_3COCl + NH_3 \rightarrow CH_3CONH_2 + HCl$

   $+ 2NH_3 \rightarrow 2RCONH_2 + H_2O$

  For example,

   $+ 2NH_3 \rightarrow 2CH_3CONH_2 + H_2O$

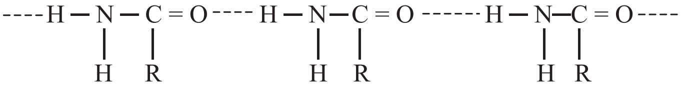
$RCOOR' + NH_3 \rightarrow RCONH_2 + R'OH$

For example,

$CH_3COOC_2H_5 + NH_3 \rightarrow CH_3CONH_2 + C_2H_5OH$

PHYSICAL PROPERTIES

- Acetamide is a colourless crystalline solid with a melting point 82°C and a boiling point 222°C. It is soluble in water and alcohol and can exist as a dimer because of hydrogen bonding.
- **Boiling point** Due to strong intermolecular hydrogen bonding amides have quite high boiling point among all the given organic compounds of comparable molecular masses.



$$----H-\underset{H}{\underset{|}{N}}-\underset{R}{\underset{|}{C}}=O----H-\underset{H}{\underset{|}{N}}-\underset{R}{\underset{|}{C}}=O------H-\underset{H}{\underset{|}{N}}-\underset{R}{\underset{|}{C}}=O----$$

CHEMICAL PROPERTIES

- **Amphoteric Nature** Due to amphoteric nature amides can react both with acid and bases to give salts as follows:

$RCONH_2 \xrightarrow{HCl} RCONH_2.HCl$

Amide hydrogen chloride

Stable in aq. solution

$2RCONH_2 \xrightarrow{HgO} (RCONH_2)_2Hg + H_2O$

Mercuric amide

$RCONH_2 \xrightarrow[\text{Ether}]{\text{Na}} RCONH.Na + \frac{1}{2} H_2$

Sodium alkanamide

- **Hydrolysis** It can be hydrolyzed by water acid, bases however the rate of hydrolysis decreases as follows:

$\xrightarrow[\text{Hydrolyses}]{\text{Bases > acid > } H_2O}$

$RCONH_2 + H_2O \xrightarrow{H^+} RCOOH + NH_3$

For example,

$CH_3CONH_2 + H_2O \xrightarrow{H^+} CH_3COOH + NH_3$

- **Dehydration** Amides can undergo dehydration by P_2O_5, $POCl_3$, $POCl_2$, to give cyanides as follows:

$RCONH_2 \xrightarrow[\Delta\, -H_2O]{P_2O_5\, /\, SOCl_2/POCl_3} RCN$

For example,

$CH_3CONH_2 \xrightarrow[\Delta\, -H_2O]{P_2O_5\, /\, SOCl_2/POCl_3} CH_3CN$

- **With Nitrous Acid (HNO_2)** Amides react with nitrous acid ($NaNO_2$ + HCl or HNO_2) to give acids.

$$RCONH_2 \xrightarrow{HNO_2} RCOOH + N_2 + H_2O$$

For example,

$$CH_3CONH_2 \xrightarrow{HNO_2} CH_3COOH + N_2 + H_2O$$

- **Reduction** Amides can be reduced with $LiAlH_4$, Na/Alcohol into amines as follows:

$$RCONH_2 + 4H \xrightarrow[\text{Ether}]{LiAlH_4} RCH_2NH_2 + H_2O$$

For example,

$$CH_3CONH_2 + 4H \xrightarrow[\text{Ether}]{LiAlH_4} \underset{\text{Ethyl amine}}{CH_3CH_2NH_2} + H_2O$$

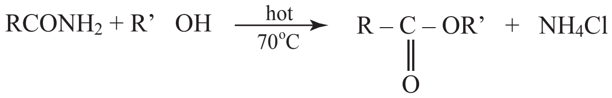
- **With PCl_5** Amides react with PCl_5 and give cyanides as follows:

$$RCONH_2 \xrightarrow{PCl_5} RCCl_2NH_2 + POCl_3 \xrightarrow{\Delta} R-CN + 2HCl$$

For example,

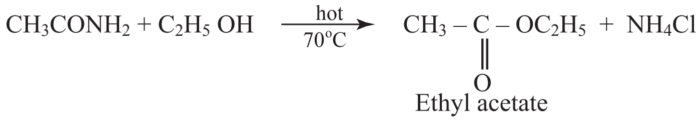
$$CH_3CONH_2 \xrightarrow[PCl_5]{} CH_3CCl_2NH_2 + POCl_3 \xrightarrow{\Delta} CH_3CN + 2HCl$$

- **With Alcohol (R – OH)** Amides react with alcohols to give esters



$$RCONH_2 + R'\ OH \xrightarrow[70^oC]{hot} R-\underset{\underset{O}{\|}}{C}-OR' + NH_4Cl$$

For example,



$$CH_3CONH_2 + C_2H_5\ OH \xrightarrow[70^oC]{hot} CH_3-\underset{\underset{O}{\|}}{C}-OC_2H_5 + NH_4Cl$$

Ethyl acetate

- **Hoffmann's Bromamide Reaction** Here amides are heated with bromine and caustic soda to give primary amines that is, conversion of – $CONH_2$ in to $-NH_2$ group. In this reaction, one carbon atom is lost as carbonate ion or potassium carbonate.

$$RCONH_2 + Br_2 + 4KOH \rightarrow RNH_2 + K_2CO_3 + 2KBr + 2H_2O$$

For example,

$$C_2H_5CONH_2 \xrightarrow{(Br_2 + KOH)} C_2H_5NH_2$$

$$C_2H_5CONH_2 + Br_2 \rightarrow C_2H_5CONHBr + HBr$$

$$HBr + KOH \rightarrow KBr + H_2O$$

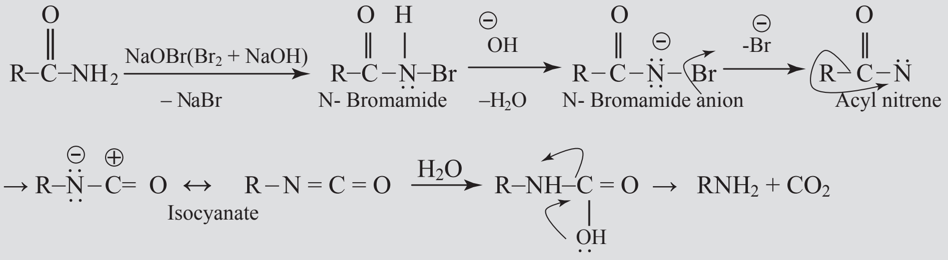
$$C_2H_5CONHBr + KOH \rightarrow C_2H_5NCO + KBr + H_2O$$

$$\underline{C_2H_5NCO + 2KOH \rightarrow C_2H_5NH_2 + K_2CO_3}$$

$$C_2H_5CONH_2 + Br_2 + 4KOH \rightarrow C_2H_5NH_2 + K_2CO_3 + 2KBr + 2H_2O$$

Mechanism

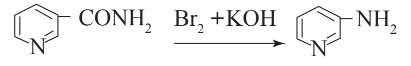
The mechanism has been suggested on the basic of the intermediates isolated during the course of reaction as follows:



$(CO_2 + 2NaOH \rightarrow Na_2CO_3 + H_2O)$

Examples

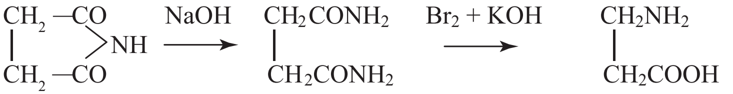
(i) Preparation of β -amino pyridine from nicotinamide



Nicotinamide

β - Aminopyridine

(ii) Synthesis of amino acids



Succinimide

β - Alanine

Phthalimide

Anthranilic acid

REMEMBER

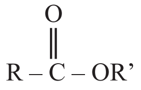
- Here $R-\overset{O}{\overset{\|}{C}}-N$ is reaction intermediate

$$R-\overset{O}{\overset{\|}{C}}-\ddot{N}: \xrightarrow{\text{Intramolecular rearrangement}} R-N=C=O$$

Acyl nitrile

Isocyanate

ESTERS



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OR'$$

- Esters are named as alkyl alkanoates.

  For example, $HCOOCH_3$ Methyl methanoate

  CH_3COOCH_3 Methyl ethanoate

  $CH_3CH_2COOC_2H_5$ Ethyl Propanoate

  $CH_3COCH_2COOC_2H_5$

  Ethyl-3-keto butanoate

  $C_6H_5COOC_6H_5$

  Phenyl benzoate

  $C_6H_5-CH=CH-COOC_2H_5$

  Ethyl z-phEnyl prop 2-enoate

Isomerism Shown By Esters Esters are functional isomers of acids and among themselves they show metamerism.

For example,

$$\left.\begin{array}{l} C_3H_6O_2 \\ (1)\ CH_3-CH_2-COOH \\ \left.\begin{array}{l}(2)\ CH_3-COOCH_3 \\ (3)\ HCOOC_2H_5\end{array}\right\}\quad \text{metamers}\end{array}\right\}\quad \text{functional}$$

Some Facts About Esters

- Esters are neutral and pleasant smelling liquids.
- Esters do not give efferences of CO_2 with aqueous sodium bi carbonate (distinguishing test from acids).
- On hydrolysis an ester gives an acid and an alcohol.
- On reduction with $LiAlH_4$ an ester gives two moles of alcohol.
- Higher esters are used as flavouring agents.

Methods of Preparation

- **By the Reaction Acid and Alcohols** When an acid react with an alcohol in presence of concentrated H_2SO_4 or HCl gas an ester is formed as follows:

$$RCOOH + HOR' \xrightarrow[H_2SO_4]{\text{conc.}} RCOOR' + H_2O$$

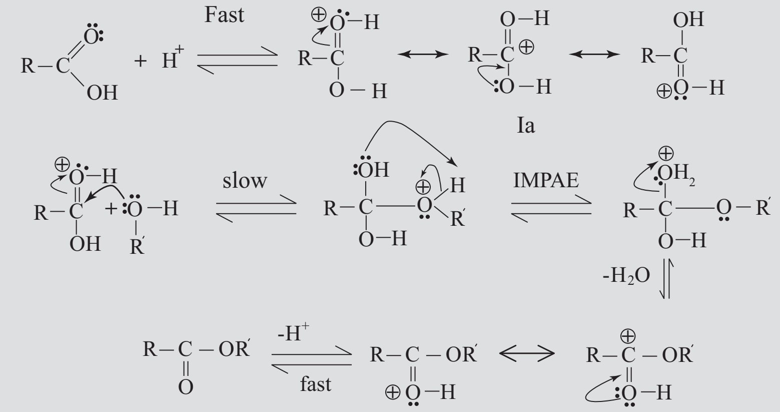
For example,

$$CH_3COOH + HOC_2H_5 \xrightarrow[H_2SO_4]{\text{conc.}} \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + H_2O$$

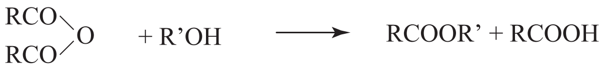
Mechanism of esterification by acid catalysis

A direct reaction between a carboxylic acid and alcohol under the catalytic effect of sulphuric acid yields an ester. This is a reversible reaction and is known as the Fischer esterification.

Mechanism

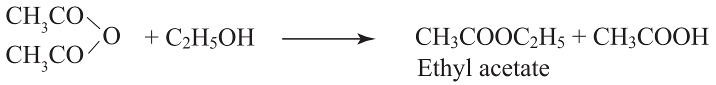


- **From Acid Anhydride** Acid anhydrides react with alcohols to give esters as follows:



$$(RCO)_2O + R'OH \longrightarrow RCOOR' + RCOOH$$

For example,



$$(CH_3CO)_2O + C_2H_5OH \longrightarrow CH_3COOC_2H_5 + CH_3COOH$$

Ethyl acetate

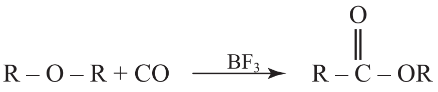
- **From Acid Chlorides**

$RCOCl + HOR' \longrightarrow RCOOR' + HCl$

For example,

$CH_3COCl + HOC_2H_5 \longrightarrow CH_3COOC_2H_5 + HCl$

- **From Ethers** Ethers react with carbon monoxide in presence of BF_3 to give esters as follows:



$$R-O-R + CO \xrightarrow{BF_3} R-\overset{\overset{\displaystyle O}{\|}}{C}-OR$$

For example,

$$CH_3-O-CH_3 + CO \xrightarrow{BF_3} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OCH_3$$

- **From Silver Salt of Acids** When silver salts of acids are treated with alkyl iodide esters are formed as follows:

$R-COOAg + I-R' \longrightarrow R-COOR' + AgI$

For example,

$$\underset{\text{Silver acetate}}{CH_3-COOAg} + I-C_2H_5 \longrightarrow CH_3-COOC_2H_5 + AgI$$

- **By Thischenko Reaction** It is the modified form of cannizzaro reaction. Here aldehydes undergo condensation in presence of aluminium ethoxide to give esters.

  For example,

  $$2CH_3CHO \xrightarrow{Al(OC_2H_5)_3} CH_3COOC_2H_5$$

PHYSICAL PROPERTIES

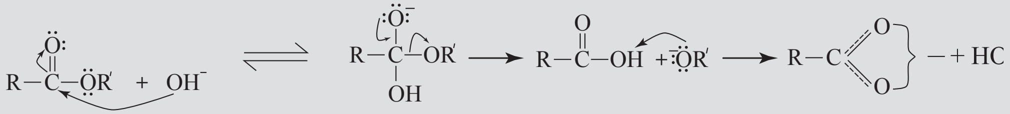
- Esters are colourless sweet smelling liquids. e.g., Ethyl acetate has a fruity smell.
- Ethyl acetate has a boiling point 350.5 K.
- Ethyl acetate is slightly soluble in water but more soluble in organic solvents like alcohol, ether etc.

CHEMICAL PROPERTIES

- **Hydrolysis** Esters undergo hydrolysis by boiling water or dilute acids or bases as follows.

  $$RCOOR' + H_2O \underset{\text{acid } H^+}{\longleftrightarrow} RCOOH + R'OH$$

Mechanism



For example,

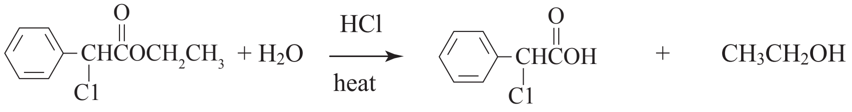
$$CH_3COOC_2H_5 + H_2O \xleftrightarrow{\text{acid } H^+} CH_3COOH + C_2H_5OH$$

$$RCOOR' + NaOH \longrightarrow RCOONa + R'OH$$

For example,

$$CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$$

- Acidic hydrolysis is reversible while basic hydrolysis is irreversible and called saponification. Example,



2- Chloro -2- phenylacetate

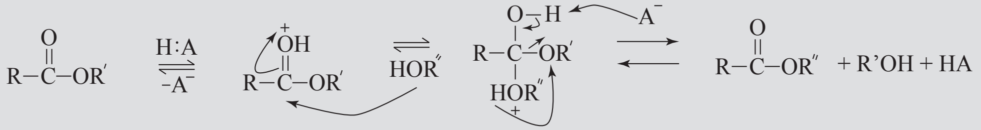
2- Chloro -2- phenylacetic acid (80 -82 %)

Ethyl alcohol

- **Splitting by ROH (Alcoholysis)** In this reaction alkyl group of an ester is substituted by alkyl group of alcohol in presence of sodium alkoxide. It is called trans esterification.

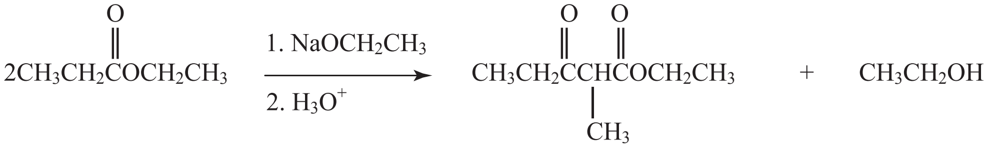
  $$RCOOR' + R''OH \xleftrightarrow{C_2H_5ONa} RCOOR'' + R'OH$$

Mechanism



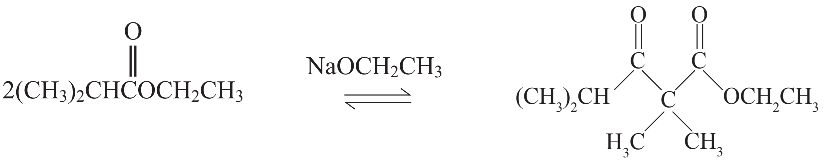
For example,

$$CH_3COOC_2H_5 + CH_3OH \xleftrightarrow{C_2H_5ONa} CH_3COOCH_3 + C_2H_5OH$$



$$2CH_3CH_2\overset{O}{\overset{\|}{C}}OCH_2CH_3 \xrightarrow[2.\ H_3O^+]{1.\ NaOCH_2CH_3} CH_3CH_2\overset{O}{\overset{\|}{C}}\underset{CH_3}{\underset{|}{C}}H\overset{O}{\overset{\|}{C}}OCH_2CH_3 + CH_3CH_2OH$$

Ethyl propanoate Ethyl 2- methyl -3- oxopentanoate (81 %) Ethanol



Ethyl 2- methylpropanoate Ethyl 2, 2, 4- trimethyl -3- oxopentanoate

Reduction

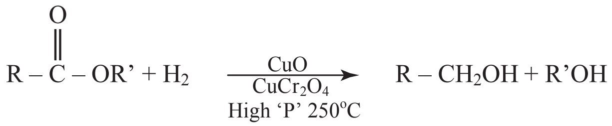
- When esters are reduced by $LiAlH_4$ or Na/C_2H_5OH alcohols are formed as follows:

$$RCOOR' + 4H \xrightarrow{LiAlH_4} RCH_2OH + R'OH$$

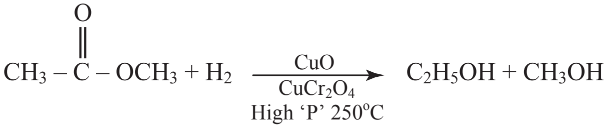
For example,

$$CH_3COOC_2H_5 + 4H \xrightarrow{LiAlH_4} 2CH_3CH_2OH$$

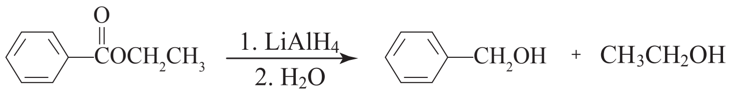
$$CH_3CH_2COOCH_3 + 4H \xrightarrow{Na\,/\,C_2H_5OH} CH_3CH_2CH_2OH + CH_3OH$$



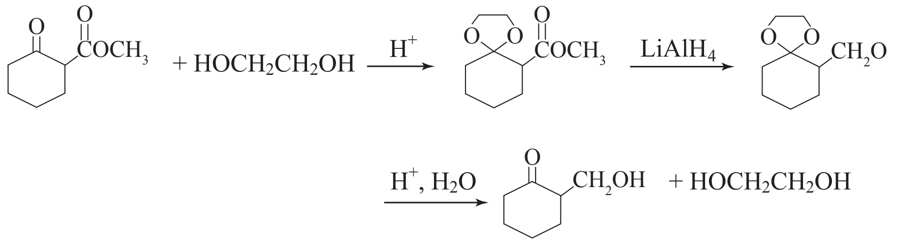
$$R - \overset{O}{\overset{\|}{C}} - OR' + H_2 \xrightarrow[\substack{CuCr_2O_4 \\ High\ 'P'\ 250^oC}]{CuO} R - CH_2OH + R'OH$$



$$CH_3 - \overset{O}{\overset{\|}{C}} - OCH_3 + H_2 \xrightarrow[\substack{CuCr_2O_4 \\ High\ 'P'\ 250^oC}]{CuO} C_2H_5OH + CH_3OH$$



Ethyl benzoate Benzyl alcohol (90 %) Ethyl alcohol



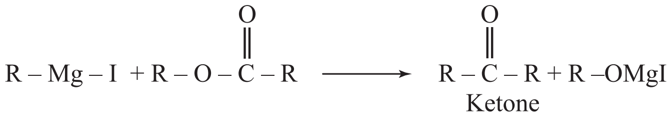
- **With Bromine** Esters react with bromine to give α-bromo substituted ester.

$$RCH_2COOR' + Br_2 \xrightarrow{\text{red P}} RCHBrCOOR' + HBr$$

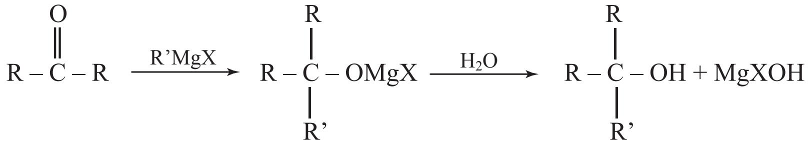
For example,

$$CH_3COOC_2H_5 + Br_2 \xrightarrow{\text{red P}} CH_2BrCOOC_2H_5 + HBr$$

- **With Grignard Reagent (R – MgX)** Grignard reagent reacts with esters to give ketones which again react with grignard reagent to give tertiary alcohols as follows:

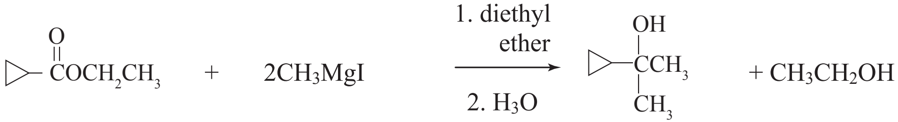


$$R-Mg-I + R-O-\overset{\overset{\displaystyle O}{\|}}{C}-R \longrightarrow \underset{\text{Ketone}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-R} + R-OMgI$$



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-R \xrightarrow{R'MgX} R-\overset{\overset{\displaystyle R}{|}}{\underset{\underset{\displaystyle R'}{|}}{C}}-OMgX \xrightarrow{H_2O} R-\overset{\overset{\displaystyle R}{|}}{\underset{\underset{\displaystyle R'}{|}}{C}}-OH + MgXOH$$

Tertiary alcohol



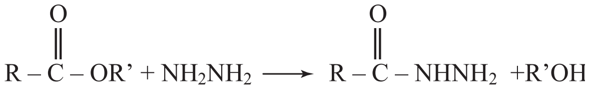
Ethyl cyclopropanecarboxylate Methylmagnesium iodide 2- Cyclopropyl -2- propanol (9 %) Ethanol

With Hydroxyl Amine Esters react with hydroxyl amine in presence of alcoholic KOH to give hydro-oxamic acid.

For example,

$$CH_3COOC_2H_5 \xrightarrow{NH_2OH} \underset{\text{Hydroxamic acid}}{CH_3CONH.OH} + C_2H_5OH$$

- **With Hydrazine** An ester reacts with hydrazine to give acid hydrazide as follows:

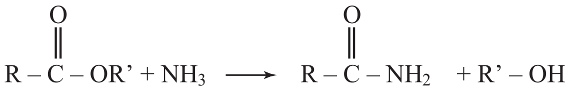


$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OR' + NH_2NH_2 \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-NHNH_2 + R'OH$$

For example,

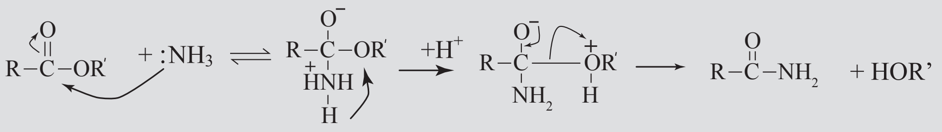
$$CH_3COOC_2H_5 \xrightarrow{NH_2NH_2} \underset{\text{Acid hydrazine}}{CH_3CONH.NH_2} + C_2H_5OH$$

Reaction With Amsmonia, Amine Esters react with ammonia or amines to give amides or alkyl substituted amides as follows:



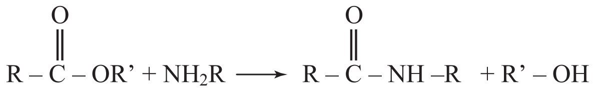
$$R-\overset{O}{\overset{\|}{C}}-OR' + NH_3 \longrightarrow R-\overset{O}{\overset{\|}{C}}-NH_2 + R'-OH$$

Mechanism



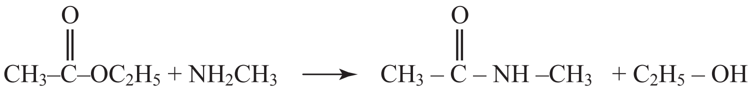
For example,

$$CH_3COOC_2H_5 + NH_3 \longrightarrow CH_3CONH_2 + C_2H_5OH$$



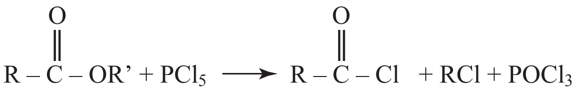
$$R-\overset{O}{\overset{\|}{C}}-OR' + NH_2R \longrightarrow R-\overset{O}{\overset{\|}{C}}-NH-R + R'-OH$$

For example,



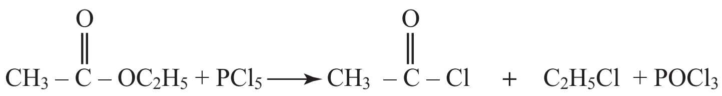
$$CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5 + NH_2CH_3 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-NH-CH_3 + C_2H_5-OH$$

- **With PCl_5 or $SOCl_2$** Esters react with these to give acid halides as follows



$$R-\overset{O}{\overset{\|}{C}}-OR' + PCl_5 \longrightarrow R-\overset{O}{\overset{\|}{C}}-Cl + RCl + POCl_3$$

For example,



$$CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5 + PCl_5 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-Cl + C_2H_5Cl + POCl_3$$

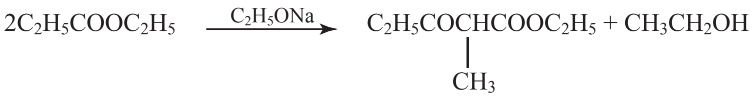
- **Claisen Condensation**

When two moles of an ester having α- hydrogen atom are condensed in presence of sodium ethoxide (strong base) a β- keto ester is formed.

For example,

When two moles of ethyl acetate are condensed ethyl acetoacetate or aceto acetic ester is formed as follows:

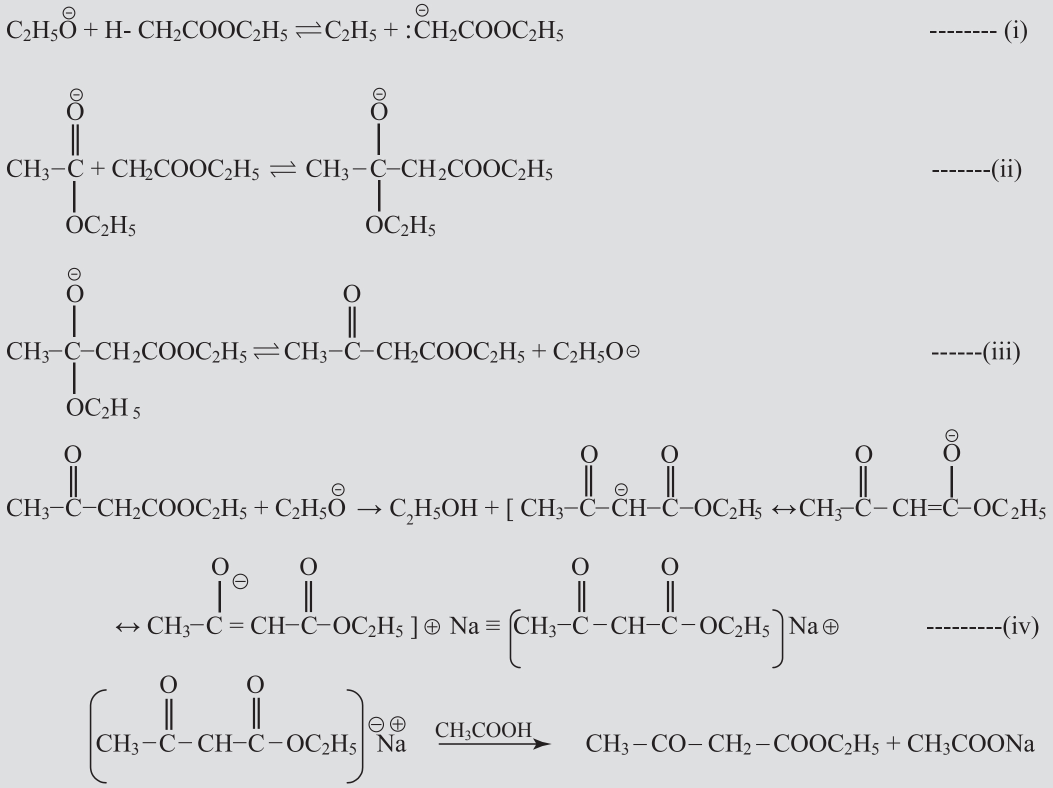
$$2CH_3COOC_2H_5 \xrightarrow{C_2H_5ONa} \underset{\text{Ethyl acetoacetate}}{CH_3COCH_2COOC_2H_5} + C_2H_5OH$$



$$2C_2H_5COOC_2H_5 \xrightarrow{C_2H_5ONa} C_2H_5CO\underset{\underset{\displaystyle CH_3}{|}}{C}HCOOC_2H_5 + CH_3CH_2OH$$

Ethyl 3-keto-2-methyl pentanoate

Mechanism



$$C_2H_5\overset{\ominus}{O} + H\text{- }CH_2COOC_2H_5 \rightleftharpoons C_2H_5 + :\overset{\ominus}{C}H_2COOC_2H_5 \qquad \text{-------- (i)}$$

$$CH_3-\underset{\underset{\displaystyle OC_2H_5}{|}}{\overset{\overset{\overset{\ominus}{O}}{\|}}{C}} + CH_2COOC_2H_5 \rightleftharpoons CH_3-\underset{\underset{\displaystyle OC_2H_5}{|}}{\overset{\overset{\overset{\ominus}{O}}{|}}{C}}-CH_2COOC_2H_5 \qquad \text{-------(ii)}$$

$$CH_3-\underset{\underset{\displaystyle OC_2H_5}{|}}{\overset{\overset{\overset{\ominus}{O}}{|}}{C}}-CH_2COOC_2H_5 \rightleftharpoons CH_3-\overset{\overset{O}{\|}}{C}-CH_2COOC_2H_5 + C_2H_5O^{\ominus} \qquad \text{------(iii)}$$

$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2COOC_2H_5 + C_2H_5\overset{\ominus}{O} \rightarrow C_2H_5OH + [\ CH_3-\overset{\overset{O}{\|}}{C}-\overset{\ominus}{C}H-\overset{\overset{O}{\|}}{C}-OC_2H_5 \leftrightarrow CH_3-\overset{\overset{O}{\|}}{C}-CH=\overset{\overset{\overset{\ominus}{O}}{|}}{C}-OC_2H_5$$

$$\leftrightarrow CH_3-\overset{\overset{O^{\ominus}}{|}}{C}=CH-\overset{\overset{O}{\|}}{C}-OC_2H_5\ ]\oplus Na \equiv \left(CH_3-\overset{\overset{O}{\|}}{C}-CH-\overset{\overset{O}{\|}}{C}-OC_2H_5\right)Na^{\oplus} \qquad \text{---------(iv)}$$

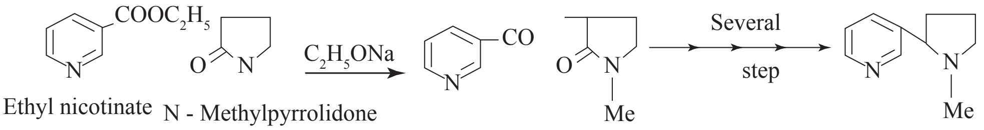
$$\left(CH_3-\overset{\overset{O}{\|}}{C}-CH-\overset{\overset{O}{\|}}{C}-OC_2H_5\right)\overset{\ominus\oplus}{Na} \xrightarrow{CH_3COOH} CH_3-CO-CH_2-COOC_2H_5 + CH_3COONa$$

Examples

(i)

$$\underset{\text{Ethyl benzoate}}{C_6H_5COOC_2H_5} + CH_3COOC_2H_5 \xrightarrow[\text{2. }H^{\oplus}]{\text{1. }C_2H_5ONa} \underset{\text{Ethyl benzoylacetate}}{C_6H_5COCH_2COOC_2H_5 + C_2H_5OH}$$

(ii)

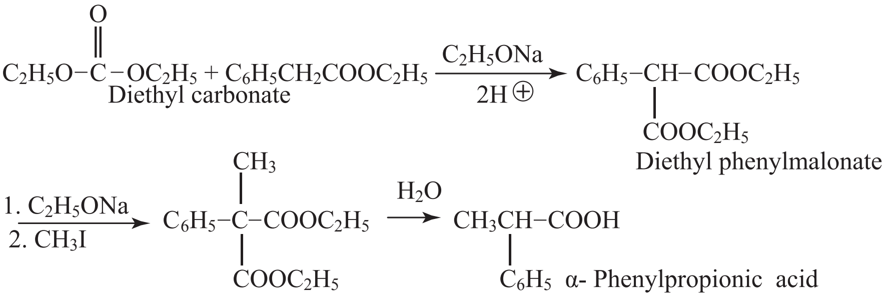


Ethyl nicotinate N - Methylpyrrolidone Nicotine

(iii)

$$C_6H_5CH_2COOC_2H_5 + HCOOC_2H_5 \xrightarrow[2H^{\oplus}]{C_6H_5ONa} C_6H_5\text{ -CH - }COOC_2H_5 + C_2H_5OH$$

(iv)



$$C_2H_5O-\overset{\overset{\displaystyle O}{\|}}{C}-OC_2H_5 + C_6H_5CH_2COOC_2H_5 \xrightarrow[2H^{\oplus}]{C_2H_5ONa} C_6H_5-\underset{\underset{\displaystyle COOC_2H_5}{|}}{CH}-COOC_2H_5$$

Diethyl carbonate

Diethyl phenylmalonate

$$\xrightarrow[2.\ CH_3I]{1.\ C_2H_5ONa} C_6H_5-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle COOC_2H_5}{|}}{C}}-COOC_2H_5 \xrightarrow{H_2O} CH_3\underset{\underset{\displaystyle C_6H_5}{|}}{CH}-COOH$$

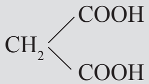
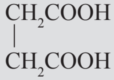
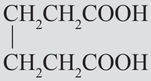
α- Phenylpropionic acid

ENHANCE YOUR KNOWLEDGE

Dibasic Acid

Such acids have two carboxylic groups with a general formula $C_nH_{2n}(COOH)_2$

For example,

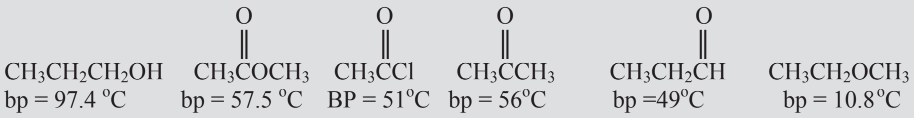
- Oxalic acid  $\begin{matrix} COOH \\ | \\ COOH \end{matrix}$ Ethan-1,2-dioic acid , Malonic acid  $CH_2\begin{matrix} \diagup COOH \\ \diagdown COOH \end{matrix}$ Propan-1,3-dioic acid
- Succinic acid  $\begin{matrix} CH_2COOH \\ | \\ CH_2COOH \end{matrix}$ Butan-1, 4-dioic acid , Adipic acid  $\begin{matrix} CH_2CH_2COOH \\ | \\ CH_2CH_2COOH \end{matrix}$ Hexan-1,6-dioic acid
- Benzoic acid is used as urinary antiseptic in medicines and in vapour form for disinfecting bronchial tubes.
- Acetic anhydride reacts with N_2O_5 to give acetyl nitrate. $(CH_3CO)_2O + N_2O_5 \rightarrow 2CH_3COONO_2$ Acetyl nitrate
- Reaction of acid chlorides with water decrease with increase of C-atoms in alkyl groups.

  $CH_3COCl > CH_3 - CH_2 - COCl > CH_3 - CH_2 - CH_2COCl > .....$

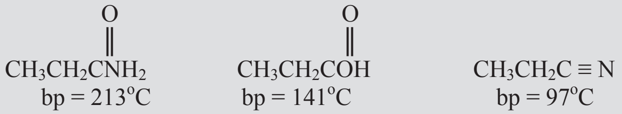
  Relative boiling points

  amides > carboxylic acids > nitriles >> esters ~ acyl chlorides ~ aldehydes ~ ketones

The boiling points of esters, acyl chlorides, aldehydes, and ketones are higher than the boiling points of ethers because of the polar carbonyl group, but are lower than the boiling points of alcohols because their molecules can't form hydrogen bonds with each other.



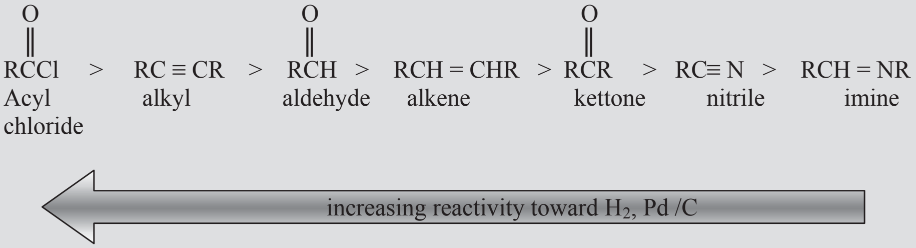
$CH_3CH_2CH_2OH$ bp = 97.4 °C; $CH_3C(=O)OCH_3$ bp = 57.5 °C; $CH_3C(=O)Cl$ BP = 51°C; $CH_3C(=O)CH_3$ bp = 56°C; $CH_3CH_2C(=O)H$ bp =49°C; $CH_3CH_2OCH_3$ bp = 10.8°C



$CH_3CH_2C(=O)NH_2$ bp = 213°C; $CH_3CH_2C(=O)OH$ bp = 141°C; $CH_3CH_2C \equiv N$ bp = 97°C

- **Blanc Rule**: It states when dicarboxylic acids having two –COOH groups on same carbon atom are heated monocarboxylic acids are formed on the other hand 1, 4 and 1, 5 dicarboxylic acids on heating with acetic anhydrides give cyclic ketones.

Relative Ease of Reduction of Functional Groups by Catalytic Hydrogenation



$RC(=O)Cl > RC \equiv CR > RC(=O)H > RCH = CHR > RC(=O)R > RC \equiv N > RCH = NR$

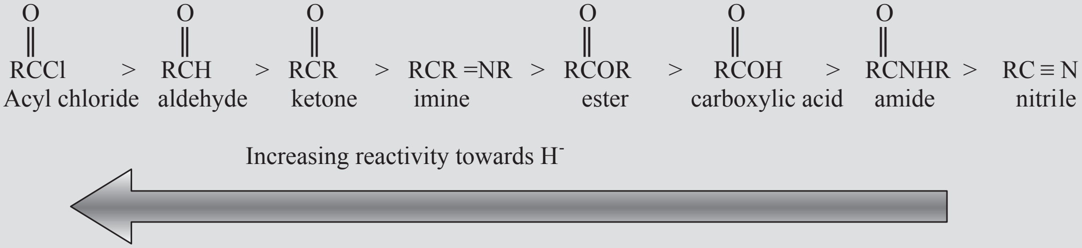
Acyl chloride > alkyl > aldehyde > alkene > kettone > nitrile > imine

increasing reactivity toward H_2, Pd /C

cannot be reduced by catalytic hydrogenation:

$RC(=O)OR$ ester; $RC(=O)NHR$ amide; $RC(=O)OH$ carboxylic acid

Relative Ease of Reduction of Functional Groups by Addition of Hydride Ion



$RC(=O)Cl > RC(=O)H > RC(=O)R > RCR{=}NR > RC(=O)OR > RC(=O)OH > RC(=O)NHR > RC \equiv N$

Acyl chloride > aldehyde > ketone > imine > ester > carboxylic acid > amide > nitrile

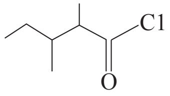
Increasing reactivity towards H^-

Cannot be reduced by hydride ion: $RCH = CHR$ Alkene; $RC \equiv CR$ alkyne

MULTIPLE-CHOICE QUESTIONS

Straight Objective Type Questions

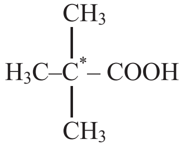
1. The IUPAC name of



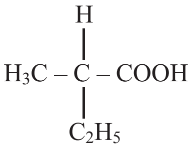
(a) 2-ethyl-3methylbutanoyl chloride
(b) 2, 3-dimethylpentanoyl chloride
(c) 3, 4-dimethylpentanoyl chloride
(d) 1-chloro-1-oxo-2, 3-dimethylpentane

2. The correct priority of functional groups in IUPAC nomenclature is
(a) Amides > acid > ester > ketone
(b) Ester > amide > ketone > acid
(c) Ketone > acid > ester > amide
(d) Acid > ester > amide > ketone

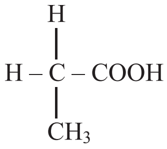
3. Which of the following shows optical isomerism?

(a) 

$$H_3C\text{–}\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C^*}}\text{– COOH}$$

(b) 

$$H_3C - \overset{\overset{\large H}{|}}{\underset{\underset{\large C_2H_5}{|}}{C}} - COOH$$

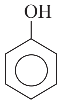
(c) 

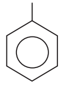
$$H - \overset{\overset{\large H}{|}}{\underset{\underset{\large CH_3}{|}}{C}} - COOH$$

(d) None of these

4. What is the main reason for the fact that carboxylic acids can undergo ionization?
(a) Resonance stabilization of the carboxylate ion
(b) Hydrogen bonding
(c) Absence of alpha hydrogen
(d) High reactivity of alpha hydrogen

5. Which of the following is the weakest acid?
(a) HCOOH (b) CH_3COOH

(c) 

(d) 

6. Which of the following orders of relative strengths of acids is correct?
(a) $ClCH_2COOH > FCH_2COOH > BrCH_2COOH$
(b) $ClCH_2COOH > BrCH_2COOH > FCH_2COOH$
(c) $BrCH_2COOH > ClCH_2COOH > FCH_2COOH$
(d) $FCH_2COOH > ClCH_2COOH > BrCH_2COOH$

7. Which one of the following acids is thermally most unstable?
(a) CH_3COCH_2COOH
(b) $CH_3COCH_2CH_2CH_2COOH$
(c) $CH_3COCOOH$
(d) $CH_3COCH_2CH_2COOH$

8. Among the following acids which has the lowest pKa value?
(a) CH_3COOH (b) HCOOH
(c) $(CH_3)_2CH - COOH$ (d) CH_3CH_2COH

9. Which one of the following is correct? Formic acid has lower pKa than that of CH_3COOH because:
(a) Formic acid is a strong reducing agent
(b) Formic acid is smaller in size than acetic acid
(c) Formic acid does not have an alkyl group
(d) Formic acid does not dissociate

10. In the propanoate ion:
(a) both the carbon-oxygen bonds are the same length.
(b) the carbon-oxygen double bond is shorter.
(c) the carbon-oxygen double bond is longer.
(d) one of the oxygen atoms bears a -1 charge.

11. The relation reactivities of acyl compounds towards nucleophillic substitution are in the order of:
(a) Acid anhydride > Amide > Ester > Acyl chloride
(b) Acyl chloride > Ester > Acid anhydride > Amide
(c) Acyl chloride > Acid anhydride > Ester > Amide
(d) Ester > Acyl chloride > Amide > Acid anhydride

12. Which of the following on oxidation followed by hydrolysis gives pyruvic acid?
(a) acetone cyanohydrin
(b) acetaldehyde cyanohydrin
(c) formaldehyde cyanohydrin
(d) none of these

13. Hydrogenation of benzoyl chloride in the presence of Pd and $BaSO_4$ gives:
(a) benzyl alcohol (b) benzaldehyde
(c) benzoic acid (d) phenol

14. The end product (B) in the following sequence of reactions

$$CH_3Cl \xrightarrow{KCN} (A) \xrightarrow{H^+/H_2O} (B) \text{ is}$$

(a) HCOOH (b) CH_3NH_2
(c) CH_3COOH (d) CH_3COCH_3

15. Which statement is true regarding reaction of an acid chloride (RCOCl) and ammonia when taken in 1 :1 molar ratio?
(a) One-half of acid chloride is converted into RCONH$_2$ and the other half into RCOONH$_4$
(b) Whole of acid is converted into RCON$_2$
(c) One - half of acid chloride is converted into RCONH$_2$ and the remaining half remains unreacted
(d) None of the three is correct.

16. Compound 'A' reacts with PCl$_5$ to give 'B' which on treatment with KCN followed by hydrolysis gave propionic acid. What are A and B respectively?
(a) C_2H_5OH & C_2H_5Cl (b) C_2H_5Cl & $C_2H_5Cl_2$
(c) C_2H_8 & C_2H_5Cl (d) C_3H_8 & C_3H_7Cl

17. Acetamide is treated separately with the following reagents. Which one of the these would give methyl amine?
(a) Sodalime (b) PCl$_5$
(c) Hot. Conc. H$_2$SO$_4$ (d) NaOH + Br$_2$

18. R – CH$_2$ – CH$_2$OH can be converted into RCH$_2$CH$_2$COOH. The correct sequence of reagent is
(a) PBr$_3$, KCN, H$^+$ (b) HCN, PBr$_3$, H$^+$
(c) KCN, H$^+$ (d) PBr$_3$, KCN, H$_2$

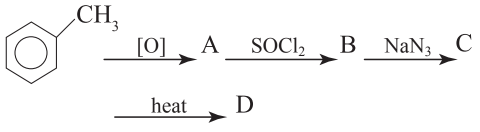
19. The hydrolysis of esters, amides, and nitriles:
(a) Must be acid-catalysed
(b) Should be carried out at pH 7.0 for optimum efficiency
(c) Can be carried out under acidic or basic conditions
(d) Must be base-catalysed

20. The end product of the reaction

$$C_2H_5OH \xrightarrow{PCl_5} C_2H_5Cl \xrightarrow{KCN} C_2H_5CN \xrightarrow{H_3O^+}$$

(a) propanol (b) propanoic acid
(c) propanamide (d) none of these

21. In the following sequence of reactions, what is D?



(a) an amide
(b) phenyl isocyanate
(c) primary amine
(d) a chain lengthened hydrocarbon

22. $CH_3CH_2COOH \xrightarrow[\text{red P}]{Cl_2} A \xrightarrow{\text{alc. KOH}} B$
What is B?
(a) CH$_3$CH$_2$CHO (b) ClCH$_2$CH$_2$COOH
(c) CH$_3$CH$_2$COCl (d) CH$_2$ = CHCOOH

23. $(CH_3)_2CO \xrightarrow[\text{(HCl)}]{\text{NaCN}} A \xrightarrow{H_3O^+} B$
in the above sequence of reactions A and B are
(a) (CH$_3$)$_2$C(OH)CN, (CH$_3$)$_2$CHCOOH
(b) (CH$_3$)$_2$C(OH)CN, (CH$_3$)$_2$C(OH)$_2$
(c) (CH$_3$)$_2$C(OH)CN, (CH$_3$)$_2$C(OH)COOH
(d) (CH$_3$)$_2$C(OH)CN, (CH$_3$)$_2$C = O

24. In the following reaction, X and Y respectively are
$X \xrightarrow[\text{Solution}]{\text{aq. NaOH}} CH_3COOH \xrightarrow{Y} (CH_3CO)_2O$
(a) CH$_3$COCH$_3$; H$_2$SO$_4$ (b) CH$_3$CH$_2$OH , NaOAc
(c) CH$_3$CN, P$_2$O$_5$ (d) CH$_3$CHO, PCl$_5$

25. What alkyllithium would react with acetic acid to form 2-butanone?
(a) methyllithium (b) vinyllithium
(c) ethyllithium (d) propyllithium

26. An organic compound reacts (i) with metallic sodium to liberate hydrogen and (ii) with Na$_2$CO$_3$ solution to liberate CO$_2$. the compound is
(a) an ether (b) an ester
(c) an alcohol (d) a carboxylic acid

27. $(CH_3CO)_2O \xrightarrow[\text{Anhyd. AlCl}_3]{\text{diethyl ether}} A.$
Product A is
(a) CH$_3$COOC$_2$H$_5$ (b) CH$_3$COOCH$_3$
(c) CH$_3$CH$_2$COOC$_2$H$_5$ (d) CH$_3$CH$_2$COOH

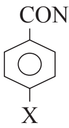
28. Which of the following converts acetic acid to acetyl chloride?
(a) Cl$_2$/P (b) HCl
(c) NaCl (d) PCl$_3$

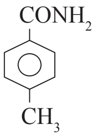
29. In the following reaction, X and Y are respectively
$CH_3COOH + NH_3 \longrightarrow X \xrightarrow{\Delta} Y + H_2O$
(a) CH$_3$NH$_2$, CH$_3$CONH$_2$
(b) CH$_3$CONH$_2$, CH$_3$COOH
(c) CH$_3$CONH$_2$, CH$_4$
(d) CH$_3$COONH$_4$, CH$_3$CONH$_2$

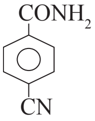
30. By aerial oxidation, which one of the following gives phthalic acid?
(a) benzene (b) naphthalene
(c) toluene (d) mesitylene

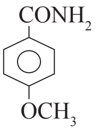
31. Acids can be reduced to aldehydes by:
(a) Conversion to the amide followed by treatment with $NaBH_4$
(b) Conversion to the anhydride followed by treatment with Mg and H_3O^+.
(c) Conversion to the acid chloride followed by treatment with $LiAlH[OC(CH_3)_3]_3$.
(d) Conversion to the ester followed by treatment with $LiAlH_4$.

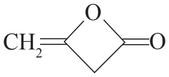
32. Which of the following can undergo Hoffmann reaction most easily?

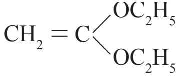
(a) 

(b) 

(c) 

(d) 

33. $CH_3CO_2C_2H_5$ on reaction with sodium ethoxide in ethanol gives A, which on heating in the presence of acid gives B. Compound B is
(a) CH_3COCH_2COOH (b) CH_3OCH_3
(c) 

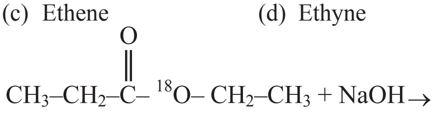
(d) 
$CH_2 = C(OC_2H_5)_2$

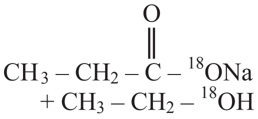
34. An acid which could not be prepared by the reaction of an organic halide with cyanide ion followed by acid hydrolysis of the nitrile is
(a) propanoic acid (b) phenylacetic acid
(c) acetic acid (d) $(CH_3)_3CCO_2H$

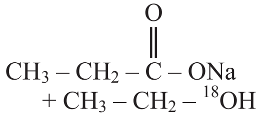
35. Acetic acid reacts with ethanol in the presence of H_2SO_4 to form X and water, which of the following is X?
(a) $CH_3COC_2H_5$ (b) CH_3COCH_3
(c) $CH_3CH_2COOC_2H_5$ (d) $CH_3COOC_2H_5$

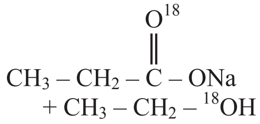
36. Self condensation of two moles of ethyl acetate in presence of sodium ethoxide yields
(a) methyl acetoacetate
(b) ethyl propionate
(c) ethyl butyrate
(d) acetoacetic ester

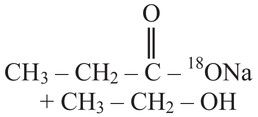
37. Product formed on electrolysis of potassium salt of fumaric and maleic acid salt is
(a) Ethene + ethyne (b) Ethane
(c) Ethene (d) Ethyne

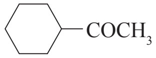
38. 
$CH_3{-}CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\,^{18}O{-}CH_2{-}CH_3 + NaOH \rightarrow$

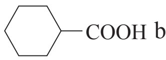
(a) 
$CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-\,^{18}ONa + CH_3-CH_2-\,^{18}OH$

(b) 
$CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-ONa + CH_3-CH_2-\,^{18}OH$

(c) 
$CH_3-CH_2-\overset{\overset{\displaystyle O^{18}}{\|}}{C}-ONa + CH_3-CH_2-\,^{18}OH$

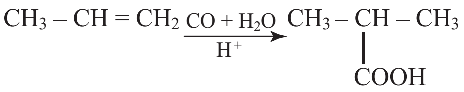
(d) 
$CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-\,^{18}ONa + CH_3-CH_2-OH$

39. The compound 

can be exclusively oxidized into 

by
(a) $K_2Cr_2O_7$ followed by H_3O^+
(b) NaCN followed by hydrolysis
(c) NaOI followed by H_3O^+
(d) Hot $KMnO_4$ followed by hydrolysis

40. The reaction,


$$CH_3-CH=CH_2 \xrightarrow[H^+]{CO + H_2O} CH_3-\underset{\underset{\displaystyle COOH}{|}}{CH}-CH_3$$

is known as:
(a) Koch reaction
(b) Kolbe's reaction
(c) Wurtz reaction
(d) Clemmensen reduction

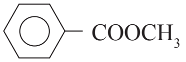
41. On mixing ethyl acetate with aqueous sodium chloride, the composition of the resultant solution is
(a) $CH_3COOC_2H_5 + NaCl$
(b) $CH_3COONa + C_2H_5OH$
(c) $CH_3COCl + C_2H_5OH + NaOH$
(d) $CH_3Cl + C_2H_5COONa$

42. The correct order of increasing boiling points of the following compounds is:
(1) CH_3COCl (2) CH_3COOCH_3
(3) $(CH_3CO)_2O$ (4) CH_3CONH_2
(a) 2 > 3 > 4 > 1 (b) 2 > 3 > 1 > 4
(c) 3 > 2 > 1 > 4 (d) 1 > 3 > 4 > 2

43. Lithium aluminum hydride reduces carboxylic acids to primary alcohols via what intermediate?
(a) a ketone (b) a methyl ester
(c) an aldehyde (d) a secondary alcohol

44. Which of the following will produce only 1 product on reduction with $LiAlH_4$?
(a) $CH_3OCOCH_2CH_3$
(b) $CH_3CH_2OCOCH_2CH_2CH_3$
(c) $CH_3CH_2OCOCH_2CH_3$
(d) $CH_3CH_2OCOCH_3$

45. Claisen condensation is not given by:

(a)


(b)

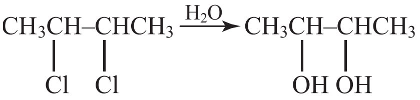

(c)


(d)

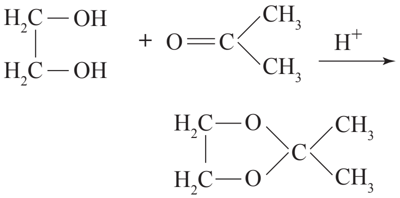

46. When $CH_2 = CH - COOH$ is reduced with $LiAlH_4$ the compound obtained will be
(a) $CH_3 - CH_2 - COOH$
(b) $CH_2 = CH - CH_2OH$
(c) $CH_3 - CH_2 - CH_2OH$
(d) $CH_3 - CH_2 - CHO$

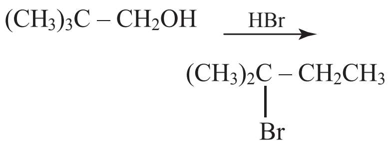
47. Which one of the following reactions is an example of asymmetric synthesis?

(a) $CH_3CHO \xrightarrow[(2)\ H_3O^+]{(1)\ HCN} CH_3CHOH.COOH$

(b)


$CH_3\underset{Cl}{CH}-\underset{Cl}{CH}CH_3 \xrightarrow{H_2O} CH_3\underset{OH}{CH}-\underset{OH}{CH}CH_3$

(c)


(d)


$(CH_3)_3C - CH_2OH \xrightarrow{HBr} (CH_3)_2\underset{Br}{C} - CH_2CH_3$

48. The reaction of ethyl p-aminobenzoate with HNO_2 and then with HBF_4 yields a compound (X), a crystalline ionic compound. Compound (X) when heated form $C_9H_9O_2$ (Y). Identify Y.
(a) ethyl-o-fluorobenzoate
(b) ethyl-p-fluorobenzoate
(c) ethyl-m-fluorobenzoate
(d) mixture of all the above

49. Consider the following reaction:

$$C_6H_5NO_2 \xrightarrow{Sn / HCl} X \xrightarrow{C_6H_5COCl} Y + HCl$$

What is Y?
(a) azo-benzene (b) hydrazo-benzene
(c) benzanilide (d) acetanilide

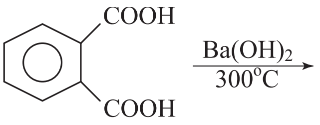
50. o-Hydroxybenzoic acid is treated with methanol in the presence of a drop of concentrated H_2SO_4. Which product is formed?
(a) Salicylic acid (b) Methyl salicylate
(c) Phthalic acid (d) Phenyl salicylate

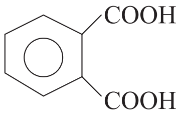
51. The methyl ester of a carboxylic acid can be synthesized directly using
(a) $SOCl_2$ (b) PCl_5
(c) CrO_2Cl_2 (d) $CH2N_2$

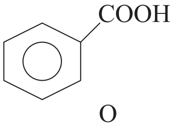
52. EtCOOH on reaction with EtMgBr gives:
(a) EtH (b) $Et_3COMgBr$
(c) EtCOEt (d) EtCOOEt

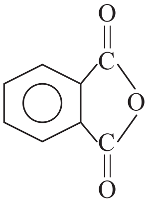
53. In the anion $HCOO^-$ the two carbon-oxygen bonds are found to be of equal length. What is the reason for it?
(a) electronic orbits of carbon atom are hybridized
(b) The C = O bond is weaker than the C–O bond
(c) The anion $HCOO^-$ has two resonating structures
(d) the anion is obtained by removal of a proton from the acid molecule

54. Identify the product

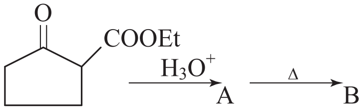
(a)


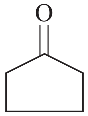
(b)


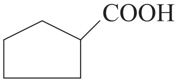
(c)


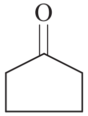
(d)


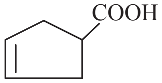
55. The compound is



(a) 

(b) 

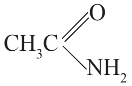
(c) 

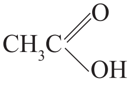
(d) 

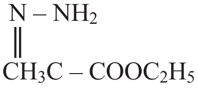
56. Which of the following acids has the smallest dissociation constant?

(a) FCH_2CH_2COOH (b) $CH_3CHFCOOH$
(c) $BrCH_2CH_2COOH$ (d) $CH_3CHBrCOOH$

57. Ethyl acetate reacts with hydrazine to give

(a) 
$CH_3C(=O)NH_2$

(b)  and C_2H_5OH
$CH_3C(=O)OH$

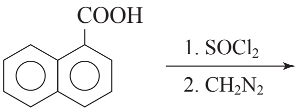
(c) 
$CH_3C(=N{-}NH_2){-}COOC_2H_5$

(d) $CH_3CONHNH_2$

58. Which compound is produced when N, N-dimethylpropanamide is treated with $LiAlH_4$?

(a) $CH_3CH_2CH_2OH$ (b) $CH_3CH_2CH_2N(CH_3)_2$
(c) $CH_3CH_2CONH_2$ (d) $CH_2CH_2CH_2NH_2$

59. The product formed in the following reaction is



(a) β-amino- α-naphthoylchloride
(b) β-amino- α-naphthanamide
(c) diazo- α-acetonaphthone
(d) α-naphthyl acetic acid

60. The end product R in the following sequence of chemical reaction is

$$CH_3-COOH \xrightarrow{Ca(OH)_2} (P) \xrightarrow{\Delta} Q \xrightarrow{NH_2OH} (R)$$

(a) Formaldehyde oxime
(b) Acetaldehyde oxime
(c) Methyl nitrate
(d) Acetoxime

Brainteasers Objective Type Questions (Single choice only)

61. The correct order of increasing acid strength of the compound

(a) CH_3O_2H (b) $MeOCH_2CO_2H$
(c) CF_3CO_2H (d) $(Me)_2-CO_2H$

is

(a) b < d < a < c (b) d < a < c < b
(c) d < a < b < c (d) a < d < c < b

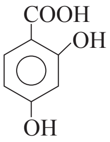
62. In the reaction

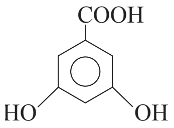
$$R-CH_2CH_2COOH \xrightarrow{Cl_2\ /red\ p} P \xrightarrow{Alc.\ KOH} Q$$

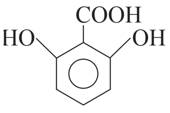
the compound Q is:

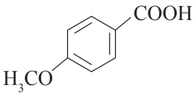
(a) $R-CH_2CH_2OH$
(b) $R-CH_2CH_2COCl$
(c) $R-CH=CH-COOH$
(d) $R-CH_2CHClCOOH$

63. For these given carboxylic acids

(I) 

(II) 

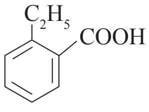
(III) 

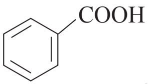
(IV) 

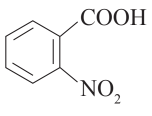
The order of increasing acidity is

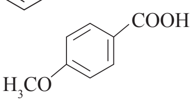
(a) I < II < IV < III (b) I < III < IV < II
(c) III < IV < I < II (d) IV < II < I < III

64. Write the correct order of acidity.

(I) 

(II) 

(III) 

(IV) 

(a) I > II > III > IV (b) IV > II > I > III
(c) II > I > III > IV (d) III > I > II > IV

65. At pH 4.5, which of the following acids would be most dissociated?

(a) p-nitrobenzoic acid ($pK_a = 3.41$)
(b) acetic acid (ethanoic acid) ($pK_a = 4.74$)
(c) hexanoic acid ($pK_a = 4.88$)
(d) octanoic acid ($pK_a = 4.89$)

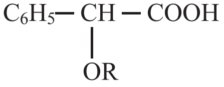
66. Consider the following acids:
(1) o-HOC_6H_4COOH
(2) o-$CH_3OC_6H_4COOH$
(3) C_6H_5COOH
Arrange these acids in the decreasing order of their acidities.
(a) 1 > 3 > 2 (b) 3 > 2 > 1
(c) 1 > 2 > 3 (d) 2 > 3 > 1

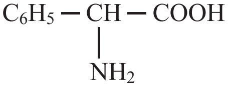
67. Arrange the following carboxylic acids in the decreasing order of the reactivities:
1. CH_3COOH 2. $ClCH_2COOH$
3. $Cl_2CHCOOH$ 4. Cl_3CCOOH
(a) 1 > 2 > 3 > 4 (b) 4 > 3 > 2 > 1
(c) 2 > 1 > 3 > 4 (d) 2 > 4 > 1 > 3

68. Place the following acid chlorides in the decreasing order of reactivity to hydrolysis
(1) C_6H_5COCl
(2) p-$O_2NC_6H_4COCl$
(3) p-$CH_3OC_6H_4COCl$
(a) 2 > 1 > 3 (b) 3 > 1 > 2
(c) 1 > 2 > 3 (d) 1 > 3 > 2

69. Consider the following acids:
(1) HCN (2) HCOOH
(3) CH_3COOH (4) $Cl - CH_2 - COOH$
The acid strengths of these acids are such that
(a) 4 > 3 > 1 > 2 (b) 1 > 3 > 2 > 4
(c) 2 > 3 > 4 > 1 (d) 4 > 2 > 3 > 1

70. Which one of the following pairs gives effervescence with aq. $NaHCO_3$?
(I) CH_3COCl (II) CH_3COCH_3
(II) CH_3COOCH_3 (IV) $CH_3COOCOCH_3$
(a) I & III (b) I & IV
(c) II& III (d) I & II

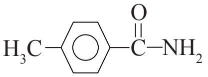
71. Which of the following carboxylic acids undergoes decarboxylation easily?
(a)

$C_6H_5 - \underset{OR}{\underset{|}{CH}} - COOH$

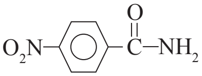
(b)

$C_6H_5 - \underset{NH_2}{\underset{|}{CH}} - COOH$

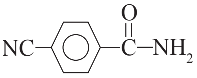
(c) $C_6H_5 - CO - CH_2 - COOH$
(d) $C_6H_5 - CO - COOH$

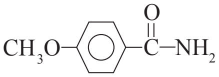
72. Consider the following acids:
(1) CH_3COOH (2) $Cl_2CHCOOH$
(3) $ClCH_2COOH$ (4) $ClCH_2CH_2COOH$
The correct sequence of acidity is
(a) 3 > 1 > 2 > 4 (b) 2 > 3 > 4 > 1
(c) 1 > 3 > 4 > 2 (d) 2 > 4 > 3 > 1

73. Arrange the following amides according to their relative when react with Br_2 in excess of strong base:

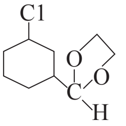
(I)


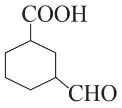
(II)


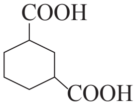
(III)


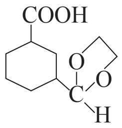
(IV)


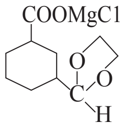
(a) I > II > IV > III (b) IV > I > III > II
(c) II > III > IV > I (d) I > IV> III > II

74.

reacted with $\xrightarrow[\text{(ii) } CO_2 \quad \text{(iii) } H_3O^+]{\text{(i) Mg, ether}}$ (P)

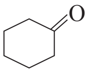
(a)


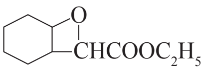
(b)


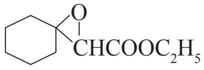
(c)


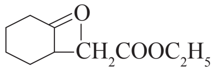
(d)


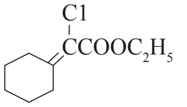
75. Perdict the nature of A in the following reaction?


$+ ClCH_2COOC_2H_5 \xrightarrow{\text{base}} (A)$

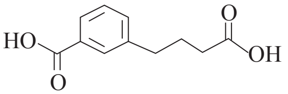
(a)


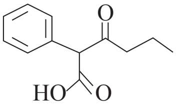
(b)


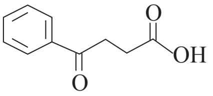
(c)


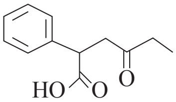
(d)


76. Which of the following undergoes decarboxylation most readily on being heated?

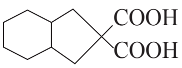
(a) 

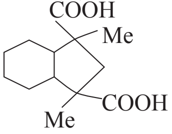
(b) 

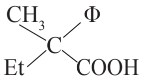
(c) 

(d) 

77. An acid (a) does not perform HVZ reaction with Br_2 -red P. (A) on heating gives (B) which can perform HVZ reaction with Br_2 -red P. (A) is

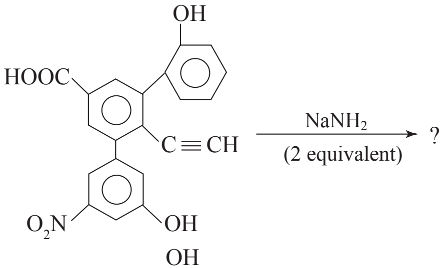
(a) 

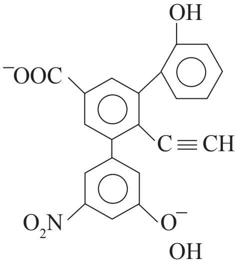
(b) 

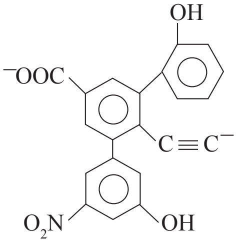
(c) 

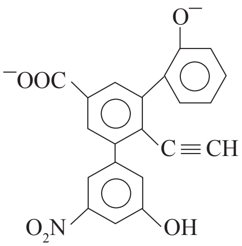
(d) None of these

78. The product of the reaction can be given as:

(a) 

(b) 

(c) 

(d) 

79. CH_3CH_2CHO $Al(OC_2H_5)_3$ [ ] C_2H_5ONa (P)
(P) is given as:
- (a) $CH_3CH_2COCH(CH_3)COOC_2H_5$
- (b) $CH_3COCH_2COOC_2H_5$
- (c) $CH_3CH_2COONa + C_2H_5OC_2H_5$
- (d) $CH_3CH_2COCH_2CH_2COOC_2H_5$

80. In the following sequence of reactions:

$CH_3CH_2OH \xrightarrow{KMnO_4}$

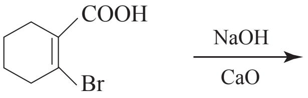
(a) $\xrightarrow{SOCl_2,\ NH_3}$

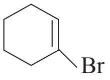
(b) $\xrightarrow{Br_2 + NaOH}$ (C)

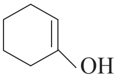
the end product (C) is

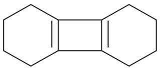
(a) Acetone	(b) Ethylamine
(c) Acetic acid	(d) Methyl amine

81. Identify the product (X) in the following reaction:



(a) 

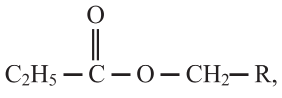
(b) 

(c) 

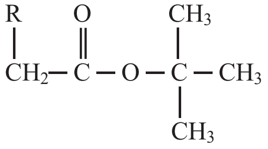
(d) can be both A and B

82. $R-CH_2-COOH + C_2H_5\overset{18}{O}H \xrightarrow{\text{conc. } H_2SO_4} (P)$

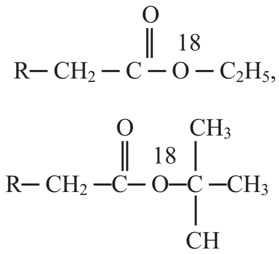
$R-CH_2-COOH + (CH_3)_3C-\overset{18}{O}H \xrightarrow{\text{conc. } H_2SO_4} (Q)$

(a) 

$C_2H_5-\overset{O}{\overset{\|}{C}}-O-CH_2-R,$

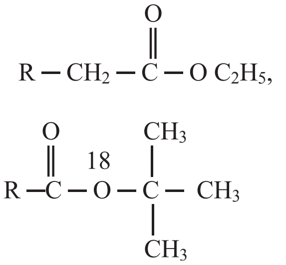


$\overset{R}{\overset{|}{CH_2}}-\overset{O}{\overset{\|}{C}}-O-\overset{CH_3}{\overset{|}{\underset{\underset{CH_3}{|}}{C}}}-CH_3$

(b) 

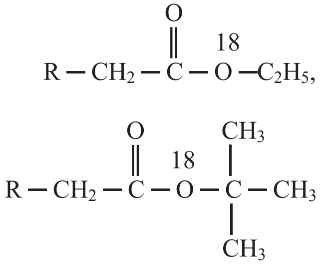
$R-CH_2-\overset{O}{\overset{\|}{C}}-\overset{18}{O}-C_2H_5$,

$R-CH_2-\overset{O}{\overset{\|}{C}}-\overset{18}{O}-\underset{CH}{\overset{CH_3}{C}}-CH_3$

(c) 

$R-CH_2-\overset{O}{\overset{\|}{C}}-O\,C_2H_5$,

$R-\overset{O}{\overset{\|}{C}}-\overset{18}{O}-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$

(d) 

$R-CH_2-\overset{O}{\overset{\|}{C}}-\overset{18}{O}-C_2H_5$,

$R-CH_2-\overset{O}{\overset{\|}{C}}-\overset{18}{O}-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$

83. Carbonation of methylmagnesium bromide gives an organic compound. This compound is also obtained by

(a) Hydrolysis of methyl formate with dilute mineral acid.
(b) Oxidation of methyl alcohol.
(c) Hydrolysis of methyl formate with dilute mineral acid.
(d) Hydrolysis of acetonitrile by a mineral acid.

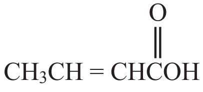
84. 2-methyl-2-ethyl-3-butenoic acid is strongly heated. The major product is

(a) 3-methyl-1-pentene
(b) 2-methyl-3-ethyl-2-butene
(c) 2-methyl-2-ethyl-1-butene
(d) 3-methyl-2-pentene

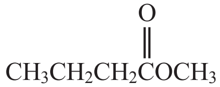
85. What is compound R here?

$CH_3CH_2CH_2X \xrightarrow{NaCN} (P) \xrightarrow{H_3O^+} (Q) \xrightarrow{CH_3OH} (R)$

(a) $CH_3CH_2CH_2CH(OCH_3)_2$
(b) $CH_3CH_2CH_2CH=NOCH\ CH_3$

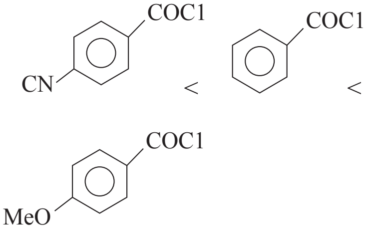
(c) 

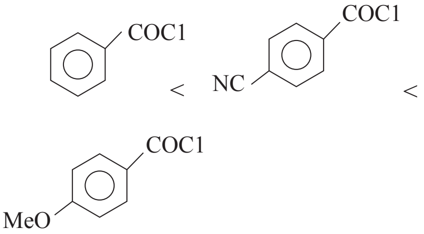
$CH_3CH=CH\overset{O}{\overset{\|}{C}}OH$

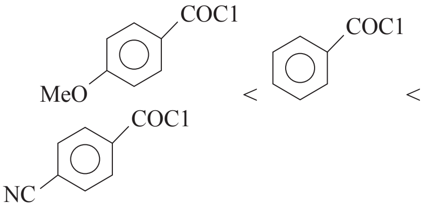
(d) 

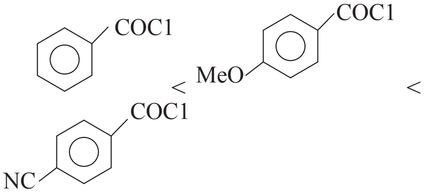
$CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}OCH_3$

86. The correct order of the ease of hydrolysis is

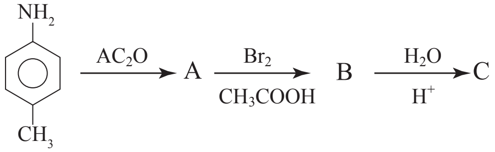
(a) 

(b) 

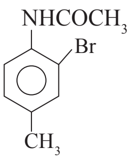
(c) 

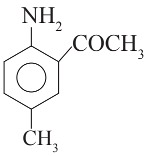
(d) 

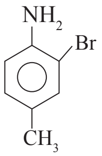
87. In the reaction

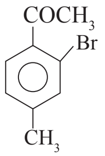


the final product C is

(a) 

(b) 

(c) 

(d) 

88. Identify (A) in the following sequence of reactions

$$C_4H_7OCl\ (A) \xrightarrow{NH_3} C_4H_9ON \xrightarrow{Br_2 + NaOH} CH_3CH_2CH_2NH_2$$

(a) $CH_3CH_2CH_2COCl$

(b) $CH_3CH_2CHClCHO$

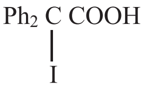
(c) $CH_3CH_2CH(OH)CH_2Cl$

(d) $CH_3CH_2COCH_2Cl$

89. Identify the product of the reaction,

$$Ph_2C(OH)COOH \xrightarrow[\text{Heat}]{\text{1 eq., red P / HI (excess)}} ?$$

(a) Ph_2CHOH

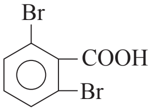
(b) 

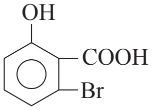
$Ph_2\underset{\underset{I}{|}}{C}COOH$

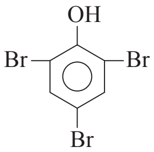
(c) $Ph_2CHCOOH$

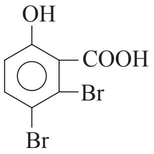
(d) None of these

90. The reaction of p-HOC_6H_4COOH with excess Br_2 forms

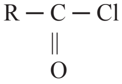
(a) 

(b) 

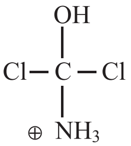
(c) 

(d) 

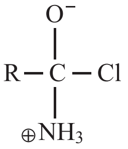
91. Which of the following is an intermediate formed in the given reaction?



$R-\underset{\underset{O}{\|}}{C}-Cl + NH_3 \rightarrow$ Intermediate $\rightarrow$ product.

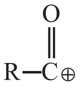
(a) 

$Cl-\overset{\overset{OH}{|}}{\underset{\underset{\oplus NH_3}{|}}{C}}-Cl$

(b) 

$R-\overset{\overset{O^-}{|}}{\underset{\underset{\oplus NH_3}{|}}{C}}-Cl$

(c) $R-NH_3$

(d) 

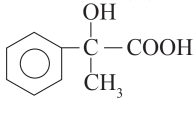
$R-\overset{\overset{O}{\|}}{C}\oplus$

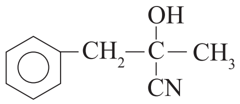
92. In a set of reactions acetic acid yielded a product (D).

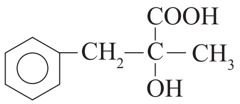
$$CH_3COOH \xrightarrow{SOCl_2} (A) \xrightarrow[\text{Anhy. }AlCl_3]{\text{Benzene}}$$

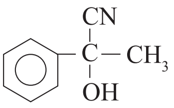
$$(B) \xrightarrow{HCN} (C) \xrightarrow{H_2O} (D)$$

The structure of (D) would be:

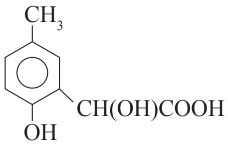
(a) 

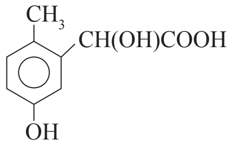
(b) 

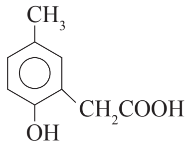
(c) 

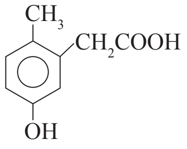
(d) 

93. p-cresol reacts with chloroform in alkaline medium to give the compound (A) which adds hydrogen cyanide to form the compound (B). The latter on acidic hydrolysis gives chiral carboxylic acid. The structure of the carboxylic acid is

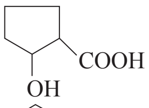
(a) 

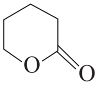
(b) 

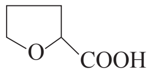
(c) 

(d) 

94. $Cl-(CH_2)_4-COOH \xrightarrow[\text{(2) }H^+]{\text{(1) }OH^-} ?$

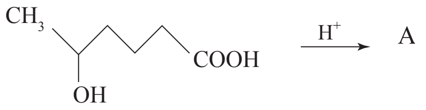
(a) 

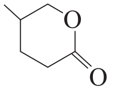
(b) 

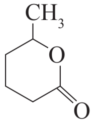
(c) 

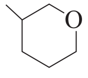
(d) $HO-(CH_2)_4-COOH$

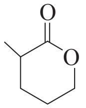
95. Compound A is



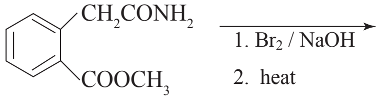
(a) 

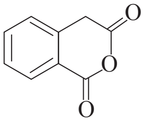
(b) 

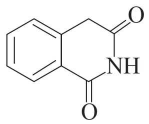
(c) 

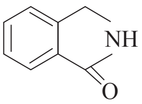
(d) 

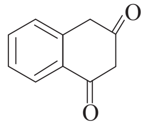
96. The following sequence of reactions on A gives



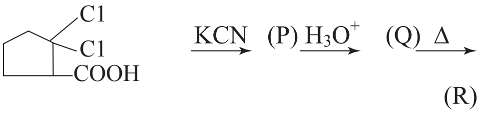
(a) 

(b) 

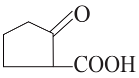
(c) 

(d) 

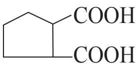
97. $(CH_2)_3(COOH)_2$ on heating gives
(a) open chain ketone
(b) monocarboxylic acid
(c) cyclic ketone
(d) cyclic anhydride

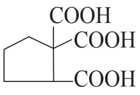
98. 

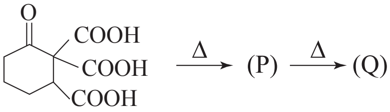
Here (R) is given as:

(a) 

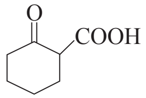
(b) 

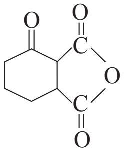
(c) 

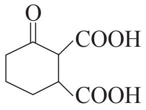
(d) 

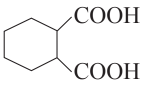
99. 

The product (Q) in this reaction is:

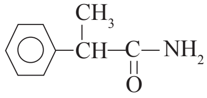
(a) 

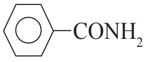
(b) 

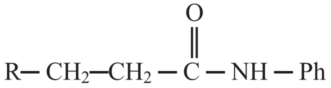
(c) 

(d) 

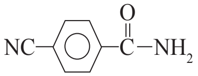
100. Which of the following compound can give Hofmann rearrangement

(I) 

(II) 

(III) 

$$R-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-NH-Ph$$

(IV) 

(a) I, II, III (b) I, II, IV
(c) II, III, IV (d) I, II, III, IV

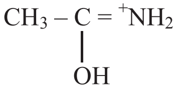
Decisive Thinking Objective Type Questions (One or more than one choice)

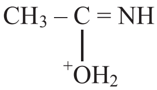
101. Which of the following reactions can give carboxylic acid?
(a) $PhCN + H_3O^+ \rightarrow$
(b) $PhOH + NaOH + CO_2 \rightarrow$
(c) $RMgX + CO_2 \rightarrow$
(d) $PhOH + CHCl_3 + NaOH \rightarrow$

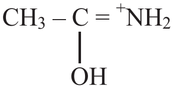
102. Identify the correct statement from the following:
(a) methyl salicylate is an ester.
(b) salicylic acid is a monobasic acid.
(c) methyl salicylate does not occur in natural oils.
(d) salicylic acid gives violet colour with neutral ferric chloride as well as brisk effervescence with sodium bicarbonate.

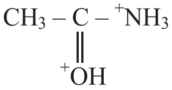
103. Which of following acids are affected on heating?
(a) Fumaric acid
(b) Succinic acid
(c) Malonic acid
(d) Maleic acid

104. Which of the following intermediate are formed during acidic hydrolysis of $MeC \equiv N$ to MeCOOH?

(a) 
$CH_3-\underset{\displaystyle |\atop OH}{C}={}^{+}NH_2$

(b) 
$CH_3-\underset{\displaystyle |\atop {}^{+}OH_2}{C}=NH$

(c) 
$CH_3-\underset{\displaystyle |\atop OH}{C}={}^{+}NH_2$

(d) 
$CH_3-\underset{\displaystyle \|\atop {}^{+}OH}{C}-{}^{+}NH_3$

105. Identify the incorrect statement about the acids, from the following:

(a) Electron releasing substituents decrease the stability of carboxylic acids.

(b) Malonic acid is a stronger acid than succinic acid.

(c) The reduction of benzoic acid with lithium aluminium hydride gives toluene.

(d) Formic acid can be halogenated in the presence of red P and Cl_2.

106. $C_4H_4O_4$ can represents

(a) A cis-dibasic acid

(b) A cyclic ester of dibasic acid

(c) An α, β unsaturated dibasic acid which on heating gives a monobasic acid

(d) An ester with keto group

107. Which of the following statement is/are true regarding esterification of a carboxylic with an alcohol?

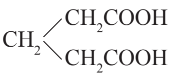
(a) The strong acid makes the carbonyl group more electrophil which is thus attacked easily by an alcohol, a weak nucleophile.

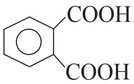
(b) Estrification can be done even in absence of a strong acid.

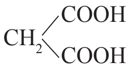
(c) It is carried out in presence of a strong acid which acts as a catalyst .

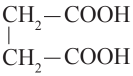
(d) The strong acid makes the carbonyl carbon more electrophilic, and hence causes the alcohol, a strong nucleophile to attack on the carbonyl carbon.

108. Which of the following can yield cyclic compound on heating?

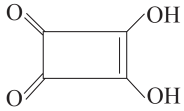
(a) 

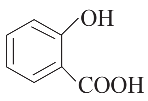
(b) 

(c) 

(d) 
$\begin{array}{l}CH_2-COOH\\ \;|\\ CH_2-COOH\end{array}$

109. Which of the following can react with $NaHCO_3$ to give CO_2?

(a) 

(b) 

(c) C_6H_5OH

(d) $CH_3COCOOH$

110. Which of the following statements is/are false?

(a) $LiAlH_4$ reacts with acid chlorides to yield secondary alcohols after hydrolysis.

(b) Two equivalents of Grignard reagent react with acid chlorides to yield tertiary alcohols after hydrolysis.

(c) $LiAlH[OC(CH_3)_3]_3$ reacts with acid chlorides to yield primary alcohols after hydrolysis.

(d) $LiAlH_4$ reacts with acid amides to give primary alcohols.

111. Which of the following on reduction with $LiAlH_4$ give ethanol?

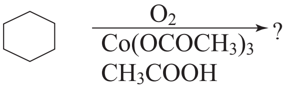
(a) CH_3CONH_2

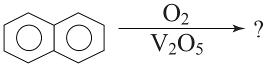
(b) CH_3COCl

(c) $CH_3COOC_2H_5$

(d) $(CH_3CO)_2O$

112. In which of these reaction phthalic acid can be formed?

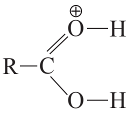
(a) 

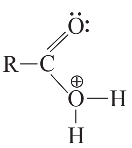
(b) 

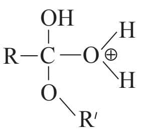
(c) 

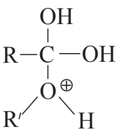
(d) 

113. Which of the following intermediates are involved in the acid catalysed esterification of carboxylic acid?

(a) 

(b) 

(c) 

(d) 

114. Which of the following statement are correct?

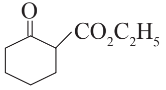
(a) RCOOR' is more reactive than ROR'

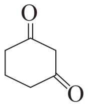
(b) RCOCl is more reactive than $RCONH_2$

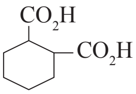
(c) $RCONH_2$ is more reactive than RNH_2

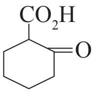
(d) RCOCl is less reactive than RCOOR'

115. Which of the following compound can not undergo decarboxylation on heating?

(a) 

(b) 

(c) 

(d) 

116. Which of the following statements are correct about HCOOH?

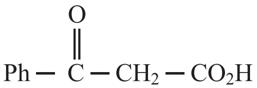
(a) It reduces Tollen's reagent

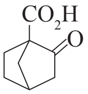
(b) It is stronger than benzoic acid

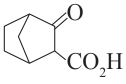
(c) It gives HCOCl with PCl_5

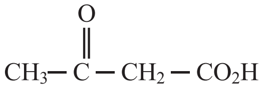
(d) It gives CO and H_2O on heating with conc. H_2SO_4

117. Which β -keto acid shown cannot undergo decarboxylation?

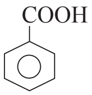
(a) 
$\mathrm{Ph-\overset{\overset{O}{\|}}{C}-CH_2-CO_2H}$

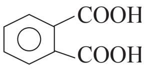
(b) 

(c) 

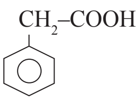
(d) 
$\mathrm{CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CO_2H}$

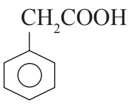
118. In which of the following pairs both members on heating with sodalime give same hydrocarbon:

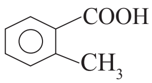
(a) 

, 

(b) 

, 

(c) 

, 

(d) $HOOC-CH_2CH_2-COOH$, $HOOC-CH_2CH_3$

119. Which of the following conditions will drive the equilibrium of the Fischer esterification towards ester formation?

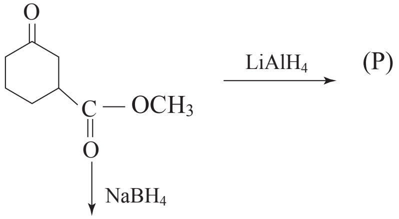
(a) addition of water

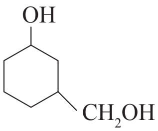
(b) addition of alcohol

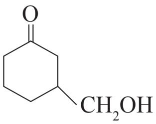
(c) addition of an inorganic acid as a catalyst

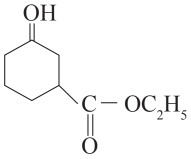
(d) removal of water as it is formed

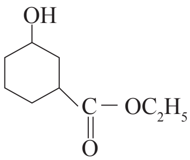
120. Identify (P) and (Q) in the following reaction:



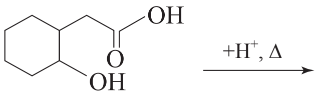
(a) (P) is 

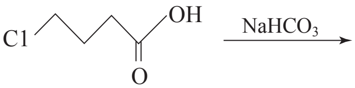
(b) (Q) is 

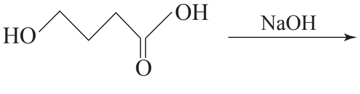
(c) (P) is 

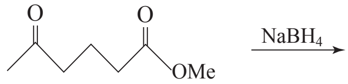
(d) (Q) is 

121. Which of the following reactions can be used to prepare lactones (cyclic ester)?

(a) 

(b) 

(c) 

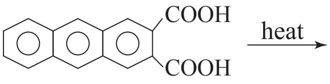
(d) 

122. In which of the following case anhydride is/are obtained:

(a) 

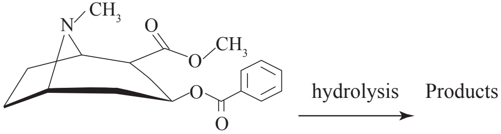
(b) 

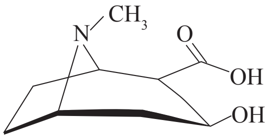
$\begin{array}{l} Ph-CH-COOH \\ \quad\ \ | \\ Ph-CH-COOH \end{array} \xrightarrow{heat}$

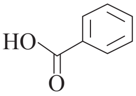
(c) 

(d) 

123. Cocaine on hydrolysis can give which of the following products?



(a) 

(b) 

(c) NH_2OH

(d) $HOCH_3$

Linked-Comprehension Type Questions

Comprehension 1

Carboxylic acids have a general formula $C_nH_{2n}O_2$. They have higher values of acidic nature. B. P. solubility in water etc. than their corresponding molecular weight alcohols, carbonyl compounds and acid derivatives. Their acidic nature in greatly influenced by the presence of electron withdrawing or releasing groups present in them.

124. How many structural and optically active isomers of carboxylic acid with molecular formula $C_6H_{12}O_2$ are possible respectively?

(a) 7, 3

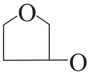
(b) 7, 3

(c) 8, 3

(d) 8, 2

125. Which of the following is correct order here?

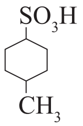
(I) B. P.: $CH_3-CH_2-CH_2-COOH >$



$OH > CH_3-CO-OCH_2-CH_3$

(II) Acidic nature: $CH_3COOH < \underset{X}{\underset{|}{CH_2}}-$

COOOH <



(III) Solubility in water: $R-OH > R-COOH > R-COOR' > R-CONH_2$

(IV) PKa in increasing order:
$CCl_3COOH < HCOOH < C_6H_5COOH < CH_3COOH$

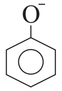
(a) I, II, III

(b) II, III, IV

(c) I, II, IV

(d) I, II, III, IV

126. Which of the following is the correct order of stability for the following?

(I) 

(II) $CH3-O^-$

(III) $H-COO^-$

(IV) 

(a) I > III > II > IV

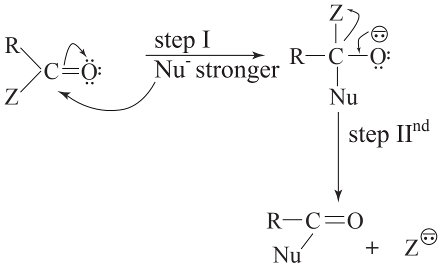
(b) III > I > II > IV

(c) I > III > IV > II

(d) I > IV > III > II

Comprehension 2

The characteristic and important reaction of carboxylic acid derivatives is nucleophillic acyl substitution which is possible only when the incoming nucleophile (Nu^- or HNu) must not be a much weaker base than the group or substituent attached to the acyl group in the acid derivative. It is a two step process involving nucleophillic attack followed by the loss of the leaving group.



127. Arrange the following in the decreasing order of leaving group ability?

(I) X^-

(II) $\bar{N}H_2$

(III) $\bar{O}H$

(IV) $\bar{O}R$

(V) $R-CO^-$

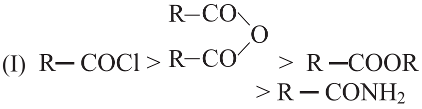
(a) I > V > III > IV > II

(b) I > V > III ≈ IV > II

(c) V > I > II > IV > III

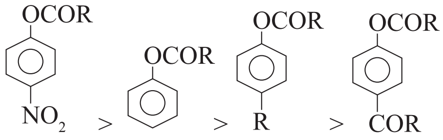
(d) V > I > III ≈ > IV > I

128. Which of these order are correct for hydrolysis?

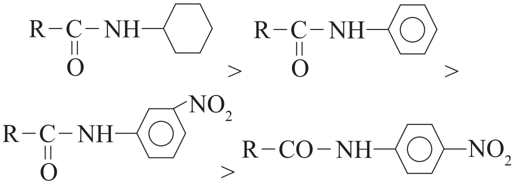


(I) $R-COCl > \begin{matrix}R-CO\\ \quad\ \ O\\ R-CO\end{matrix} > R-COOR > R-CONH_2$

(II)



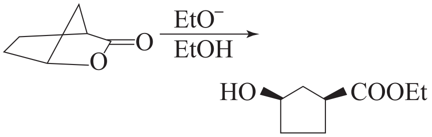
(III)



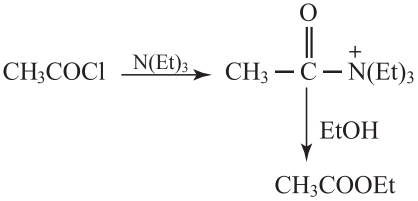
(a) I, III (b) II, III
(c) I, II (d) I, II, III

129. Which of these reactions are examples of nucleophilic acyl substitution?

(I)

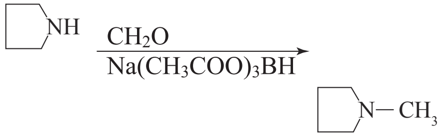


(II)

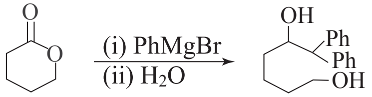


$$CH_3COCl \xrightarrow{N(Et)_3} CH_3-\overset{O}{\overset{\|}{C}}-\overset{+}{N}(Et)_3 \xrightarrow{EtOH} CH_3COOEt$$

(III)



(IV)



(a) I, III only (b) I, I only
(c) I, II, III (d) I, II, IV

Comprehension 3

Claisen condensation involves a Carbon-carbon bond formation reaction between to esters or one esters with a carbonyl compound. It is highly endothermic so it can not take place without a stoichiometric amount of base strong enough to deprotonate the resulting 3-keto esters.

The common bases used are C_2H_5ONa , NaH, $NaNH_2$ etc., Mixed Claisen condensation between to esters are non selective unless they are intramolecular (Dieckmann condensation) or one of the component is devoid of α –hydrogen.

130. Which of the following statements are correct regarding Claisen condensation?

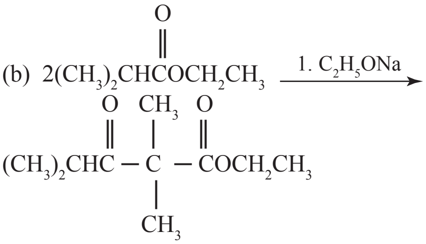
(I) It starts with the formation of resonance stabilised anion or enolate.
(II) One component must behave like in all partner and the other one like acylation partner.
(III) It is completely irreversible reaction.
(IV) Deprotonation of keto esters drives equilibrium.

(a) I , II , III (b) II, III, IV
(c) I, II, IV (d) I, II, III, IV

131. Which of the following reaction is not case of Claisen condensation?

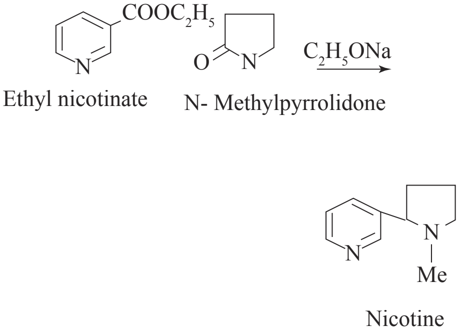
(a) $C_6H_5COOC_2H_5 + CH_3COOC_2H_5 \xrightarrow[2.\ H^+]{1.\ C_2H_5ONa} C_6H_5COCH_2COOC_2H_5 + C_2H_5OH$

(b)



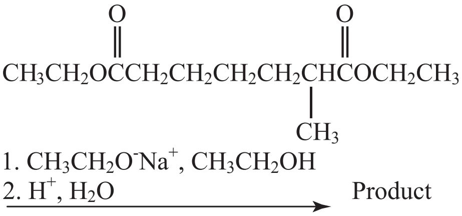
$$2(CH_3)_2CH\overset{O}{\overset{\|}{C}}CH_2CH_3 \xrightarrow{1.\ C_2H_5ONa} (CH_3)_2CH\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-\overset{O}{\overset{\|}{C}}OCH_2CH_3$$

(c)

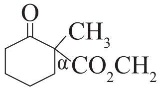


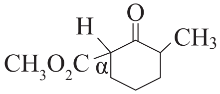
(d) $C_6H_5CH_2COOC_2H_5 + HCOOC_2H_5 \xrightarrow[2H^+]{C_6H_5ONa} C_6H_5\text{ -CH - }COOC_2H_5 + C_2H_5OH$

132.

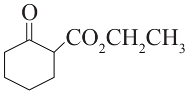


$$CH_3CH_2O\overset{O}{\overset{\|}{C}}CH_2CH_2CH_2CH_2\underset{CH_3}{\underset{|}{C}}H\overset{O}{\overset{\|}{C}}OCH_2CH_3 \xrightarrow[2.\ H^+,\ H_2O]{1.\ CH_3CH_2O^-Na^+,\ CH_3CH_2OH} \text{Product}$$

(a) 

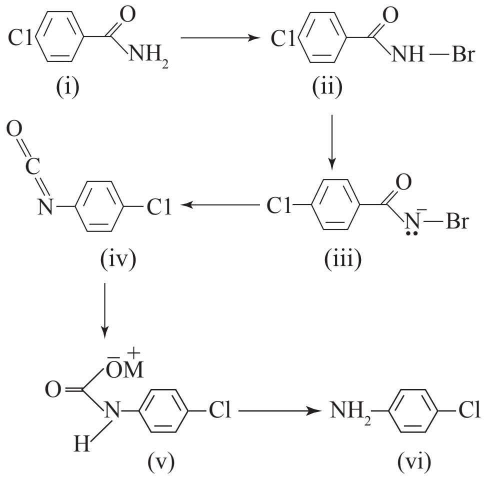
(b) 

(c) Both A and B

(d) 

Comprehension 4

$RCONH_2$ is converted into RNH_2 by means of Hofmann bromamide degradation. [2006]



In this reaction, RCONHBr is formed from which this reaction has derived its name. Electron donating group at phenyl activates the reaction. Hofmann degradation reaction is an intramolecular reaction.

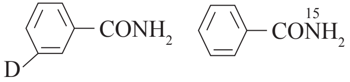
133. How can the conversion of (i) and (ii) be brought about?

(a) KBr (b) KBr + CH_3ONa
(c) KBr + KOH (d) Br_2 + KOH

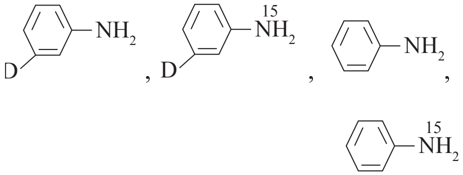
134. Which is the rate determining step in Hofmann bromamide degradation ?

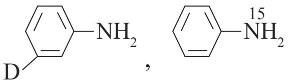
(a) Formation of (i) (b) Formation of (ii)
(c) Formation of (iii) (d) Formation of (iv)

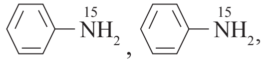
135. What are the constituent amines formed when the mixture of (i) and (ii) undergoes Hofmann bromamide degradation ?



(i) (ii)

(a) 

(b) 

(c) 

(d) 

Assertion-Reason Type Questions

In the following question two statements (Assertion) A and Reason (R) are given Mark.

(a) if A and R both are correct and R is the correct explanation of A.
(b) if A and R both are correct but R is not the correct explanation of A.
(c) if A is true but R is false.
(d) if A is false but R is true.
(e) if A and R both are false.

136. **(A):** Resonance energy of carboxylate ion is much greater than that of undissociated carboxylic acid.

(R): Carboxylate ion is a resonance hybrid of equivalent resonating structures.

137. **(A):** Sulphanilic acid exists as a dipolar ion where as p-aminobenzoic acid does not.

(R): Carboxyl group being more acidic than the SO_3H group can easily transfer H^+ to the amino group.

138. **(A):** Claisen Condensation involves the self condensation of ester molecules having α hydrogen.

(R): Claisen condensation occurs in the presence of a strong base such as sodium ethoxide.

139. **(A):** Ethyl acetoacetate gives reddish violet colour on treatment with ferric chloride.

(R): It exists predominantly in the keto form.

140. **(A):** The C—O bond length is shorter in an ester as compared to an anhydride .

(R): A degree of cross conjugation exist in the anhydride that decreases the delocalization to each carbonyl oxygen.

141. **(A):** CH_3COOH but not HCOOH can be halogenated in presence of red P and Cl_2.

(R): Both formic acid and CH_3COOH are highly soluble in water.

142. (A): In sodium formate, both the C – O bonds have same value 1.27 Å.
(R): Same bond length is due to the phenomenon of resonance.

143. (A): Formic acid gives rise to nucleophillic addition reactions.
(R): Carbon oxygen bond length in formic acid are 1.23 Å and 1.36 Å.

144. (A): The second dissociation constant of maleic acid is greater than fumaric acid.
(R): Higher the dissociation constant of acid more is acidic character.

145. (A): Nitration of benzoic acid gives m-nitrobenzoic acid.
(R): Carboxyl group increases the electron density at the meta position.

146. (A): m-Chlorobenzoic acid is a stronger acid than p-chlorobenzoic acid.
(R): In m-chlorobenzoic acid both –I effect and +R effect of Cl operate but in p-chlorobenzoic acid only +R effect of Cl operates.

147. (A): Both formic acid and oxalic acid decolourize $KMnO_4$ solution.
(R): Both are easily oxidized to CO_2 and H_2O.

148. (A): RCOCl, $(RCO)_2O$ and RCOOR' all react with Grignard reagents to form 3° alcohols.
(R): RCOCl reacts with R_2Cd to form ketones but $(RCO)_2O$ and RCOOR' do not react at all.

149. (A): p-Hydroxybenzoic acid has lower boiling point than o-hydroxybenzoic acid.
(R): o- Hydroxybenzoic acid has intramolecular hydrogen bonding.

150. (A): Acetamide reacts with Br_2 in presence of methanolic CH_3ONa to form methyl N- methylcarbomate.
(R): Methyl isocyanate is formed as an intermediate which reacts with methanol to form methyl N-methylcarbamate.

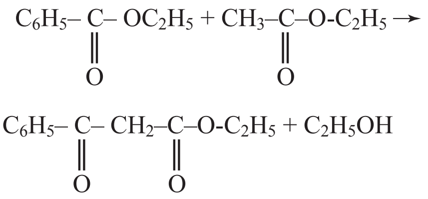
151. (A): Acid catalysed hydrolysis of ester is reversible on the other hand base catalysed hydrolysis is irreversible.
(R): In acid catalysed ester hydrolysis carboxylic acid is formed on which nucleophile attack of alcohol is possible while in base catalysed ester hydrolysis carboxylate anion is formed on which nucleophillic attack is not possible.

Matrix-Match Type Questions

152. Match the following:

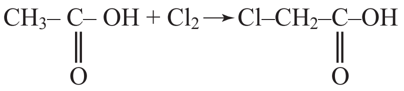
Column I (Reagents)

(a)



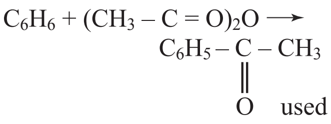
$$C_6H_5-\underset{\underset{O}{\|}}{C}-OC_2H_5 + CH_3-\underset{\underset{O}{\|}}{C}-O-C_2H_5 \rightarrow C_6H_5-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-O-C_2H_5 + C_2H_5OH$$

(b)



$$CH_3-\underset{\underset{O}{\|}}{C}-OH + Cl_2 \rightarrow Cl-CH_2-\underset{\underset{O}{\|}}{C}-OH$$

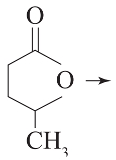
(c)



$$C_6H_6 + (CH_3-C=O)_2O \longrightarrow C_6H_5-\underset{\underset{O}{\|}}{C}-CH_3$$

used

(d)



$CH_3CH(OH)CH_2CH_2CH_2OH$

Column II

(P) Anhydrous $ZnCl_2$
(q) $C_2H_5O^{\ominus}$
(r) P
(s) $LiAlH_4$

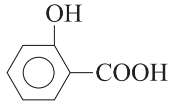
153. Match the following:
Column I (reaction)

(a) $C_6H_5CHO + NaOH \longrightarrow C_6H_5COOH + C_6H_5CH_2OH$

(b) $C_6H_6 + CH_3Cl \xrightarrow{\text{Anhyd. } AlCl_3} C_6H_5CH_3$

(c) $RCOCl + H_2 \xrightarrow{Pd/BaSO_4} RCHO$

(d) $C_6H_5OH + NaOH + CO_2 \xrightarrow{\text{1. heat, 2. } H^+}$

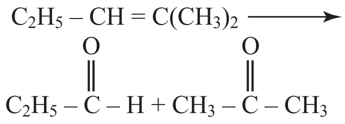


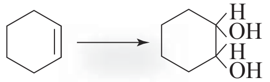
Column II (Name of Reactions)

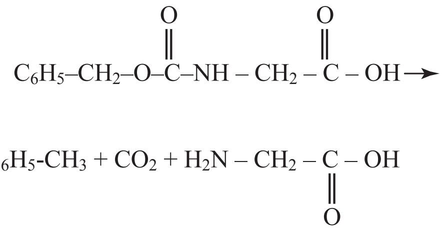
(p) Rosenmund reduction
(q) Kolbe's reaction
(r) Claisen reaction
(s) Cannizzaro reaction
(t) Friedal-Craft's reaction

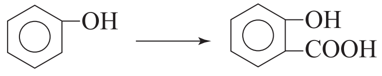
154. Match the following:

Column I

(a)

$$C_2H_5-CH=C(CH_3)_2 \longrightarrow C_2H_5-\overset{\overset{O}{\|}}{C}-H+CH_3-\overset{\overset{O}{\|}}{C}-CH_3$$

(b)


(c)

$$C_6H_5-CH_2-O-\overset{\overset{O}{\|}}{C}-NH-CH_2-\overset{\overset{O}{\|}}{C}-OH \longrightarrow C_6H_5-CH_3+CO_2+H_2N-CH_2-\underset{\underset{O}{\|}}{C}-OH$$

(d)


Column II

(p) $KMnO_4$

(q) $CHCl_3$ + aq. NaOH

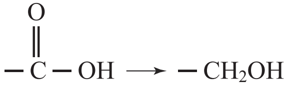
(r) O_3 .Zn + H_2O

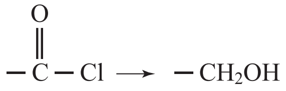
(s) H_2 / Pd – C

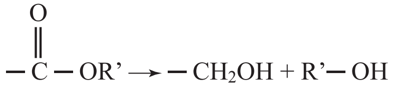
The correct matching is

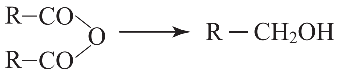
155. Match the following:

Column I (Reactions)

(a)

$$-\overset{\overset{O}{\|}}{C}-OH \longrightarrow -CH_2OH$$

(b)

$$-\overset{\overset{O}{\|}}{C}-Cl \longrightarrow -CH_2OH$$

(c)

$$-\overset{\overset{O}{\|}}{C}-OR' \longrightarrow -CH_2OH+R'-OH$$

(d)


Column II (Reductants)

(p) $LiAlH_4$ (q) $NaBH_4/C_2H_5OH$

(r) B_2H_6 /THF (s) H_2 /Pd

156. Match the following:

Column I

(a) CH_3COCHO

(b) 1, 2-cyclohexanedione

(c) PhCH(OH)CHO

(d) $CH_3CH_2CH(OH)COCH_3$

Column II

(p) PhCH = O + HCOOH

(q) $CH_3CH_2CHO + HOOCCH_3$

(r) $HOOC(CH_2)_4COOH$

(s) $CH_3COOH + HCOOH$

157. Match the following:

Column I [IIT 2009]

(a) $CH_3CH_2CH_2CN$

(b) $CH_3CH_2OCOCH_3$

(c) $CH_3-CH=CH-CH_2OH$

(d) $CH_3CH_2CH_2CH_2NH_2$

Column II

(p) Reduction with Pd – C / H_2

(q) Reduction with $SnCl_2$ / HCl

(r) Development of foul smell on treatment with chloroform and alcoholic KOH

(s) Reduction with diisobutylaluminium hydride (DIBAL – H)

(t) Alkaline hydrolysis

The IIT-JEE Corner

158. When propionic acid is treated with aqueous sodium bicarbonate, CO_2 is liberated. The C of CO_2 comes from:

(a) Bicarbonate

(b) Methyl group

(c) Carboxylic acid group

(d) Methylene group

[IIT 1999]

159. Benzoyl chloride is prepared from benzoic acid by:

(a) Cl_2, hv (b) SO_2Cl_2

(c) $SOCl_2$ (d) Cl_2, H_2O

[IIT 2000]

160. Identify the correct order of boiling points of the following compounds: [2002]

$CH_3CH_2CH_2CH_2OH$ (1), $CH_3CH_2CH_2CHO$ (2),

$CH_3CH_2CH_2COOH$ (3)

(a) 1 > 2 > 3

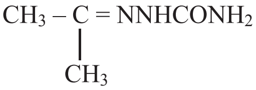
(b) 3 > 1 > 2

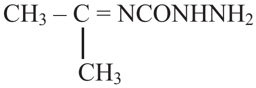
(c) 1 > 3 > 2

(d) 3 > 2 > 1

161. Compound 'A' (molecular formula C_3H_8O) is treated with acidified potassium dichromate to form a product 'B' (molecular formula C_3H_6O). 'B' forms a shining silver mirror on warming with ammonical silver nitrate. 'B' when treated with an aqueous solution of $H_2NCONHNH_2$ HCl and sodium acetate gives a product ‘C’. Identify the structure of ‘C’.

(a) $CH_3CH_2CH = NNHCONH_2$

(b) 
$CH_3 - \underset{CH_3}{\underset{|}{C}} = NNHCONH_2$

(c) 
$CH_3 - \underset{CH_3}{\underset{|}{C}} = NCONHNH_2$

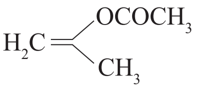
(d) $CH_3CH_2CH = NCONHNH_2$.

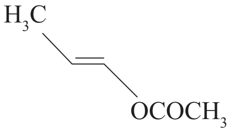
[IIT 2002]

162. An enantiomerically pure acid is treated with recemic mixture of an alcohol having one chiral carbon. The ester formed will be: **[2003]**

(a) Optically active mixture
(b) Pure enantiomer
(c) Meso compound
(d) Racemic mixture

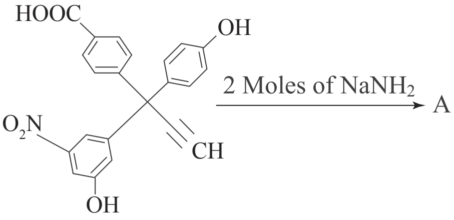
163. The product of acid hydrolysis of P and Q can be distinguished by:

P = 

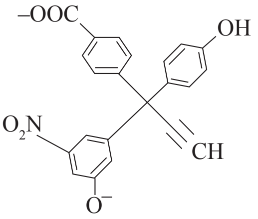
Q = 

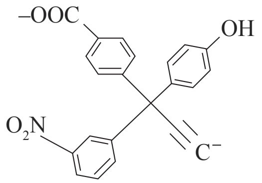
(a) Lucas reagent
(b) 2, 4-DNP
(c) Fehling’s solution
(d) $NaHSO_3$.

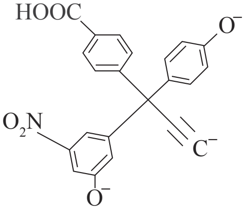
[IIT 2003]

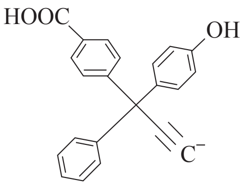
164. 

[IIT 2003]

(a) 

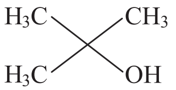
(b) 

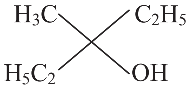
(c) 

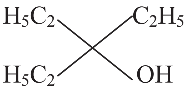
(d) 

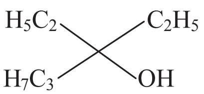
165. Ethyl ester $\xrightarrow{CH_3MgBr}$ P,

The product ‘P’ will be: **[2003]**

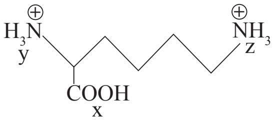
(a) 

(b) 

(c) 

(d) 

166. In the compound given below



The correct order of acidity of the positions (X), (Y) and (Z) is

(a) X > Y > Z
(b) Y > X > Z
(c) Z > X > Y
(d) X > Z > Y

[IIT 2004]

167. Benzamide on reaction with $POCl_3$ gives:

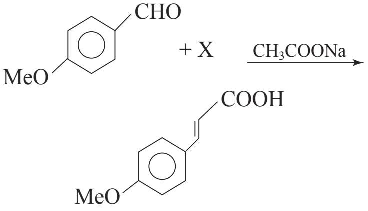
(a) aniline
(b) chlorobenzene
(c) benzylamine
(d) benzonitrile

[IIT 2004]

168. To convert 2-butanone into propionic acid
(a) NaOH + NaI/H^+
(b) Fehling's test
(c) I_2 / NaOH / H^+
(d) Tollen's reagent.

[IIT 2005]

169. Identify (X) in the following reaction.



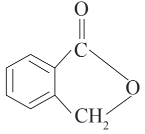
(a) CHO – COOH
(b) CH_3COOH
(c) $BrCH_2COOH$
(d) $(CH_3CO)_2O$

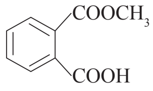
[IIT 2005]

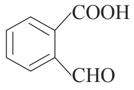
170. When benzene sulphonic acid and p-nitrophenol are treated with $NaHCO_3$, the gases released respectively are:
(a) SO_2, NO_2
(b) SO_2, NO
(c) SO_2, CO_2
(d) CO_2, CO_2

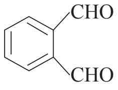
[IIT 2006]

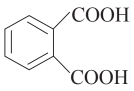
171. Which of the following reactants on reaction with conc. NaOH followed by acidification gives the following lactone as the only product?



(a) 

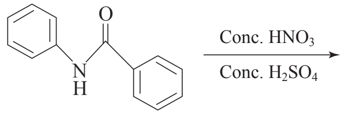
(b) 

(c) 

(d) 

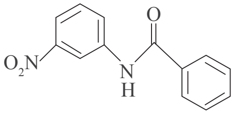
[IIT 2006]

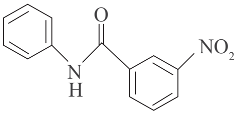
172. In the following reaction

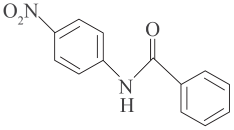


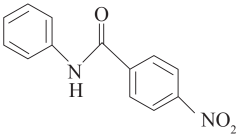
X **[IIT 2007]**

the structure of the major product 'X' is

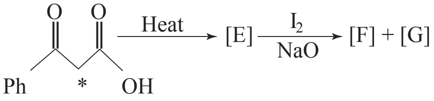
(a) 

(b) 

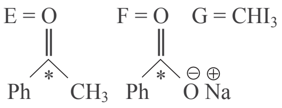
(c) 

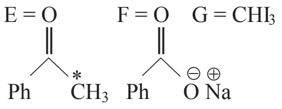
(d) 

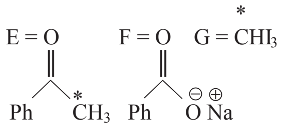
173. In the following reaction sequence, the correct structure of E, F and G are **[2008]**

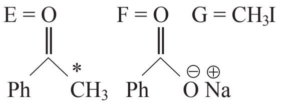


(* implies ^{13}C labeled carbon)

(a) 

(b) 

(c) 

(d) 

ANSWERS

Straight Objective Type Questions

1. (b) **2.** (d) **3.** (b) **4.** (a) **5.** (c) **6.** (d) **7.** (c) **8.** (b) **9.** (c) **10.** (a)
11. (c) **12.** (b) **13.** (b) **14.** (c) **15.** (c) **16.** (a) **17.** (d) **18.** (a) **19.** (c) **20.** (b)
21. (b) **22.** (d) **23.** (c) **24.** (c) **25.** (c) **26.** (d) **27.** (a) **28.** (d) **29.** (d) **30.** (b)
31. (c) **32.** (d) **33.** (c) **34.** (d) **35.** (d) **36.** (d) **37.** (d) **38.** (b) **39.** (c) **40.** (a)
41. (a) **42.** (a) **43.** (c) **44.** (a) **45.** (d) **46.** (b) **47.** (a) **48.** (b) **49.** (c) **50.** (b)
51. (d) **52.** (a) **53.** (c) **54.** (c) **55.** (a) **56.** (c) **57.** (d) **58.** (b) **59.** (c) **60.** (d)

Brainteasers Objective Type Questions

61. (c) **62.** (c) **63.** (d) **64.** (d) **65.** (a) **66.** (c) **67.** (b) **68.** (a) **69.** (d) **70.** (b)
71. (a) **72.** (b) **73.** (b) **74.** (a) **75.** (b) **76.** (b) **77.** (a) **78.** (a) **79.** (a) **80.** (d)
81. (c) **82.** (d) **83.** (d) **84.** (d) **85.** (d) **86.** (c) **87.** (c) **88.** (a) **89.** (c) **90.** (c)
91. (b) **92.** (a) **93.** (a) **94.** (b) **95.** (a) **96.** (c) **97.** (d) **98.** (c) **99.** (b) **100.** (b)

Decisive Thinking Objective Type Questions

101. (a), (b), (c) **102.** (a),(b),(d) **103.** (b), (c), (d) **104.** (a), (b), (c) **105.** (a),(c),(d)
106. (a), (b), (c) **107.** (a), (c) **108.** (a), (b), (d) **109.** (a), (b) ,(d) **110.** (a), (c), (d)
111. (b), (c), (d) **112.** (b), (c), (d) **113.** (a), (c), (d) **114.** (a), (b), (c) **115.** (a), (b),(c)
116. (a), (b), (d) **117.** (a), (b), (c) **118.** (a), (c), (d) **119.** (b), (d) **120.** (a), (d)
121. (a), (b), (d) **122.** (a), (c), (d) **123.** (a), (b), (d)

Linked-Comprehension Type Questions

124. (c) **125.** (c) **126.** (b) **127.** (b) **128.** (c) **129.** (b) **130.** (c) **131.** (b) **132.** (b) **133.** (d)
134. (d) **135.** (b)

Assertion-Reason Type Questions

136. (a) **137.** (c) **138.** (a) **139.** (b) **140.** (a) **141.** (b) **142.** (a) **143.** (d) **144.** (d) **145.** (c)
146. (a) **147.** (a) **148.** (b) **149.** (d) **150.** (a) **151.** (a)

Matrix-Match Type Questions

152. (a) - (q), (b) - (r), (c) - (p), (d) - (s)
153. (a) - (r), (b) - (t), (c) - (p), (d) - (q)
154. (a) - (r) , (b) - (p), (c) - (s), (d) - (q)
155. (a) - (p, r, s), (b) - (p, q, s),(c) - (p, r, s), (d) - (p, r, s)
156. (a) - (s), (b) - (r), (c) - (p), (d) - (q)
157. (a) - (p, q, s, t), (b) - (s, t), (c) - (p), (d) - (r)

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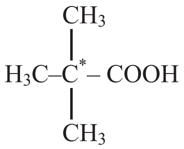
158. (a) **159.** (c) **160.** (b) **161.** (a) **162.** (a) **163.** (c) **164.** (a) **165.** (c) **166.** (a) **167.** (d)
168. (c) **169.** (d) **170.** (d) **171.** (c) **172.** (c) **173.** (c)

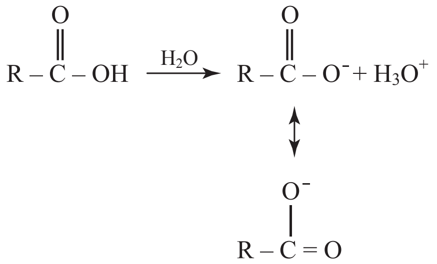
HINTS AND EXPLANATION

Straight Objective Type Questions

3. 

$$H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C^*}}-COOH$$

It contains a chiral carbon (C^*) atom, so it shows optical isomerism.

4. 

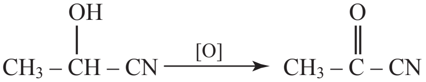
$$R-\overset{\overset{O}{\|}}{C}-OH \xrightarrow{H_2O} R-\overset{\overset{O}{\|}}{C}-O^- + H_3O^+ \;\updownarrow\; R-\overset{\overset{O^-}{|}}{C}=O$$

Because of resonance stabilization of carboxylate ion, the equilibrium shifts in the forward direction, thereby forming more and more of hydronium ions.

5. Its dissociation constant is less as compound to carboxylic acids.

8. Since it is the strongest acid here so it will have lowest pKa value.

9. Formic acid has lower pKa value than that of CH_3COOH because formic acid does not have an alkyl group.

12. 

$$CH_3-\overset{\overset{OH}{|}}{C}H-CN \xrightarrow{[O]} CH_3-\overset{\overset{O}{\|}}{C}-CN$$

Acetaldehyde Cyanohydrin

$$\xrightarrow{H^+/H_2O} CH_3COCOOH$$

Pyruvic acid

13. $C_6H_5COCl + H-H \xrightarrow[\text{-KCl}]{\text{Pd-BaSO}_4}$

C_6H_5CHO
Benzaldehyde

14. $CH_3Cl \xrightarrow{KCN} CH_3CN \xrightarrow{H^+/H_2O}$

CH_3COOH
(B)

16. $\underset{(A)}{C_2H_5OH} \xrightarrow{PCl_5} \underset{(B)}{C_2H_5Cl} \xrightarrow{KCN}$

$C_2H_5CN \xrightarrow{H_2O} C_2H_5COOH$
Propionic acid

17. $\underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow{NaOH + Br_2} \underset{\text{Methyl amine}}{CH_3NH_2}$

It is Hoffman's bromide reaction.

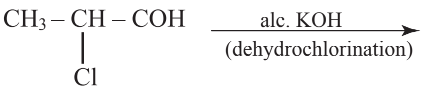
18. $RCH_2CH_2OH \xrightarrow{PBr_3} RCH_2CH_2Br \xrightarrow{KCN}$

$RCH_2CH_2CN \xrightarrow{H^+/H_2O} RCH_2CH_2COOH$

20. $C_2H_5OH \xrightarrow{PCl_5} C_2H_5Cl \xrightarrow{KCN} C_2H_5CN$

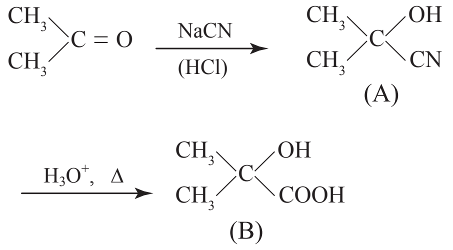
$\xrightarrow{H_3O^+}$

22. $CH_3CH_2COOH \xrightarrow[\text{H.V.Z. reaction}]{Cl_2,\text{ red P}}$



$$CH_3-\underset{\underset{Cl}{|}}{C}H-COH \xrightarrow[\text{(dehydrochlorination)}]{\text{alc. KOH}}$$

$CH_2 = CH - COOH$

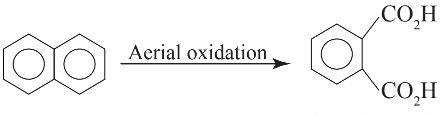
23. 

26. $R-COOH + Na \rightarrow R-COONa + H_2$

$2R-COOH + Na_2CO_3 \rightarrow 2R-COONa + H_2O + CO_2$

27. $(CH_3CO)_2O \xrightarrow[\text{Anhyd. AlCl}_3]{\text{diethyl ether}} \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5}$

28. $3CH_3COOH + PCl_3 \rightarrow 3CH_3COCl + H_3PO_3$

30. 

naphthalene phthalic acid

33. It is an example of claisen condensation.

35. $CH_3COOH + C_2H_5OH \xrightarrow{H_2SO_4} CH_3COOC_2H_5 + H_2O$

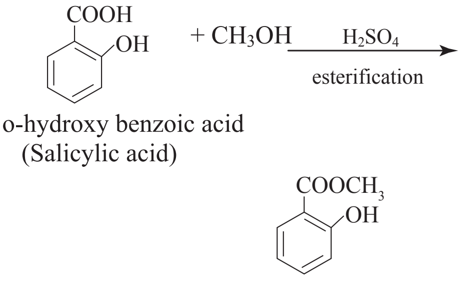
36. $CH_3COOC_2H_5 + CH_3COOC_2H_5 \xrightarrow{CH_3CH_2ONa} CH_3COCH_2COOC_2H_5$
Ethyl acetoacetate

40. Aqueous NaCl in neutral so there is no reaction between ethyl acetate and aqueous NaCl.

44. $LiAlH_4$ in ether reduces ethyl acetate into ethyl alcohol.

$$CH_3COOC_2H_5 + 2H_2 \xrightarrow[\text{Ether}]{LiAlH_4} 2CH_3CH_2OH$$

50.

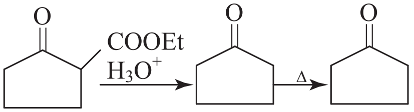


o-hydroxy benzoic acid
(Salicylic acid)

Methyl salicylate
(ester)

54. In presence of $Ba(OH)_2$ when heated phthalic acid undergoes decarboxylation.

55.

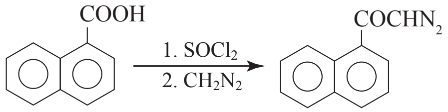


β-keto acid undergoes decarboxylation when heated.

56. Stronger – I group attached closer to – COOH makes the acid stronger, that is, acid has the larger dissociation constant – Br shows poor(- I) effect and also far away from –COOH group that is, option (c) has smallest dissociation constant.

57. When hydrazine attacks ethyl acetate, the leaving group $–OC_2H_5$ is replaced by $NHNH_2$ to give $CH_3CONHNH_2$.

59.



α-naphtholic acid diazo α-aceto--naphthone

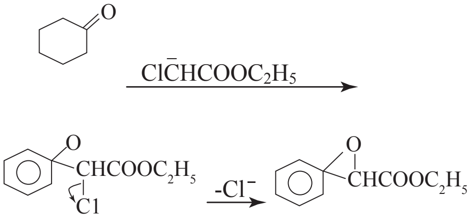
Brainteasers Objective Type Questions

66. Both o-substituted acids are stronger than C_6H_5COOH, due to ortho effect. Since$–OCH_3$ is bulkier (ortho effect) than –OH group, so it might be more acid strengthening. But salicylate ion has the ability to undergo intramolecular hydrogen bonding (chelation), which stabilizes conjugate base and therefore, enhances the acidity.

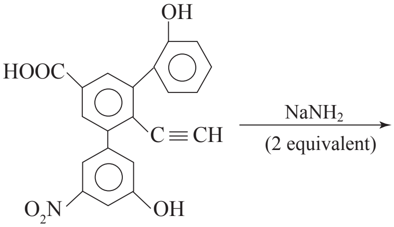
69. HCN is a very weak acid. CH_3COOH is a weaker acid than HCOOH, because $CH_3–$ is electron donating, acid weakening group. $Cl – CH_2COOH$ is a stronger acid than CH_3COOH as Cl is electron withdrawing, acid strengthening group.

70. Acid chloride and acid anhydride are extremely reactive out of acid derivatives. They react independently with water even in the absence of catalyst to give carboxylic acid , which will ultimately reacts with $NaHCO_3$ to give sodium salt of acid and CO_2. Ester reacts with water in presence of acid catalyst to produce acid . Acetone in inert toward $NaHCO_3$ solution.

75. It is a case of Darzen glycidic ester synthesis:



78.



80. $CH_3CH_2OH \xrightarrow[\text{Oxidation}]{KMnO_4} \underset{(A)}{CH_3COOH}$

$\xrightarrow{SOCl_2} CH_3COCl \xrightarrow{NH_3}$

$\underset{(B)}{CH_3CONH_2} \xrightarrow[\text{Hoffmann bromamide reaction}]{Br_2 + NaOH}$

$\underset{(C)}{CH_3NH_2} + Na_2CO_3 + NaBr + H_2O$

83. Carbonation of CH_3MgBr forms CH_3COOH

$$CH_3MgBr + CO_2 \longrightarrow CH_3CO_2MgBr$$

$$\xrightarrow{H_2O} CH_3COOH + MgBr(OH)$$

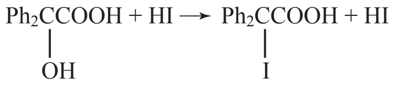
Hydrolysis of acetonitrile by a mineral acid also forms CH_3COOH.

$$CH_3CN \xrightarrow{H_3O^+} CH_3CONH_2 \xrightarrow{H_3O^+} CH_3COOH + NH_4^+$$

86. As electron withdrawing group (CN) increases the nucleophilicity of the carbonyl carbon of acid chloride during hydrolysis so the correct of order of ease of hydrolysis is C

88. $\underset{(A)}{CH_3CH_2CH_2COCl} \xrightarrow{NH_3}$

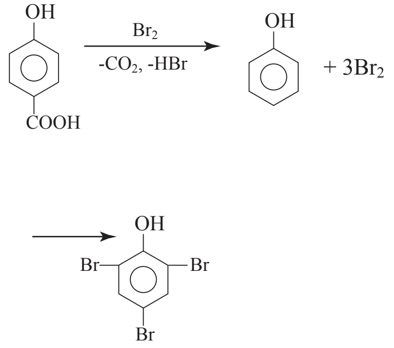
$$CH_3CH_2CH_2CONH_2 \xrightarrow{Br_2 + NaOH} CH_3CH_2CH_2NH_2$$

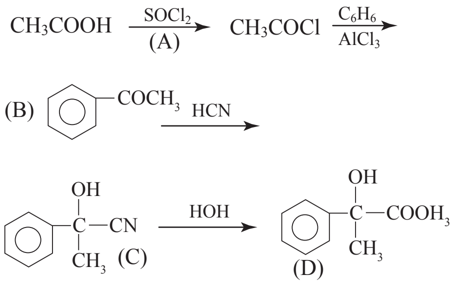
89. 

$$\underset{\substack{|\\OH}}{Ph_2CCOOH} + HI \longrightarrow \underset{\substack{|\\I}}{Ph_2CCOOH} + HI$$

$\rightarrow Ph_2\ CHCOOH + I$

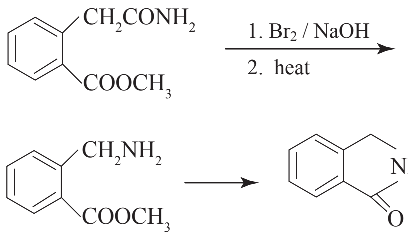
(As hydrogen iodide is a very powerful reducing agent)

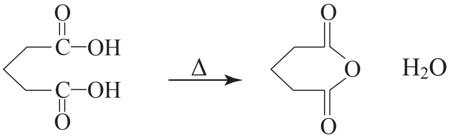
90. 

92. 

93. –OH group is o, p-directing and hydrolysis of cyanohydrins gives α-hydroxy acids.

94. The OH^- reacts first replacing the bromide ion at the end chain to form $HO-(CH_2)_4-COOH$ which reacts further intra molecularity in the presence of acid (H^+) to form cyclic six membered structure – a lactone.

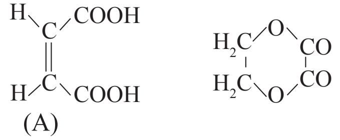
96. 

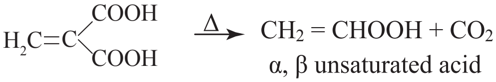
97. 

Decisive Thinking Objective Type Questions

103. Methyl salicylate occurs in essential oils of winter green and sweet birch.

106. $C_4H_4O_4$ can be





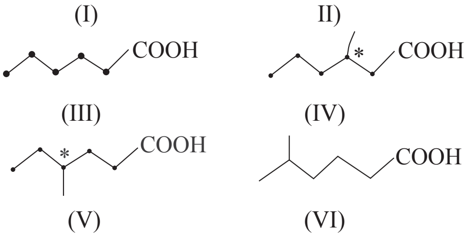
$CH_2 = CHOOH + CO_2$

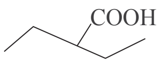
α, β unsaturated acid

111. As CH_3CONH_2 on reduction with $LiAlH_4$ gives ethyl amine.

Linked-Comprehension Type Questions

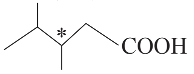
124. It has 8 structural isomers and out of them 3 are optically active as follows:

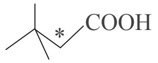




(VII)

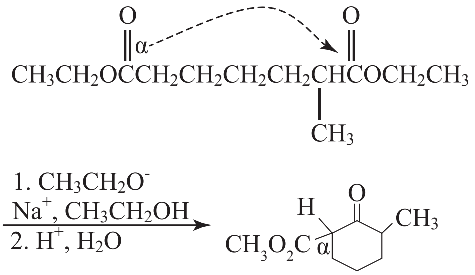
(VIII)



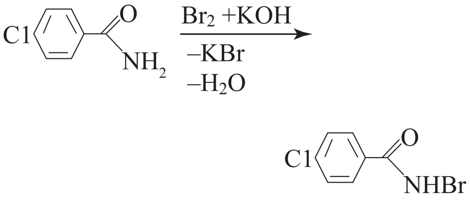


131. In case of option B, the reactant compound ethyl 2- methylpropanoate does not have any α -hydrogen atom so reaction is not possible.

132.



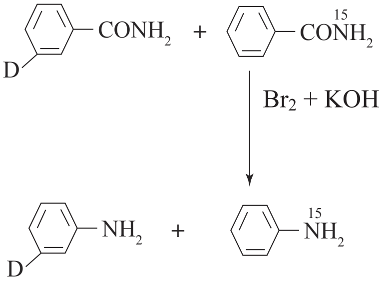
133.



N- bromo derivative

134. The rate determining step is elimination of Br^- to from isocyanate as it is the slowest step of this conversion.

135.



As the overall reaction is intermolecular, so there will be no effect on product formation.

Assertion-Reasoning Questions

137. Assertion is correct but reason is wrong. Carboxylic acid being less acidic than he $–SO_3H$ group.

139. Assertion and reason both are correct but does not give correct explanation reddish violet colour on treatment with $FeCl_3$ due to enol form.

141. The Hell Volhard Zelinsky (HVZ) reaction shows halogen substitution at α-carbon atom. HCOOH has no such α-carbon atom and thus does not undergo HVZ reaction.

145. Carboxyl group only marginally decreases the electron density at m-position relative to o- and p-.

146. –I and +R effect in m-chlorobenzoic acid outweighs +R effect in p-chlorobenzoic acid.

147. Both formic acid and oxalic acid behave as reducing agent and decolourise acidified $KMnO_4$ solution.

$$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$

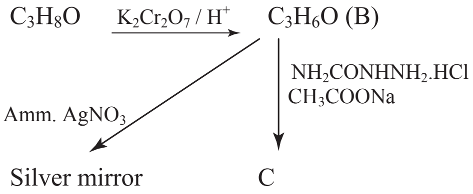
148. RCOCl, $R(CO)_2O$ and RCOOR' all add two molecules of Grignard reagents to give 3° alcohols.

The IIT-JEE Corner

158. $$C_2H_5COOH + NaHCO_3 \longrightarrow C_2H_5COONa + H_2O + CO_2$$

160. In these C forms dimmer due to hydrogen bonds and compound A, form hydrogen bonds. Hence in these stronger hydrogen bond is in compound C than compound A. Compound B does no form hydrogen bond. Thus, they follow the following order of mol. wt. 3 > 1 > 2. So they have same order in their boiling point .

161.



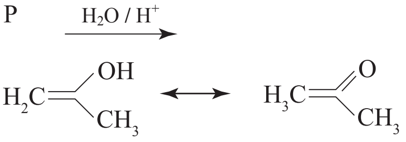
Here B is an aldehyde as it gives silver mirror test with ammonical $AgNO_3$ solution. Tollen's reagent B is formed by oxidation of A, so A must be 1° alcohol $(CH_3CH_2CH_2 – OH)$.

$$\underset{(B)}{CH_3CH_2 – CH = O} + H_2NCONHNH_2HCl$$

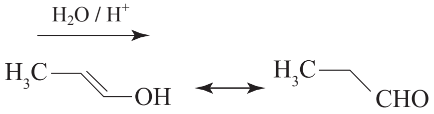
$$\xrightarrow[\text{-HCl, - H}_2\text{O}]{\text{sod. Acetate}} CH_3–CH_2–CH=N.NHCONH_2$$

162. When optically active acid reacts with racemic mixture of an alcohol. It forms two types of isomeric esters. In each, the configuration of the chiral center of acid will remain the same.

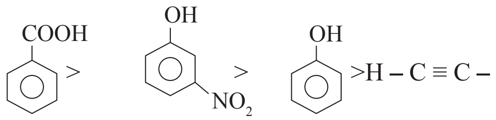
163. P



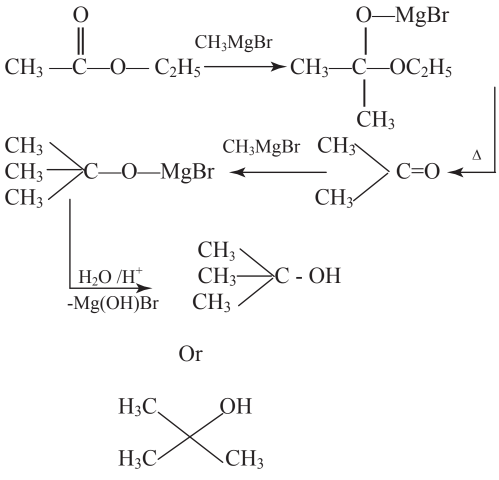
Q



164. The acidic strength of the attached groups is in the following order:



165.



Thus ketone is further reacted with excess CH_3MgBr and to give t -alcohol as the final product.
Hence it is tertiary butyl alcohol.

166. Carboxylic acids are stronger acids than N^+H_3, therefore, X is the strongest acid. since –COOH has –I effect which decreases with distance, therefore, effect is more pronounced on Y than on Z. As a result, Y is more acidic than Z. therefore X > Y > Z.

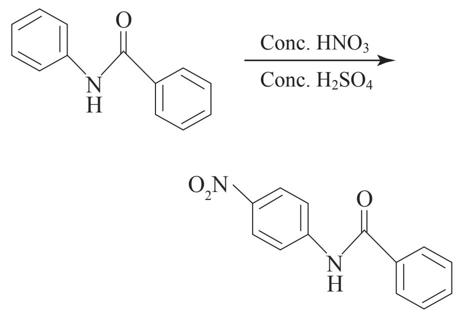
167. $C_6H_5CONH_2 \xrightarrow[-H_2O]{POCl_3} C_6H_5C \equiv N$ benzonitrile

168. $CH_3-CO-CH_2-CH_3 \xrightarrow{NaOH + I_2}$
2-butanone

$Cl_3-CO-CH_2CH_3 \xrightarrow{H^+}$

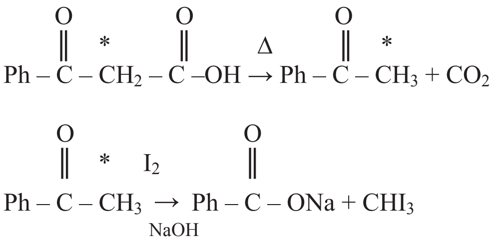
$CHI_3 + CH_3CH_2COOH$
Propanoic acid

172.



Due to presence of lone pair of electron on nitrogen atom, it will activate the ring and it will stabilize intermediate cation at o- and p- positions.

173.



$$Ph-\overset{O}{\overset{\|}{C}}-\overset{*}{C}H_2-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{\Delta} Ph-\overset{O}{\overset{\|}{C}}-\overset{*}{C}H_3+CO_2$$

$$Ph-\overset{O}{\overset{\|}{C}}-\overset{*}{C}H_3 \xrightarrow[NaOH]{I_2} Ph-\overset{O}{\overset{\|}{C}}-ONa+CHI_3$$

SUBJECTIVE SOLVED EXAMPLES

1. Complete the following reaction with appropriate structure.

(i) $C_6H_5COOH + CH_3MgI \rightarrow …… + ….$

[IIT 1993]

Solution

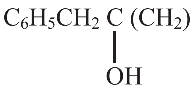
$C_6H_5COOH + CH_3MgI \rightarrow CH_4 + C_6H_5COOMgI$

(ii) $C_6H_5CH_2CO_2CH_3 \xrightarrow[2.\ H^+]{1.CH_3MgBr\ (excess)}$

[IIT 1994]

Solution

$C_6H_5CH_2CO_2CH_3 \xrightarrow[2.\ H^+]{1.\ 2CH_3MgBr\ (excess)}$



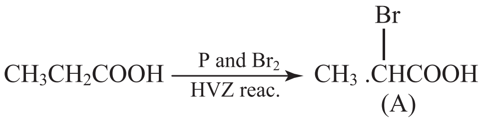
$C_6H_5CH_2\underset{\underset{OH}{|}}{C}(CH_2)$

(iii) $CH_3CH_2\ COOH \xrightarrow{P\ \&\ Br_2} (A)$

$\xrightarrow[2.\ H^+]{1.alc.\ KOH\ (excess)} (B)$

[IIT 1995]

Solution



$CH_3CH_2COOH \xrightarrow[HVZ\ reac.]{P\ and\ Br_2} CH_3\ .\overset{\overset{Br}{|}}{C}HCOOH$ (A)

$\xrightarrow[2.\ H^+]{1.\ alc.\ KOH\ (excess)} CH_2 = CHCOOH$ (B)

(iv) $C_6H_5CHO + CH_3COOC_2H_5$

$\xrightarrow[C_2H_5OH\ and\ heat]{NaOC_2H_5\ in\ absolute} (D)$

[IIT 1995]

Solution

$C_6H_5CHO + CH_3COOC_2H_5 \xrightarrow[C_2H_5OH\ and\ heat]{NaOC_2H_5\ in\ absolute}$

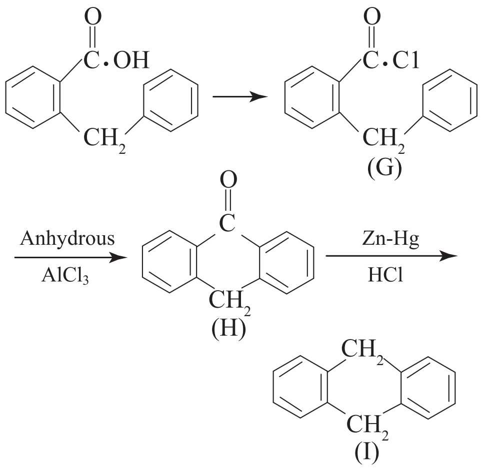
$C_6H_5CH = CHCOOC_2H_5$ (D)

(v) $o\text{-}HOOC - C_6H_4 - CH_2 - C_6H_5 \xrightarrow{SOCl_2}$

$(G) \xrightarrow{anhyd.\ AlCl_3} (H) \xrightarrow[HCl]{Zn\text{-}Hg} (I)$

[IIT 1995]

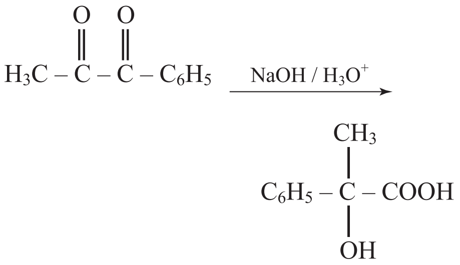
Solution



(vi) $H_3CCOCOC_6H_5 + NaOH/H_3O^+ \longrightarrow (J)$

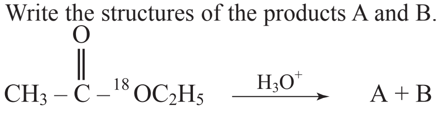
[IIT 1997]

Solution



$H_3C - \overset{\overset{O}{\|}}{C} - \overset{\overset{O}{\|}}{C} - C_6H_5 \xrightarrow{NaOH\ /\ H_3O^+} C_6H_5 - \overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}} - COOH$

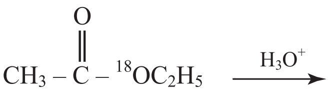
(vii) Write the structures of the products A and B.



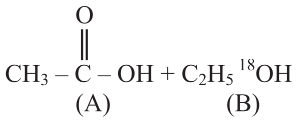
$CH_3 - \overset{\overset{O}{\|}}{C} - {}^{18}OC_2H_5 \xrightarrow{H_3O^+} A + B$

[IIT 2000]

Solution



$CH_3 - \overset{\overset{O}{\|}}{C} - {}^{18}OC_2H_5 \xrightarrow{H_3O^+}$



$$\underset{(A)}{CH_3-\overset{\overset{O}{\|}}{C}-OH} + \underset{(B)}{C_2H_5\,{}^{18}OH}$$

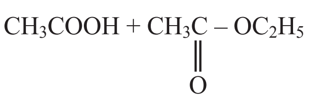
(Ester hydrolysis involves acyl-oxygen fission)

(viii) Complete the following with appropriate structures:

(1) $(CH_3CO)_2O \xrightarrow{C_2H_5OH} CH_3COOH + ?$

Solution

$(CH_3CO)_2O \quad C_2H_5OH$

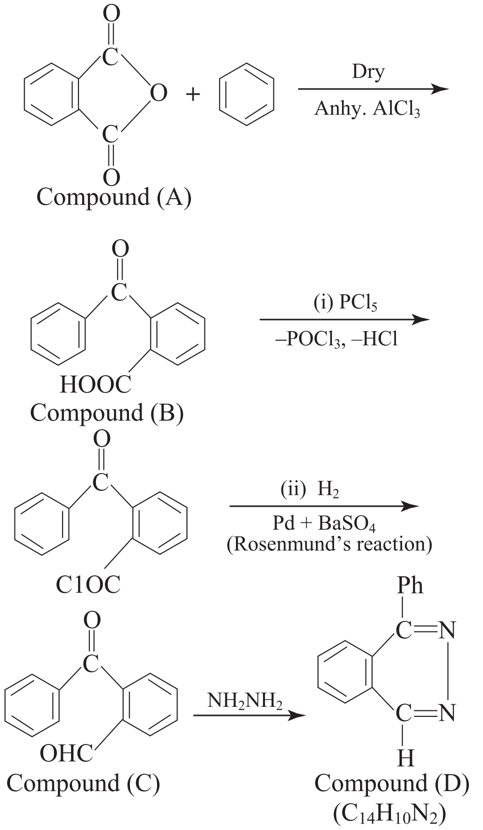


$$CH_3COOH + CH_3\underset{\underset{O}{\|}}{C}-OC_2H_5$$

2. An organic compound (A) $C_8H_4O_3$, in dry benzene in the presence of anhydrous $AlCl_3$ gives compound (B). The compound B, on treatment with PCl_5, followed by reaction with H_2 / Pd ($BaSO_4$) gives compound (C). Which on reaction with hydrazine gives a cyclised compound (D) ($C_{14}H_{10}N_2$)? Identify A, B, C and D. Explain the formation of D from C.

[IIT 2000]

Solution



Compound (A)

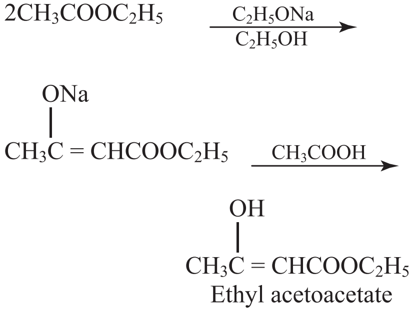
Compound (B)

Compound (C)

Compound (D) ($C_{14}H_{10}N_2$)

3. (i) Write the chemical equation to show what happens when ethyl acetate is treated with sodium ethoxide in ethanol and the reaction mixture is acidified.

Solution



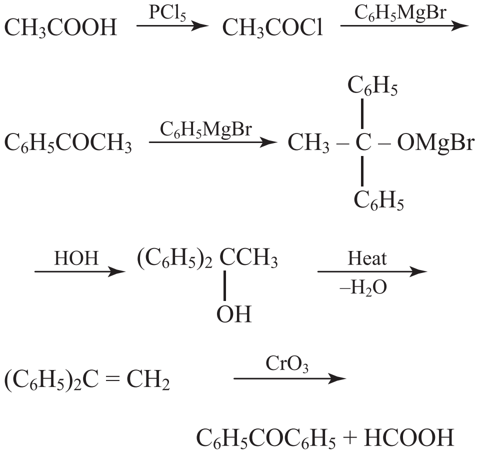
$$2CH_3COOC_2H_5 \xrightarrow[C_2H_5OH]{C_2H_5ONa}$$

$$CH_3\overset{\overset{ONa}{|}}{C} = CHCOOC_2H_5 \xrightarrow{CH_3COOH} \underset{\text{Ethyl acetoacetate}}{CH_3\overset{\overset{OH}{|}}{C} = CHCOOC_2H_5}$$

(ii) Ethanoic acid to a mixture of methanoic acid and diphenyl ketone.

[IIT 1990]

Solution



$$CH_3COOH \xrightarrow{PCl_5} CH_3COCl \xrightarrow{C_6H_5MgBr}$$

$$C_6H_5COCH_3 \xrightarrow{C_6H_5MgBr} CH_3-\underset{\underset{C_6H_5}{|}}{\overset{\overset{C_6H_5}{|}}{C}}-OMgBr$$

$$\xrightarrow{HOH} (C_6H_5)_2\underset{\underset{OH}{|}}{C}CH_3 \xrightarrow[-H_2O]{Heat}$$

$$(C_6H_5)_2C = CH_2 \xrightarrow{CrO_3}$$

$$C_6H_5COC_6H_5 + HCOOH$$

4. State the conditions under which the following preparation are carried out. Give the necessary equations which need not to be balanced.
Acetic acid from methyl iodide.

Solution

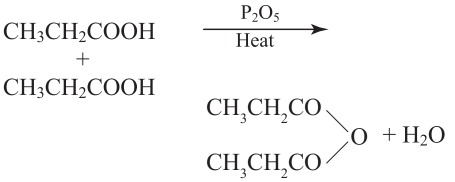
$$CH_3I + KCN\ (alc.) \xrightarrow{-KI} CH_3CN$$

$$\xrightarrow{H^+ / H_2O} CH_3COOH$$

5. Write down the reactions involved in the preparation of the following using the reagents indicated against it in parenthesis:
Propionic anhydride from propionaldehyde [$AgNO_3$ /NH_4OH, P_2O_5]

Solution

$$CH_3CH_2CHO + [O] \xrightarrow[\text{Tollen's reagent}]{AgNO_3\,/\,NH_4OH} CH_3CH_2COOH + 2Ag$$



$$CH_3CH_2COOH + CH_3CH_2COOH \xrightarrow[\text{Heat}]{P_2O_5} (CH_3CH_2CO)_2O + H_2O$$

Propionic anhydride

6. (i) Show with balanced equation what happens when the following are mixed:
   "Chloral is heated with aqueous hydroxide"

Solution

$$\underset{\text{Chloral}}{2CCl_3CHO} \xrightarrow{NaOH} CCl_3COONa + CCl_3CH_2OH$$

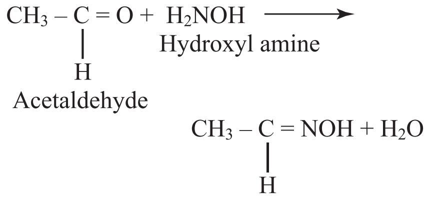
This reaction is known as Cannizaro reaction.

(ii) Write down the reactions involved in the preparation of the following using the reagents indicated against in parenthesis:

"Acetoxime from acetaldehyde"

[$K_2Cr_2O_7$ / H^+, $Ca(OH)_2$ and $NH_2OH.HCl$]

Solution

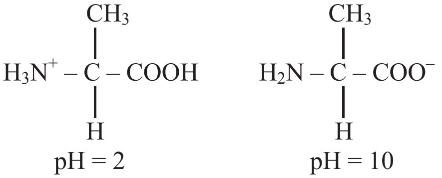


$$\underset{\text{Acetaldehyde}}{CH_3-\underset{\displaystyle H}{\underset{|}{C}}=O} + \underset{\text{Hydroxyl amine}}{H_2NOH} \longrightarrow \underset{\text{Acetoximde}}{CH_3-\underset{\displaystyle H}{\underset{|}{C}}=NOH} + H_2O$$

7. Write the structures of alanine at pH = 2 and pH = 10.

[IIT 2000]

Solution



$$H_3N^+-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle H}{\underset{|}{C}}}}-COOH \qquad H_2N-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle H}{\underset{|}{C}}}}-COO^-$$

pH = 2　　pH = 10

8. (i) Arrange the following in order of their increasing reactivity towards HCN:

   CH_3CHO, CH_3COCH_3, $HCHO$, $C_2H_5COCH_3$

Solution

$C_2H_5COCH_3 < CH_3COCH_3 < CH_3CHO < HCHO$

(ii) Arrange the following in increasing ease of hydrolysis

$CH_3COOC_2H_5$, CH_3COCl, $(CH_3CO)_2O$, CH_3CONH_2,

Solution

$CH_3CONH_2 < CH_3COOC_2H_5 < (CH_3CO)_2O < CH_3COCl$

9. An organic compound (A) on treatment with acetic acid in the presence of sulphuric acid produces an ester (B), (A) on mild oxidation gives (C), (C) with 50% potassium hydroxide followed by acidification with dilute hydrochloric acid generates (A) and (D), (D) with phosphorous pentachloride followed by reaction with ammonia gives (E), (E) on dehydration produces hydrocyanic acid. Identify the compounds A, B, C, D and E.

Solution

(i) (A) on mild oxidation gives (C), which reacts with 50% KOH to produce (A) and (D). As (C) is an aldehyde having no α-H-atom (as it gives Cannizzaro's reaction). So (A) is an alcohol.

$$\underset{(A)}{-CH_2OH} \xrightarrow{[O]} \underset{(C)}{-CHO} \xrightarrow{KOH}$$

$$\begin{array}{l} -COOK + \underset{(A)}{-CH_2OH} \\ \big\downarrow H_2O \\ \underset{(D)}{-COOH} \end{array}$$

(ii) (D) on reaction with PCl_5 followed with action of NH_3 gives (E) which on dehydration produces HCN.

$$\underset{(D)}{-COOH} \xrightarrow{PCl_5} -COCl \xrightarrow{NH_3} \underset{(E)}{CONH_2}$$

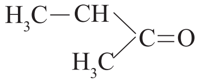
$$\xrightarrow{\text{Dehydration}} HCN$$

(iii) Step (ii) shows that: (E) = $HCONH_2$

(D) = HCOOH

so (C) = HCHO and (A) = CH_3OH

(iv) (A) also reacts with acid to form ester (B).

$\xrightarrow{[O]}$  $+ CH_3COOH$

Butanone-2 (C) Acetic acid (B)

$$\underset{(A)}{CH_3OH} + CH_3COOH \rightarrow \underset{\text{Ester (B)}}{CH_3COOCH_3} + H_2O$$

Therefore

(A) = CH_3OH

(B) = CH_3COOCH_3

(C) = HCHO

(D) = HCOOH

(E) = $HCONH_2$

10. The sodium salt of a carboxylic acid A, was produced by passing a gas B into an aqueous solution of caustic alkali at an elevated temperature and pressure. A, on heating in presence of sodium hydroxide followed by treatment with sulphuric acid gave a dibasic acid, C. A sample of 0.4 g of acid C, on combustion gave 0.08 g of water and 0.39 g of carbon dioxide. The silver salt to the acid weighing 1.0 g on ignition yielded 0.71 g of silver as residue. Identify A, B and C.

[IIT 1990]

Solution

(i) (A) is sodium salt of a carboxylic acid formed by a gas (B) on reaction with NaOH at high pressure and temperature. This reaction is a characteristic reaction of CO_2 and NaOH at high pressure and temperature.

$$\underset{(B)}{CO_2} + NaOH \xrightarrow{\text{Pressure, Temperature}} HCOONa$$

$$\xrightarrow{H_2O} \underset{(A)}{HCOOH}$$

(ii) (A) on heating in presence of NaOH followed by H_2SO_4 gives a dibasic acid (C).

$$\underset{(A)}{HCOOH} \xrightarrow{NaOH,\ \Delta} \underset{\text{Sodium formate}}{HCOONa} \xrightarrow{\Delta}$$

$$\underset{\text{Sodium oxalate}}{\begin{array}{l} COONa \\ | \\ COONa \end{array}} \xrightarrow[\Delta]{H_2SO_4} \underset{\text{(C) Oxalic acid}}{\begin{array}{l} COOH \\ | \\ COOH \end{array}}$$

(iii) The data given for (C) also confirms that it is oxalic acid.

For empirical formula of (C):

Element	**Percentage**	**Relative no. of atoms = %/ at. mass**	**Simplest ratio**
C	$\frac{12}{44}\times\frac{0.39}{0.40}\times 100$ = 26.59	$\frac{26.59}{12}$ = 2.21	1
H	$\frac{2}{18}\times\frac{0.08}{0.40}\times 100$ = 2.22	$\frac{2.22}{1}$ = 2.22	1
O	100 – (26.59 + 2.22) = 71.19	$\frac{71.19}{16}$ = 4.44	2

So empirical formula of (C) is CHO_2.

Empirical formula weight = 45

Molecular weight of (C):

$$\frac{\text{Weight of Ag}}{\text{Eq. wt of Ag}} = \frac{\text{Weight of Ag salt}}{E + 108}$$

Here E is the equivalent wt. of anion of acid

$$\text{So } \frac{0.71}{108} = \frac{1}{E + 108}.$$

E = 44 i.e., equivalent wt of anion of acid

Eq. wt. of acid = 44 + 1 = 45

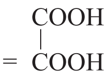
Molecular wt. of acid = 90

$$n = \frac{\text{Molecular weight}}{\text{Empirical formula weight}}$$

$$= \frac{90}{45} = 2$$

Molecular formula = (Empirical formula)$_n$

$= (CHO_2)_2$



$$= \begin{array}{c} COOH \\ | \\ COOH \end{array}$$

(C) Oxalic acid

11. (i) $C_6H_5COOH \xrightarrow{PCl_5} (C) \xrightarrow{NH_3}$

$(D) \xrightarrow{P_2O_5} C_6H_5CN \xrightarrow{H_2 / Ni} (E)$

Identify C, D and E.

[IIT 1991]

Solution

$C_6H_5COOH \xrightarrow{PCl_5} C_6H_5COCl \xrightarrow{NH_3}$

$C_6H_5CONH_2 \xrightarrow{P_2O_5} C_6H_5CN \xrightarrow{H_2 / Ni}$

$C_6H_5CH_2NH_2$

(ii) $H_3C - CH = CH - CHO \xrightarrow{NaBH_4}$

$(F) \xrightarrow{HCl, ZnCl_2} (G) \xrightarrow{KCN, H^+} (H)$

Identify F, G and H.

[IIT 1991]

Solution

$H_3C - CH = CH - CHO \xrightarrow{NaBH_4}$

$CH_3CH = CH - CH_2 - OH \xrightarrow[ZnCl_2]{HCl}$

$CH_3 - CH = CHCH_2Cl \xrightarrow{KCN, H^+}$

$CH_3CH = CH - CH_2COOH$

12. Compound 'X', containing chlorine on treatment with strong ammonia gives a solid 'Y' which is free from chlorine. 'Y' analysed as C = 49.31%, H = 9.59 % and N = 19.18 % and reacts with B_2 and caustic soda to give a basic compound 'Z'. 'Z' reacts with HNO_2 to give ethanol. Suggest structures for 'X', 'Y' and 'Z'.

[IIT 1992]

Solution

For empirical formula of (Y)

Element	%	Relative no. of atoms	Simplest ratio
C	49.31	4.10	3
H	9.59	9.59	7
N	19.18	1.37	1
O	21.92	1.37	1

Thus empirical formula of (Y) is C_3H_7NO.

(Y) reacts with Br_2 and NaOH to give (Z) and (Z) reacts with HNO_2 to give ethanol and thus empirical formula of (Y) seems to be molecular formula with $-CONH_2$ group.

$$\underset{(Y)}{CH_3CH_2CONH_2} + Br_2 + 4KOH \longrightarrow$$

$$\underset{(Z)\text{ basic}}{CH_3CH_2NH_2} \xrightarrow{HNO_2} \underset{\text{Ethanol}}{CH_3CH_2OH}$$

(Y) is formed from (X) having Cl on treatment with NH_3 so (X) is CH_3CH_2COCl i.e., propanoyl chloride.

$$\underset{(X)}{CH_3CH_2COCl} + NH_3 \rightarrow \underset{(Y)}{CH_3CH_2CONH_2}$$

13. An organic compound 'A' on treatment with ethyl alcohol gives a carboxylic acid 'B' and compound 'C'. Hydrolysis of 'C' under acidic conditions gives 'B' and 'D'. Oxidation of 'D' with $KMnO_4$ also gives 'B'. 'B' on heating with $Ca(OH)_2$ gives 'E' (molecular formula, C_3H_6O). 'E' does not give Tollen's test and does not reduce Fehling's solution but forms a 2,4-dinitrophenyl hydrazone. Identify A, B, C, D and E.

[IIT 1992]

Solution

(i) Compound (A) $\xrightarrow{C_2H_5OH}$ Carboxylic acid (B) + Compound (C)

(ii) Compound (C) $\xrightarrow[H_2O / H^+]{\text{Hydrolysis}}$ Compound (B) + Compound (D)

(iii) Compound (D) $\xrightarrow{\text{Oxidation with } KMnO_4}$ Compound (B)

As compound (D) is primary alcohol so compound (D) and (B) have same number of carbon atoms. Compound (B) (carboxylic acid) and (D) (p-alcohol) are produced with hydrolysis of compound (C). So compound (C) is ester.

As compound (B) and (C) are formed by the reaction of compound (A) with C_2H_5OH. So compound (A) is acid anhydride and compound (C) is ethyl ester when compound (C) is ethyl ester therefore, compound (D) is ethyl alcohol and compound (B) is CH_3COOH due to reaction (ii) and (iii).

$$\underset{\text{Compound (A)}}{(CH_3CO)_2O} + C_2H_5OH \longrightarrow \underset{\text{Compound (B)}}{CH_3COOH} + \underset{\text{Compound (C)}}{CH_3COOC_2H_5}$$

$$\underset{\text{Compound (C)}}{CH_3COOC_2H_5} + H_2O \xrightarrow{H^+} \underset{\text{Compound (B)}}{CH_3COOH} + \underset{\text{Compound (D)}}{C_2H_5OH}$$

$$\underset{\text{Compound (D)}}{C_2H_5OH} + [O] \xrightarrow{\text{Oxidation with } KMnO_4}$$

$$CH_3CHO \xrightarrow{[O]} \underset{\text{Compound (B)}}{CH_3COOH}$$

Compound (B) on heating with $Ca(OH)_2$ gives compound (E) (C_3H_6O) which does not give Tollen's test and does not reduce Fehling's solution but form 2, 4-dinitrophenyl hydrazone. So compound (E) is ketone (i.e., CH_3COCH_3).

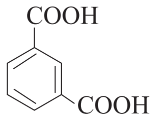
$$2CH_3COOH + Ca(OH)_2 \xrightarrow[-2H_2O]{}$$

$$(CH_3COO)_2Ca \xrightarrow[-CaCO_3]{\Delta} \underset{\text{Compound (E)}}{CH_3COCH_3}$$

14. Write down the structures of E and F.

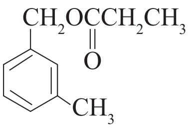
$$E\ (C_{11}H_{14}O_2) \xrightarrow{OH^-} F + CH_3CH_2COO^-$$

$$F \xrightarrow[2.\ H^+]{1.\ KMnO_4/\ OH^-}$$



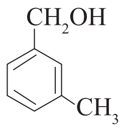
[IIT 1997]

Solution



(E) an ester

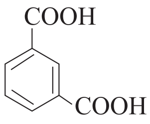
$$\xrightarrow{OH^-}$$



$+ CH_3CH_2COO^-$

(F)

$\downarrow$ Oxidation



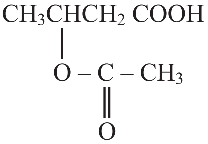
(ii) Write down the structures of G and H where G is $C_4H_8O_3$.

$$\begin{tikzcd}
\text{Acetate} & (G) \arrow[l, "Ac_2O", "\text{Pyridine}"'] \arrow[r, "NaHCO_3"] \arrow[d, "CrO_3"] & CO_2 \\
 & H \arrow[d, "\text{Warm}"] & \\
 & CH_3COCH_3 + CO_2 &
\end{tikzcd}$$

[IIT 1997]

Solution

$$\underset{(G)}{CH_3\ CH(OH)CH_2COOH} \xrightarrow[\text{Pyridine}]{(CH_3CO)_2O}$$



$$CH_3\underset{\substack{|\\ O-\underset{\substack{\|\\ O}}{C}-CH_3}}{C}HCH_2\ COOH$$

$$\underset{(G)}{CH_3\ CH(OH)CH_2COOH} \xrightarrow{NaHCO_3} CO_2$$

$$\underset{(G)}{CH_3\ CH(OH)CH_2COOH} \xrightarrow{CrO_3}$$

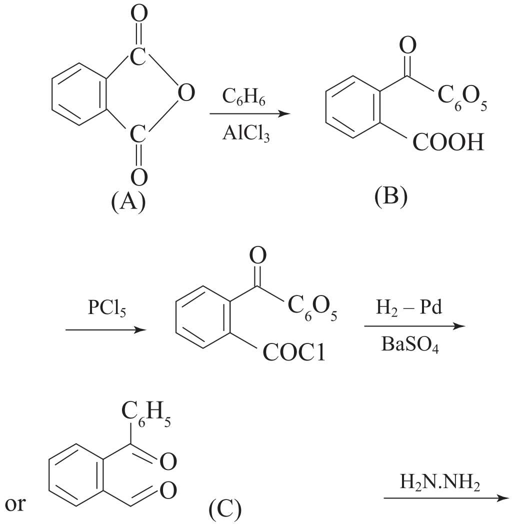
$$\underset{(H)}{CH_3CHCH_2COOH} \xrightarrow{\Delta} CH_3COCH_3 + CO_2$$

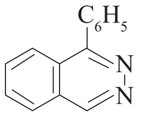
15. An organic compound A, $C_8H_4O_3$, in dry benzene in the presence of anhydrous $AlCl_3$ gives compound B. The compound B on treatment with PCl_5, followed by reaction with H_2 / Pd ($BaSO_4$) gives compound

C, which on reaction with hydrazine gives a cyclic compound D ($C_{14}H_{10}N_2$). Identify A, B, C and D. Explain the formation of D from C.

[IIT 2000]

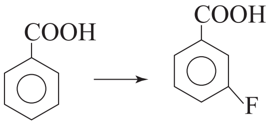
Solution





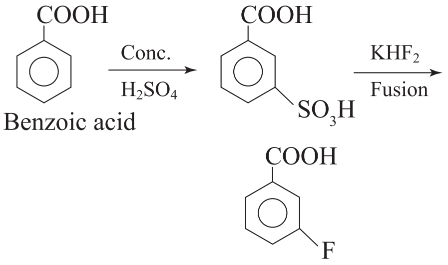
(D)

16. Convert (in not more than 3 steps)



[IIT 2003]

Solution



ORGANIC CHEMISTRY BASED ON FUNCTIONAL GROUP-III

(NITROGEN CONTAINING COMPOUNDS)

CHAPTER 8

CHAPTER CONTENTS

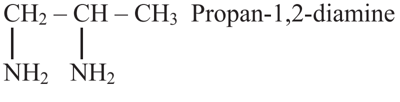
(Introduction, Preparations, Properties of Nitrogen Containing Compounds)
Basicity of substituted anilines and aliphatic amines, preparation from nitro compounds, reactions with nitrous acid, azo coupling reaction of diazonium salts, carbyl amine reaction and various level of multiple-choice questions.

AMINES

INTRODUCTION AND NOMENCLATURE

- Amines are the alkyl or aryl derivatives of ammonia.
- Amines have a general formula $C_nH_{2n+3}N$.
- There are three types of amines primary (RNH_2), secondary (R_2NH) and tertiary (R_3N).
- All the three types of amine are obtained from ammonia by replacing H-atoms by alkyl or aryl groups.
- Amines are named as Aminoalkanes or Alkanamines in case of primary amines.

For example, $CH_3CH_2CH_2NH_2$ Propanamine



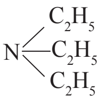
$$\underset{NH_2}{\underset{|}{CH_2}} - \underset{NH_2}{\underset{|}{CH}} - CH_3$$ Propan-1,2-diamine

- Secondary amines are named as N-Alkyl alkanamine.

For example, $C_2H_5NHCH_2CH_2CH_3$
N-Ethyl propanamine

- Tertiary amines are named as N,N-dialkyl alkanamine.

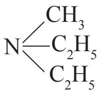
For example,



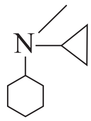
N, N-diethyl ethanamine

- Tertiary amines are also named as N-alkyl N'-alkyl alkanamine.

  For example,



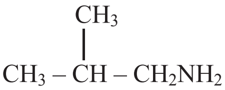
N-ethyl N'methyl ethanamine

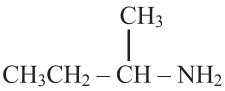


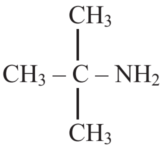
N-cyclopropyl N-methyl cyclohexanamine

- Amines show functional, chain, position and metamerism isomerisms.
- p, s, t amines are functional isomers.
- $C_4H_{11}N$ has 4-primary, 3-secondary and 1-tertiary amines that is, 8 in all.
- 1, 2, 5, 4 show chain and position isomerisms.
- 5, 6, or 7 are metamers.
- 6, 7 are positions isomers.
- 1---4, or 5, 6, 7 or 8 are functional isomers.

(1) $CH_3CH_2CH_2CH_2NH_2$

(2)

$CH_3 - \overset{\overset{CH_3}{|}}{CH} - CH_2NH_2$

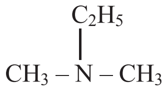
(3)

$CH_3CH_2 - \overset{\overset{CH_3}{|}}{CH} - NH_2$

(4)

$CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - NH_2$

(5) $C_2H_5 - NH - C_2H_5$

(6) $CH_3 - NH - CH_2CH_2CH_3$

(7) $CH_3 - NH - CH\,(CH_3)_2$

(8)

$CH_3 - \overset{\overset{C_2H_5}{|}}{N} - CH_3$

METHODS OF PREPARATION FOR ALL TYPES OF AMINE

- **By Hoffmann's Method** Here Alkyl halide is treated with alcoholic ammonia as follows:

$$RX + NH_3 \xrightarrow{\Delta} RNH_2 + HX$$

$$RNH_2 + RX \longrightarrow R_2NH + HX$$

$$R_2NH + RX \rightarrow R_3N + HX$$

$$R_3N + RX \rightarrow \underset{\text{Quaternary ammonium salt}}{R_4N^+ X^-}$$

- When NH_3 is in excess $R-NH_2$ is the major product and when $R-X$ is in excess quaternary ammonium salt is the major product.
- It is called ammonolysis of alkyl halides. It is a nucleophillic substitution reaction.
- **By Ammonolysis of Alcohols** Here vapours of alcohol and ammonia are passed over heated Alumina or Thoria at 350°C as follows:

$$ROH + NH_3 \xrightarrow[350^{o}C]{Al_2O_3} RNH_2 + H_2O$$

$$RNH_2 + ROH \rightarrow R_2NH + H_2O$$

$$R_2NH + ROH \rightarrow R_3N + H_2O$$

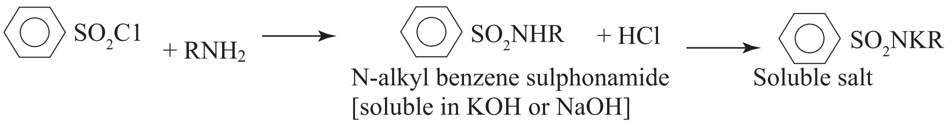
Separation of Primary, Secondary, Tertiary Amine and Quaternary Ammonium Salt

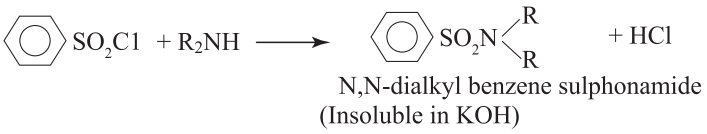
- The mixture is first treated with aq. KOH where the quaternary halide forms quaternary ammonium hydroxide a solid product.
- The mixture is distilled where primary, secondary and tertiary amines are distilled leaving salt residue in the flask.
- The mixture of primary, secondary, tertiary amines can be separated by any of the following methods.

By Fractional Distillation When the mixture is subjected to a fractional distillation by which all the three amines are separated but the method is applicable only when the three amines differ considerably in their boiling points.

By Hinsberg's Method Here the mixture of amines is treated with Hinsberg reagent (Benzene sulphonyl Chloride).

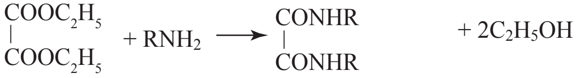
- Here only primary and secondary amines react while tertiary does not react with it.
- The mixture is distilled to remove unreacted tertiary amine.
- The remaining mixture is treated with aq. KOH in which the derivative of primary amine become soluble and that of secondary amine remains insoluble.





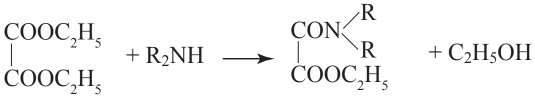
By Hoffmann's Method

- Here the mixture of amines is heated with diethyl oxalate.
- Here primary amine forms a solid product., secondary amine forms an oily product while tertiary amine does not react.
- The mixture is distilled where unreacted tertiary amines distilled over first followed by the oily product of secondary amine. The derivative of primary amine is left in the flask.
- The derivatives of primary and secondary amines on hydrolysis generate amines.



$$\begin{matrix}\mathrm{COOC_2H_5}\\|\\\mathrm{COOC_2H_5}\end{matrix} + \mathrm{RNH_2} \longrightarrow \begin{matrix}\mathrm{CONHR}\\|\\\mathrm{CONHR}\end{matrix} \quad + 2\mathrm{C_2H_5OH}$$

Di alkyloxamide (solid)



$$\begin{matrix}\mathrm{COOC_2H_5}\\|\\\mathrm{COOC_2H_5}\end{matrix} + \mathrm{R_2NH} \longrightarrow \begin{matrix}\mathrm{CON}\begin{smallmatrix}\mathrm{R}\\\mathrm{R}\end{smallmatrix}\\|\\\mathrm{COOC_2H_5}\end{matrix} \quad + \mathrm{C_2H_5OH}$$

Di alkyl oxamic ester
(oily liquid)

METHODS FOR PRIMARY AMINES ONLY

- **From Acids**

$$\mathrm{RCOOH} + \mathrm{NH_3} \longrightarrow \mathrm{RCOONH_4} \xrightarrow{\Delta}$$

$$\mathrm{RCONH_2} \xrightarrow{\mathrm{Br_2/KOH}} \mathrm{RNH_2}$$

For example,

$$\mathrm{CH_3COOH} + \mathrm{NH_3} \longrightarrow \mathrm{CH_3COONH_4} \xrightarrow{\Delta}$$

$$\mathrm{CH_3CONH_2} \xrightarrow{\mathrm{Br_2/KOH}} \mathrm{CH_3NH_2}$$

- **By Schmidt Reaction**

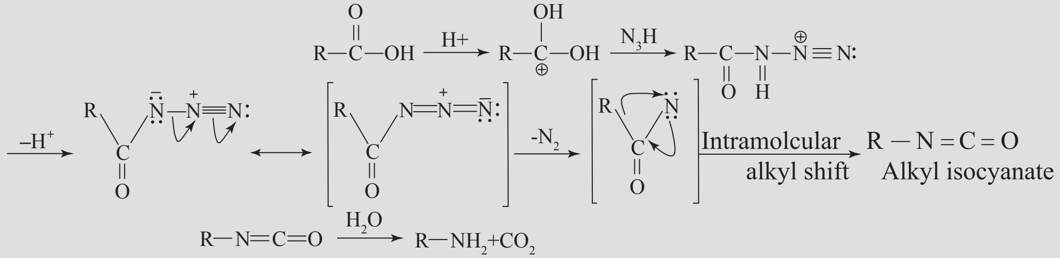
$$\mathrm{RCOOH} + \underset{\text{Hydrazoic acid}}{\mathrm{N_3H}} \xrightarrow[\mathrm{H_2SO_4}]{\text{conc.}} \mathrm{RNH_2} + \mathrm{N_2} + \mathrm{CO_2}$$

For example,

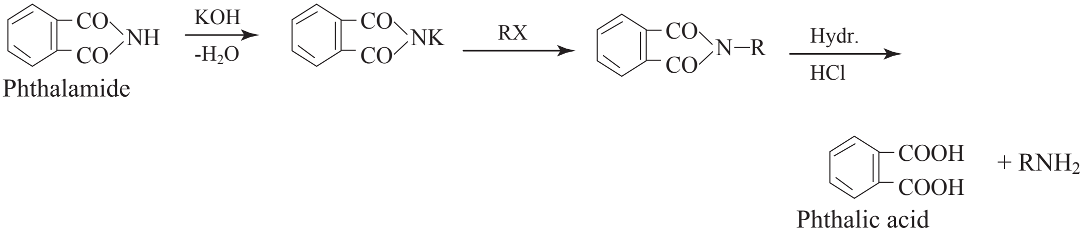
$$\mathrm{CH_3COOH} + \mathrm{N_3H} \xrightarrow{\text{conc. }\mathrm{H_2SO_4}} \mathrm{CH_3NH_2} + \mathrm{N_2} + \mathrm{CO_2}$$

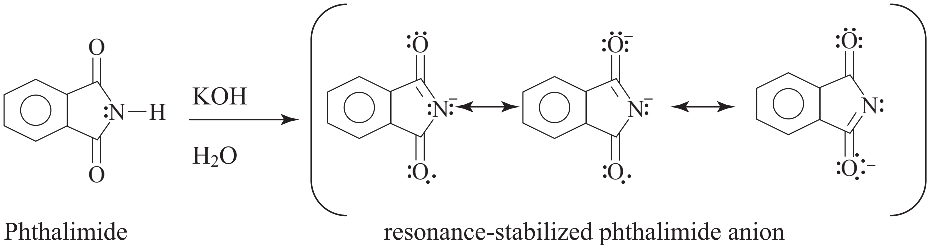
- In this reaction alkyl isocyanate and acyl azide are the reaction intermediates and they give primary amines as the final product by Curtius degradation method.

Mechanism

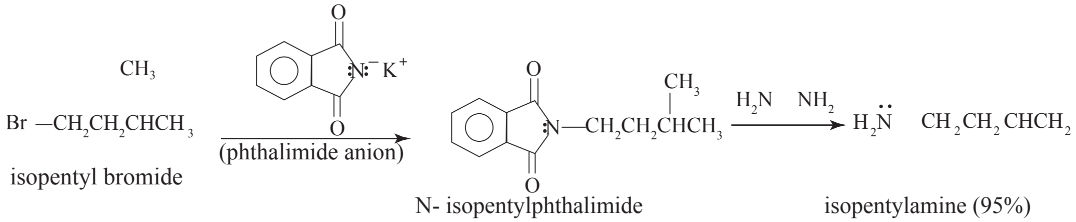


- **By Gabriel Phthalamide Synthesis** Here primary amines are formed by the reaction of potassium phthalamide and alkyl halide and the rate of reaction can be increase by using solvents like dimethyl furan and crowns ethers etc.





For example,



- $C_6H_5 - NH_2$ can not prepared here as C_6H_6 does not under go nucleophillic substitution under mild conditions.

- **By Reduction of Cyanides**

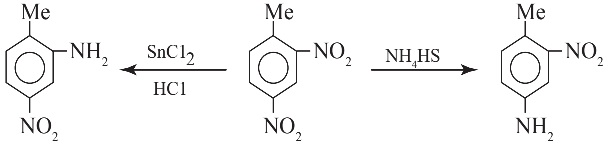
$$RCN + 4H \xrightarrow[\text{Na + alc.}]{\text{LiAlH}_4} RCH_2NH_2$$

For example,

$$CH_3CN + 4H \xrightarrow[\text{Na + alc.}]{\text{LiAlH}_4} CH_3CH_2NH_2$$

- **By Reduction of Nitro Alkanes**

$$RCH_2NO_2 + 6H \xrightarrow[\text{LiAlH}_4]{\text{Sn/HCl}} RCH_2NH_2 + 2H_2O$$



For example,

$$CH_3CH_2NO_2 + 6H \xrightarrow[\text{LiAlH}_4]{\text{Sn/HCl}} CH_3CH_2NH_2 + 2H_2O$$

By Reduction of Amides

$$RCONH_2 + 4H \xrightarrow[C_2H_5OH/Na]{LiAlH_4} RCH_2NH_2 + H_2O$$

For example,

$$CH_3CONH_2 + 4H \xrightarrow[C_2H_5OH/Na]{LiAlH_4} CH_3CH_2NH_2 + H_2O$$

By Reduction of Oximes

$$RCH = NOH + 4H \xrightarrow[\substack{OR \\ Na/C_2H_5OH}]{LiAlH_4} RCH_2NH_2 + H_2O$$

For example,

$$CH_3CH = NOH + 4H \xrightarrow[\substack{OR \\ Na/C_2H_5OH}]{LiAlH_4} CH_3CH_2NH_2 + H_2O$$

From Alkyl Halides and Alcohols

$$\underset{}{RX} + \underset{excess}{NH_3} \longrightarrow RNH_2 + HX$$

$$ROH + \underset{excess}{NH_3} \xrightarrow[350^{\circ}C]{Al_2O_3} RNH_2 + H_2O$$

For example,

$$C_2H_5Cl + \underset{excess}{NH_3} \longrightarrow C_2H_5NH_2 + HCl$$

$$C_2H_5OH + \underset{excess}{NH_3} \xrightarrow[350^{\circ}C]{Al_2O_3} C_2H_5NH_2 + H_2O$$

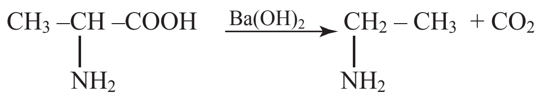
From Grignard Reagent

$$RMgX + NH_2Cl \longrightarrow RNH_2 + XMgCl$$

For example,

$$C_2H_5MgCl + NH_2Cl \longrightarrow C_2H_5NH_2 + MgCl_2$$

By Decarboxylation of α-Amino Acids



$$CH_3-\underset{\displaystyle NH_2}{\underset{|}{CH}}-COOH \xrightarrow{Ba(OH)_2} \underset{\displaystyle NH_2}{\underset{|}{CH_2}}-CH_3 + CO_2$$

By Hydrolysis of Isocyanides and Isocyantes

$$RNC + 2H_2O \xrightarrow{H^+} RNH_2 + HCOOH$$

$$RNCO + 2KOH \xrightarrow{H} RNH_2 + K_2CO_3$$

For example,

$$C_2H_5NC + 2H_2O \xrightarrow{H^+} C_2H_5NH_2 + HCOOH$$

$$C_2H_5NCO + 2KOH \xrightarrow{H} C_2H_5NH_2 + K_2CO_3$$

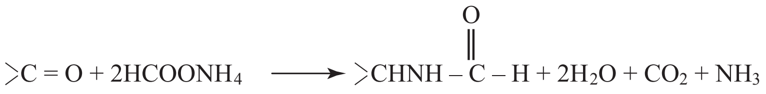
- **By the Reaction of Azide With NaBH4**

$$\underset{\text{Sod. azide}}{R-X + NaN_3} \longrightarrow \underset{\text{Alkyl azide}}{RN_3} \xrightarrow[H_2O]{NaBH_4} RNH_2$$

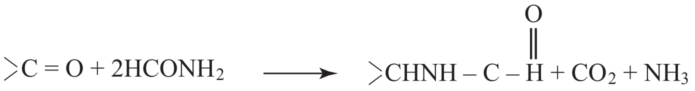
For example,

$$C_2H_5Cl + \underset{\text{Sod. azide}}{NaN_3} \longrightarrow \underset{\text{Ethyl azide}}{C_2H_5N_3} \xrightarrow[H_2O]{NaBH_4} C_2H_5NH_2$$

- **By Leuckart Reaction** Aldehydes or ketones on reaction with ammonium formate or with formamide, give formyl derivatives of primary amine.

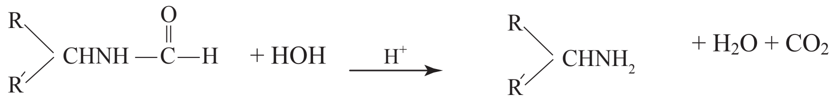


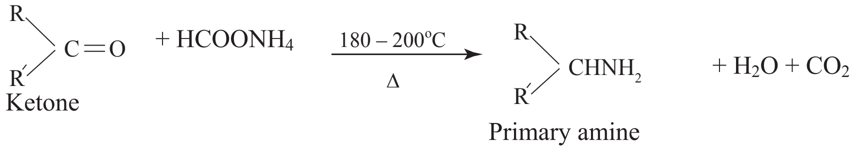
$$>C=O + 2HCOONH_4 \longrightarrow >CHNH-\overset{\overset{O}{\|}}{C}-H + 2H_2O + CO_2 + NH_3$$



$$>C=O + 2HCONH_2 \longrightarrow >CHNH-\overset{\overset{O}{\|}}{C}-H + CO_2 + NH_3$$

- These formyl derivatives are easily hydrolyzed by acids into primary amines.





METHODS FOR SECONDARY AMINES

$$RN \equiv C + 4[H] \xrightarrow{Pt} \underset{\text{Secondary amine}}{RNHCH_3}$$

For example,

$$C_2H_5N \equiv C + 4[H] \xrightarrow{Pt} \underset{\substack{\text{N-methyl}\\ \text{ethanamine}}}{C_2H_5NHCH_3}$$

Mannich Reaction

$$R-CONHR' + 4[H] \xrightarrow{LiAlH_4} RCH_2NHR' + H_2O$$

For example,

$$CH_3-CONHCH_3 + 4[H] \xrightarrow{LiAlH_4} \underset{\text{N-methyl ethanamine}}{CH_3CH_2NHCH_3} + H_2O$$

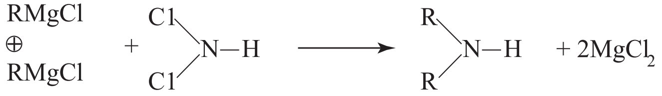
Hydrolysis of Dialkyl Cyanamide

$$R_2N-CN + 2H_2O \xrightarrow{H^+} R_2NH + CO_2 + NH_3$$

For example,

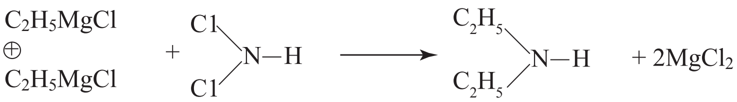
$$(CH_3)_2N-CN + 2H_2O \xrightarrow{H^+} \underset{\text{N-methyl methanamine}}{(CH_3)_2NH} + CO_2 + NH_3$$

Using Grignard Reagent



Dichloroamine Secondary amine

For example,



Dichloroamine N-ethyl ethanamine

METHODS FOR TERTIARY AMINES

Reduction of N, N-Disubstituted Amides

$$RCONR'_2 \xrightarrow[4[H]]{LiAlH_4} RCH_2NR'_2 + H_2O$$

For example,

$$CH_3CON(CH_3)_2 \xrightarrow[4[H]]{LiAlH_4} \underset{\text{N,N-dimethyl ethanamine}}{CH_3CH_2N(CH_3)_2} + H_2O$$

By Decomposition of Tetra-Ammonium Hydroxides

$$(R)_4NOH \xrightarrow{\Delta} (R)_3N + \text{Alkene} + H_2O$$

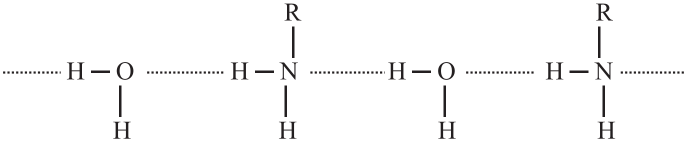
For example,

$$(C_2H_5)_4NOH \xrightarrow{\Delta} \underset{\text{N,N-diethyl ethanamine}}{(C_2H_5)_3N} + C_2H_4 + H_2O$$

PHYSICAL PROPERTIES

- The first two members (methyl amine and ethyl amine) are gases with ammonical smell while rest members are liquid or solid.

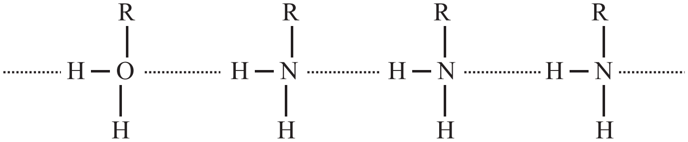
Solubitity Lower aliphatic amines are soluble in water due to hydrogen bonding but higher aliphatic and aromatic amines are insoluble in water due to larger non-polar part.



Solubility $\propto$ 1/molecular weight

For example, $CH_3NH_2 > C_2H_5NH_2 > C_3H_7NH_2 > \ldots\ldots$

Boiling point Boiling point of amines are higher than hydrocarbons and haloalkanes of comparable molecular masses, because in amines intermolecular hydrogen bonding is present.



The electrobnegative of N is lower than oxygen, therefore, intermolecular hydrogen bonding is weaker in amines than alcohols and acids. Therefore, boiling point of amines is lesser than alcohols and carboxylic acids. Thus boiling point follows order.

Amines < Alcohols < Catrboxylic acids

- These are inflammable and basic in nature.

CHEMICAL PROPERTIES

Basic Nature

- Amines are basic in nature as Nitrogen atom has one lone pair of electrons to donate, so they form salts with acids.

$RNH_2 + HCl \rightarrow RNH_3^+Cl^-$

$2R - NH_2 + H_2PtCl_6 \rightarrow (R^+NH_3)_2PtCl_6^{-2}$

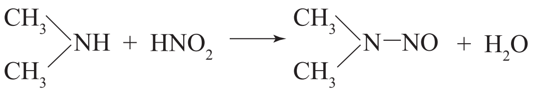
Chloro platinate

$AgCl + 2R - NH_2 \rightarrow [R - NH_2 \rightarrow Ag \leftarrow NH_2R]^+ Cl^-$

- ***Nitrous Acid HNO_2*** A primary amine gives alcohol with it while a secondary amine gives nitroso amine and a tertiary amine forms trialkyl ammonium nitrate. [Test of distinguishing Aminel]

$CH_3CH_2NH_2 + HNO_2 \rightarrow C_2H_5OH + N_2 + H_2O$

(N free)



(oily product
Nitroso amine)

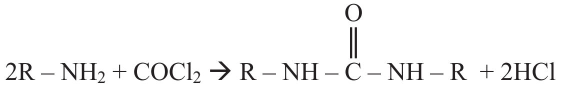
$(CH_3)_3N + HNO_2 \rightarrow (CH_3)_3 N^+ NO_2^-$

- ***With NOCl*** A primary amine gives alkyl halide while a secondary amine gives an oily product and a tertiary amine does not react with it.

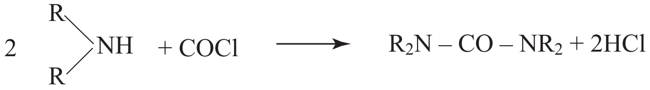
  $CH_3CH_2NH_2 + NOCl \rightarrow CH_3CH_2Cl + N_2 + H_2O$

Nitroso amine
oily product

- ***Libermann's Nitroso Test*** When nitroso amine is heated with phenol in the presence of sulphuric acid a red colour is formed which changes to blue and finally green.
- ***With COCl$_2$*** This reaction is given by primary amine and secondary amines only.



$$2R - NH_2 + COCl_2 \rightarrow R - NH - \overset{\overset{\displaystyle O}{\|}}{C} - NH - R + 2HCl$$



- ***Acetylation or Reaction With CH$_3$COCl*** This reaction is used to confirm the presence of NH_2 group.

  $CH_3COCl + RNH_2 \rightarrow \underset{\text{N-alkyl ethanamide}}{CH_3CONHR} + HCl$

Oxidation

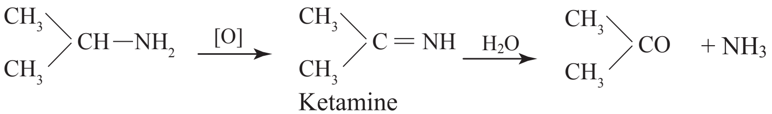
A primary amine on oxidation gives aldimine which on hydrolysis gives aldehyde.

For example,

$$CH_3CH_2NH_2 \xrightarrow[KMnO_4]{[O]} \underset{\text{aldimine}}{CH_3CH{=}NH} \xrightarrow{H_2O} \underset{\text{Acetaldehyde}}{CH_3CHO + NH_3}$$

A secondary amine on oxidation gives ketamine which on hydrolysis gives ketone.

For example,



Ketamine

A secondary amine on oxidation by H_2O_2 or caro acid gives dialkyl hydroxylamine as follows

$$R_2NH \xrightarrow[\text{or } H_2SO_5]{H_2O_2} R_2N - OH$$

A secondary amine on oxidation by $KMnO_4$ gives tetralkyl hydrazine as follows

$$R_2NH \xrightarrow{KMnO_4} R_2N - NR_2 + H_2O$$

- A tertiary amine on oxidation by caroacid or Fenton's reagent gives t-amine oxide.

$$R_3N + [O] \xrightarrow[\substack{O_3 \\ H_2SO_5}]{H_2O_2} R_3N \rightarrow O$$

- ***Carbyl Amine Reaction*** It is a test of a primary amine. Here a pungent bad smelling compound isocyanide(carbyl amine) is formed by the reaction between a primary amine chloroform and base like KOH. Here reaction intermediate is Dichloro carbene.

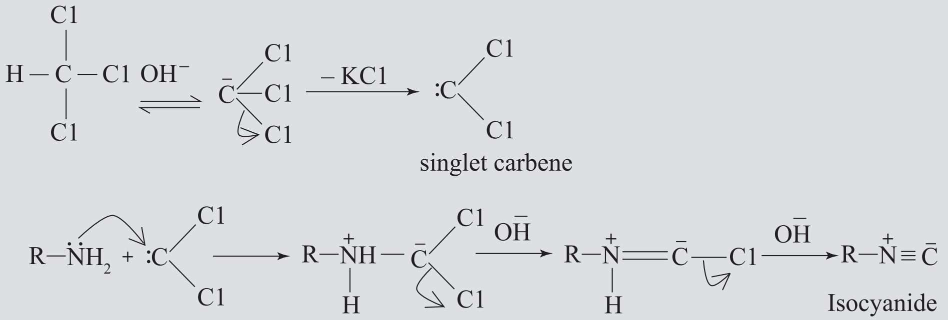
$$RNH_2 + CHCl_3 + 3KOH \xrightarrow{\text{alc. KOH}} RNC + 3KCl + 3H_2O$$

For example,

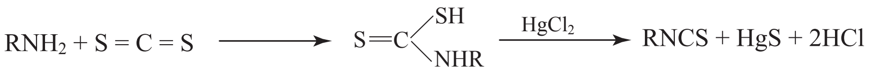
$$CH_3NH_2 + CHCl_3 + 3KOH \xrightarrow{\text{alc. KOH}} \underset{\text{Methyl isocyanide}}{CH_3NC} + 3KCl + 3H_2O$$

$$C_6H_5NH_2 + CHCl_3 + 3KOH \xrightarrow{\text{alc. KOH}} \underset{\text{Phenyl isocyanide}}{C_6H_5NC} + 3KCl + 3H_2O$$

Mechanism

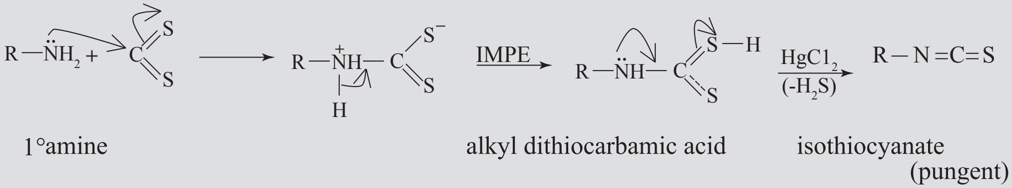


- ***Hoffmann's Mustard Oil Reaction*** It is a test of primary amine. Here primary amine gives alkyl isothiocyanate having mustard oil like smell as follows



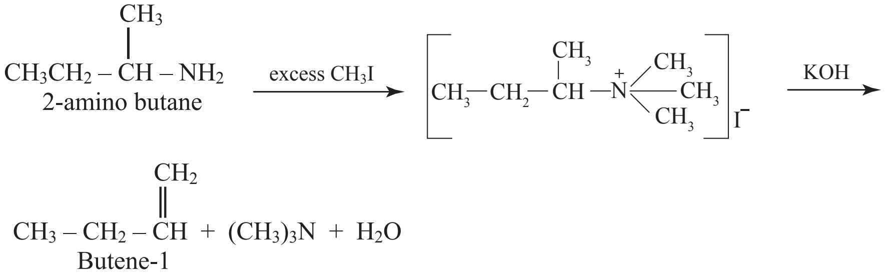
$$RNH_2 + S = C = S \longrightarrow S{=}C\langle{}^{SH}_{NHR} \xrightarrow{HgCl_2} RNCS + HgS + 2HCl$$

Mechanism



- ***Hoffmann's Exhaustive Methylation and degradation*** It involve formation of alkene by following Hoffman rule that is, less stable alkene will be the major product.

For example,



$$CH_3CH_2-\overset{\overset{CH_3}{|}}{CH}-NH_2 \xrightarrow{\text{excess } CH_3I} \left[CH_3-CH_2-\overset{\overset{CH_3}{|}}{CH}-\overset{+}{N}(CH_3)_3\right]I^- \xrightarrow{KOH}$$

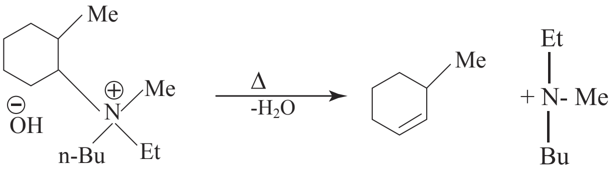
2-amino butane

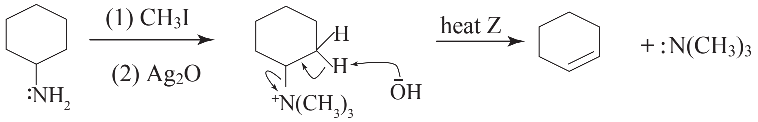
$$CH_3-CH_2-\overset{\overset{CH_2}{\|}}{CH} + (CH_3)_3N + H_2O$$

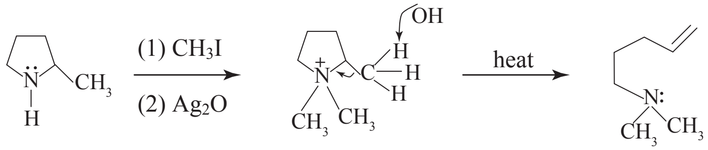
Butene-1

The above elimination is governed by Hoffmann rule. According to this rule elimination of the β-hydrogen atom takes place from the carbon containing more hydrogen atoms or a less stable alkene is formed here.

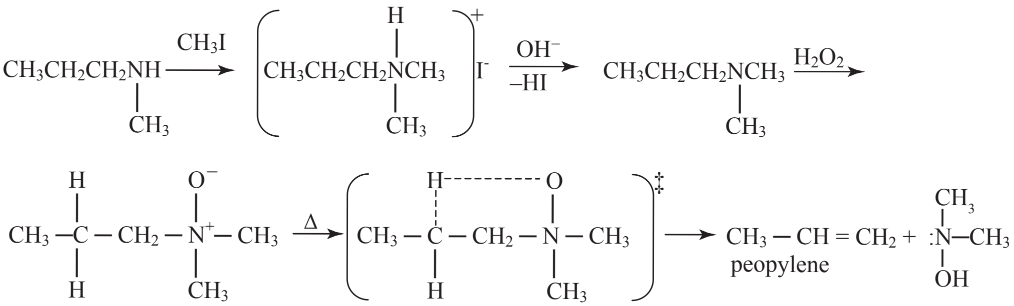
For example,







Cope Elimination of 3° Amine Oxides



$$CH_3CH_2CH_2\underset{\underset{CH_3}{|}}{N}H \xrightarrow{CH_3I} \left(CH_3CH_2CH_2\overset{\overset{H}{|}}{\underset{\underset{CH_3}{|}}{N}}CH_3\right)^+ I^- \xrightarrow[-HI]{OH^-} CH_3CH_2CH_2\underset{\underset{CH_3}{|}}{N}CH_3 \xrightarrow{H_2O_2}$$

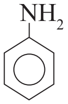
$$CH_3-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-CH_2-\overset{\overset{O^-}{|}}{\underset{\underset{CH_3}{|}}{N^+}}-CH_3 \xrightarrow{\Delta} \left(CH_3-\overset{\overset{H\text{-----}}{\vdots}}{\underset{\underset{H}{|}}{C}}-CH_2-\overset{\overset{O}{|}}{\underset{\underset{CH_3}{|}}{N}}-CH_3\right)^{\ddagger} \longrightarrow CH_3-CH=CH_2 + :\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{N}}-CH_3$$

peopylene

3° amine oxide

N, N -
Dimethyl - hydroxylamine

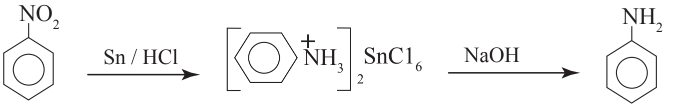
ANILINE OR AMINO BENZENE



- It is also called Benzenamine or Phenyl amine.

Methods of Preparation

- **By Reduction of Nitro Benzene**

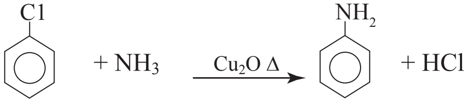


Aniline chlorostannate (salt) ppt

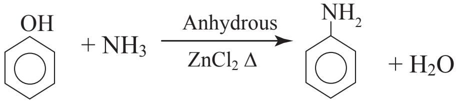
Aniline

- In commercial preparation Fe + HCl is used.

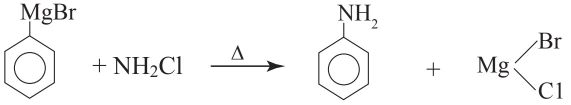
- **From Chlorobenzene**



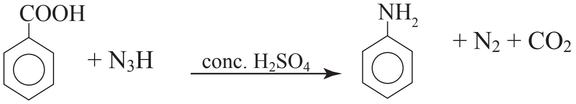
- **From Phenol**



- **From Phenyl Magnesium Bromide**

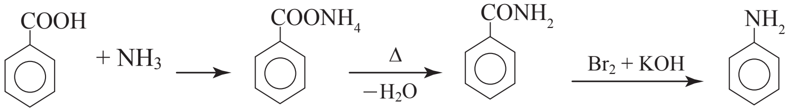


- **Schmidt Reaction**



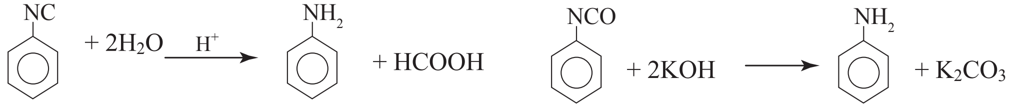
Hydrazoic acid

- **From Benzoic Acid**



Ammonium benzoate Benzamide Aniline

- The conversion of Benzamide into aniline is by Hoffmann bromamide reaction.
- **By the Hydrolysis of Isocyanide and Isocyanate**



- **From Benzene Sulphonic acid**

Sodium benzene Sulphonate

Aniline

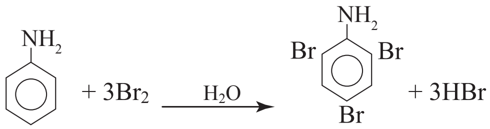
PHYSICAL PROPERTIES

- Pure aniline is a colourless oily liquid but on standing it becomes dark brown due to action of light and air.
- Its boiling point is 183°C.
- It is soluble in water but volatile in steam.
- It can be purified by steam distillation.

CHEMICAL PROPERTIES

1 Electrophilic Substitution –NH_2 group in aniline is highly ring activating as the lone pair of electron present on nitrogen atom becomes delocalized due to resonance to increase electron density at ortho and para positions.

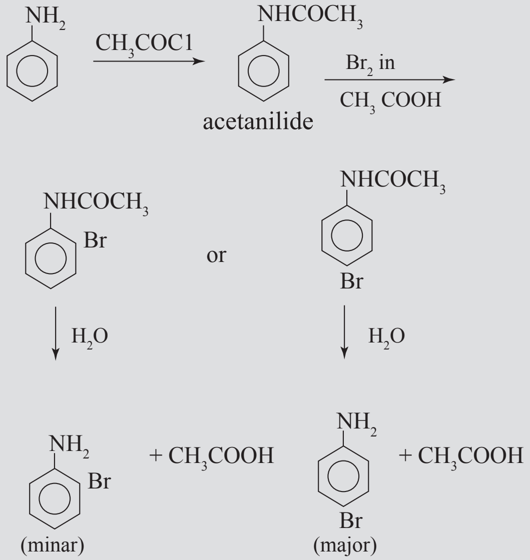
- ***Halogenation***



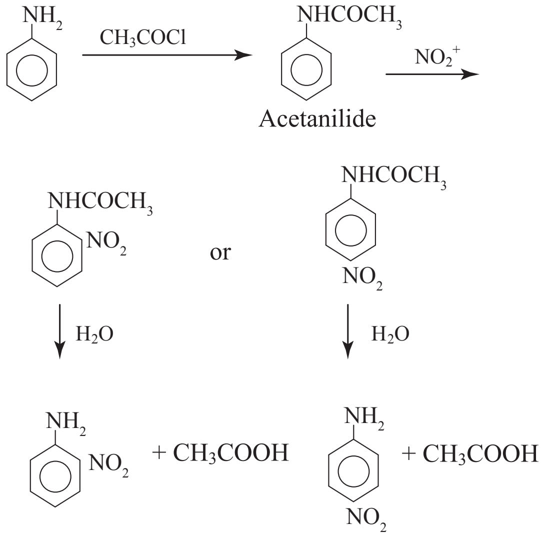
2,4,6 tribromo aniline

REMEMBER

- If we want to convert aniline into ortho, para bromoanilines, aniline is first converted into Acetanilide and then bromination is carried out.

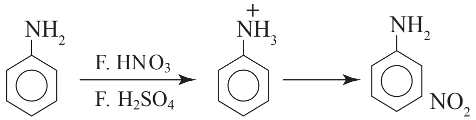


- ***Nitration***



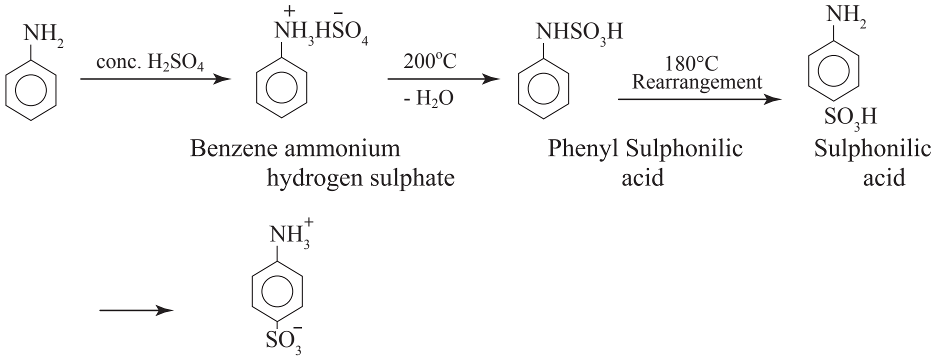
Acetanilide

- Direct nitration is not possible as HNO_3 is a strong oxidizing agent so oxidizes NH_2 group also, hence first protect NH_2 group by acetylation before nitration.



m-nitroaniline

- ***Sulphonation***



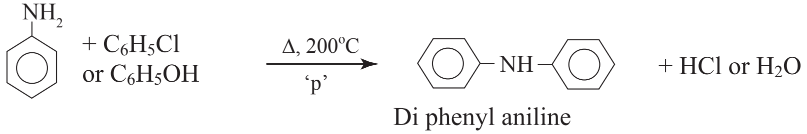
Benzene ammonium hydrogen sulphate

Phenyl Sulphonilic acid

Sulphonilic acid

Zwitter ion

- ***Arylation*** Aniline react with chlorobenzene or phenol to give diphenyl aniline.



Di phenyl aniline

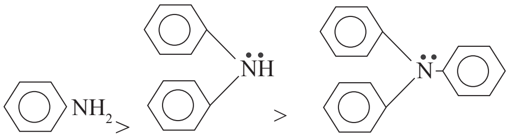
- ***Friedal Craft Reaction*** Aniline fails to give Friedal craft reaction as aniline act as a Lewis base so $AlCl_3$ being an electrophile form salt with it. that is, $C_6H_5NH_2^+ . AlCl_3^-$

2 Reactions Due to NH_2 Group

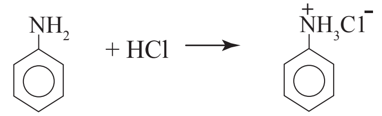
- ***Basic Nature*** Aniline is weak base as nitrogen atom has one lone pair of electron however this lone pair of electron is delocalized due to resonance.

$$\text{Basic nature} \propto \frac{1}{\text{Resonance}}$$

For example,

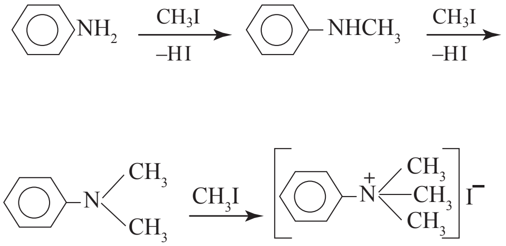


- ***Salt Formation***



Aniline hydrogen chloride

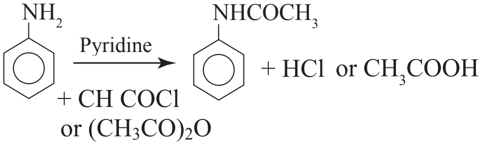
- ***Alkylation***



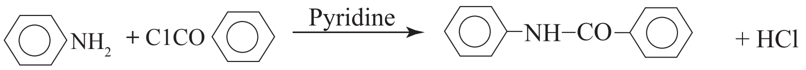
t-amine

Tri methyl phenyl ammonium iodide

- ***Acylation***

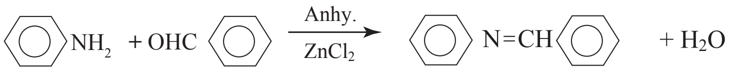


- ***Benzylation (Schotten Baumen's Reaction)***



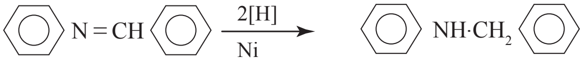
Benzoyl chloride Benzanilide

- ***With Benzaldehyde***



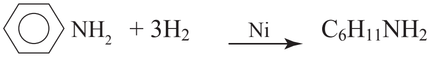
Benzal aniline or
Schiff's base or Anils or Benzilidine

- Schiff base on hydrogenation gives Benzylphenyl aniline.

- 

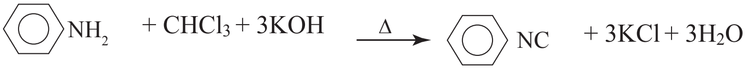
Benzyl phenyl aniline

- ***Reduction***



Amino cyclohexane

- ***Carbyl Amine Reaction*** It is a test of primary amines and chloroform here pungent bad smelling iso-cyanites are formed. Here dichlorocarbene is reaction intermediate.

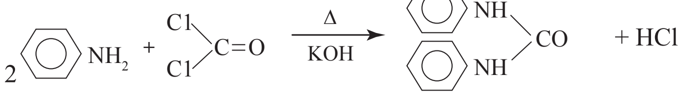


Phenyl Isocyanide

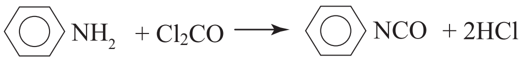
- ***With HNO_2*** When aniline is treated with a mixture of sodium nitrite and hydrogen chloride in cold Benzene di azonium chloride is formed and it is called Diazotization reaction.

Benzene di azonium chloride

- ***With Phosgene***

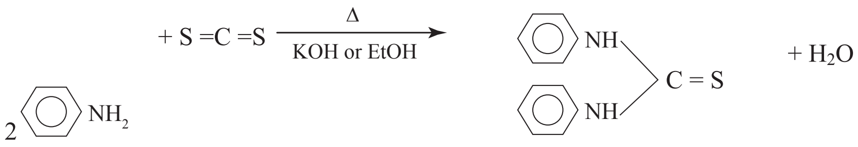


Di phenyl urea

- 

Phenyl Iso cyanate

- ***With CS₂***



Di phenyl thio urea

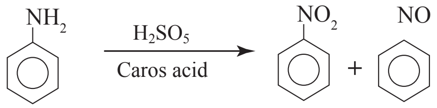
- ***With Benzene Chlorosulphonic Acid***

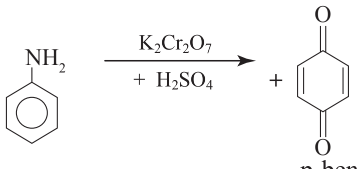
N-phenyl benzene sulphanamide
(Hinsberg Reagent)

REMEMBER

- Aniline is used in making Schiff base (Anti oxidant in rubber industry) and some sulphadrugs etc.
- Aniline in sulphuric acid with $K_2Cr_2O_7$ first give a red colour which finally changes into deep blue colour.

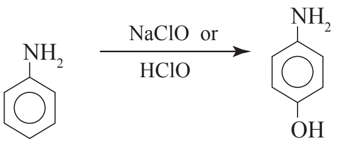
- ***Oxidation*** Aniline gives different products on oxidation as follows:



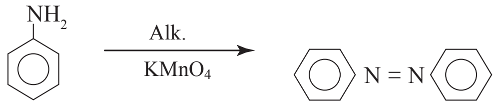
- 

p-benzoquinone

- 

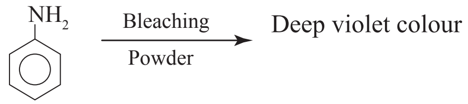
- 

p-Amino phenol

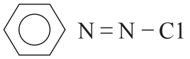
- 

Azo benzene

- 

- 

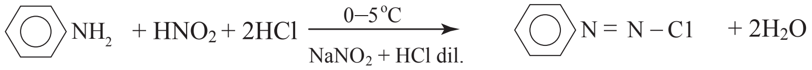
BENZENE DIAZONIUM CHLORIDE



Diazotization When an aromatic primary amine is treated with nitrous acid and HCl between 0 –5°C it undergoes diazotization to give benzene di azonium chloride. The reaction is known as diazo reaction and the process is known as diazotization.

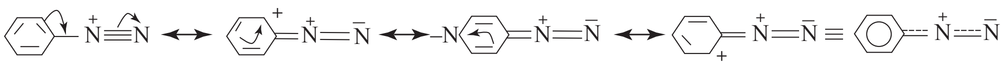
Benzene di azonium chloride

Or



Benzene di azonium chloride

Stability of Diazonium Salts Aromatic diazonium salts are more stable than the aliphatic diazonium salts. This is due to the dispersal of the positive charge on the nitrogen atom of the diazonium salt over the ring due to conjugation.



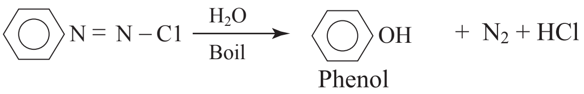
Since no conjugation is noticed n aliphatic diazonium salts, these are comparatively less stable compounds.

Synthetic Applications

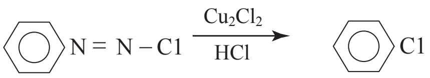
- The solution of Benzene diazonium chloride is used as such for various synthetic application.
- **Synthesis of Benzene** 

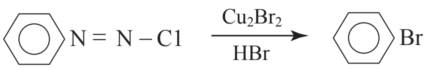
Benzene

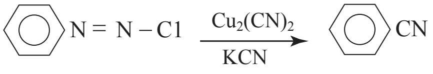
- **Synthesis of Phenol**



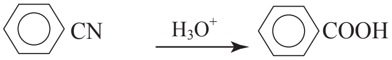
- **Sand mayer's Reaction**

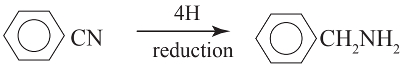




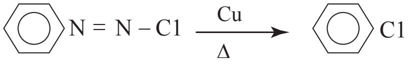


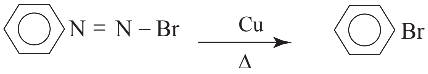
- Cyanobenzene on hydrolysis give benzoic acid and on reduction gives benzyl amine as follows:



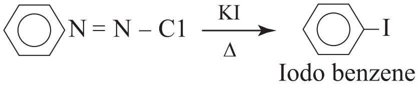


- **Gattermann Reaction**

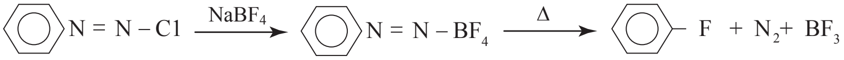


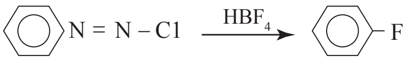


- **Synthesis of Iodo Benzene**

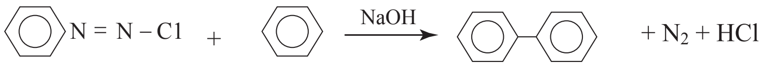


- **Synthesis of C_6H_5F**



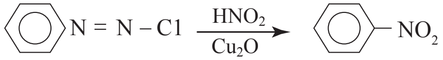
- 

- **Gomberg Reaction**

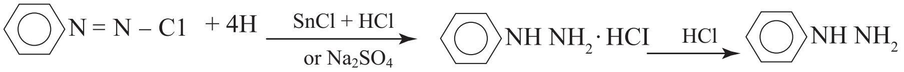


Bi phenyl

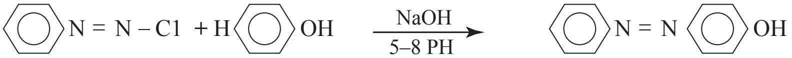
- **Synthesis of Nitro Benzene**



- **Synthesis of Phenyl Hydrazine**



- **Coupling Reactions** Here diazonium salt undergoes coupling with phenol, aniline etc., to give coloured azo compounds.
- ***With Phenol***

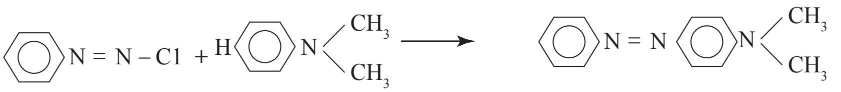


p-hydroxy azo benzene
(orange dye)

- ***With Aniline***

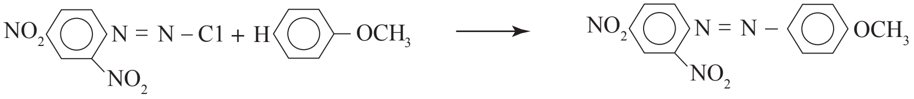
p-aminoazo benzene
(orange red dye)

- ***With N,N-Dimethyl Aniline***

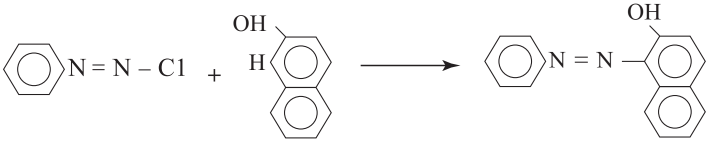


para amino N-N - dimethyl azo benzene
(butter yellow)

- ***With Anisole***



- ***With Alkaline Solution of β–Naphthol***
  (Test of NH_2 Group):



Phenyl azo β– naphthol
(orange red dye) [Scarlet]

- Formation of an orange red dye with alk. Solution of β– naphthol confirms the presence of aromatic p-amino group.
- If a compound reacts with HNO_2 but does not form a dye with β– naphthol compound may contain NH_2 group in the side chain.

REMEMBER

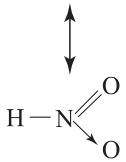
In case p-position is occupied, the coupling reaction occures at o-position also.

With Amines acidic conditions are prefered due to more reactivity of $Ar\overset{+}{N}_2$ and non-conversion of $ArNH_2$ into $Ar\overset{+}{N}H_3$.

ALKYL NITRITES AND NITRO ALKANES

- HNO_2 exists in following two tautomeric forms:

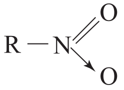
$H-O-N=O$
Nitrite form



Nitro form

- Alkyl derivatives of the nitrite form are called alkyl nitrites while the alkyl derivatives of nitro form are called nitroalkanes.

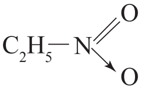
$R-O-N=O$
Alkyl nitrite



Nitroalkane

For example,

$C_2H_5-O-N=O$
Ethyl nitrite



Nitroethane

ALKYL NITRITE (R – O – N = O)

Methods of Preparation

- Alkyl nitrite is prepared by adding conc. H_2SO_4 to aqueous solution of sodium nitrite and alcohol.

  $NaNO_2 + H_2SO_4 \rightarrow NaHSO_4 + HONO$
  $ROH + HONO \rightarrow RONO + H_2O$

  For example,

  $NaNO_2 + H_2SO_4 \rightarrow NaHSO_4 + HONO$

  $C_2H_5OH + HONO \rightarrow C_2H_5ONO + H_2O$

- Alkyl nitrite is also obtained by the reaction of alkyl iodide and potassium nitrite as follows

  $RI + KNO_2 \rightarrow RONO + KI$

  For example,

  $C_2H_5I + KNO_2 \rightarrow C_2H_5ONO + KI$

- Alkyl nitrite can also be prepared by the action of nitrogen trioxide on alcohol.

  For example,

  $2C_2H_5OH + N_2O_3 \rightarrow C_2H_5ONO + H_2O$

Physical Properties

- At ordinary temperature ethyl nitrite is a gas which can be liquefied on cooling into a colourless liquid (boiling point 290 K) having characteristic smell of apples.
- It is insoluble in water but soluble in alcohol, ether etc.
- It has an important property of dilating the blood vessels so reduces hypertension and severe pain of Angina pectoris.

Chemical Properties

- **Hydrolysis** Alkyl nitrite can be hydrolyzed by water, dilute alkali or dilute acid forming alcohol and nitrous acid.

  $RONO + H_2O \rightarrow ROH + NH_3 + H_2O$

  For example,

  $C_2H_5ONO + H_2O \rightarrow C_2H_5OH + NH_3 + H_2O$

- **Reduction** On reduction with Sn/HCl it gives alcohol, ammonia or hydroxyl amine.

  $RONO + 6[H] \xrightarrow[\text{Sn + HCl}]{} ROH + NH_3 + H_2O$

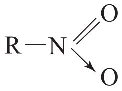
  $RONO + 4[H] \xrightarrow{\text{Sn + HCl}} ROH + NH_2OH$

For example,

$$C_2H_5ONO + 6[H] \xrightarrow{Sn + HCl} C_2H_5OH + NH_3 + H_2O$$

$$C_2H_5ONO + 4[H] \xrightarrow{Sn + HCl} C_2H_5OH + NH_2OH$$

NITRO ALKANES



METHOD OF PREPARATION

- **From Alkyl Halide** When alkyl halides and alcoholic silver nitrate solution are treated nitroalkanes are formed as follows:

  $$RX + AgNO_2 \longrightarrow RNO_2 + AgX$$

  For example,

  $$C_2H_5Br + AgNO_2 \longrightarrow C_2H_5NO_2 + AgBr$$

- **From α-Halo Substituted Acids**

  $$\underset{\text{Chloroacetic acid}}{ClCH_2COOH} + NaNO_2 \xrightarrow{\Delta} \underset{\text{Nitroacetic acid}}{O_2NCH_2COOH} + NaCl$$

  $$O_2NCH_2COOH \xrightarrow{\Delta} CH_3NO_2$$

- **By Nitration of Paraffin**

  $$R - CH_3 + HONO_2 \xrightarrow{400^\circ C} RCH_2NO_2 + H_2O$$

  For example,

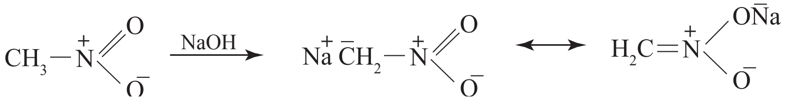
  $$CH_3 - CH_3 + HONO_2 \xrightarrow{400^\circ C} CH_3CH_2NO_2 + H_2O$$

PHYSICAL PROPERTIES

- Nitroalkanes are colourless liquids with pleasant smell.
- These are partially soluble in water but readily soluble in organic solvents.
- They have high value of boiling points due to their polar nature.

CHEMICAL PROPERTIES

- **Acidic Character** These are slightly acidic due to presence of α-hydrogen atom so react with strong alkali like aqueous NaOH to form salts.



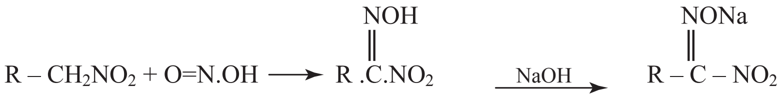
$$CH_3-\overset{+}{N}\begin{smallmatrix}\diagup O\\ \diagdown O^-\end{smallmatrix} \xrightarrow{NaOH} \overset{+}{Na}\,\overset{-}{C}H_2-\overset{+}{N}\begin{smallmatrix}\diagup O\\ \diagdown O^-\end{smallmatrix} \longleftrightarrow H_2C=\overset{+}{N}\begin{smallmatrix}\diagup O\overset{-}{Na}\\ \diagdown O^-\end{smallmatrix}$$

- ***With Halogens*** Nitroalkanes are easily halogenated in alkaline solution at α-position.

For example,

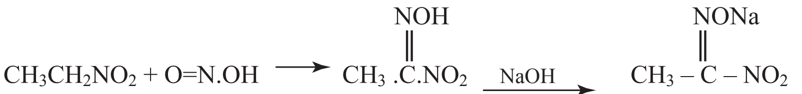
$$CH_3NO_2 \xrightarrow{3Cl_2.NaOH} CCl_3NO_2 + 3HCl$$

- ***With Nitrous Acid*** Primary nitroalkanes react with nitrous acid to give nitrolic acid which dissolves in NaOH into red solution of sodium nitrolate.



$$R-CH_2NO_2 + O{=}N.OH \longrightarrow R.\overset{\overset{NOH}{\|}}{C}.NO_2 \xrightarrow{NaOH} R-\overset{\overset{NONa}{\|}}{C}-NO_2$$

For example,

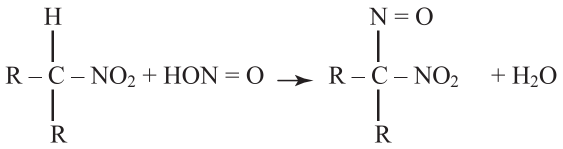


$$CH_3CH_2NO_2 + O{=}N.OH \longrightarrow CH_3.\overset{\overset{NOH}{\|}}{C}.NO_2 \xrightarrow{NaOH} CH_3-\overset{\overset{NONa}{\|}}{C}-NO_2$$

Nitrolic acid

Sodium nitrolate (red colour)

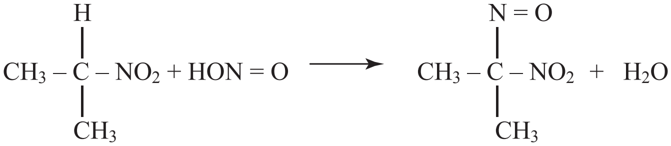
- Secondary nitroalkanes give blue solution of pseudonitroles.



$$R-\overset{\overset{H}{|}}{\underset{\underset{R}{|}}{C}}-NO_2 + HON=O \longrightarrow R-\overset{\overset{N=O}{|}}{\underset{\underset{R}{|}}{C}}-NO_2 + H_2O$$

Pseudonitrol

For example,



$$CH_3-\overset{\overset{H}{|}}{\underset{\underset{CH_3}{|}}{C}}-NO_2 + HON=O \longrightarrow CH_3-\overset{\overset{N=O}{|}}{\underset{\underset{CH_3}{|}}{C}}-NO_2 + H_2O$$

- Tertiary nitroalkanes do not give this reaction due to absence of α-hydrogen atom.
- **Hydrolysis** Primary nitroalkanes undergo acidic hydrolysis to give acids as follows:

$$RCH_2NO_2 + H_2O \xrightarrow[HCl]{} RCOOH + NH_2OH$$

For example,

$$CH_3CH_2NO_2 + H_2O \xrightarrow[HCl]{} CH_3COOH + NH_2OH$$

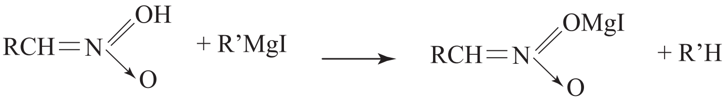
- Secondary nitroalkanes on hydrolysis give ketones as follows:

$$2R_2CHNO_2 \xrightarrow{HCl} 2R_2CO + N_2O + H_2O$$

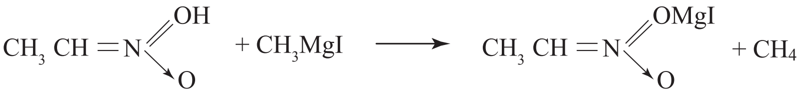
For example,

$$2(CH_3)_2CHNO_2 \xrightarrow{HCl} 2(CH_3)_2CO + N_2O + H_2O$$

- **Reaction With Grignard Reagent** Nitroalkane in Aci-form gives alkanes with Grignard reagent as follows:

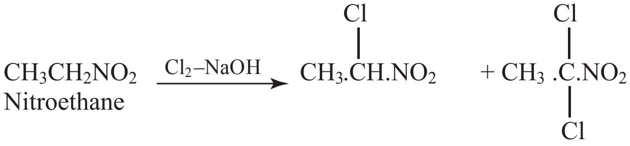


For example,



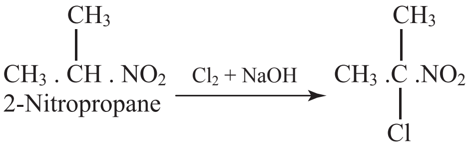
- **Halogenation** Nitroalkanes undergo halogenation at α-position.

For example,



$$\underset{\text{Nitroethane}}{CH_3CH_2NO_2} \xrightarrow{Cl_2-NaOH} CH_3.\overset{\overset{Cl}{|}}{C}H.NO_2 + CH_3\ .\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}}.NO_2$$

$$\underset{\text{Nitromethane}}{CH_3NO_2} \xrightarrow{Cl_2 + NaOH} \underset{\text{Chloropicrin}}{CCl_3.NO_2}$$



$$\underset{\text{2-Nitropropane}}{CH_3\ .\ \overset{\overset{CH_3}{|}}{C}H\ .\ NO_2} \xrightarrow{Cl_2 + NaOH} CH_3\ .\underset{\underset{Cl}{|}}{\overset{\overset{CH_3}{|}}{C}}\ .NO_2$$

- **Reduction** Nitroalkanes undergo reduction as follows:
- Reduction by Sn + HCl or $LiAlH_4$ gives primary amine as follows:

$$RNO_2 + 6[H] \xrightarrow[Sn + HCl]{} RNH_2 + 2H_2O$$

For example,

$$\underset{\text{Nitroethane}}{C_2H_5NO_2 + 6[H]} \xrightarrow{Sn + HCl} \underset{\text{Ethyl amine}}{C_2H_5NH_2} + 2H_2O$$

- Reduction with zinc dust and NH_4Cl gives hydroxylamines as follows:

$$RNO_2 + 4[H] \xrightarrow[Zn + NH_4Cl]{} RNHOH + H_2O$$

For example,

$$C_2H_5NO_2 + 4[H] \xrightarrow{Zn + NH_4Cl} \underset{\text{Ethyl hydroxyl amine}}{C_2H_5NHOH} + H_2O$$

- Reduction with $SnCl_2$/HCl gives a mixture of oxime and hydroxyl amine as follows:

$$RCH_2NO_2 \xrightarrow{SnCl_2 / HCl} RCH_2NHOH + RCH{=}NOH$$

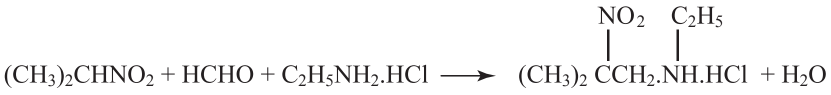
For example,

$$CH_3CH_2NO_2 \xrightarrow{SnCl_2 / HCl} CH_3CH_2NHOH + CH_3CH{=}NOH$$

- **Mannich Reaction** It involves condensation between nitroalkane, formaldehyde, primary amine and hydrogen chloride as follows:

For example,

$$R_2CHNO_2 + HCHO + R'NH_2.HCl \longrightarrow R_2\overset{NO_2}{\overset{|}{C}}CH_2.\overset{R'}{\overset{|}{N}}H.HCl + H_2O$$



$$(CH_3)_2CHNO_2 + HCHO + C_2H_5NH_2.HCl \longrightarrow (CH_3)_2\overset{NO_2}{\overset{|}{C}}CH_2.\overset{C_2H_5}{\overset{|}{N}}H.HCl + H_2O$$

Heating Effect

- On moderate heating below 300°C – alkene is formed.

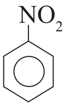
$$RCH_2.CH_2.NO_2 \xrightarrow{>300^oC} R.CH = CH_2 + HNO_2$$

- On heating rapidly explosion takes place.

For example,

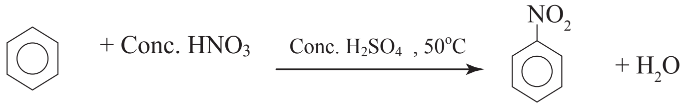
$$CH_3NO_2 \xrightarrow{\Delta} CO_2 + ½ N_2 + 3/2 H_2$$

NITRO BENZENE

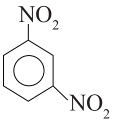


- It is called Oil of Mirbane and have bitter almond smell.

METHODS OF PREPARATION

- 

If temperature is above 100°C further nitration takes place and the product is m-dinitrobenzene.



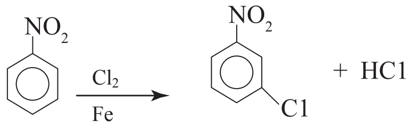
PHYSICAL PROPERTIES

- It is a light brown coloured oily liquid with a boiling point of 210°C.
- It is insoluble in water, volatile in steam.
- It can be purified by steam distillation.

CHEMICAL PROPERTIES

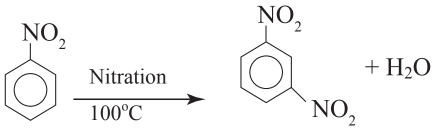
Due to Benzene Ring

- Nitro group deactivate the benzene ring therefore further substitution takes place only at m-position and rate is much slower than that of benzene.
- **Halogenation**



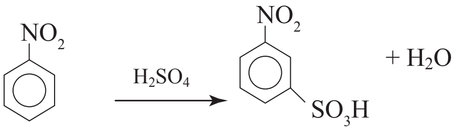
m-chloronitro benzene

- **Nitration**



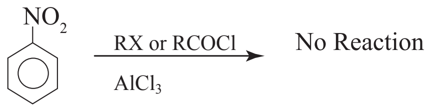
m-dinitro benzene

- **Sulphonation**



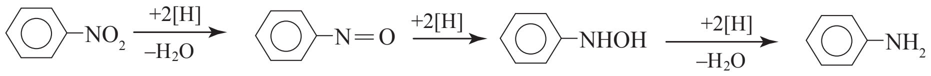
m-nitro benzenesulphonic acid

- **Friedal Craft Reaction**



Friedal Craft reaction is not possible in any of the m-directing groups like $-NO_2$ –CHO, etc.

Reduction of Nitro Benzene



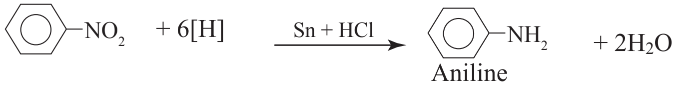
Nitroso benzene

Phenylhydroxy amine

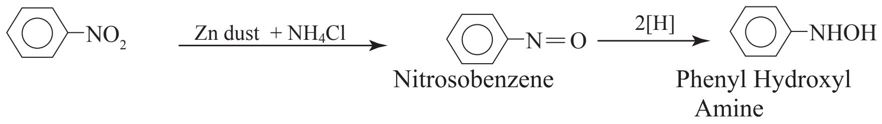
Aniline

Different product can be obtained from nitro benzene on reduction but the nature of the product depends upon the reducing agent used.

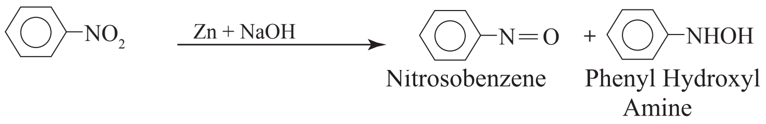
- **In Strong Acid Medium**



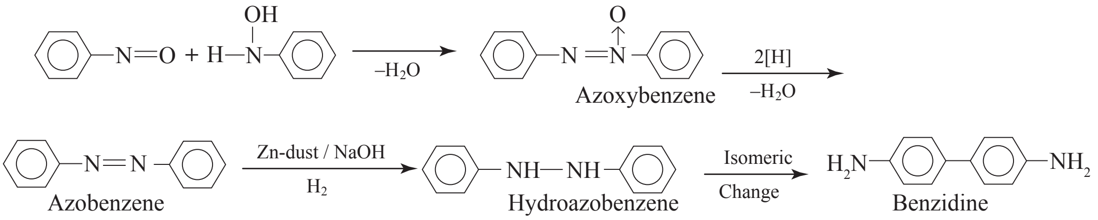
- **In Neutral Medium**



- **In Basic Medium**

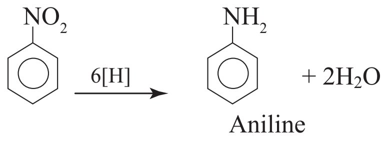


- Nitrosobenzene and Phenylhydroxy amine further react to give following products depending upon reagent used as follows:

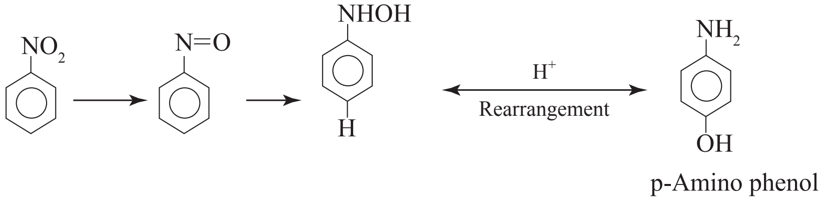


- With Zinc dust/NaOH or sodium amalgam Azobenzene and Hydrazobenzene are formed.
- With Sodium Arsenite and NaOH Azoxybenzene is formed.
- **Electrolytic Reduction**

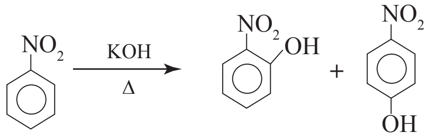
In Weak Acidic Medium



In Strong Acidic Medium



- **With Solid KOH** It is an example of nucleophillic substitution reaction.

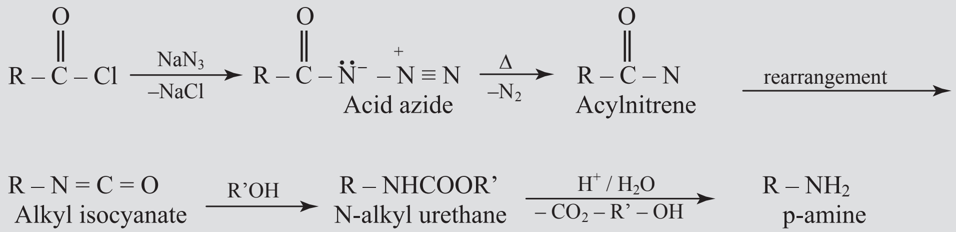


'o' and 'p' Nitrophenol

- The $-NO_2$ group is very firmly linked to B-nucleus more over partial double bond character develops due to resonance so Nitro benzene become inert and does not give displacement reaction.
- Nitrobenzene is used in the manufacture of azodyes, aniline and as a perfume material in shoe polish and soaps.

ENHANCE YOUR KNOWLEDGE

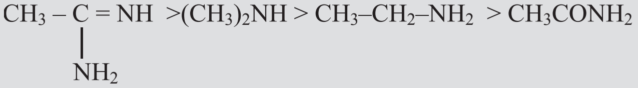
- **Curtius Rearrangement:** $RCON_3$) into a primary amine in acidic or alkaline medium is known as Curtius degradation



$$R-\overset{\overset{O}{\|}}{C}-Cl \xrightarrow[-NaCl]{NaN_3} \underset{\text{Acid azide}}{R-\overset{\overset{O}{\|}}{C}-\ddot{N}^{-}-\overset{+}{N}\equiv N} \xrightarrow[-N_2]{\Delta} \underset{\text{Acylnitrene}}{R-\overset{\overset{O}{\|}}{C}-N} \xrightarrow{\text{rearrangement}}$$

$$\underset{\text{Alkyl isocyanate}}{R-N=C=O} \xrightarrow{R'OH} \underset{\text{N-alkyl urethane}}{R-NHCOOR'} \xrightarrow[-CO_2-R'-OH]{H^+/H_2O} \underset{\text{p-amine}}{R-NH_2}$$

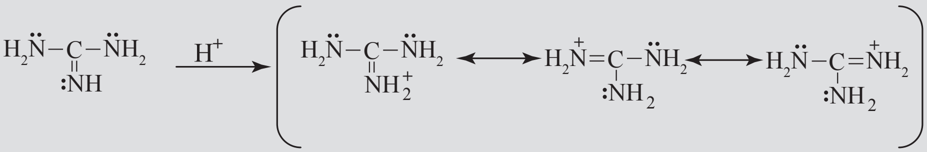
- The bad smell produced during putrefaction of dead animals is due to the formation of amines by the bacterial oxidation of body proteins.
- 4 per cent alcoholic solution of ethyl nitrite is called as "Sweet spirit of nitre" and is used Diuretic.
- Basic nature in decreasing order:



$$CH_3-\underset{\underset{NH_2}{|}}{C}=NH > (CH_3)_2NH > CH_3-CH_2-NH_2 > CH_3CONH_2$$

Unlike other amines (RNH_2), $H_2\ddot{N}-\underset{\underset{:NH}{\|}}{C}-\ddot{N}H_2$ is a strong base as The cation formed by addition of H^+ has three

Equivalent contributing structures. This greatly stablilizes the conjugate acid making it very weak and the base strong.



$$H_2\ddot{N}-\underset{\underset{:NH}{\|}}{C}-\ddot{N}H_2 \xrightarrow{H^+} \left[H_2\ddot{N}-\underset{\underset{NH_2^+}{\|}}{C}-\ddot{N}H_2 \longleftrightarrow H_2\overset{+}{N}=\underset{\underset{:NH_2}{|}}{C}-\ddot{N}H_2 \longleftrightarrow H_2\ddot{N}-\underset{\underset{:NH_2}{|}}{C}=\overset{+}{N}H_2 \right]$$

The reactivity of $C_6H_5\overset{+}{N}_2$ can be enhanced by adding strong E.W.G like $-NO_2$ at O, P positions and than coupling is posible even with Anisole, Mesitylene etc. also.

MULTIPLE CHOICE QUESTIONS

Straight Objective Type Questions (Single Choice only)

1. Amines can behave as
(a) Neutral compound
(b) Lewis acids
(c) Aprotic acid
(d) Lewis base

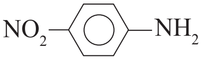
2. How many primary amines are possible with the formula of $C_4H_{11}N$?
(a) 1 (b) 3
(c) 5 (d) 4

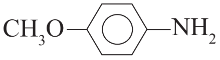
3. Which of the following will be most basic?
(a) Benzylamine (b) Aniline
(c) p-Methoxyaniline (d) p-Methylaniline
(e) p-Nitroaniline

4. In HS^-, I^-, RNH_2 and NH_3 order of proton accepting tendency will be
(a) $I^- > NH_3 > RNH_2 > HS^-$
(b) $HS^- > RNH_2 > NH_3 > I^-$
(c) $RNH_2 > NH_3 > HS^- > I^-$
(d) $NH_3 > RNH_2 > HS^- > I^-$

5. Increase order of basic nature in aqueous solutions
(a) $CH_3NH_2 > (CH_3)_2NH > NH_3 > C_6H_5NH_2$
(b) $(CH_3)_2NH > CH_3NH_2 > NH_3 > C_6H_5NH_2$
(c) $C_6H_5NH_2 > NH_3 > CH_3NH_2 > (CH_3)_2NH$
(d) $NH_3 > C_6H_5NH_2 > CH_3NH_2 > (CH_3)_2NH$

6. Which of the following is least basic?

(a) 

(b) 

(c) 

(d) All are equally basic.

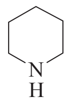
7. Intermolecular hydrogen bonding is strongest in
(a) Methylamine (b) Phenol
(c) Formaldehyde (d) Methanol

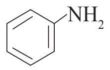
8. Which one of the following is the strongest base in aqueous solution?
(a) Aniline (b) Dimethyl amine
(c) Methyl amine (d) Trimethyl amine

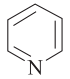
9. Among the following is weakest base is:
(a) $C_6H_5CH_2NHCH_3$ (b) $C_6H_5CH_2NH_2$
(c) CH_3NHCHO (d) $O_2N.CH_2NH_2$

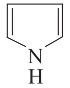
10. The indicator that is obtained by coupling the diazonium salt of sulphanilic acid with N,N-dimethylaniline is
(a) Methyl red (b) Phenolphthalein
(c) Indigo (d) Methyl orange
(e) Phenanthroline

11. The strongest base among the following is

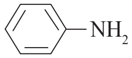
(a) 

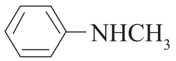
(b) 

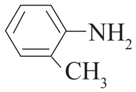
(c) 

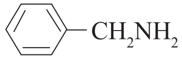
(d) 

12. Which of the following is the strongest base?

(a) 

(b) 

(c) 

(d) 

13. The compound that is most reactive towards electrophillic nitration is
(a) benzene (b) nitrobenzene
(c) benzoic acid (d) toluene

14. Among the following compounds $C_3H_7NH_2$, NH_3, CH_3NH_2, $C_2H_5NH_2$ and $C_6H_5NH_2$, the least basic compound is
(a) NH_3 (b) $C_2H_5NH_2$
(c) $C_6H_5NH_2$ (d) CH_3NH_2
(e) $C_3H_7NH_2$

15. Which one of the following methods is neither meant for the synthesis not for separation of amines?
(a) Hinsberg method (b) Hoffmann method
(c) Wurtz reaction (d) Curtius reaction

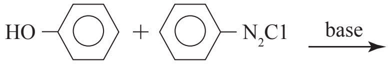
16. In the Hinsberg test,
(a) the hydrogen attached to nitrogen is made more acidic in the primary amine sulphonamides by the electron withdrawing nature of SO_2 group.
(b) a tertiary amine, if it is water insoluble, readily reacts with benzene sulphonyl chloride and aqueous KOH, forming a clear solution.
(c) only a primary amine reacts with sulphonyl chloride to form a sulphonamide and not a secondary amine, so that 1° and 2° amines can be distinguished by the Hinsberg test.
(d) secondary amines reacts with benzene sulphonyl chlorine to form a sulphonamide which will

dissolve in aqueous KOH solution to form a water soluble potassium salt.

17. Which of the following reagents can not be used to distinguish primary amines from other compounds?
(a) Action of nitrous acid
(b) Carbylamine reaction
(c) Libermann's nitroso reaction
(d) Hinsberg reaction

18. The compound which one reaction with aqueous nitrous acid at low temperature produces an oily nitrosamine is
(a) methylamine (b) ethylamine
(c) triethylamine (d) diethylamine

19. The product of the reaction



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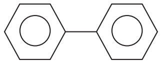

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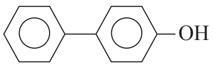

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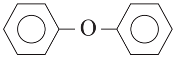

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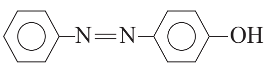
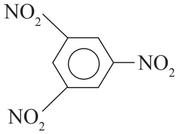


20. Reaction of cyclohexanone with dimethylamine in the presence of catalytic amount of an acid forms a compound if water during the reaction is continuously removed. The compound formed is generally known as:
(a) An amine
(b) An enamine
(c) A imine
(d) A schiff's base

21. $C_6H_5CONHCH_3$ can be converted into $C_6H_5CH_2NHCH_3$ by
(a) $NaBH_4$ (b) $H_2 – Pd/C$
(c) Zn – Hg/HCl (d) $LiAlH_4$

22. The major product (70% - 80%) of reaction between m-dinitrobenzene with $(NH_4)_2S_X$ is

(a)


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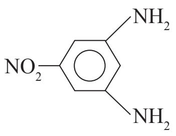

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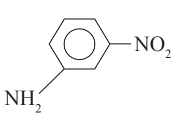

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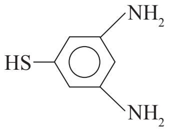
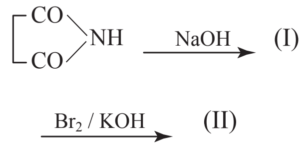


23. Acetamide is treated separately with the following reagents. Which one of these would give methylamine?
(a) sodalime (b) PCl_5
(c) NaOH + Br_2 (d) hot conc. H_2SO_4

24. In the above sequence, (II) is



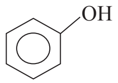
(a) α-alanine (b) β-alanine
(c) γ-amino butyric acid (d) Ethylene diamine

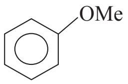
25. What is the end product C in this series

$$CH_3CN \xrightarrow{Na/C_2H_5OH} A \xrightarrow{HNO_2} B \xrightarrow{Cu/573K} C$$

(a) CH_3COOH (b) CH_3CH_2NHOH
(c) CH_3CONH_2 (d) CH_3CHO.

26. Which of the following compound does not give Friedal Crafts reaction?

(a)


(b)


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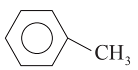

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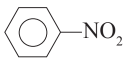
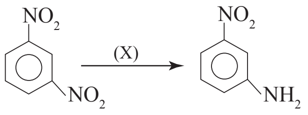


27. Which of the following exists as zwitter ion?
(a) p-aminoacetophenone
(b) Sulphanilic acid
(c) Salicylic acid
(d) p-aminophenol

28. When aniline is converted to benzene diazonium chloride, excess dil. HCl is used:
(a) to suppress the decomposition of the diazonium ion
(b) to keep the diazonium salt in solution
(c) to generate the nitrosonium ion which is the attacking species
(d) to inverse the nucleophilicity of the amine group

29. Identify (X) in the following reaction:



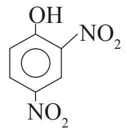
(a) Sn/HCl (b) $LiAlH_4$
(c) Na_2S (d) All of these

30. Carbylamine test is performed in alcoholic KOH by heating a mixture of:
(a) trihalogenated methane and a primary amine.
(b) an alkyl halide and a primary amine.
(c) an alkyl cyanide and a primary amine.
(d) chloroform and silver powder.

31. Which one of the following on reduction with lithium aluminium hydride yields a secondary amine?
(a) Nitroethane (b) Methyl isocyanide
(c) Acetamide (d) Methyl cyanide

32. An aliphatic amine on treatment with alcoholic carbon disulphide and mercuric chloride forms ethyl isothiocyanate, the reaction is known as:
(a) Hoffmann's mustard oil reaction
(b) Hoffmann's bromamide degradation reaction
(c) Hoffmann's reaction
(d) Hoffmann's rearrangement

33.



It is obtained when
(a) m-dinitrobenzene is treated with alkaline potassium ferri cyanide.
(b) 2; 4-diaminophenol is oxidized with $CHCl_3$ and H_2O_2.
(c) m-dinitrobenzene is treated with conc. H_2SO_4.
(d) phenol is carefully nitrated under the influence of a nitrating mixture.

34. In the reaction given below the product Y is

$$C_6H_6 \xrightarrow[H_2SO_4]{HNO_3} X \xrightarrow[FeCl_3]{Cl_2} Y$$

(a) 4-nitrochlorobenzene
(b) 3-nitrochlorobenzene
(c) 1-nitrochlorobenzene
(d) none of the above

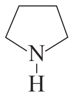
35. ____________ may be prepared by heating _____
(a) propyl alcohol with KCN
(b) butyl alcohol with KCN
(c) butyl chloride with KCN
(d) propyl chloride with KCN

36. $CH_3CH_2CONH_2 \xrightarrow{X} CH_3CH_2CH_2NH_2$
(X) is
(a) Ni/H_2 (b) $LiAlH_4$
(c) Zn (d) Pt/H_2

37. The correct sequence of reagents used for conversion of aniline into Benzylamine is
(a) $NaNO_{2/}HCl$, CuCN, Sn/HCl
(b) $NaNO_2/HCl$, CuCN, H_3O^+
(c) $NaNO_2/HCl$, Cu^+/H_3PO_2 , CH_3NH_2
(d) None of these

38. Aliphatic nitrites are prepared by the treatment of alkyl halides with:
(a) Sodium isocyanide (b) Cyanamide
(c) Potassium nitrite (d) Sodium isocyanate

39. Which one of the following compound will with acetone to give a product having carbon nitrogen double bond?
(a) $(CH_3)_3N$ (b) $C_6H_5NHNH_2$
(c) $C_6H_5NHC_6H_5$ (d)



40. The following reaction gives:

$$\text{4-nitrotoluene} \xrightarrow[H_2SO_4]{K_2Cr_2O_7} ?$$

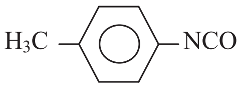
(a) 4-nitrobenzyl alcohol (b) 4-nitrobenzaldehyde
(c) 4-nitrobenzoic acid (d) 4-aminotoluene

41. Nitrosoamines ($R_2N-N=O$) are insoluble in water. On heating them with conc. H_2SO_4. They give secondary amines. The reaction is called
(a) Fries's reaction
(b) Etard's reaction
(c) Liberman nitroso reaction
(d) Perkin's reaction

42. Towards electrophillic substitution the most reactive will be
(a) nitrobenzene (b) aniline
(c) aniline hydrochloric (d) N-acetylaniline

43. The reaction of $CHCl_3$ and alcoholic KOH with p-toluidine gives:

(a)



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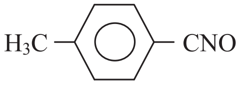

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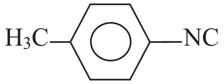

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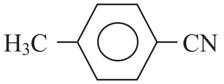

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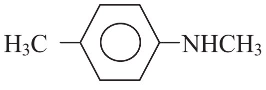
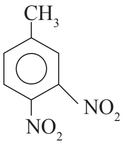
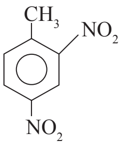
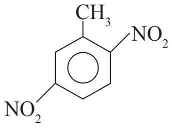
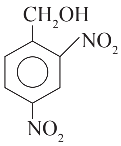


44. p-Nitrotoluene on further nitration gives

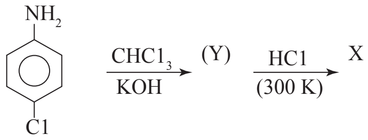
(a) 

(b) 

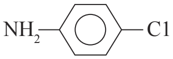
(c) 

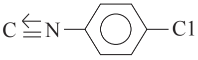
(d) 

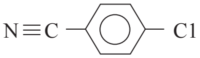
45. Identify X in the sequence given below:

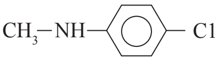


+ methanoic acid

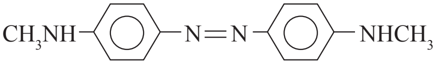
(a) 

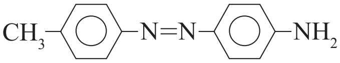
(b) 

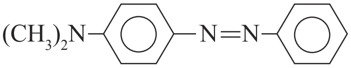
(c) 

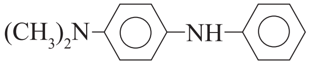
(d) 

46. Aniline when diazotized in cold and then treated with dimethyl aniline gives a coloured product. Its structure would be:

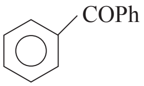
(a) 

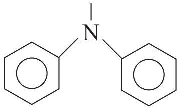
(b) 

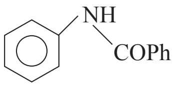
(c) 

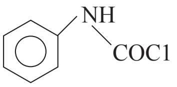
(d) 

47. The following reaction yields which of the given products?

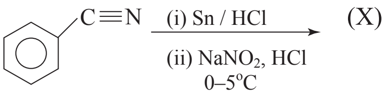
(a) 

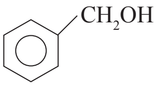
(b) 

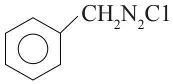
(c) 

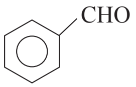
(d) 

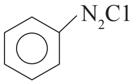
48. Identify (X) in the following reaction:

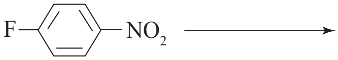


(a) 

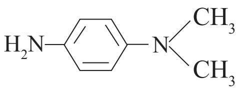
(b) 

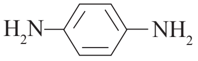
(c) 

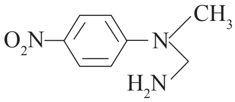
(d) 

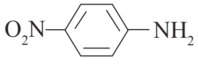
49. 

$\xrightarrow[\text{(ii) } H_2 / \text{Ni } 0\text{–}5^\circ\text{C}]{\text{(i) } NaNO_2 / HCl}$ (B) is

(a) 

(b) 

(c) 

(d) 

50. (P) + (Q) $\xrightarrow[\text{methanol}]{NaBH_3CN}$ $C_6H_5CH_2NHCH_2CH_3$

(P) and (Q) are

(a) $C_6H_5CHO + C_2H_5NH_2$
(b) $C_6H_5CH_2OH + C_2H_5NH_2$
(c) $C_6H_6 + CH_3.NH.CH_2.CH_3$
(d) $C_6H_5CHO + CH_3.NH.CH_2.CH_3$

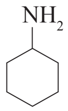
Brainteasers Objective Type Questions (Single choice only)

51. Among the following the dissociation constant is highest for.

(a) $CH_3C \equiv CH$ (b) C_6H_5OH
(c) $CH_3NH_3^+Cl^-$ (d) $C_6H_5CH_2OH$

52. Arrange the following in increasing basicity order

I. $Cl_2CHCH_2NH_2$ II. $Cl_3CH_2NH_2$

III. 

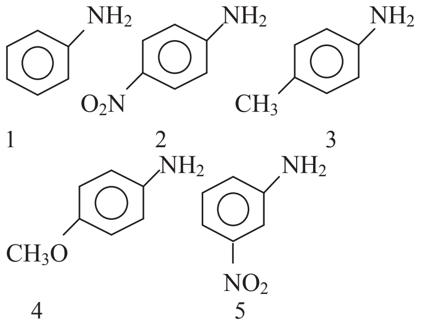
IV. $CF_3CH_2NH_2$

(a) I < III < II < IV
(b) II< IV < III < I
(c) IV < II < I < III
(d) I < II < IV < III

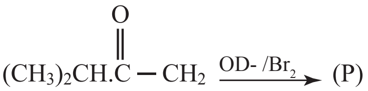
53. At what pH phenol reacts with benzene diazonium chloride to give coupling product?

(a) pH = 9 (b) pH = 14
(c) pH = 2 (d) pH = 7

54. The correct order of increasing basic nature of the following bases is



(a) 2 < 5 < 1 < 3 < 4 (b) 5 < 2 < 1 < 4 < 3
(c) 2 < 5 < 4 < 3 < 1 (d) 2 , 5 < 1 < 4 < 3

55. 
$(CH_3)_2CH.\overset{\overset{\large O}{\|}}{C}-CH_2 \xrightarrow{OD^-/Br_2} (P)$

Product P is given as:

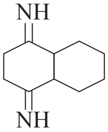
(a) $(CH_3)_2CHNHD$ (b) $(CH_3)_2CHNH_2$
(c) $(CH_3)_2CHND_2$ (d) no reaction

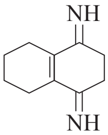
56. In the following reaction X is

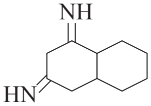
$$\begin{tikzcd}
X \arrow[r, "bromination"] & Y \arrow[r, "NaNO_2", "+HCl"'] & Z \arrow[d, "H_3PO_2"] \\
& & \text{Tribromobenzene}
\end{tikzcd}$$

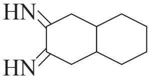
(a) benzoic acid (b) salicylic acid
(c) aniline (d) phenol

57. Which of the following imene is least stable?

(a) 

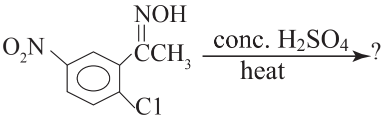
(b) 

(c) 

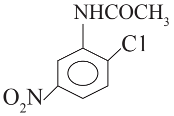
(d) 

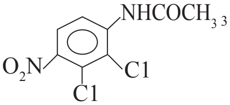
58. Which of the following is a correct statement about pyrrole and pyridine?

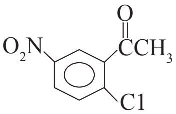
(a) Both pyrrole and pyridine are very weak bases because both can weakly accept it loses its aromatic properties.
(b) Both pyrrole and pyridine are strongly bases because both have N atoms that can readily accept protons.
(c) Pyridine is a weaker base than pyrrole because the lone pair electrons on its N atom are part of the aromatic electron system.
(d) Pyrrole I a weaker base than pyridine because when it accepts a proton it loses its aromatic properties.

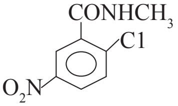
59. 

product is:

(a) 

(b) 

(c) 

(d) 

60. Identify X and Y in the following sequence:

$C_2H_5Br \xrightarrow{X} \text{product} \xrightarrow{Y} C_3H_7NH_2$

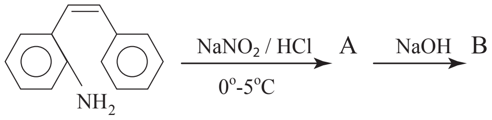
(a) X = KCN, Y = $LiAlH_4$
(b) X = KCN, Y = H_3O^+
(c) X = CH_3Cl, Y = $AlCl_3/HCl$
(d) X = CH_3NH_2, Y = HNO_2

61. Identify the final product (C) in the following sequence of reactions

$C_6H_5COOH \xrightarrow{SOCl_2} A \xrightarrow{NH_3} B \xrightarrow{H_2/Ni} C$

(a) $C_6H_5CH_2NH_2$
(b) m-$CH_3C_6H_4NH_2$
(c) $C_6H_5NH_2$
(d) o- and P-$CH_3C_6H_4NH_2$

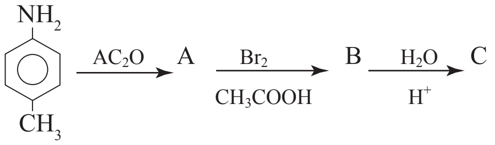
62. Identify the end product 'B' here:



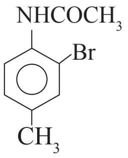
(a) phenanthrene (b) benzene
(c) naphthalene (d) Anthracene

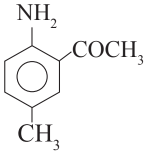
63. Aniline first reacts with acetyl chloride producing compound (A). (A) reacts with nitric acid/sulphuric acid mixture and produces compound (B), which hydrolyses to compound (C). What is the identity of (C)?
(a) Sulphanilic acid
(b) p-Nitroaniline
(c) Acetanilide
(d) p-Nitroacetanilide

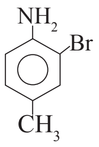
64. In the reaction

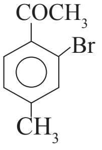


the final product C is

(a)


(b)


(c)


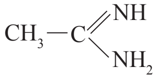
(d)


65. $CH_3CH_2Cl \xrightarrow{NaCN} (A) \xrightarrow{Ni/H_2} (B) \xrightarrow{\text{Acetic anhydride}} (C)$

(C) in the above reaction is:

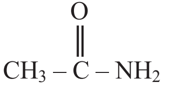
(a) $CH_3CH_2CH_2NHCOCH_3$
(b) $CH_3CH_2CH_2NH_2$
(c) $CH_3CH_2CH_2CONHCOCH_3$
(d) $CH_3CH_2CH_2CONHCH_3$

66. The correct order of basicities of the following compounds is

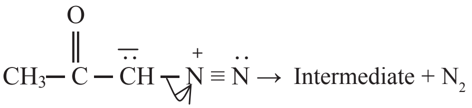
1. 

2. $CH_3CH_2NH_2$

3. $(CH_3)_2NH$

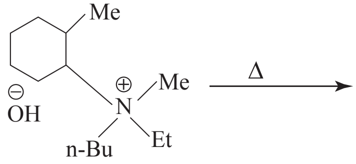
4. 
$CH_3-\overset{\overset{O}{\|}}{C}-NH_2$

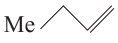
(a) 2 > 1 > 3 > 4 (b) 1 > 3 > 2 > 4
(c) 3 > 1 > 2 > 4 (d) 1 > 2 > 3 > 4

67. 
$CH_3-\overset{\overset{O}{\|}}{C}-\overset{-}{C}H-\overset{+}{N}\equiv \ddot{N} \rightarrow$ Intermediate + N_2

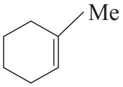
The nature of its reaction intermediate in this reaction is?
(a) Carbanion (b) Carbonium ion
(c) Carbene (d) Free radial

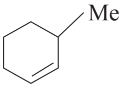
68. The alkene formed as a major product in the given elimination reaction is



(a)


(b) $CH_2 = CH_2$

(c)


(d)


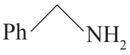
69. The number of moles of NaOH consumed in Hoffmann Bromamide reaction?
(a) 2 (b) 3
(c) 1 (d) 4

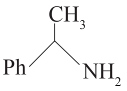
70. Identify R in the following reaction

$PhCOOH \xrightarrow[PBr_3]{LiAlH_4} P \xrightarrow{KCN} Q \xrightarrow[\text{(ii) NaOBr}]{\text{(i) Partial hydrolysis}} R$

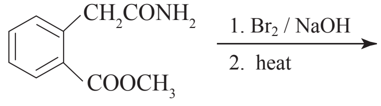
(a)


(b)

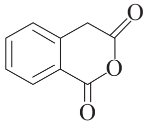

(c)


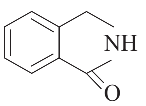
(d)


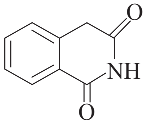
71. The following sequence of reactions on A gives

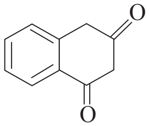


(A)

(a) 

(b) 

(c) 

(d) 

72. Which of the following statements relating to aniline is not true?

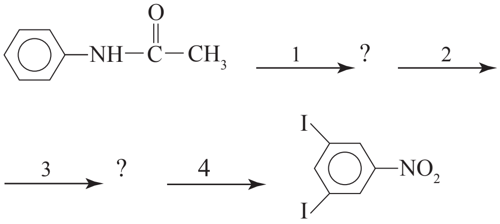
(a) Aniline on Schotten-Baumann reaction gives benzanilide.

(b) Aniline cannot be prepared by the reduction of benzonitrile with $LiAlH_4$.

(c) On heating with conc. H_2SO_4 at 180°C, aniline gives sulphanilic acid.

(d) Aniline liberates nitrogen on treatment with ice cold nitrous acid.

73. The correct sequence of reagents in the following conversion



is

(a) H_2O/H^+, $NaNO_2/HCl$, Cu, I_2

(b) H_2O/H^+, $NaNO_2/HCl$, $NaNO_2$ + Cu, I_2/HgO

(c) H_2O/H^+, I_2, Sn + HCl, $NaNO_2$

(d) None

74. In a set of reactions propionic acid yielded a compound D.

$CH_3CH_2COOH \xrightarrow{SOCl_2} B \xrightarrow{NH_3} C \xrightarrow[Br_2]{KOH} D$

The structure of D would be

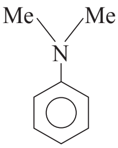
(a) $CH_3CH_2NHCH_3$

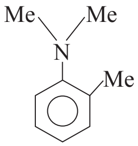
(b) $CH_3CH_2NH_2$

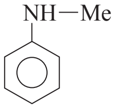
(c) $CH_3CH_2CH_2NH_2$

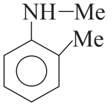
(d) $CH_3CH_2CONH_2$

75. In which of the following substituted aromatic amines coupling with diazonium ion is minimum?

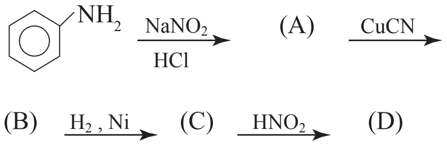
(a) 

(b) 

(c) 

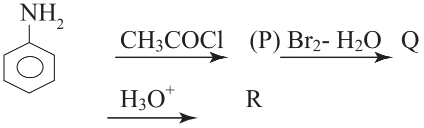
(d) 

76. Aniline in a set of reactions yielded a product (D)

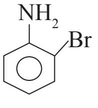


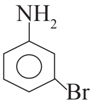
The structure of the product (D) would be

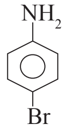
(a) $C_6H_5CH_2OH$
(b) C_6H_5NHOH
(c) $C_6H_5NHCH_2CH_3$
(d) $C_6H_5CH_2NH_2$

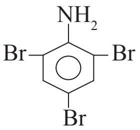
77. 

Here R is?

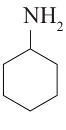
(a) 

(b) 

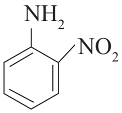
(c) 

(d) 

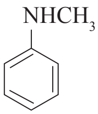
78. The correct order of decreasing base strength among the amines given is



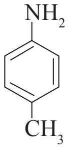
(I)



(II)



(III)



(IV)

(a) I > III > IV > II
(b) IV > III > I > II
(c) I > IV > III > II
(d) I > III > IV > II

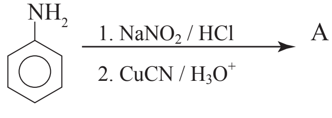
79. In a set of reactions propionic acid yielded a compound D.

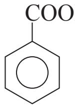
$$CH_3CH_2COOH \xrightarrow{SOCl_2} B \xrightarrow{NH_3} C \xrightarrow[Br_2]{KOH} D$$

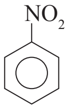
The structure of D would be

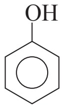
(a) $CH_3CH_2NHCH_3$ (b) $CH_3CH_2NH_2$
(c) $CH_3CH_2CH_2NH_2$ (d) $CH_3CH_2CONH_2$

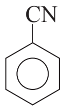
80. Identify 'A' in the following reaction:



(a) 

(b) 

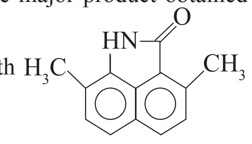
(c) 

(d) 

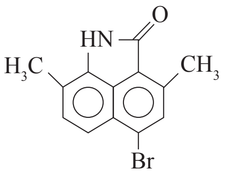
81. Among the following statements on the nitration of aromatic compounds, the false one is

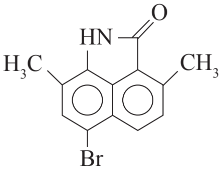
(a) the rate of nitration of benzene is almost the same as the hexadeuterobenzene.
(b) the rate of nitration of toluene is greater than that of benzene.
(c) nitration is an electrophilic substitution reaction.
(d) the rate of nitration of benzene is greater than that of hexadeuterobenzene.

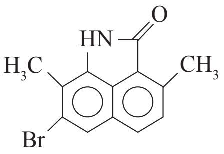
82. The major product obtained when Br_2/Fe is treated with

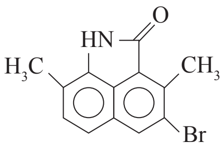


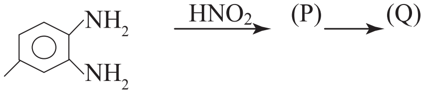
is

(a) 

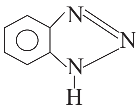
(b) 

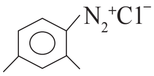
(c) 

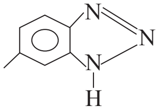
(d) 

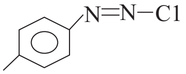
83. 

Here the product Q is given as:

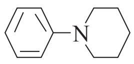
(a) 

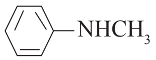
(b) 

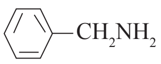
(c) 

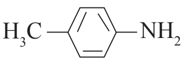
(d) 

84. Which of amines yields N- nitroso amine on treatment with nitrous acid ($NaNO_2$, HCl)?

(a) 

(b) 

(c) 

(d) 

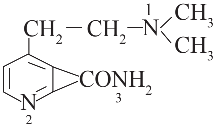
85. $C_5H_{13}N$ reacts with HNO_2 to give an optically active alcohol. The compound is

(a) N –methylbutan-2-amine
(b) Pentan-2-amine
(c) N,Ndimethylpropan-2-amine
(d) Pentan-1-amine

86. Identify compound (c) in the following sequence of reactions

$$(A) \xrightarrow{Br_2 + NaOH} R-N{=}C{=}O \xrightarrow{H_2O} (B) \xrightarrow{R-N=C=C} (C)$$

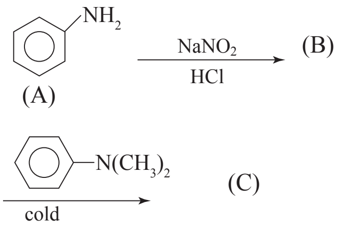
(a) RNHCOR (b) RNHCONHR
(c) RNH_2 (d) $RCONH_2$

87. 

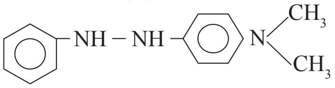
Which of the following order is correct to express basicity on the indicated N-atoms?

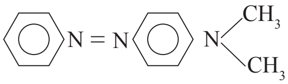
(a) 2 > 1 > 3
(b) 2 > 3 > 1
(c) 1 > 2 > 3
(d) 1 > 3 > 2

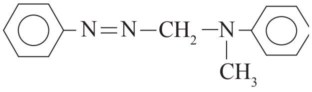
88. In a reaction of aniline a coloured product (C) was obtained.

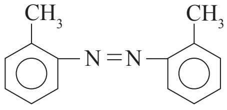


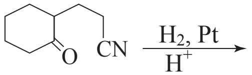
The structure of (C) would be

(a) 

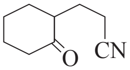
(b) 

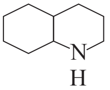
(c) 

(d) 

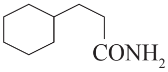
89. 

The product can be given as?

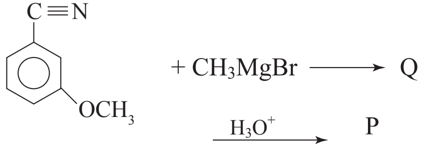
(a) 

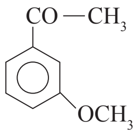
(b) 

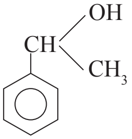
(c) 

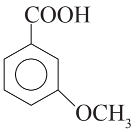
(d) 

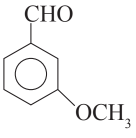
90. The product 'P' in the

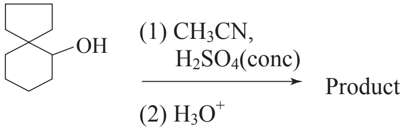


(a) 

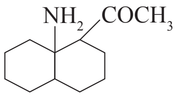
(b) 

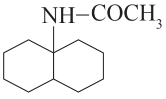
(c) 

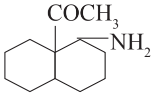
(d) 

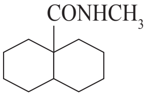
91. 

Here the product can be given as :

(a) 

(b) 

(c) 

(d) 

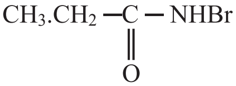
92. Given the following sequence of reaction

$$CH_3CH_2I \xrightarrow{NaCN} A \xrightarrow[\text{Partial Hydrolysis}]{OH^-} B$$

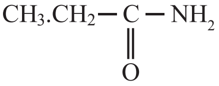
$$\xrightarrow{Br_2/NaOH} C$$

The major product 'C' is:

(a) $CH_3CH_2NH_2$

(b) 
$CH_3.CH_2-\underset{\underset{O}{\|}}{C}-NHBr$

(c) $CH_3.CH_2-COONH_4$

(d) 
$CH_3.CH_2-\underset{\underset{O}{\|}}{C}-NH_2$

93. Which one of the following is not the correct reaction of aryl diazonium salts?

(a) $C_6H_5N_2^+Cl^- + Cu_2Cl_2 \rightarrow C_6H_5Cl$

(b) $C_6H_5N_2^+Cl^- + HBF_4$ heat C_6H_5F

(c) $C_6H_5N_2^+Cl^- + H_3PO_2 \rightarrow C_6H_5PO_4$

(d) $C_6H_5N_2^+Cl^- + SNCl_2/HCl \rightarrow C_6H_5NHNH_2$

Decisive Thinking Objective Type Questions (One or more than one choice)

94. Which of the following reactions yield an amine?

(a) $R-X + NH_3 \rightarrow$

(b) $R-CH=NOH + [H] \xrightarrow{Na,\ C_2H_5OH}$

(c) $R-CN + H_2O \xrightarrow{H^+}$

(d) $R-CONH_2 + 4[H] \xrightarrow{LiAlH_4}$

95. Reaction of $RCONH_2$ with a mixture of Br_2 and KOH gives RNH_2 as the main product. The intermediate involved in the reaction are

(a) RCONHBr
(b) R – NHBr
(c) R – N = C = O
(d) $RCONBr_2$

96. Which of the following arylamines can from a diazonium salt on reaction with sodium nitrite in hydrochloric acid?

(a) 4- Chloro -2- nitroaniline
(b) N- Ethyl -2- methylaniline
(c) m- Ethylaniline
(d) p- Aminoacetophenone

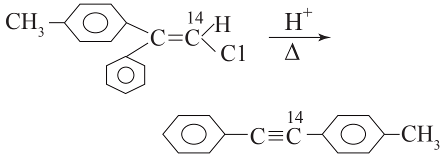
97. The coupling reaction of a diazonium salt is written as:

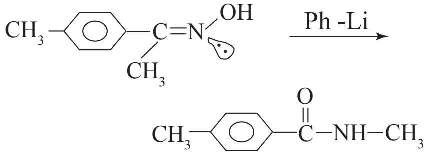
$[Ar - N^{\oplus} \equiv N: \leftrightarrow Ar - N = \ddot{N}^{\oplus}]\ddot{C}l^{\ominus} + H\text{-}Ar'$
$Ar - N = N - Ar' + H^{\oplus}\ Cl^{\ominus}$

Out the following generalizations regarding this reaction, which one is/are correct?

(a) The aromatic ring attacked by the diazonium ion must contain an electron withdrawing substituent.
(b) The positively charged nitrogen of the diazonium salt represents an electrophile.
(c) The coupling with amines takes place in neutral or weakly acidic solution.
(d) The coupling with phenols occurs in alkaline medium.

98. Which of the following reaction/s represent major product here?

(a)


(b)


(c)

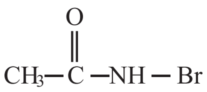

(d)

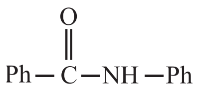
$R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{Br_2+KOH} R-NH_2$

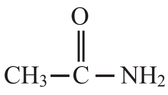
99. Among the following which can act as an intermediate in Hoffmann rearrangement?

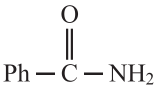
(a) RNCO (b) $RCO\ddot{N}$
(c) RCONHBr (d) RNC

100. Which of the following can give Hoffmann bromamide reaction?

(a)

$CH_3-\overset{O}{\overset{\|}{C}}-NH-Br$

(b)

$Ph-\overset{O}{\overset{\|}{C}}-NH-Ph$

(c)

$CH_3-\overset{O}{\overset{\|}{C}}-NH_2$

(d)

$Ph-\overset{O}{\overset{\|}{C}}-NH_2$

101. Amines are prepared by Hoffmann's method, in which ammonolysis of alkyl halide is done. Which alkyl halide cannot be used in this reaction?

(a) 3° halide; (b) vinyl halide;
(c) aryl halide (d) 1° halide;

102. Which of the following cannot be identified by carbyl amine test?

(a) $C_3H_7NH_2$
(b) $C_6H_5NH_2$
(c) $C_2H_5 - NH - C_2H_5$
(d) $(C_3H_7)_3N$

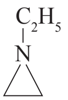
103. Which of the following compound will dissolve in an alkali solution after it has undergone reaction with Hinsberg's reagent?

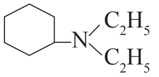
(a) N- methyl ethanamine
(b) N, N -dimethyl aniline
(c) diethyl amine
(d) Isopropyl amine

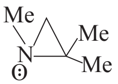
104. Which of the following reagents can be used in Backmann rearrangement:

(a) TsOH (b) BF_3
(c) $R-SO_2Cl$ (d) $Ph-Li$

105. Which of the following amines can not be resolved into enantiomers?

(a)


(b)


(c)


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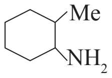
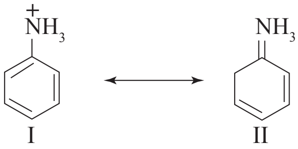


106. Examine the following two structures for the anilinium ion and choose the incorrect statement from the ones given below:

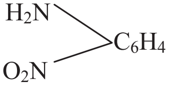


(a) II is not an acceptable canonical structures because carbonium ions are less stable than ammonium ions.
(b) II is an acceptable canonical structure.
(c) II is not an acceptable canonical structure because the nitrogen has ten valence electrons.
(d) II is not an acceptable canonical structure because it is non aromatic

107. Which will go for diazotization?

(a) $C_6H_5NH_2$ (b) $C_6H_5CH_2NH_2$

(c)


(d)


108. Which is/are the property of ethanenitrile (CH_3CN)?
- (a) It gives carbylamine reaction with chloroform.
- (b) It tautomerises to give methyl isocyanide.
- (c) Undergoes acidic hydrolysis to give carboxylic acid.
- (d) Undergoes alkaline hydrolysis to give salt of carboxylic acid.

109. When nitrobenzene is treated with Br_2 in presence of $FeBr_3$, the major product formed is m-bromonitrobenzene. The statements which is/are not related to obtain the m-isomer are
- (a) the electron density on meta carbon is more than at ortho and para positions.
- (b) the intermediate carbonium ion formed after initial attack of Br^+ at the meta positions is least destabilized.
- (c) loss of aromaticity when Br^+ attacks at the ortho and para positions and not at m-position.
- (d) easier loss of H^+ to regain aromaticity from the meta position than from ortho and para positions.

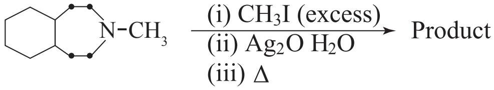
110. Which compounds can give Lassaigne test for nitrogen?

(a) NH_2OH	(b) CH_3CONH_2
(c) $C_6H_5N_2Cl$	(d) NH_2-CH_2-COOH

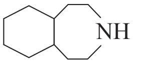
111. p – Chloroaniline and anilinium hydro- chloride can be distinguished by

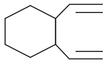
(a) Sandmeyer reaction	(b) $NaHCO_3$
(c) $AgNO_3$	(d) Carbylamine test

112. Among the following statements on the nitration of aromatic compounds, the false one is
- (a) the rate of nitration of benzene is almost the same as the hexadeuterobenzene.
- (b) the rate of nitration of toluene is greater than that of benzene.
- (c) the rate of nitration of benzene is greater than that of hexadeuterobenzene.
- (d) nitration is an electrophilic substitution reaction.

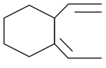
113.


Here the product formed can be?

(a)


(b)


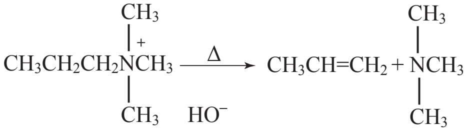
(c) $(CH_3)_3N$

(d)


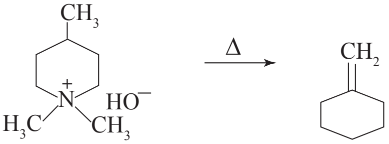
114. The amine which will liberate nitrogen on reaction with nitrous acid is

(a) Ethylamine	(b) sec-butyl amine
(c) Isopropyl amine	(d) Trimethyl amine

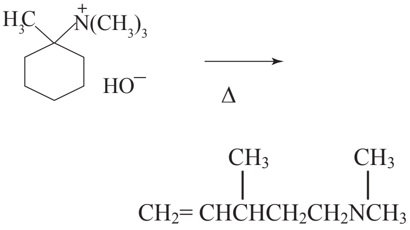
115. In which of the following reactions the major product is given correctly?

(a)


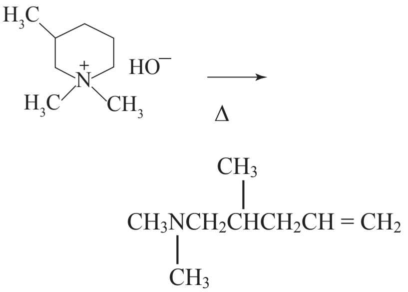
$$CH_3CH_2CH_2\overset{+}{N}(CH_3)_3\ HO^- \xrightarrow{\Delta} CH_3CH{=}CH_2 + N(CH_3)_3$$

(b)


$+ N(CH_3)_3$

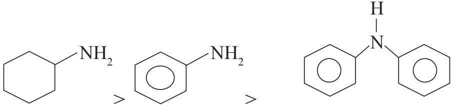
(c)


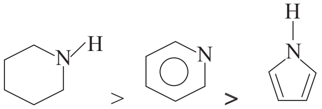
$$CH_2{=}CH\underset{}{\overset{CH_3}{C}}HCH_2CH_2\overset{CH_3}{N}CH_3$$

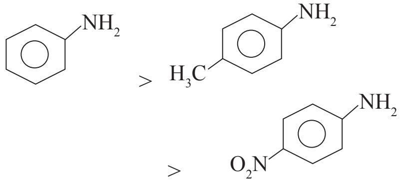
(d)


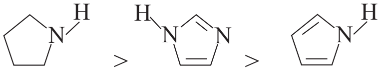
$$CH_3\underset{CH_3}{N}CH_2\overset{CH_3}{C}HCH_2CH=CH_2$$

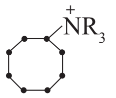
116. Which of the following sets represent decreasing order of basicity?

(a)


(b)


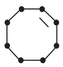
(c)


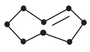
(d)


117. 

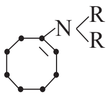
$\xrightarrow[Ag_2O\ H_2O]{\Delta}$ Product

Here products formed are

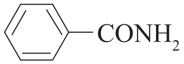
(a) 

(b) 

(c) NR_3

(d) 

118. The reaction that will give a primary amine is/are

(a) 

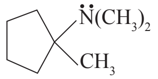
$\xrightarrow{Br_2 / KOH}$

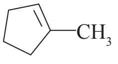
(b) $CH_3CN \xrightarrow{Na / C_2H_5OH}$

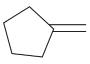
(c) $(CH_3)_2CH - Cl \xrightarrow{\text{(i) KCN, (ii) Zn/HCl}}$

(d) $CH_3CONH . C_2H_5 \xrightarrow{LiAlH_4}$

119. The products expected when the following compound is treated with H_2O_2 and heated:



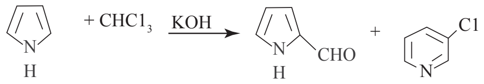
(a) 

(b) 

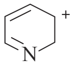
(c) $+ (CH_3)_2N — OH$

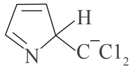
(d) 

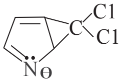
120. Pyrrole is treated with alkaline chloroform to get two products P and Q as follows:

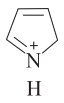


Which of the following intermediate is/are likely to be formed here?

(a) 

(b) 

(c) 

(d) 

Linked-Comprehension Type Questions

Comprehension 1

Amines are organic compounds which are alkyl or aryl derivatives of ammonia. They are capable of showing chain, position , functional, isomerism etc. They are basic a nature due to presence of one lone pair of electron on nitrogen atom. Their basicity is in influenced by the presence of electron realizing or electron withdrawing groups, steric effect, solvations effect and resonance etc.

121. Which of the following is most basic in gaseous state?

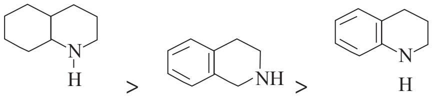
(a) $(C_2H_5)_2NH$ (b) $(C_2H_5)_3N$
(c) $C_2H_5\ NH_2$ (d) $C_2H_5\ CN$

122. Which of the following represent the correct order of basic nature?

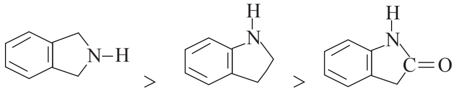
(I) Benzyl amine
(II) Guanidine
(III) Di methyl amine
(IV) Aniline

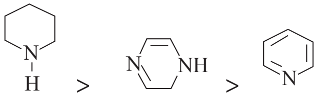
(a) II > I > III > IV (b) II > III > I > IV
(c) III > II > I > IV (d) III > I > II > IV

123. Which of the following represents the correct order of basic nature?

(I) 

(II) $RCONH_2 > RCH_2NH_2 > RCH_2CN$

(III) 

(IV) 

(a) I, II, III (b) II, III, IV
(c) I, III, IV (d) I, II, III, IV

Comprehension 2

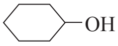
The most important reaction of all kind of amines is their reaction with nitrous acid. It is also a distinguish test as primary, secondary, tertiary, aromatic amines give different products on reaction with nitrous acid. Primary amines react with nitrous acid to give alcohols as the major product along with some other minor product like alkene etc. In case of aromatic amines the reaction is called diazotization and the product obtained is of great synthetics importance. In case of some cyclic primary amines ring expansion and conpraction is also observed.

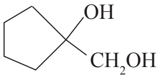
124. When propanamine reacts with nitrous acid which of the following statements are true?

(I) Here reaction intermediate is secondary corbocation
(II) Here the product formed are propene, 2- chloro propane and propanol -2
(III) It involves hydride shift
(IV) Here one of the product is optically active also

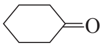
(a) I, II, III (b) I, II
(c) I, II, IV (d) II, III, IV

125. The major product obtained in this reaction can be given as

(a) 

(b) 

(c) 

(d) 

126. Which of these compound can give an N- nitroso amine on reaction with nitrous acid?

(I) $C_6H_5CONHC_2H_5$

(II) $C_2H_5NHC_2H_5$

(III) $C_6H_5NHC_2H_5$

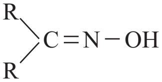
(IV) $C_6H_5NHC_6H_{11}$

(a) I, II, III (b) I, III, IV

(c) II, III, IV (d) I, II, III, IV

Comprehension 3

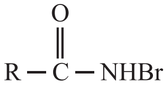
Primary amines are formed by the reduction of

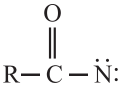
$R-NO_2$, $R-CONH_2$, $R-CN$, 
$\begin{matrix}R\\ \end{matrix}\!\!>C=N-OH$ with R above and R below

These are also obtained by various rearrangements like Hofmann bromamide, Curtius, Schmidt, Lossen Rearrangements etc. In all these rearrangements the amine formed has one C-atom less than the reactant compound used for their preparation

127. In Hoffmann bromamide reaction the correct sequence of intermediate formed can be given as

(I) $R-N=C=O$ (II) $R-\overset{\ominus}{N}-\overset{\oplus}{C}=O$

(III) 
$R-\overset{\overset{O}{\|}}{C}-NHBr$

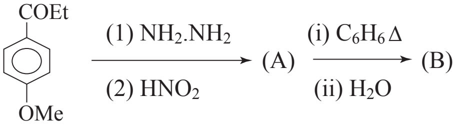
(IV) 
$R-\overset{\overset{O}{\|}}{C}-\ddot{N}:$

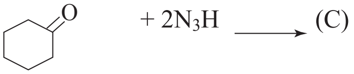
(a) II, III, IV, I

(b) III, II, IV, I

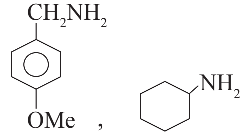
(c) III, IV, II, I

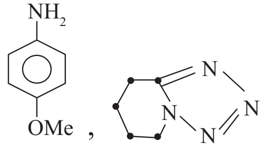
(d) IV, I, II, III

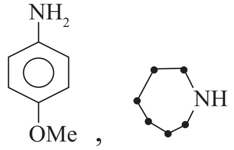
128. (I) 

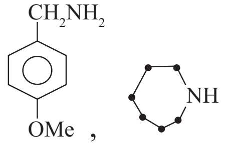
(II) 

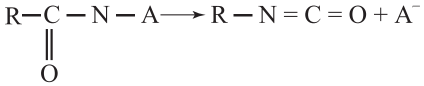
Here the products B and C can be given as respectively

(a) 

(b) 

(c) 

(d) 

129. 
$R-\underset{\underset{O}{\|}}{C}-N-A \longrightarrow R-N=C=O+A^-$

Which is correctly matched here?

(I) $A = -Br$ or $-Cl$	Hoffmann rearrangement
(II) $A = -N_2^+$	Curtius rearrangement
(III) $A - OCOR$	Lossen rearrangement
(IV) $A - OCOR$	Schmidt reaction

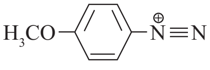
(a) I, II, IV (b) I, II, III

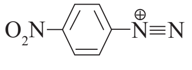
(c) II, III, IV (d) I, II, III, IV

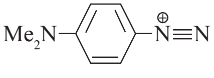
Comprehension 4

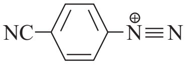
When an aromatic primary amine is treated with $NaNO_2$ + HCl at 0–5°C, a diazonium salt is formed and the reaction is called diazo reaction. In this reaction mineral acid must be added to prevent the coupling reaction of diazonium salt with excess of aryl amine. The diazonium salt is very widely used in the synthesis of a number of organic compounds. Its coupling reaction is highly useful in the synthesis of a number of coloured dyes.

130. For the following diazonium ions the decreasing order of reactivity of these ions in azo-coupling reactions (under similar conditions) can be given as

(I) 

(II) 

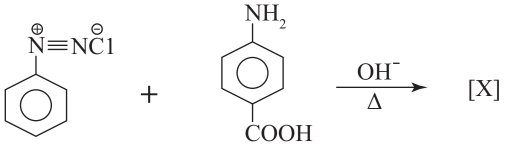
(III) 

(IV) 

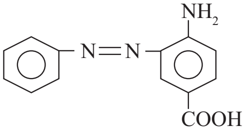
(a) II > IV > III > I (b) II > IV > I > III

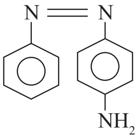
(c) II > I > IV > III (d) II > III > IV > I

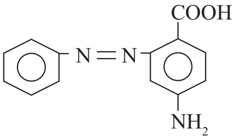
131. In the given reaction,

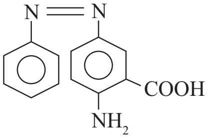


Product [X] will be

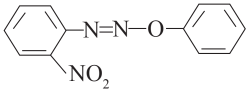
(a) 

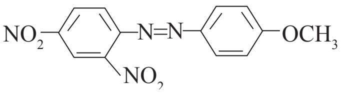
(b) 

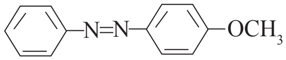
(c) 

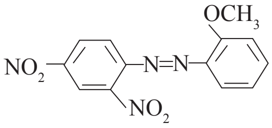
(d) 

132. When 2, 4- dinitro aniline reacts with $NaNO_2$ + HCl at 5°C followed by reaction with anisole, a coloured compound is formed which can be given as:

(a) 

(b) 

(c) 

(d) 

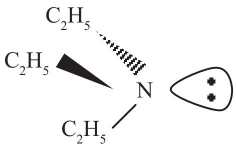
Assertion-Reason Type Questions

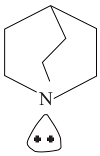
In the following question two statements (Assertion) A and Reason (R) are given Mark.

(a) if A and R both are correct and R is the correct explanation of A.
(b) if A and R both are correct but R is not the correct explanation of A.
(c) A is true but R is false.
(d) A is false but R is true.

133. **(A):** Me_3N reacts with BF_3 whereas Ph_3N does not
(R): The electron pair on the nitrogen in Ph_3N is delocalized in the benzene ring and is not available to boron in BF_3.

134. **(A):** Treithylamine (a) gives no detectable adduct with trimethylborane whereas quinuclidine (b) forms a very stable adduct.

(a) 

(b) 

(R): The ethyl groups shield the nitrogen atom of the amine to prevent any reaction of triethylamine with trimethylborane. In quinuclidine, in contrast, the carbon atom are pinned at the back in the ring system. Therefore, the nitrogen atom is free to attack trimethylborane and hence form a stable adduct.

135. **(A):** Oxidation of aminonaphthalene yields phthalic acid.
(R): An amino group attached to the benzene rings renders it sensitive oxidation.

136. **(A):** Treatment of alkyl halide with alcoholic solution of potassium cyanide gives isocyanide.
(R): Cyanides are used for preparation of amines and carboxylic acids.

137. **(A):** Nitration mixture used for carrying out nitration of benzene consists of conc. HNO_3 + conc. H_2SO_4.
(R): In presence of H_2SO_4 , HNO_3 acts as a base and produces NO_2^+ ions.

138. **(A):** Acetamide reacts with Br_2 in presence of methanolic CH_3ONa to form methyl N- methylcarbamate.
(R): Methyl isocyanate is formed an intermediate which reacts with methanol to from methyl N- methylcarbamate.

139. **(A):** Aniline is a weaker base than cyclohexyl amine.
(R): Aniline undergoes halogenation even in the absence of a catalyst.

140. **(A):** Oxidation of 1-nitro naphthalene gives o-nitro phthalic acid whereas 1-amino naphthalene on oxidation gives phthalic acid.
(R): An amino group attached to the benzene ring makes it resistant to oxidation whereas nitro group makes the benzene ring susceptible to oxidation.

141. **(A):** Diazo-coupling reactions occur in strong alkaline medium.
(R): In strong alkaline medium, the concentration of diazonium ion decreases rapidly.

142. **(A):** Nitroalkanes, but not nitroarenes can be distilled at normal atmospheric pressure.
(R): Nitroalkanes are sparingly soluble in water while nitroarenes are insoluble.

143. **(A):** In order to convert R – Cl to pure R – NH_2, Gabriel phthalimide synthesis can be used.
(R): With proper choice of alkyl halides, phthalimide synthesis can be used to prepare 1^o, 2^o or 3^o amines.

144. **(A):** In Hoffmann bromamide reaction, the amine formed has one carbon atom less than the parent 1^o amide.
(R): N-methyl acetamide undergoes Hofmann bromamide reaction.

145. **(A):** Nitration of aniline can be done conveniently by protecting the amino group by acetylation.
(R): Acetylation increases the electron density in the benzene ring.

146. **(A):** In strongly acidic solutions, aniline becomes more reactive towards electrophilic reagents.
(R): The amino group being completely protonated in strongly acidic solution, the lone pair of electrons on the nitrogen is no longer available for resonance.

147. **(A):** Aniline on reaction with $NaNO_2$/HCl at 0^oC followed by coupling with β- naphthol gives a dark blue coloured precipitate. **[IIT 2008]**
(R): The colour of the compound formed in the reaction of aniline with $NaNO_2$/HCl at 0^oC followed by coupling with β- naphthol is due to the extended conjugation.

Matrix-Match Type Questions

148. Match the following:

Column I

(a) Curtius reaction
(b) Gabriel phthalimide reaction
(c) Lossen rearrangement
(d) Schmidt reaction

Column II

(p) $R-CO-NH-O-CO-R' \xrightarrow{OH^-} R-N=C=O$
(q) $RCON_3 \xrightarrow[-N_2]{\Delta} R-N=C=O \xrightarrow{H_2O} RNH_2 + CO_2$
(r) Conversion of an alkile phthalimide into RNH_2
(s) Involves SN^2 displacement
(t) $RCOOH + N_3H \xrightarrow{H_2SO_4} RNH_2 + CO_2 + N_2$

149. Match the following:

Column I

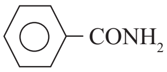
(a) $C_2H_5NH_2$
(b) $(C_2H_5)_2NH$
(c) $(C_2H_5)_3N$
(d) $C_6H_5NH_2$

Column II

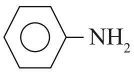
(p) Reaction with $NaNO_2$ + dil. HCl
(q) Reaction with $CHCl_3$ + KOH
(r) Formation of N- nitroso di-ethyl amine with HNO_2
(s) Formation of tri -ethyl ammonium nitrite with HNO_2

150. Match the following:

Column I (Reactants)

(a) $RX + KCN \xrightarrow{\text{ethanol}}$
(b) $RX + CH_3COOAg$
(c) $CH_3C \equiv N \xrightarrow{LiAlH_4}$
(d)  $\xrightarrow[\text{degradation}]{\text{Hofmann's}}$

Column II (Products)

(p) 
(q) RCN
(r) CH_3COOR
(s) $CH_3CH_2NH_2$
(t) RNC

151. Match the following:

Column I
(compound)

(a) Acetamide (b) Phthalimide
(c) Benzonitrile (d) Grignard reagent

Column II
(Nature)

(p) Acidic (q) Basic
(r) Nautral (s) Amphotertic

152. Match the following:

List I
(Condition of reaction of nitrobenzene)

(a) Sn and HCl (b) Zn and NH_4Cl
(c) Methanolic NaOMe (d) . Zn and KOH

List II

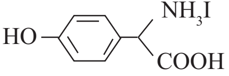
(Products formed)

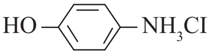
(p) Hydrazobenzene
(q) Azoxybenzene
(r) Phenyl hydroxyl amine
(s) Aniline

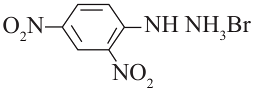
153. Match the following:

Column I

(a) $H_2N - NH_3Cl$

(b) 

(c) 

(d) 

Column II

(p) sodium fusion extract of the compound gives Prussian blue colour with $FeSO_4$.
(q) gives positive $FeCl_3$ test.
(r) gives white precipitate with $AgNO_3$.
(s) reacts with aldehyde to form the corresponding hydrazone derivatives.

[IIT 2008]

154. Match each of the compound in **Column I** with its characteristic reaction(s) in **Column II**.

Column I

(a) $CH_3CH_2CH_2CN$
(b) $CH_3CH_2OCOCH_3$
(c) $CH_3 - CH = CH - CH_2OH$
(d) $CH_3CH_2CH_2CH_2NH_2$

Column II

(p) Reduction with $Pd - C/H_2$
(q) Reduction with $SnCl_2/HCl$
(r) Development of foul smell on treatment with chloroform and alcoholic KOH
(s) Reduction with diisobutylaluminium hydride (DIBAL – H)
(t) Alkaline hydrolysis

[IIT 2009]

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155. Nitrobenzene can be prepared from benzene by using a mixture of conc. HNO_3 and conc. H_2SO_4. In the nitrating mixture, nitric acid acts as a

(a) base (b) acid
(c) reducing agent (d) catalyst

[IIT 1997]

156. Benzenediazonium chloride on reaction with phenol in weakly basic medium gives

(a) diphenyl ether
(b) o – Hydroxyazobenzene
(c) chlorobenzene
(d) benzene

[IIT 1998]

157. p – Chloroaniline and anilinium hydro- chloride can be distinguished by

1. Sandmeyer reaction 2. $NaHCO_3$
3. $AgNO_3$ 4. Carbylamine test

(a) 1, 2,4 (b) 1,2,3
(c) 1,3,4 (d) 1,2

[IIT 1998]

158. Among the following compounds, which will react with acetone to give a product containing > C = N–?

1. $C_6H_5NH_2$ 2. $(CH_3)_3N$
3. $C_6H_5NHC_6H_5$ 4. $C_6H_5NHNH_2$

(a) 3, 4 (b) 1, 3, 4
(c) 1, 3 (d) 1, 4

[IIT 1998]

159. A positive carbylamine test is given by

(1) N, N-Dimethylaniline
(2) 2, 4-Dimethylaniline
(3) N – methyl – o – methylaniline
(4) p – Methylbenzylamine

(a) 2, 4 (b) 2, 3
(c) 1, 2, 4 (d) 2, 3, 4

[IIT 1999]

160. One mole of calcium phosphide on reaction with excess of water gives

(a) one mole of phosphine
(b) two moles of phosphoric acid
(c) two moles of phosphine
(d) one mole of phosphorus pentoxide

[IIT 1999]

161. The correct sequence of reagents used for conversion of aniline into Benzylamine is

(a) $NaNO_{2/}HCl$, CuCN, Sn/HCl
(b) $NaNO_2/HCl$, CuCN, H_3O^+
(c) $NaNO_2/HCl$, Cu^+/H_3PO_2, CH_3NH_2
(d) None

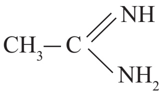
[IIT 2000]

162. Among the following, the strongest base is

(a) $C_6H_5NH_2$ (b) $p - NO_2 - C_6H_4NH_2$
(c) $m - NO_2 - C_6H_4NH_2$ (d) $C_6H_5CH_2NH_2$

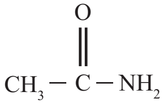
[IIT 2000]

163. The correct order of basicities of the following compounds is

1. 
$CH_3-C(=NH)NH_2$

2. $CH_3CH_2NH_2$

3. $(CH_3)_2NH$

4. 
$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2$

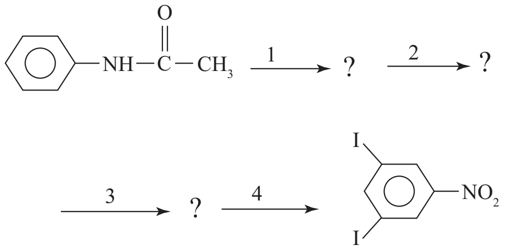
(a) $2 > 1 > 3 > 4$
(b) $1 > 3 > 2 > 4$
(c) $3 > 1 > 2 > 4$
(d) $1 > 2 > 3 > 4$

[IIT 2001]

164. The compound that will react most readily with NaOH to form methanol is
(a) $(CH_3)_4\,N^+\,I^-$
(b) CH_3OCH_3
(c) $(CH_3)_3S^+\,I^-$
(d) $(CH_3)_3CCl$

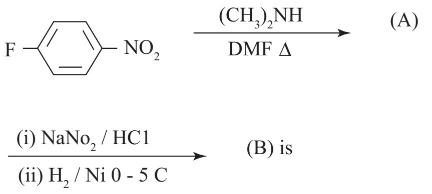
[IIT 2001]

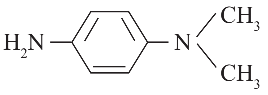
165. The correct sequence of reagents in the following conversion



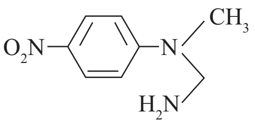
is
(a) H_2O/H^+ , $NaNO_2/HCl$, Cu, I_2
(b) H_2O/H^+, $NaNO_2/HCl$, $NaNO_2$ + Cu, I_2/HgO
(c) H_2O/H^+, I_2, Sn + HCl, $NaNO_2$
(d) None

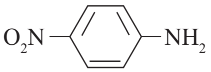
[IIT 2002]

166. 

(a) 

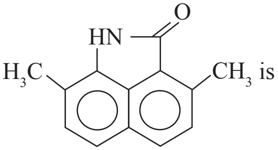
(b) 

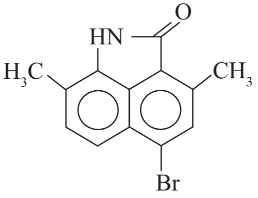
(c) 

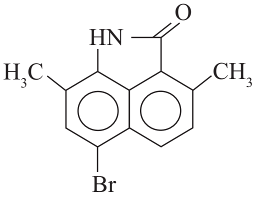
(d) 

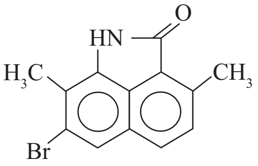
[IIT 2003]

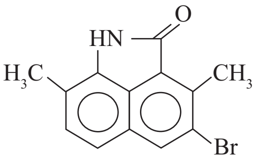
167. The major product obtained when Br_2/Fe is treated

with  is

(a) 

(b) 

(c) 

(d) 

[IIT 2004]

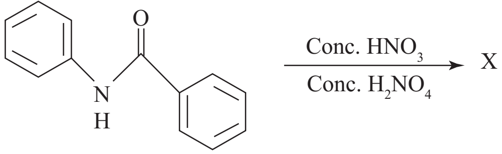
168. Benzamide on reaction with $POCl_3$ gives:
(a) aniline (b) chlorobenzene
(c) benzyl amine (d) benzonitrile

[IIT 2004]

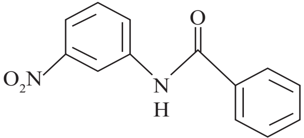
169. $CH_3NH_2 + CHCl_3 + KOH \rightarrow$ Nitrogen containing compound + KCl + H_2O. Nitrogen containing compound is
(a) $CH - C \equiv N$
(b) $CH_3 - NH - CH_3$
(c) $CH_3 - \overset{-}{N} \equiv \overset{+}{C}$
(d) $CH_3\overset{+}{N} \equiv \overset{-}{C}$

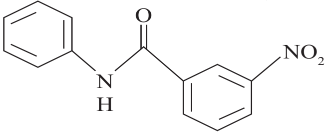
[IIT 2006]

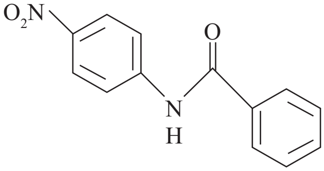
170. In the following reaction

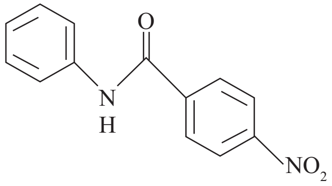


the structure of the major product 'X' is

(a)


(b)


(c)


(d)


[IIT 2007]

ANSWERS

Straight Objective Type Questions

1. (d) **2**. (d) **3**. (a) **4**. (c) **5**. (b) **6**. (a) **7**. (d) **8**. (b) **9**. (d) **10**. (d)
11. (a) **12**. (b) **13**. (d) **14**. (c) **15**. (c) **16**. (a) **17**. (c) **18**. (d) **19**. (d) **20**. (b)
21. (c) **22**. (c) **23**. (c) **24**. (b) **25**. (d) **26**. (d) **27**. (b) **28**. (c) **29**. (c) **30**. (a)
31. (b) **32**. (a) **33**. (a) **34**. (b) **35**. (d) **36**. (b) **37**. (a) **38**. (c) **39**. (b) **40**. (c)
41. (c) **42**. (b) **43**. (c) **44**. (b) **45**. (a) **46**. (c) **47**. (c) **48**. (a) **49**. (a) **50**. (a)

Brainteasers Objective Type Questions

51. (c) **52**. (c) **53**. (a) **54**. (a) **55**. (c) **56**. (c) **57**. (b) **58**. (d) **59**. (a) **60**. (a)
61. (a) **62**. (d) **63**. (b) **64**. (c) **65**. (a) **66**. (b) **67**. (c) **68**. (b) **69**. (d) **70**. (c)
71. (b) **72**. (d) **73**. (b) **74**. (b) **75**. (d) **76**. (a) **77**. (c) **78**. (d) **79**. (b) **80**. (a)
81. (d) **82**. (b) **83**. (c) **84**. (b) **85**. (b) **86**. (b) **87**. (c) **88**. (b) **89**. (b) **90**. (a)
91. (b) **92**. (a) **93**. (c)

Decisive Thinking Objective Type Questions

94. (a), (b), (d) **95.** (a), (c) **96.** (a), (c), (d) **97.** (b), (c), (d) **98.** (a), (b), (d)
99. (a), (b), (c) **100.** (a), (c), (d) **101.** (a), (b), (c) **102.** (c), (d) **103.** (b), (d)
104. (a), (b), (c) **105.** (a), (b), (c) **106.** (c), (d) **107.** (a), (c), (d) **108.** (b), (c), (d)
109. (c), (d) **110.** (b), (d) **111.** (a), (b), (c) **112.** (b), (c), (d) **113.** (b), (c)
114. (a), (b), (c) **115.** (a), (b), (c), (d) **116.** (a), (b), (c) **117.** (a), (b), (c) **118.** (a), (b), (c)
119. (a), (b), (c) **120.** (b), (c)

Linked-Comprehension Type Questions

121. (b) **122**. (b) **123**. (c) **124**. (a) **125**. (d) **126**. (c) **127**. (c) **128**. (b) **129**. (b) **130**. (b)
131. (b) **132**. (b)

Assertion-Reason Type Questions

133. (a) **134**. (a) **135**. (b) **136**. (d) **137**. (a) **138**. (a) **139**. (b) **140**. (c) **141**. (d) **142**. (b)
143.(c) **144**. (c) **145**. (c) **146**. (d) **147**. (d)

Matrix-Match Type Questions

148. (a) - (q), (b) - (r, s), (c) - (p), (d) - (t)
149. (a) - (p, q), (b) - (p, r), (c) - (p, s), (d) - (p, q)
150. (a) - (q), (b) - (r), (c) - (s), (d) - (p)
151. (a) - (r), (b) - (p), (c) - (r), (d) - (q)
152. (a) - (s), (b) - (r), (c) - (q), (d) - (p)
153. (a) - (r, s), (b) - (p, q), (c) - (p, q), (d) - (p, s)
154. (a) p, q, s, t (b) s, t (c) p (d) r

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155. (a) **156**. (b) **157**. (b) **158**. (d) **159**. (a) **160**. (c) **161**. (a) **162**. (d) **163**. (b) **164**. (c)
165. (b) **166**. (a) **167**. (b) **168**. (d) **169**. (d) **170**. (c)

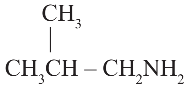
HINTS AND EXPLANATIONS

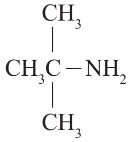
Straight Objective Type Questions

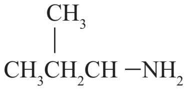
1. R – NH_2 (Amines) behaves as a Lewis base because it is capable of donating a lone pair of electron.

2. There are four possible single primary amines of the formula $C_4H_{11}N$.

(i) $CH_3CH_2CH_2CH_2NH_2$

(ii)

$CH_3CH(CH_3) – CH_2NH_2$

(iii)

$CH_3C(CH_3)_2 – NH_2$

(iv)

$CH_3CH_2CH(CH_3) – NH_2$

4. Strong base has higher tendency to accept the proton increasing order of acid

$RNH_3^+ < NH_4^+ < H_2S < I^-$

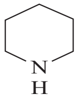
Increasing order of base is

$RNH_2 > NH_3 > HS^- > I^-$

6. It is due to electron withdrawing nature of NO_2 group.

7. The strongest intermolecular hydrogen bonding is present in methanol.

9. The weakest base is $O_2N.CH_2NH_2$ as this base has $–NO_2$ group which has a tendency to withdraw electrons (Strong –I group).

11.

(Piperidine) is the strongest base here.

13. Toluene has electron-donating methyl group and hence reacts fastest while others have either electron withdrawing groups (i.e., -COOH and $–NO_2$ etc.) or no substituent.

15. In Wurtz reaction alkyl halide reacts with sodium metal in the presence of dry ether to give alkane.

18. Secondary amines (aliphatic as well as aromatic) react with nitrous acid to form N-nitrosoamines.

$(C_2H_5)_2NH + 10\ HONO \rightarrow (C_2H_5)_2N – N = O + H_2O$

N-nitrosodiethylamine

21. This conversion can be affected by Clemmensen's reduction.

$C_6H_5CONHCH_3 \xrightarrow[C_6H_5CH_2NHCH_3]{Zn\text{-}Hg / HCl}$

22. $(NH_4)_2Sx$ reduces one $–NO_2$ to $–NH_2$ group.

23. $\underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow{NaOH + Br_2} \underset{\text{methylamine}}{CH_3NH_2}$

25. $CH_3CN \xrightarrow{Na/C_2H_5OH} CH_3CH_2NH_2 \xrightarrow{HNO_2}$

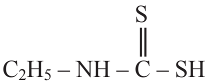
$CH_3CH_2OH \xrightarrow{Cu/573K} CH_3CHO$

30. Chloroform or trihalogenated methane (CHX_3) when heated with a primary amine, and alcoholic caustic potash give carbylamines (isocyanides) having very unpleasant smell.

$CHX_3 + RNH_2 + 3KOH \rightarrow RNC + 3KX + 3H_2O$

31. $CH_3NC + 4H \xrightarrow{LiA1H_4} CH_3NHCH_3$

32. $C_2H_5-NH_2 + S=C=S \xrightarrow[\text{(alco)}]{}$



$$C_2H_5-NH-\overset{\overset{\displaystyle S}{\|}}{C}-SH$$

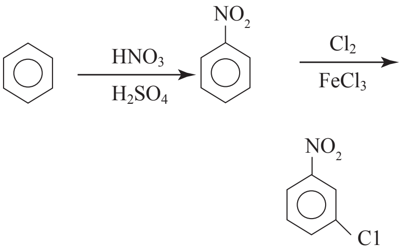
$$\downarrow HgCl_2$$

$HgS + 2HCl + C_2H_5-N=C=S$
Ethyl isothiocyanate
(with mustard oil smell)

This reaction is also known as Hoffmann's mustard oil reaction.

33. n-dinitrobenzene undergoes oxidation on treatment with alkaline potassium ferricyanide to give the dinitrophenol.

34.



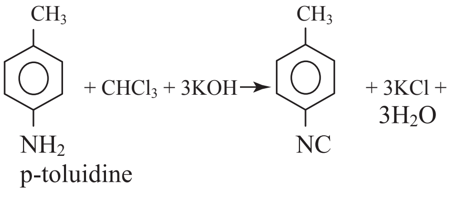
35. $CH_3CH_2CH_2-Cl + KCN \xrightarrow{-KC}$
$CH_3CH_2CH_2CN + CH_3CH_2CH_2NC$
(major) (minor)

41. It is Liberman nitroso reaction.

42. In aniline, lone pair enters the ring and the ring is activated for electrophillic attack. In nitrobenzene and N-acetyl aniline

$C_6H_5-NH-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$ due to electron withdrawing group. The ring is deactivated for electrophillic attack.

43. This is an example of carbylamine reaction.
The reaction sequence is as follows:

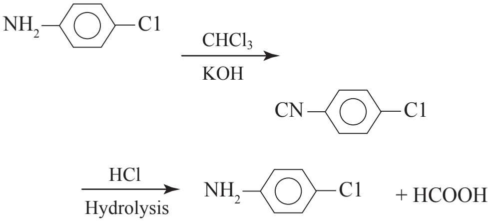


p-toluidine

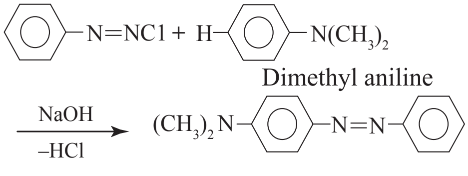
44.

$-NO_2$ group is meta directing while CH_3 group is ortho directing.

45.



46. Aniline when diazotized in cold (0–5°C) gives benzene diazonium chloride which undergoes coupling reaction with N,N-dimethyl aniline to give p-(N,N-dimethyl) amino azo benzene dye.



50. It is reductive amination reaction using sodium cyanoborohydride instead of hydrogen as the reducing agent

$C_6H_5CHO + C_2H_5NH_2 \xrightarrow[\text{methanol}]{NaBH_3CN}$

$C_6H_5CH_2NHCH_2CH_3$
N-ethyl benzylamine

Brainteasers Objective Type Questions

51. Among the following compounds, only $CH_3NH_3^+Cl$ is the ionic compound, hence dissociation constant is maximum for it.
$CH_3NH_3^+Cl^- \rightleftharpoons CH_3NH_3^+ + Cl^-$
So dissociation constant

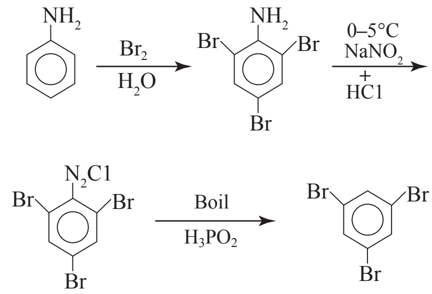
$$K = \frac{[CH_3NH_3^+]\,[Cl^-]}{[CH_3NH_3^+Cl^-]}$$

52. As basic nature decreases by the presence of electron attracting groups (–I).

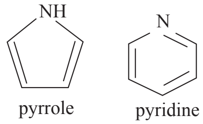
54. As the presence of electron-withdrawing (–I or –M group) like $-NO_2$ at p-position decreases the basicity, so (2) will be least basic, whereas presence of electron –donating (+ I or + M) group like $-OCH_3$ at p-position in (4) increases basicity so(4) is most basic. Here the correct order of increasing basic character is

$2 < 5 < 1 < 3 < 4$

56.



58. Consider the structures of pyrrole and pyridine.



Pyrrole is a weaker base than pyridine because when pyrrole accepts a proton it loses its aromatic properties. When it accepts a proton, the sp^2N atom is converted to a sp^3 N, which makes the molecule nonaromatic.

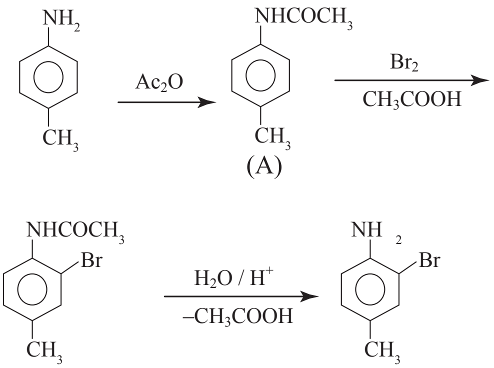
60. $C_2H_5Br \xrightarrow{KCN\ (X)} C_2H_5CN \xrightarrow{LiAlH_4\ (Y)}$

$C_2H_5CH_2NH_2\ (C_3H_7NH_2)$

61. $C_6H_5COOH \xrightarrow{SOCl_2} C_6H_5COCl \xrightarrow{NH_3}$

$C_6H_5CONH_2 \xrightarrow{H_2 / Ni} C_6H_5CH_2NH_2$

62.



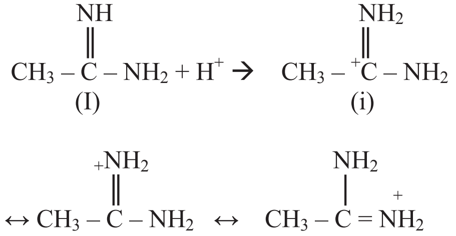
65. $CH_3CH_2Cl \xrightarrow{NaCN} \underset{(A)}{CH_3CH_2CN}$

$\xrightarrow{Ni/H_2} \underset{(B)}{CH_3CH_2CH_2NH_2}$

$\xrightarrow[-CH_3COOH]{\text{Acetic anhydride}} \underset{(C)}{CH_3CH_2CH_2NHCOCH_3}$

(Acylation)

66. 2° amines are more basic than 1° amines. Amides are least basic because lone pair on N is delocalized over C = O group.



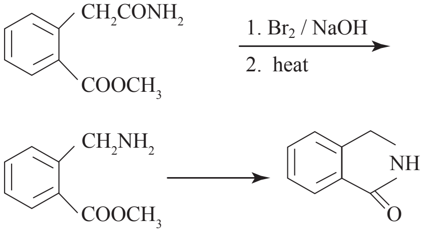
$$\underset{(I)}{CH_3-\overset{\overset{\large NH}{\|}}{C}-NH_2} + H^+ \rightarrow \underset{(i)}{CH_3-\overset{\overset{\large NH_2}{\|}}{\overset{+}{C}}-NH_2}$$

$$\leftrightarrow CH_3-\overset{\overset{\large {}^+NH_2}{\|}}{C}-NH_2 \leftrightarrow CH_3-\overset{\overset{\large NH_2}{|}}{C}=\overset{+}{N}H_2$$

The conjugate acid (i) obtained by addition of a proton to I is stabilized by resonance and hence the compound I is most basic. Thus the order of basic nature is

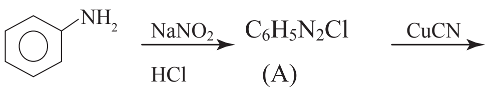
$1 > 3 > 2 > 4.$

71.



72. Aniline gives phenyldiazonium chloride ($PhN^+ \equiv N\ Cl^-$) – a salt on treatment with ice cold nitrous acid. It liberates nitrogen, only on further treatment with water

76.

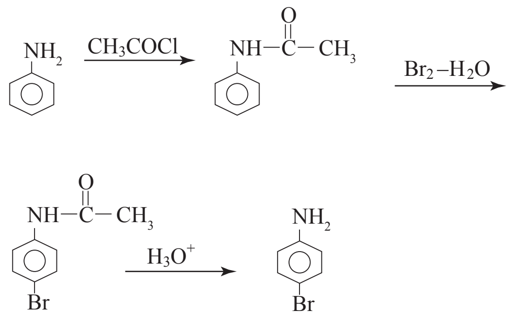


$C_6H_5NH_2 \xrightarrow[HCl]{NaNO_2} \underset{(A)}{C_6H_5N_2Cl} \xrightarrow{CuCN}$

$\underset{(B)}{C_6H_5CN} \xrightarrow{H_2,Ni} \underset{(C)}{C_6H_5CH_2NH_2}$

$\xrightarrow{HNO_2} C_6H_5CH_2OH\ (D)$

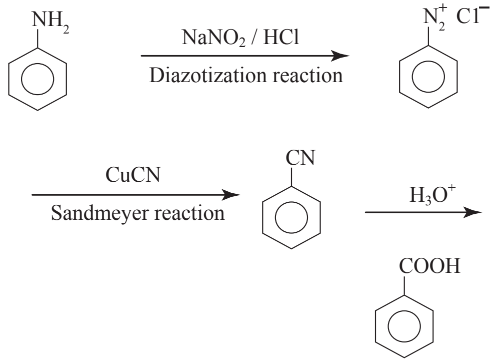
77.



79.

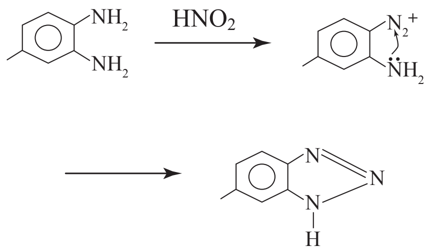
$$\underset{(A)}{CH_3CH_2COOH} \xrightarrow{SOCl_2} \underset{(B)}{CH_3CH_2COCl} \xrightarrow{NH_3} \underset{(C)}{CH_3CH_2CONH_2} \xrightarrow[\text{Hoffman bromamide Reaction}]{KOH + Br_2} \underset{(D)}{CH_3CH_2NH_2}$$

80.

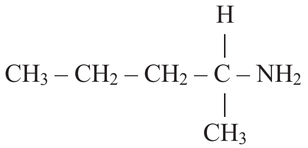


82. The benzene ring to which >NH group is directly attached is activated while the ring to which >C = O group is directly attached is deactivated towards electrophillic substitution. In addition the >NH group is ortho-para directing.

83.

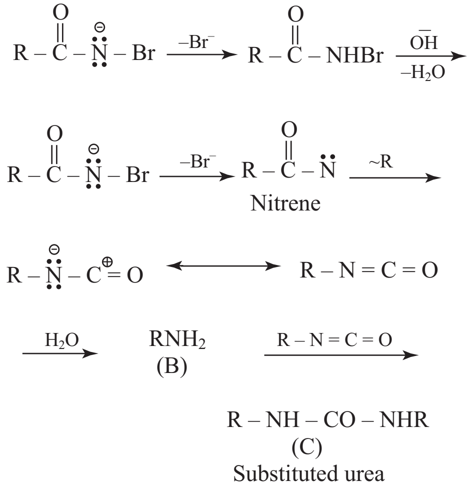


85. As HNO$_2$ reacts to give an alcohol means the compound is a primary amine so $C_5H_{13}N$ is $C_5H_{11}NH_2$. Optically active alcohol means C_5H_{11}-segment contains a chiral carbon.

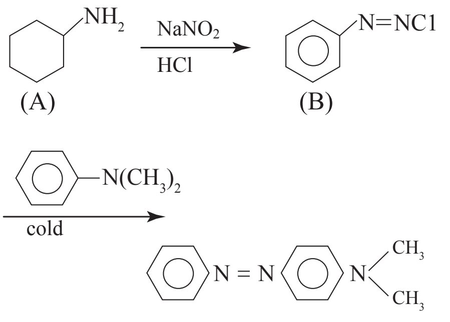


$$CH_3-CH_2-CH_2-\underset{CH_3}{\overset{H}{C}}-NH_2$$

86. (A) undergoes Hoffmann rearrangement to form isocyanate.

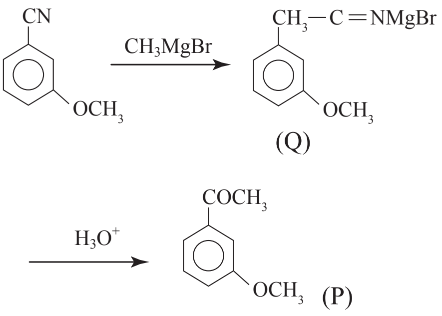


88.

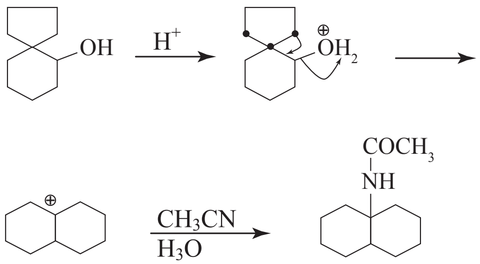


(C), Butter yellow
p-Dimethyl amino azobenzene

90. The reaction sequence is as follows:



91.



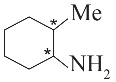
92. First reaction is nucleophillic substitution producing a cyanide [3 carbon containing]. This on partial hydrolysis would give 3 carbon amide, which on Hofmann-Bromamide reaction would give a two carbon primary amine. Therefore, etrhylamine is the final product (C).

93. $C_6H_5N_2^+Cl^-$ on reaction will hypo phosphorous acid (H_3PO_2) given benzene .

Decisive Thinking Objective Type Questions

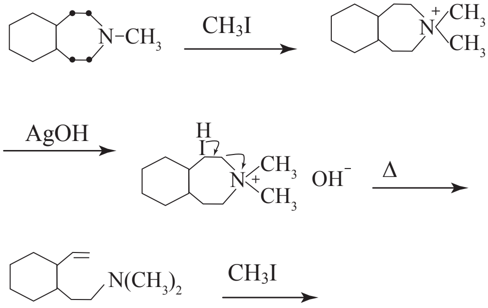
97. The aromatic ring attached by the diazonium ion may contain an electron withdrawing or an electron donating substituent. But experiments have been shown that whatever be the nature of the substituent in the second components, o- and p-substitution occurs predominantly but some m-product is also formed.

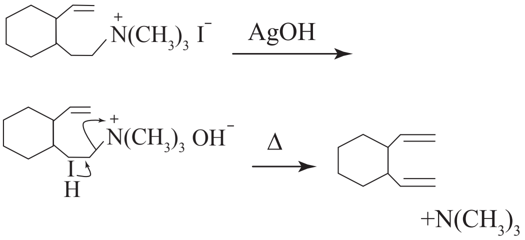
101. 3° halides give alkenes vinyl and aryl halides do not undergo SN^2 reaction.

105. As  has optical activity due to chiral-centres so it can be resolved here.

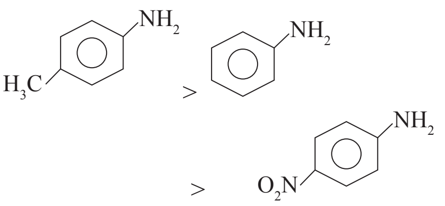
110. Because at the required temperature of Lassaigne test, N_2 expels out in the form of a gas in $C_6H_5N_2Cl$ NH_2OH does not contain carbon.

113.



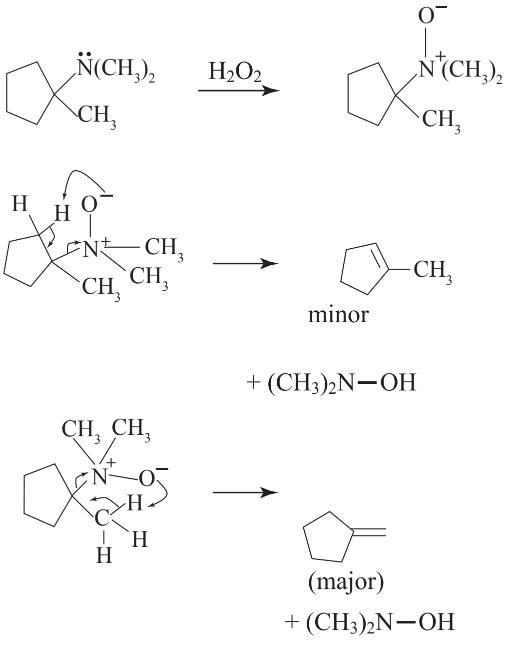


116. As the correct order of basicity for option C is



118. As secondary amide on reduction gives a secondary amine.

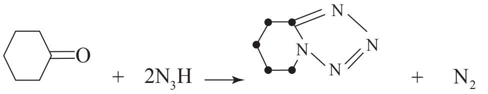
119. Oxidation converts the tertiary amine to an oxide. Cope elimination can give either of two alkenes. We expect the less hindered elimination to be favoured, giving the Hofmann product.



Linked-Comprehension Type Questions

123. As in case of (II) the correct order of basic nature is:
$RCH_2NH_2 > RCONH_2 > RCH_2CN$

128.



Assertion-Reason Type Questions

133. Both assertion and reason are correct and give correct explanation.

137. $HNO_3 + 2H_2SO_4 \leftrightarrow 2HSO_4^- + NO_2^+ + H_3O^+$

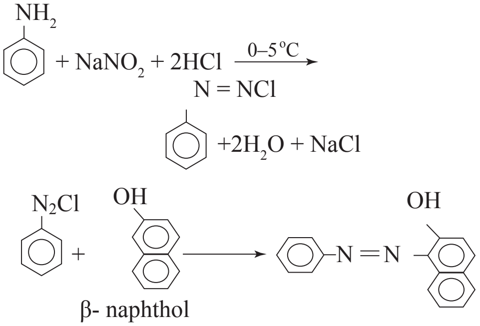
142. Nitroarenes cannot be distilled under normal atmospheric pressure . This is because either they decompose or they explode on strong heating.

143. Only primary aliphatic amines can be prepared by Gabriel phthalimide reaction.

144. Only 1° amides undergo Hofmann bromamide reaction. Since $CH_3CONHCH_3$ is a 2° amine therefore, it does not undergo Hofmann bromamide reaction.

145. Acetylation decreases the electron density in the benzene ring thereby preventing oxidation.

147.



β- naphthol

phenyl azo β- naphthol
(Red dye)

The IIT-JEE Corner

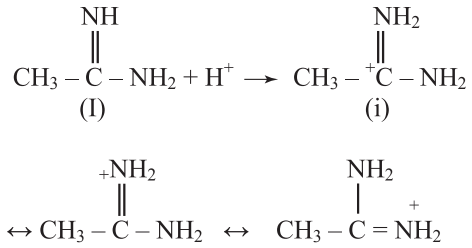
155. $H^+ + \underset{\text{(from } H_2SO_4\text{) (base)}}{HO - NO_2} \rightarrow (H_2O^+ - NO_2)$

$\rightarrow H_2O + \overset{+}{N}O_2$

159. Carbylamine test is given by 1° amines only ($R - NH_2$).

162. Benzyl amine ($C_6H_5CH_2NH_2$ i.e., aliphatic amine) with $-NH_2$ group in the side chain behaves like alkyl amines (aliphatic amines) which are more basic as compared with aryl amines which are stabilized due to resonance. On attachment of electron attractive group, basic character is decreased so benzyl amine is more basic in these amines.

163. 2° amines are more basic than 1° amines. Amides are least basic because lone pair on N is delocalized over C = O group.



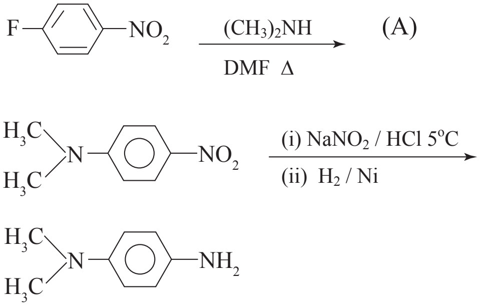
$$\underset{\text{(I)}}{CH_3 - \overset{\overset{\displaystyle NH}{\|}}{C} - NH_2} + H^+ \longrightarrow \underset{\text{(i)}}{CH_3 - \overset{\overset{\displaystyle NH_2}{\|}}{\overset{+}{C}} - NH_2}$$

$$\leftrightarrow CH_3 - \overset{\overset{\displaystyle {}^{+}NH_2}{\|}}{C} - NH_2 \leftrightarrow CH_3 - \overset{\overset{\displaystyle NH_2}{|}}{C} = \overset{+}{N}H_2$$

The conjugate acid (i) obtained by addition of a proton to I is stabilized by resonance and hence the compound I is most basic. Thus the order of basic nature is
1 > 3 > 2 > 4.

164. Due to higher electron negativity of N (3.0) than S (2.8), positively charged nitrogen will make CH_3 group more electron deficient than S. Thus $(CH_3)_4N^+I^-$ will undergo nucleophillic substitution more readily than $(CH_3)_3S^+I^-$.

166.

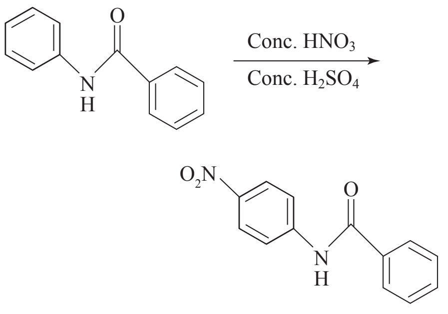


167. The benzene ring to which >NH group is directly attached is activated while the ring to which >C= O group is directly attached is deactivated towards electrophillic substitution. In addition the >NH group is ortho-para directing.

168. Benzamide on treatment with $POCl_3$ gives benzonitrile (phenyl cyanide) because in this reaction $POCl_3$ acts as a dehydrating agent and on dehydration of benzamide, benzonitrile is formed.

169. Isocyanide test/Carbylamine reaction

170.



Due to presence of lone pair of electron on nitrogen atom, it will activate the ring and it will stabilize intermediate cation at o- and p- positions.

SUBJECTIVE SOLVED EXAMPLES

1. Show with equations how the following compounds are prepared (equations need not be balanced):

(i) n-propyl amine from ethyl chloride (in two steps)

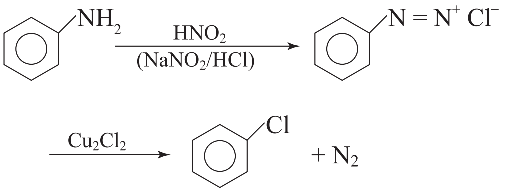
Solution

$$CH_3CH_2Cl + \text{alc. KCN} \longrightarrow CH_3CH_2CN$$

$$\xrightarrow[\text{Reduction}]{H_2 / Ni} CH_3CH_2CH_2NH_2$$

(ii) Chlorobenzene from aniline (in two steps)

Solution



(iii) Aniline from benzene

Solution

$$C_6H_6 \xrightarrow[\text{conc. } HNO_3]{\text{conc. } H_2SO_4} C_6H_5NO_2 \xrightarrow{Sn / HCl} \underset{\text{Aniline}}{C_6H_5NH_2}$$

(iv) Acetoxime from acetaldehyde using the reagents, $[K_2Cr_2O_7 /H^+$, $Ca(OH)_2$ and $NH_2OH.HCl]$

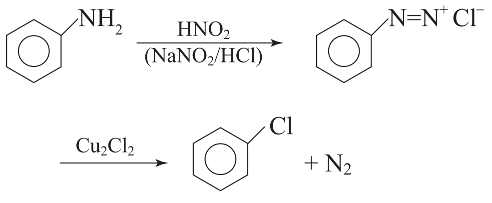
Solution

$$CH_3CHO + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3COOH$$

$$\xrightarrow{Ca(OH)_2} CH_3COCH_3 \xrightarrow{NH_2OH.HCl} \underset{\text{Acetoxime}}{(CH_3)_2C = NOH}$$

(v) Aniline to chlorobenzene

Solution



(vi) Benzaldehyde to cyanobenzene. (In not more than 6 steps).

Solution

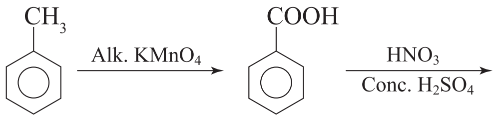
$$C_6H_5CHO \xrightarrow{\text{Oxidation}} C_6H_5COOH \xrightarrow[\text{(ii) } \Delta]{\text{(i) } NH_3}$$

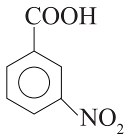
$$C_6H_5CONH_2 \xrightarrow[KOH]{Br_2} C_6H_5NH_2 \xrightarrow[0^\circ C]{HONO}$$

$$C_6H_5N_2Cl \xrightarrow{CuCN} \underset{\text{Cyanobenzene}}{C_6H_5CN}$$

(vii) How will you convert toluene to m-nitrobenzoic acid?

Solution



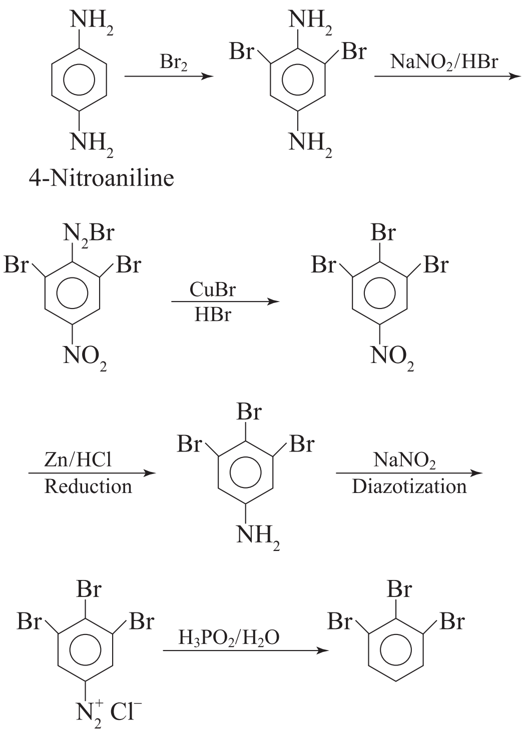


m-nitrobenzoic acid

(viii) 4-Nitroaniline to 1,2,3-tribromobenzene

[IIT 1990]

Solution

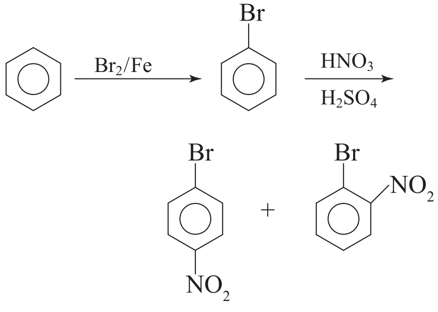


1,2,3-tribromobenzene

(ix) Outline a synthesis of p-bromonitrobenzene from benzene in two steps.

[IIT 1993]

Solution



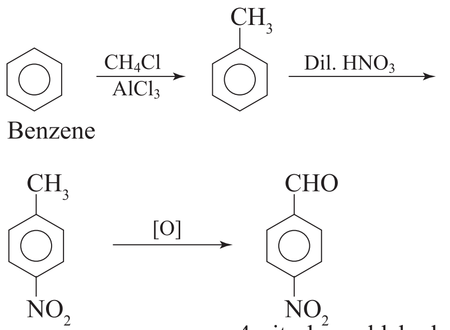
p-bromonitrobenzene o-bromonitrobenzene

On fractional crystallization para isomer crystallizes first.

(x) 4-Nitrobenzaldehyde from benzene.

[IIT 1994]

Solution

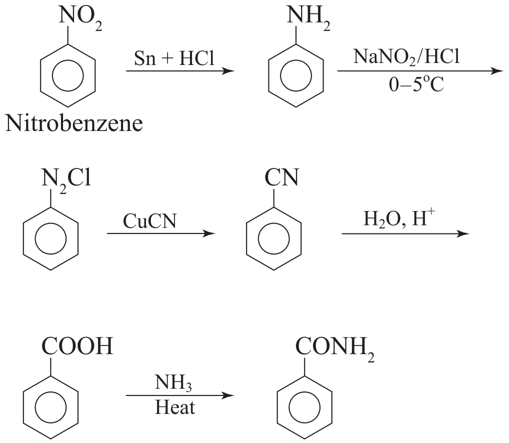


4-nitrobenzaldehyde

(xi) Benzamide from nitrobenzene

[IIT 1994]

Solution

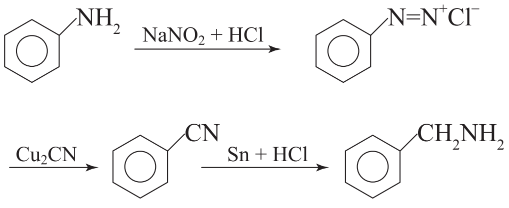


Benzamide

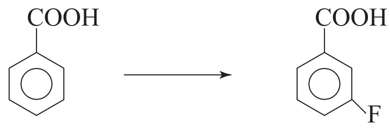
(xii) Aniline → Benzylamine (in 3 steps)

[IIT 2000]

Solution



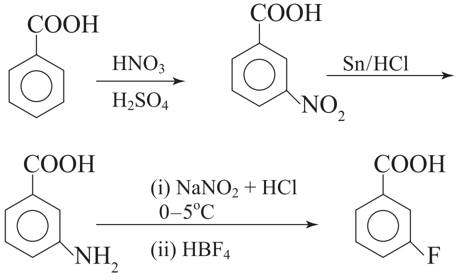
(xiii)



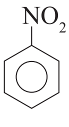
(in not more than 3 steps)

[IIT 2003]

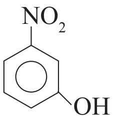
Solution



(xiv) Convert



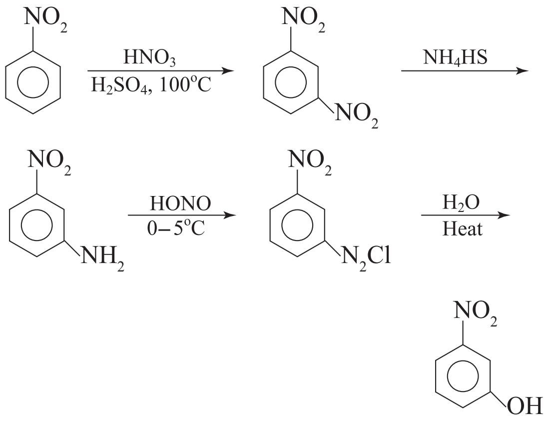
to



in not more than four steps.

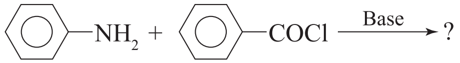
[IIT 2004]

Solution

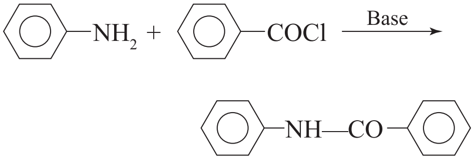


2. Complete the following with appropriate structures:

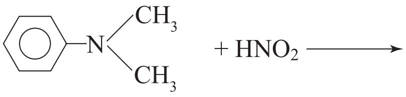
(i)



Solution

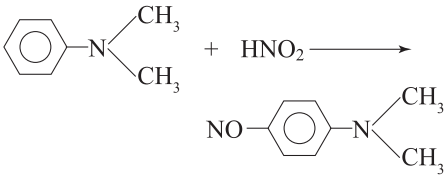


(ii)

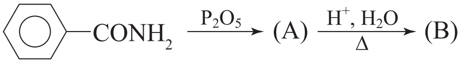


[IIT 1992]

Solution

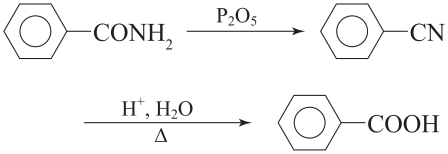


(iii)



[IIT 1992]

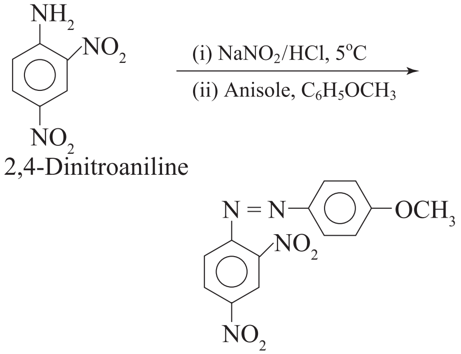
Solution



(iv) 2, 4-Dinitroaniline $\xrightarrow[\text{2.Anisole}]{\text{1.NaNO}_2\text{ \& HCl at }5^{\circ}\text{C}}$ (C)

[IIT 1995]

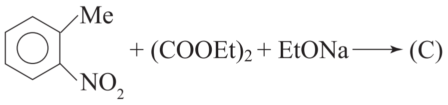
Solution



2,4-Dinitroaniline

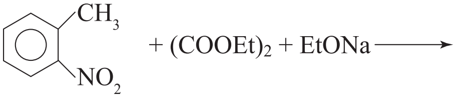
(C)

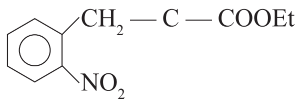
(v)



[IIT 1997]

Solution





(vi) $CH_3CH_2NH_2 \xrightarrow{(CH_3CO)_2O,\ \Delta}$ 2 Products

[IIT 1998]

Solution

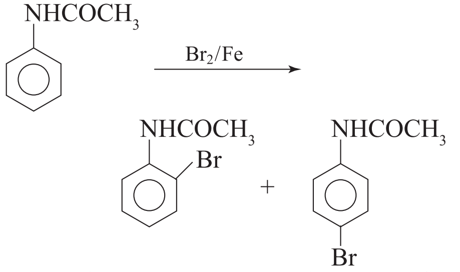
$$CH_3 - CH_2 - NH_2 \xrightarrow{(CH_3CO)_2O,\ Heat}$$

$$CH_3 - CH_2 - NH - COCH_3 + CH_3COOH$$

(vii) $CH_3CONHC_6H_5 \xrightarrow{Br_2,Fe}$ 2 Products

[IIT 1998]

Solution



o-isomer (minor) p-isomer (major)

3. Write balanced equations for the following reaction:

   Acetamide is reacted with bromine in the presence of potassium hydroxide.

Solution

Hoffmann degradation reaction is as follows:

$$\underset{\text{Acetamide}}{CH_3CONH_2} + Br_2 + 4KOH \rightarrow$$

$$\underset{\text{Methylamine}}{CH_3NH_2} + K_2CO_3 + 2KBr + 2H_2O$$

4. Give a chemical test and the reagents used to distinguish between the following pair of compounds: Ethylamine and diethylamine.

Solution

Carbylamine reaction is a distinction test for primary amines. All primary amines (aliphatic or aromatic) on heating with alcoholic KOH and $CHCl_3$ give unpleasant or foul smell of isocyanide which is easily detected.

$$C_2H_5NH_2 + CHCl_3 + \text{alc. } 3KOH \rightarrow$$

$$\underset{\text{Ethyl isocyanide}}{C_2H_5NC} + 3KCl + 3H_2O$$

5. An organic compound A, containing C, H, N and O on analysis gives 49.32 % carbon, 6.59 % hydrogen and 19.18 % nitrogen. A on boiling with NaOH gives off NH_3 and a salt which on acidification gives a monobasic nitrogen free acid B. The silver salt of B contains 59.67 % silver. Deduce the structures of A and B.

Solution

Calculation of Empirical formula:

Element	%	Mole	Simplest ratio
C	49.32	49.32 / 12 = 4.11	3
H	9.59	9.59 / 1 = 9.59	7
N	19.18	19.18 / 14 = 1.37	1
O	21.91	21.91 / 16 = 1.37	1

Empirical formula of (A) will be C_3H_7NO and empirical formula weight = 73

Calculation of molecular weight of (B):

As Meq of Ag = meq. of Ag salt

$$\frac{\text{Weight of Ag}}{\text{Eq. wt. of Ag}} = \frac{\text{Weight of salt}}{\text{Eq. wt. of salt}}.$$

$$\frac{59.67}{108} = \frac{100}{E_{Salt}}.$$

$E_{Salt} = 181$

$E_{Salt} = E_{Ag} + E_{Anion}$

$E_{Anion} = 181 - 108 = 73$

For monobasic acid (B), adding one H,

Molecular weight = Eq. wt = 73 + 1 = 74

(B) being monobasic may be represented as

$C_n H_{2n+1}$ COOH

$74 = 12n + (2n + 1).1 + 12 + 16 + 16 + 1$

On solving

$n = 2$

$B = C_2H_5COOH$

Deduction of (A):

As (B) is obtained by the reaction of A with NaOH followed by hydrolysis, so (A) is an amide, CH_3CH_2-$CONH_2$.

$$\underset{\text{(A) Propanamide}}{CH_3CH_2CONH_2} \xrightarrow{NaOH}$$

$$CH_3CH_2COONa + NH_3 \xrightarrow{HOH}$$

$$\underset{\substack{\text{(B)} \\ \text{Ethanoic acid}}}{CH_3CH_2COOH}$$

6. A mixture of two aromatic compounds A and B was separated by dissolving a chloroform followed by extraction with aqueous KOH solution. The organic layer containing compound A, when heated with alcoholic solution of KOH produced a compound C (C_7H_5N) associated with an unpleasant odour. The alkaline aqueous layer on the other hand, when heated with chloroform and then acidified gave a mixture of two isomeric compounds D and E of molecular formula $C_7H_6O_2$. Identify the compounds A, B, C, D, E and write their structures.

[IIT 1990]

Solution

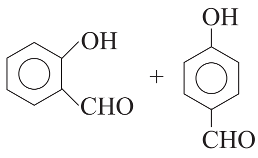
(i) Given

$$\text{Mixture of A and B} \xrightarrow{CHCl_3 + KOH\ (aq)}$$

$$\underset{(A)}{\text{Organic layer}} + \underset{(B)}{\text{Alkaline aqueous layer}}$$

(ii) As organic layer on treating with alc. KOH produces (C) of unpleasant odour (C_7H_5N), so (C) is C_6H_5NC. This is Carbylamine reaction. Hence (A) is $C_6H_5NH_2$.

$$C_6H_5OH + CHCl_3 + KOH \xrightarrow{H^+}$$



o-hydroxy benzaldehyde + p-hydroxy benzaldehyde

$$\underset{\text{(A) Aniline}}{C_6H_5NH_2} + CHCl_3 + 3KOH\ (aq) \longrightarrow \underset{(C)}{C_6H_5NC} + 3KCl + 3H_2O$$

(iii) Alkaline layer on treating with $CHCl_3$ followed with acidification gives two isomers (D) and (E) ($C_7H_6O_2$). This is Riemer-Tiemann reaction and (B) is C_6H_5OH.

7. A basic, volatile nitrogen compound gave a foul smelling gas when treated with chloroform and alcoholic potash. A 0.295 g sample of the substance dissolved in aqueous HCl and treated with $NaNO_2$ solution at 0°C, liberated a colourless odourless gas whose volume corresponds to 112 ml at STP. After the evolution of the gas was complete, the aqueous solution was distilled to give an organic liquid which did not contain nitrogen and which on warming with alkali and iodine gave a yellow precipitate. Identify the original substance. Assume that it contains one N atom per molecule.

[IIT 1993]

Solution

A basic volatile nitrogen compound is primary amine.

$$R - NH_2 + CHCl_3 + 3KOH\ (alc.) \longrightarrow \underset{\text{Foul smelling gas}}{RNC} + 3KCl + 3H_2O$$

$$\underset{\text{(It contains one N-atom)}}{R - NH_2} + NaNO_2 + \text{dil. HCl} \xrightarrow{0°C} R - OH + \underset{\text{(Colourless gas)}}{NaCl} + 2H_2O$$

At STP 112 ml of colourless gas is evolved with 0.295 g of sample of substance after treatment with aq. HCl and $NaNO_2$ at 0°C.

So at STP 22400 ml colourless gas will be evolved with $\frac{0.295 \times 22400}{112} = 59\ g$ of sample of such substance after above treatment.

Thus, the molecular weight of RNH_2 is 59.

Weight of R + 14 + 2 = 59

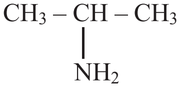
Weight of R = 43

Hence R is C_3H_7- [weight of $C_3H_7- = 43$]

Therefore the given substance may be

(i) $CH_3 - CH_2 - CH_2 - NH_2$

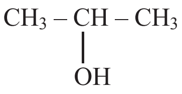
or

(ii) 

$$CH_3 - \underset{\substack{| \\ NH_2}}{CH} - CH_3$$

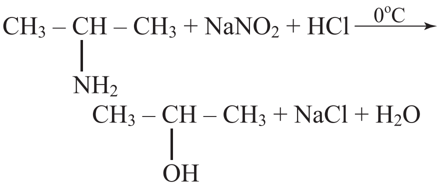
In these substances

(i) gives $CH_3 - CH_2 - CH_2OH$ with dil. HCl and $NaNO_2$ at 0°C which does not give yellow precipitate (iodoform test) with I_2 and alkali, while substance (ii) gives

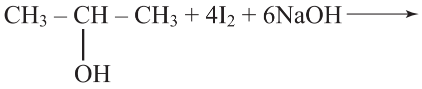


$$CH_3 - \underset{\substack{| \\ OH}}{CH} - CH_3$$

on treatment with dil. HCl and $NaNO_2$ at 0°C which gives yellow precipitate with I_2 and alkali.



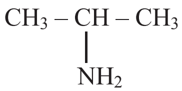
$$CH_3 - \underset{\substack{| \\ NH_2}}{CH} - CH_3 + NaNO_2 + HCl \xrightarrow{0°C} CH_3 - \underset{\substack{| \\ OH}}{CH} - CH_3 + NaCl + H_2O$$



$$CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3 + 4I_2 + 6NaOH \longrightarrow$$

$CHI_3\downarrow + CH_3COONa + 5NaI + 5H_2O$
Iodoform
(yellow ppt.)

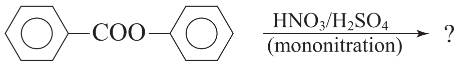
So the basic substance is



$$CH_3-\underset{\displaystyle NH_2}{\underset{|}{CH}}-CH_3$$

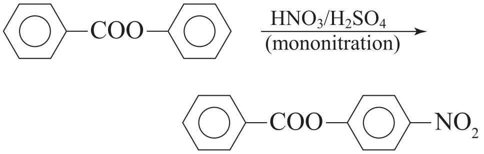
8. Identify the major product in the following reactions:

(i)

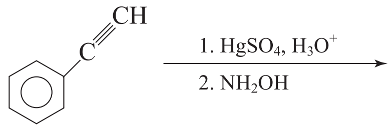


[IIT 1993]

Solution

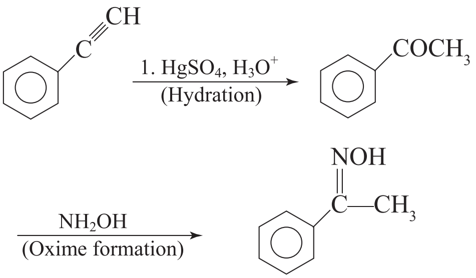


(ii)

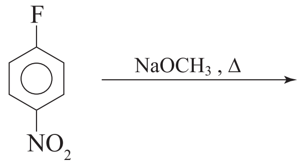


[IIT 1997]

Solution

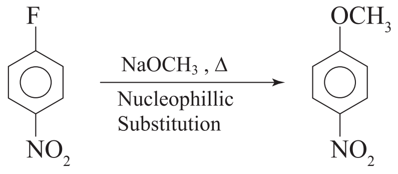


(iii)

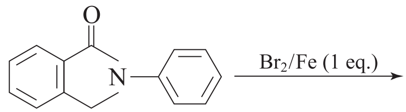


[IIT 2000]

Solution

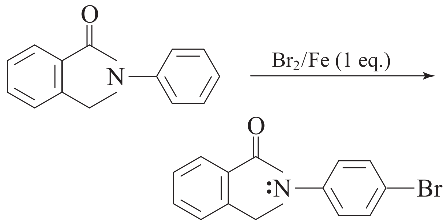


(iv)



[IIT 2000]

Solution



Deactivated benzene ring due to >C = O

Activated benzene ring due to –N<

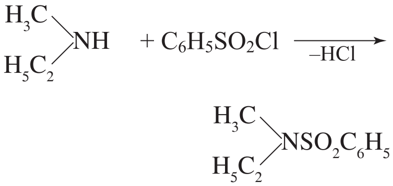
9. Identify, A (C_3H_9N) reacts with benzenesulphonyl chloride to give a solid insoluble in alkali.

[IIT 1993]

Solution

A (C_3H_9N) is a secondary amine

$CH_3 - NH - C_2H_5$ (ethylmethylamine).



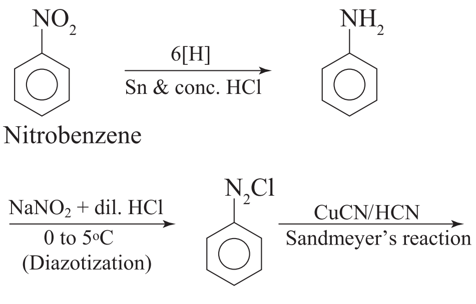
N,N-ethylmethylbenzene sulphonamide
(Insoluble in alkali)

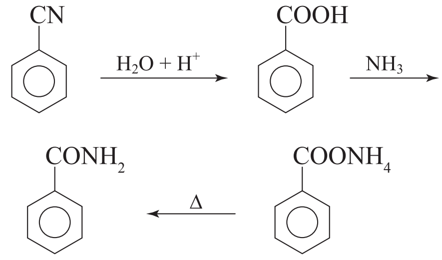
10. How will you bring about the following conversion?

"Benzamide from nitrobenzene"

[IIT 1994]

Solution





Benzamide

11. Write the structure of the foul-smelling compound obtained when aniline is treated with chloroform in the presence of KOH.

[IIT 1996]

Solution

$C_6H_5NH_2 + CHCl_3 + 3KOH \rightarrow$

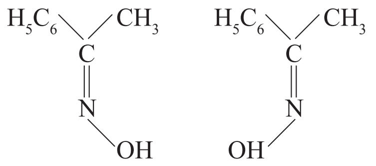
$C_6H_5N \equiv C + 3KCl + 3H_2O$

12. Acetophenone on reaction with hydroxylamine hydrochloride can produce two isomeric oximes. Write structures of the oximes.

[IIT 1997]

Solution

The structures of two isomeric oximes are as follows:

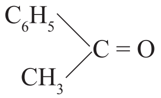


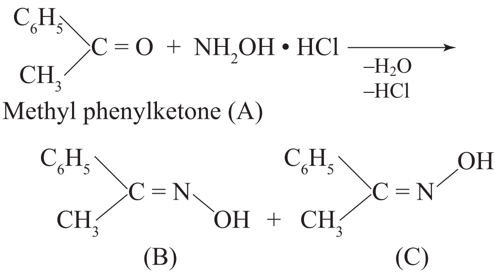
13. Compound A (C_8H_8O) on treatment with NH_2OH. HCl gives B and C. B and C rearrange to give D and E respectively, on treatment with acid. B, C, D and E are all isomers of molecular formula (C_8H_9NO). When D is boiled with alcoholic KOH an oil F (C_6H_7N) separates out. F reacts rapidly with CH_3COCl to give back D. On the other hand, E on boiling with alkali followed by acidification gives a white solid G ($C_7H_6O_2$), Identify (A – G).

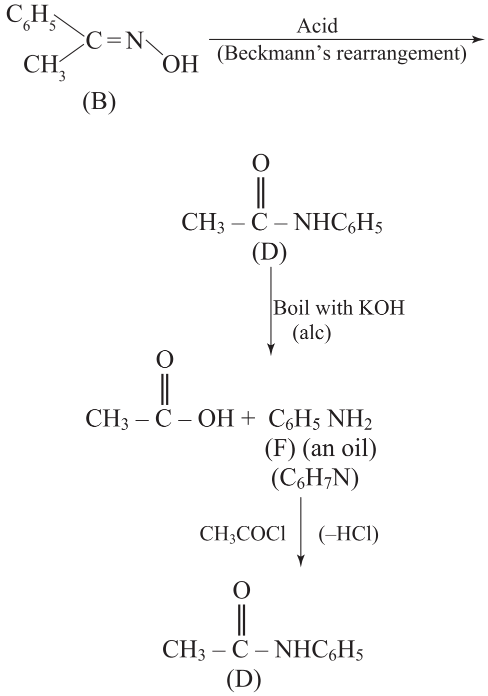
[IIT 1999]

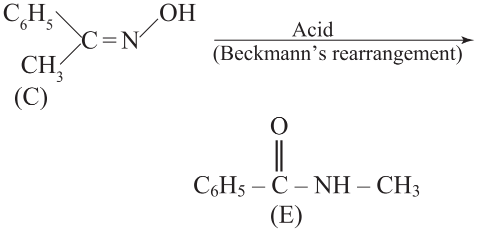
Solution

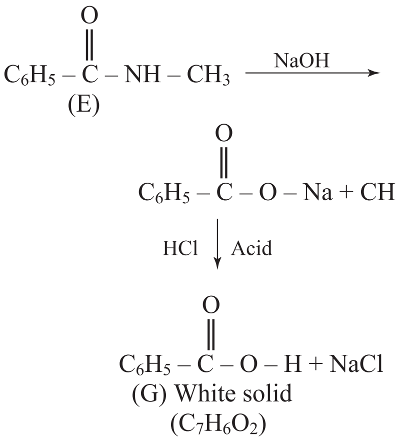
Compound A (C_8H_8O) is reacted with $NH_2OH.HCl$ and to give B and C. Hence, there are oximes. So compound A is carbonyl compound and forms oximes which show the phenomenon of geometrical isomerism. The possible structure of A may be









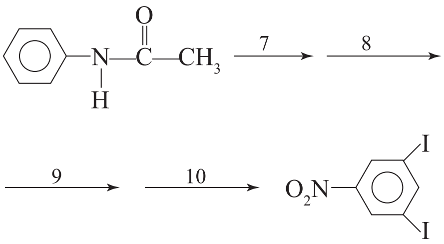


$$\underset{(E)}{C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-NH-CH_3} \xrightarrow{NaOH} C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-O-Na + CH_3NH_2 \xrightarrow[Acid]{HCl} C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-O-H + NaCl$$

(G) White solid

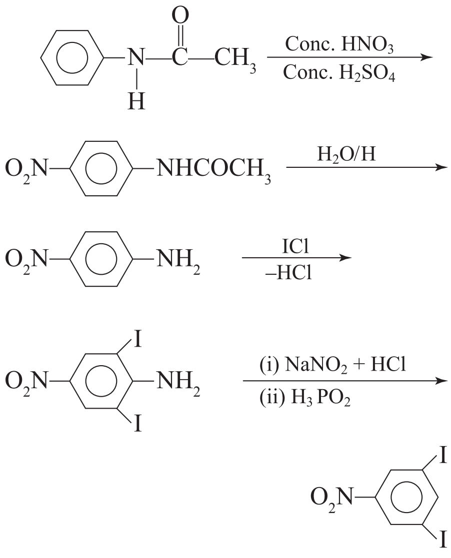
($C_7H_6O_2$)

14. Complete the following reaction with appropriate reagents:



[IIT 1999]

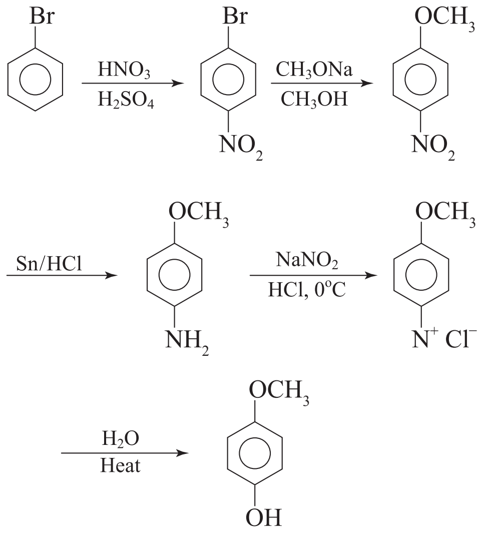
Solution



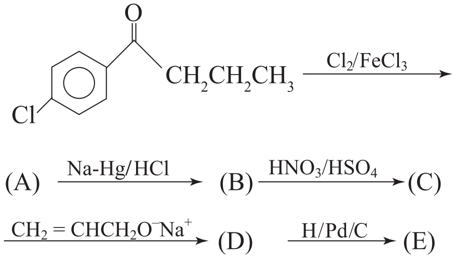
15. How would you synthesise 4-methoxyphenol from bromobenzene in not more than five steps? State clearly the reagents used in each step and show the structures of the intermediates compounds in your synthetic scheme.

[IIT 2001]

Solution

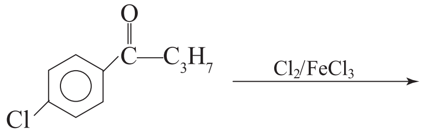


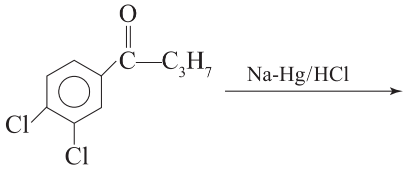
16. Write structures of the products A, B, C, D and E in the following schemes.



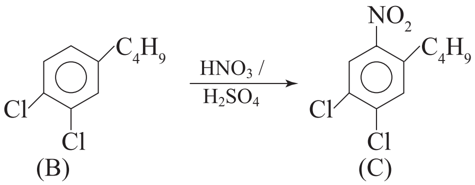
[IIT 2002]

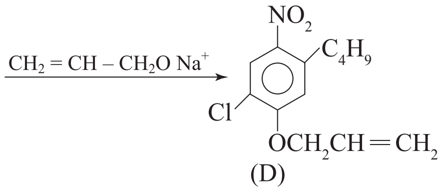
Solution



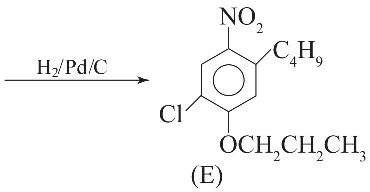


(A)





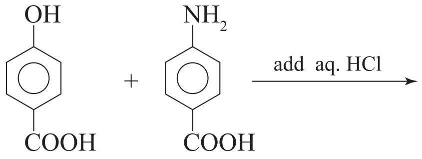
(only –C para to –NO_2 gp is replaced)



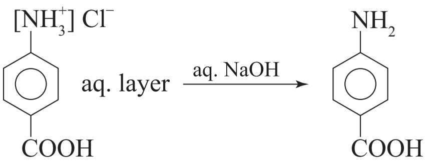
17. There is a solution of p-hydroxy benzoic acid and p-amino benzoic acid. Discuss one method by which we can separate them and also write down the confirmatory tests of the functional groups present.

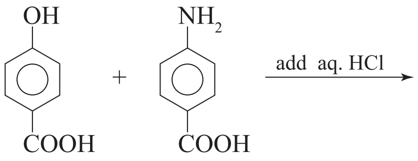
[IIT 2003]

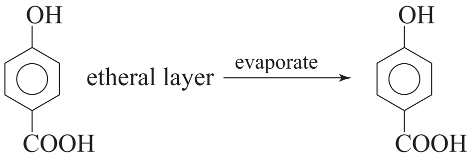
Solution



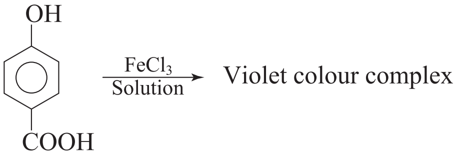
Shake with ether



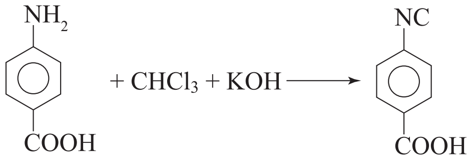




Test of Phenolic group:



Test of Primary amino group:



Characteristic foul smell of isocyanide

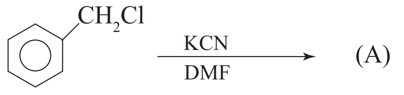
Test of –COOH group:

$$-COOH \xrightarrow{NaHCO_3} CO_2 \xrightarrow{\text{lime water}}$$

With effervescence

Milky solution

18. Identify (A) to (D) in the following series of reactions.

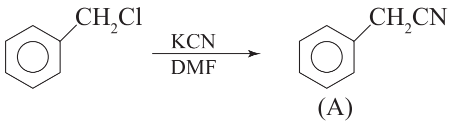


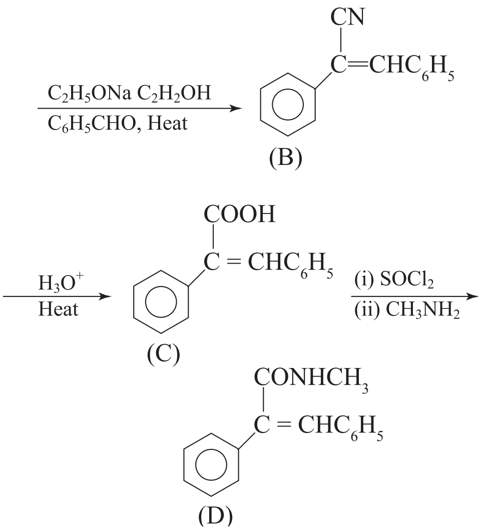
$$\xrightarrow[C_6H_5CHO,\ \Delta]{C_2H_5ONa,\ C_2H_5OH} (B) \xrightarrow[\Delta]{H_3O^+} (C)$$

$$\xrightarrow{(i)\ SOCl_2\ \ (ii)\ CH_3NH_2} (D)$$

[IIT 2004]

Solution





19. $$C_5H_{13}N \xrightarrow[-N_2]{\text{aq. NaNO}_2\text{/HCl}}$$
(optical active)

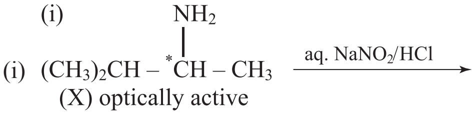
$$Y + \text{Some other products}$$
(Tertiary alcohol)

(i) Identify (X) and (Y).
(ii) Is (Y) optically active?
(iii) Give structures of intermediate, if any, in the formation of (Y) from (X).

[IIT 2005]

Solution

(i)



(i) $(CH_3)_2CH-\overset{*}{C}H(NH_2)-CH_3 \xrightarrow{\text{aq. NaNO}_2\text{/HCl}}$
(X) optically active

$(CH_3)_2C(OH)-CH_2CH_3 + NaCl + N_2 + H_2O$
(Y) 3° tertiary

(ii) (Y), a tertiary alcohol is optically inactive.

(iii) Formation of (Y) from (X).

20. Nitrobenzene is formed as the major product along with a minor product in the reaction of benzene with a hot mixture of nitric acid and sulphuric acid. The minor product consists of carbon 42.86 %, hydrogen 2.40 %, nitrogen 16.67 % and oxygen 38.07 %.

(i) Calculate the empirical formula of the minor product.

(ii) When 5.5 g of the minor product is dissolved in 45 g of benzene, the boiling point of the solution is 1.84°C higher than that of pure benzene. Calculate the molar mass of the minor product and determine its molecular and structural formula.

[IIT 1999]

Solution

Element	%	Relative number	Ratio of atoms
C	42.86	$\frac{42.86}{12}=3.57$	$\frac{3.57}{1.19}=3.00$
H	2.40	$\frac{2.40}{1}=2.40$	$\frac{2.40}{1.19}=2.00$
N	16.67	$\frac{16.67}{14}=1.19$	$\frac{1.19}{1.19}=1.00$
O	38.07	$\frac{38.07}{16}=2.37$	$\frac{2.37}{1.19}=2.00$

So empirical formula of minor product
$= C_3H_2NO_2$

Mol. wt. of minor product (m)

$$= \frac{1000 \times K_b}{\Delta T_b} \times \frac{w}{W}.$$

$$= \frac{1000 \times 2.53}{1.84} \times \frac{5.5}{45} = 168$$

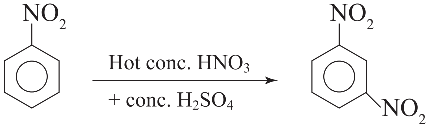
Suppose the molecular formula of minor product
$= n \times C_3H_2NO_2$

$$n = \frac{\textit{Molecular weight}}{\textit{Wt. of empirical formula}}.$$

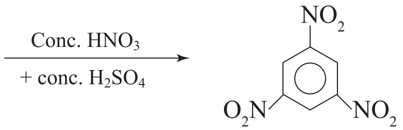
$$= \frac{168}{36+2+14+32} = 2$$

So empirical formula of minor product
$= 2 \times (C_3H_2NO_2)$
$= C_6H_4N_2O_4$

So



m-dinitrobenzene
(Minor product $C_6H_4N_2O_4$)



Trinitrobenzene
(Major product)

Questions For Self Assesments

21. An aromatic compound contains 69.4% carbon and 5.8% hydrogen. A sample of 0.303 g of this compound was analysed for nitrogen by Kjeldahl's method. The ammonia evolved was absorbed in 50 ml of 0.05 M sulphuric acid. The excess of acid required 25 ml of 0.1 M sodium hydroxide for neutralization. Determine the molecular formula of the compound if its molecular weight is 121. Draw two possible structures for this compound.

22. Give reasons for the following:

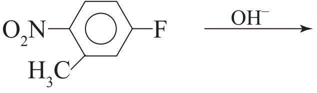
(i) Cyclohexyl amine is a stronger base than aniline.

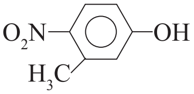
(ii) o-Nitrophenol is steam volatile whereas p-nitrophenol is not.

(iii) Dimethylamine is a stronger base than trimethylamine.

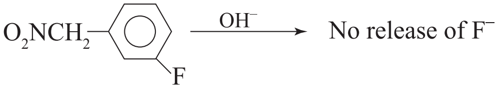
(iv) Nitrobenzene does not undergo Friedel-Crafts alkylation.

(v) (a)





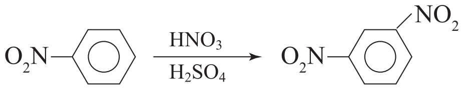
but (b)



[IIT 2005]

(vi)

but

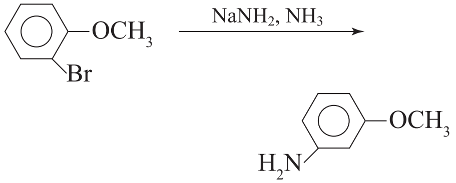


23. Arrange the following in:

(i) Increasing basicity
p-toluidine, N,N-dimethyl-p-toluidine, p-nitroaniline, aniline

(ii) methylamine, dimethylamine, aniline, N-methylamine in increasing order of base strength.

24. Explain briefly the formation of the products giving the structures of the intermediates.



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POLYMERS AND BIOMOLECULES

CHAPTER 9

CHAPTER CONTENT

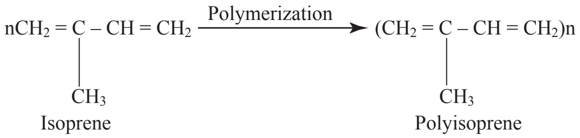
Properties and uses of some important polymers; Natural rubber, Cellulose, Nylon, Teflon and PVC. Carbohydrates : Classification ; Mono-and di-saccharides (Glucose and sucrose), Oxidation, Reduction, Glycoside formation and hydrolysis of sucrose: Amino acids peptides; General structure (Only primary structure of peptides) and Physical properties and various level of multiple-choice questions

INTRODUCTION

- A polymer is a large but a single chain-like molecule in which the repeating units derived from small molecules called monomers are held together.The process by which monomers are transformed into a polymer is called polymerization.The number of monomers which are joined together in a polymer are called Degree of Polymerization. A polymer always has a repeating structure unit or monomer while a macromolecule may or may not have such a unit.
- There are many natural polymers often called bipolymers, such as carbohydrates and proteins.
- Most synthetic polymers are long chain organic molecules and contain thousands of monomer units; such molecules have very high molecular mass and often called macromolecules.
- All polymers are macromolecules but all macromolecules are not polymers.
  For example, Haemoglobin and chlorophyll are only macromolecules and not polymers

CLASSIFICATION OF POLYMERS

- **Natural Polymer or Biopolymers** Natural polymers include starch, cellulose and natural rubber.
- Starches are polymers of glucose.
- Cellulose is also a polymer of glucose. It is made by plants from glucose produced during photosynthesis.
- Protein is obtained as a result of polymerization of α-aminoacids.
- Natural rubber is a polymer consisting of repeated units of the hydrocarbons 2-Methyl-1, 3-butadiene (isoprene).



$$n\underset{\underset{\text{Isoprene}}{CH_3}}{CH_2 = \overset{|}{C} – CH = CH_2} \xrightarrow{\text{Polymerization}} \underset{\underset{\text{Polyisoprene}}{CH_3}}{(CH_2 = \overset{|}{C} – CH = CH_2)n}$$

Synthetic Polymers

- Synthetic polymers are man-made polymers, for example, polythene, polystyrene, PVC, bakelite, nylon and Dacron.

CLASSIFICATION BASED ON SYNTHESIS

ADDITION OR CHAIN GROWTH POLYMERS It involves the repeated addition of monomers to the polymer chain. The monomers are unsaturated compounds. These are chain growth polymers.

CHAIN GROWTH POLYMERIZATION

	Monomer	Polymer
(a)	Ethylene	Polythene
(b)	Propylene	Polypropylene
(c)	Butadiene	Polybutadiene
(d)	Tetraflouoro-ethylene	Polytetraflouoroethelene (Teflon or PTFE)
(e)	Vinyl chloride	Polyvinyl chloride (PVC)

- This type of polymerization takes place by ionic as well as free radical mechanism.
- Ionic polymerization occurs in following two ways:

(a) Cationic Polymerization Here polymerization is initiated by a cation forming cationic intermediate using Lewis acids like BX_3 , AlX_3 etc.
Cationic polymerization occurs in monomer having electron releasing groups as follows
Initiation Step:

$MH + CH_2 = CH – R \rightarrow CH_3 – {}^{+}CHRM^{–}$
Lewis acid

Propagation Step:

$${}^{+}CH_3 – CHRM^{–} + CH_2 = CH – R \longrightarrow CH_3 – CHR – CH_2 – {}^{+}CHRM^{–}$$

Termination Step:

$$CH_3 – CHR – CH_2 – {}^{+}CHRM^{–} + n \ldots\ldots \longrightarrow \underset{\text{Polymer}}{CH_3 – CHR(CH_2 – CHR)_n – CH = CHR}$$

(b) Anionic Polymerization Here a negative ion or group is added in the polymerization for an ionic intermediate in initiation step like KNH_2.
Monomers having electron attracting groups undergo this type of polymerization.

For examle, Formation of polystyrene from styrene occurs in presence of KNH_2.

$$KNH_2 + CH_2 = CH\text{Ø} \rightarrow H_2N\,.CH_2 – {}^{–}CH\text{Ø}K^{+}$$

$$H_2N – CH_2 – {}^{–}CH\text{Ø}K^{+} + n\ldots\ldots \longrightarrow H_2N.\,CH_2 – CH\text{Ø} –(CH_2 – CH\text{Ø})_n – CH = CH\text{Ø}$$

- **Condensation or Step Growth Polymers**
  It involves a series of condensation reactions involving two monomers. Each monomer normally contains two functional groups.
- **Step Growth Polymerization**

	Monomer	Polymer
(a)	Adipic acid and Hexamethylene-diamine	Nylon-66
(b)	Phenol and formaldehyde	Bakelite
(c)	Terephthalic acid and ethylene	glycol Polyester (Terylene)

CLASSIFICATION BASED ON STRUCTURE

- **Linear Polymers** Such polymers have long straight chain of monomers. Such polymer chains give a close packed structure also.
- Such polymers have high tensile strength, high density, high melting points.

  For example, polythene, nylon etc.
- **Branch Chain Polymers** Here polymers have braches along with main chain of monomers.
- Such polymers have low melting point, low tensile strength, low density etc., due to lack of well packing.

  For example, Amylopectin, glycogen etc.
- **Three Dimensional Network or Crossed Linked Polymers** Such polymers have three dimensional cross linked structures. Such polymers are hard, brittle and rigid.

  For example, Bakelite, melmac etc.

CLASSIFICATION BASED ON MOLECULAR FORCES

- **Elastomers** In elastomers the polymer chains are held together by the weakest intermolecular forces or Vander Waal's forces.

  For example, Vulcanized rubber.
- **Fibers** Such polymers are used for making fibers possessing high tensile strength and high modulus. This can be attributed to the strong intermolecular forces like hydrogen bonding eg- polyamides

  (For example, Nylon-66).
- **Thermoplastics** The intermolecular forces of attraction in thermoplastic polymers are intermediary to those of elastomers and fibres. As a result, these can be easily moulded by heating. Thermoplastic polymers are formed by addition and condensation reactions and have linear structure and get soften on heating.
- In thermoplastic polymers there is no cross-linking between chains

  For example, Polythene, polystyrene etc.
- **Thermosetting** These polymers are normally made from relatively low molecular mass semi-fluid polymers which when heated in a mould become infusible and form an insoluble hard mass. This happens due to extensive cross-linking between different polymer chains.

For example, bakelite, urea-formaldehyde etc.

- Thermosetting polymers are formed by condensation reactions and have cross linked structures and do not get soften on heating.

SOME COMMERCIALLY IMPORTANT POLYMERS AND THEIR USES

(A) ADDITION POLYMERS

Polyolefins

- ***Poly Ethylene*** It is obtained from ethylene. ($CH_2 = CH_2$) It has low density. Polythene is a chain growth polymer used in making packing materials only.

  High densiy and low density polythenes: When ethylene is polymerized at high pressure of 1000 to 2000 atm and at temperature of 350 K to 570 K in presence of traces of oxygen peroxide highly branched polyethylene is formed called low density polythene. But when polymerization of ethene is carried in the persence of Zeigler-Natta catalyst at about 330 K to 350 K and at one atmospheric pressure linear structure polythene is formed, called high density polythene.

- ***Poly Propylene*** It is obtained from propylene

  ($CH_3 – CH = CH_2$)

  It is additional homopolymer of propene formed by free radical or Zeigler-Natta polymerization, It is used in packing of bags, carpet fiber etc.

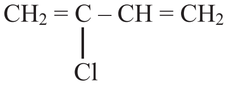
- ***Poly Styrene*** It is obtained from styrene

  ($C_6H_5 – CH = CH_2$)

  It is addition homopolymer with a linear chain like structure. It is used as insulator, wraping material and in the manufacture of toys etc.

Polydienes

- ***Neoprene*** It is obtained from Chloroprene



$$CH_2 = \underset{\displaystyle Cl}{\underset{|}{C}} – CH = CH_2$$

  2-chloro buta-1, 3-diene

  It is addition homopolymer with rubber like structure and properties. It is used in making printing rollers, shoe-hells etc.

- ***Buna–S (Butadiene-Styrene)*** It is obtained from polymerization of butadiene and styrene.

  $CH_2 = CH – CH = CH_2$ (Butadiene)
  $C_6H_5 – CH = CH_2$ (Styrene)

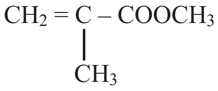
  It is an addition copolymer with a rubber like structure. It is used in making automobile tyre, water proof shoes etc.

  Buna-N (Butadiene-Acrylonitrile) It is obtained from butadiene and acrylonitrile. It is an addition copolymer with a rubber like structure. It is used in making adhesive, oil seals etc.

  $CH_2 = CH – CH = CH_2$ (Butadiene)
  $CN – CH = CH_2$ (Acrylonitrile)

Polyacrylates

- ***Polymethyl Methaacrylate (PMMA)*** It is an addition homopolymer of methyl methacrylate



$$CH_2 = \underset{\displaystyle CH_3}{\underset{|}{C}} - COOCH_3$$

It is hard, transparent and better than glass in optical clarity. It is used in making lenses, sign boards, air craft windows etc.

- ***Polyethyl Acrylate*** It is an addition homopolymer of ethylacrylate $CH_2 = CH - COOC_2H_5$
  It is used in making films, pipes etc.
- ***Polyacrylonitrile (PAN)*** It is an addition homopolymer of acrylonitrile ($CH_2 = CH - CN$)
  It is a hard and high melting point material and used in the manufacture of synthetic fiber, clothes, carpets etc.

Polyhalolefins

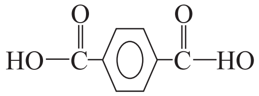
- ***Poly Tetra Fluoro Ethylene or Teflon (PTFE)*** It is chain growth homopolymer of tetrafluoroethylene ($CF_2 = CF_2$)

  It is flexible and inert to solvent acids etc so it is used in making non-sticky utensils and also in making gaskets, pumps etc.
- ***Polyvinyl Chloride (PVC)*** It is a chain growth homopolymer of vinyl chloride ($CH_2 =CH - Cl$)
  It is used in making raincoat, hand bags and insulator for wires and cables etc.
- ***Polymonochloro Trifluoro Ethylene (PCTFE)***
  It is a chain growth homopolymer of monochloro tri fluoro ethylene ($CF_2 = CFCl$)
  It is just like Teflon.

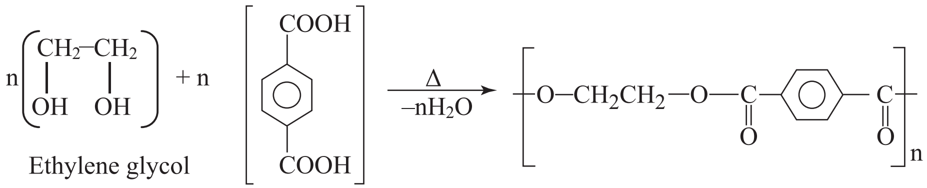
CONDENSATION POLYMERS

Polyesters

- ***Terylene or Dacron*** It is a step growth, linear copolymer of ethylene glycol ($HOCH_2 - CH_2OH$) and terephthalic acid



  It is a durable fiber used in making wash and wear fabrics and safety belts etc.

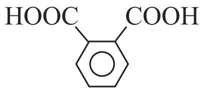


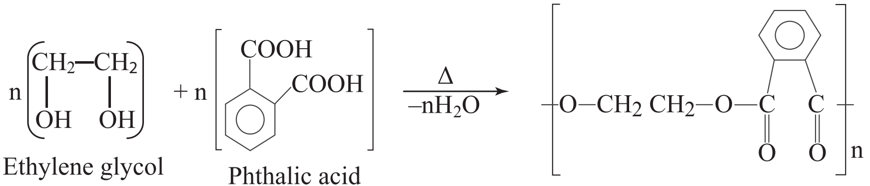
Ethylene glycol

Terephthalic acid

Dacron or Terylene

- ***Glyptal or Alkyd Resin*** It is a step growth, linear copolymer of ethylene glycol ($HOCH_2 - CH_2OH$) and phthalic acid





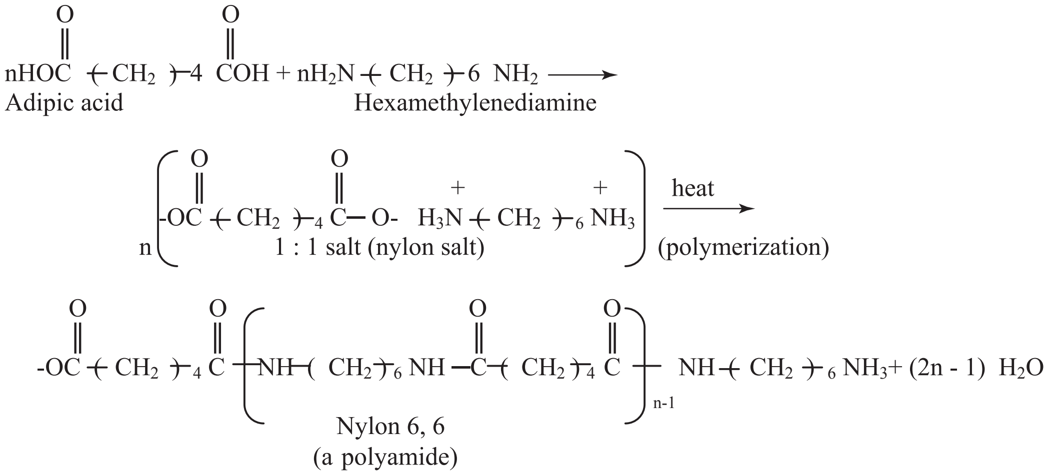
Ethylene glycol Phthalic acid

Glyptal

It is used in making paints, lacquers etc.

Polyamides

- ***Nylon-66*** It is a step growth, linear copolymer of adipic acid [$HOOC-(CH_2)_4-COOH$] and Hexamethylenediamine [$H_2N-(CH_2)_6-NH_2$]. It is used in making carpets, toothbrushes bristles, parachutes etc.



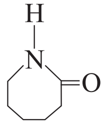
$$\underset{\text{Adipic acid}}{nHO\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}OH} + \underset{\text{Hexamethylenediamine}}{nH_2N-(CH_2)_6-NH_2} \longrightarrow$$

$$n\left(\underset{\text{1 : 1 salt (nylon salt)}}{-O\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-O^{-}\quad \overset{+}{H_3N}-(CH_2)_6-\overset{+}{NH_3}}\right) \xrightarrow[\text{(polymerization)}]{\text{heat}}$$

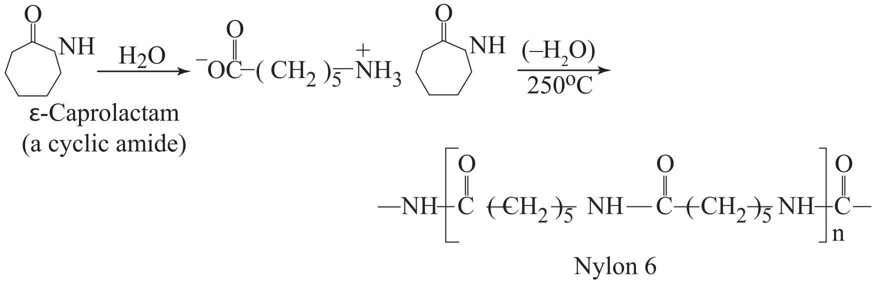
$$-O\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-\left(NH-(CH_2)_6-NH-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}\right)_{n-1}-NH-(CH_2)_6-NH_3 + (2n-1)\,H_2O$$

Nylon 6, 6
(a polyamide)

Nylon-6 It is a step growth, linear homopolymer of



caprolactam. It is used in making fabrics and tyre coarse.



ε-Caprolactam
(a cyclic amide)

Nylon 6

- ***Nylon –6, 10*** It is a step growth, linear copolymer of sebacic acid [$HOOC - (CH_2)_8 - COOH$] and Hexamethylenediamine [$H_2N - (CH_2)_6 - NH_2$]. It is used in making carpets, parachutes etc.

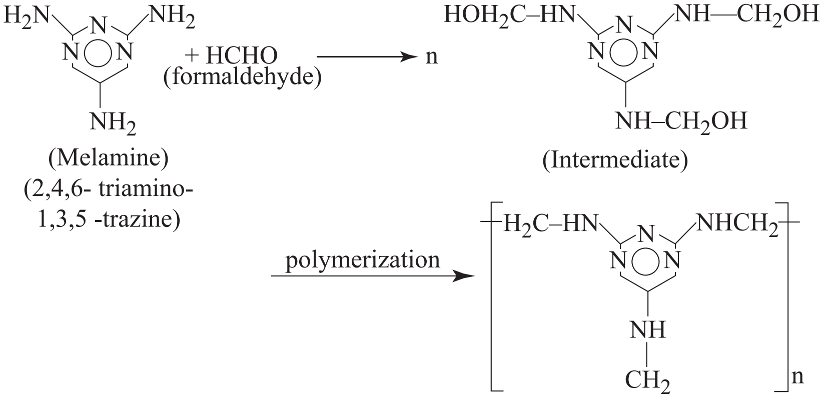
  $$\underset{\text{Hyexamethylene diamine}}{nNH_2 - (CH_2)_6 - NH_2} + \underset{\text{Sebacic acid}}{nCOOH - (CH_2)_8 - COOH}$$

  $$\xrightarrow[\text{Nylon-6,10}]{-2n\ H_2O} -(CO-(CH_2)_8 - CO - NH - (CH_2)_6 - NH - CO - (CH_2)_8 - CO -)\ n$$

- ***Nylon –2 Nylon-6*** It is a biodegradable step growth polymer and polyamide of glycine (NH_2CH_2COOH) and ∈ −aminocaproic acid ($NH_2(CH_2)_5COOH$).

Formaldehyde Resins

- **Bakelite or Phenol Formaldehyde Resin** It is a step growth, branched thermosetting copolymer of phenol and formaldehyde It is used as binding glue in varnish, lacquers, when it is in low degree of polymerization. It is used in making combs, electrical goods, gramophone records when it is in high degree of polymerization.
- **Melmac or Melamine Formaldehyde Resin** It is a step growth, branched thermosetting copolymer of melamine (2, 4, 6-triamino-1, 3, 5 tri azine) and formaldehyde. It is used in making non-breakable plastic crockery



Melamine polymer

- **Poly β-Hydroxy Butyrate–co β-Hydroxy Valarate (PHBV)** It is a step growth copolymer of β-hydroxy butyrate ($CH_3CHOH\ CH_2COOH$) and β-hydroxy valarate [$CH_3CHOH(CH_2)COOH$]. It is used in the packing of orthopedic devices.

SOME MORE POLYMERS

- **Dextron** It was the first biodegradable polyester and a polymer of polyglycolic and poly lactic acid. It is used for stitching wounds after operation.
- **Kevlar** It is a nylon polymer formed by the condensation of terephthalic and 1,4-diaminobenzene. It is used in making bullet proof vestes.
- **Nomax** It is a polyamide of m-phthalic acid and m-diaminobenzene. It is used in clothing of fire fighters, astronauts etc., as it is fire resistant.
- **Lexan** It is a polyester formed by the condensation of diethyl carbonate and bis phenol. It is used in making bullet proof windows and helmets.
- **Super Glue** It is a polymer of methyl α-cyano acrylate.
- **Novolac** It is a linear condensation polymer of phenol and formaldehyde.
- **ABS- Rubber** It is copolymer of buta-1,3-diene styrene and acrylonitrile.

ENHANCE YOUR KNOWLEDGE

- **Vulcanization** It was introduced by Charles Goodyear. He dropped a mixture of natural rubber and sulphur on to a hot stove and observed that rubber became quite strong and elastic and tougher than the natural rubber that is, Vulcanization is a process of treating natural rubber under heat and sulphur. Sulphur introduces cross-links due to which rubber becomes harder, tougher and more elastic.
- Linear polymers generally have higher magnitude of intermolecular forces of attraction and thus possess high density, high melting point and high tensile strength.
- Branch chain polymers generally have low density, low tensile strength and low melting point.
- Thermosetting polymers cannot be remoulded but thermoplastic polymers can be remoulded
- Rayon was originally called artificial silk but now a days it is a name given to artificial fibers derived from cellulose.
- Rayon can absorb over 90 per cent of its own mass of water and it does not stick to wound.
- Natural silk contains nitrogen while artificial silk may not have nitrogen.
- 80 per cent of world production of artificial silk is from Viscose Rayon.
- Natural silk on burning gives a smell of burning hair and shrinks into a ball of cinder while artificial silk gives a thread of ash.
- Terylene is a British name of Dacron.
- The family of fibers prepared from polymerisation of acrylonitrile is called Orlon.
- Co-polymer of vinyl chloride 90 per cent and vinyl acetate 10 per cent is called VINYON.
- Co-polymer of a acrylonitrile 40 per cent and vinyl chloride 60 per cent is called DYNEL.
- 15 Co-polymer of vinyl chloride and vinyledene chloride is called SARAN.
- 16 Thiokol is another variety of synthetic rubber which is a copolymer of ethylene chloride and sodium tetrasulphide (Na_2S_4).
- Gutta piareha rubber is very hard horny material consisting of trans 1, 4-polyisoprene polymer.
- Natural rubber is cis-polyisoprene and is prepared from Latex which is obtained from rubber tree (Hevea brasiliensis).
- **Plasticizer** Those plastics which do not soften very much on heating can be made soft and readily workable by the addition of certain organic compounds called plasticizers.

  For example, Dialkyl phthalates.
- **Average Molecular Weight** If $N_1, N_2, N_3 \ldots N_i$ are the number of molecules with molecular masses $M_1, M_2, M_3 \ldots . M_i$ respectively then

  (a) Weight Average Molecular Weight

  Wt = Average molecular mass ($\bar{M}_w$) is given by

  $$(\bar{M}_w) = \frac{\Sigma N_i M_i^2}{\Sigma N_i M_i}$$

  (b) Number Average Molecular Weight It is given as

  $$(\bar{M}_n) = \frac{\Sigma N_i M_i}{\Sigma N_i}$$

Poly Dispersity Index (PDI) It is the ratio of ($\bar{M}_w$) and ($\bar{M}_n$).

PDI = ($\bar{M}_w$)/($\bar{M}_n$)

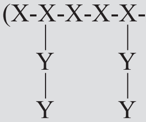
PDI is one for natural polymers but for synthetic polymers it is greater than one.

- The empirical formula of natural rubber is C_5H_8 it on heating gives CO_2 and H_2O.
- If polymers are made of a single monomer they are called Homopolymer

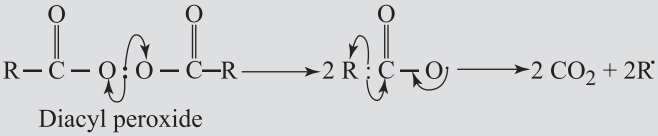
  For example, polythene, PVC.
- If one or two type of monomers form a polymer a polymer is called copolymer.

  For example, Buna-S is a polymer of Buta-1,3-diene and styrene.

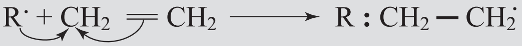
Copolymers may be random type (-Y-X-X-Y-Y-X-Y-X-X-), alternate type (-X-Y-X-Y-X-Y-X-Y-), block polymer (–X-X-X-X-Y-Y-Y-Y-Y-X-X-X-X –) and graft copolymer (X-X-X-X-X-X-X)



Radical Polymerization of Ethene

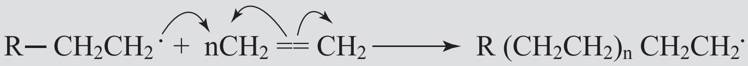


Step 2



The diacyl peroxide dissociates and releases carbon dioxide gas.
Alkyl radicals are produces, which in turn initiate chains.

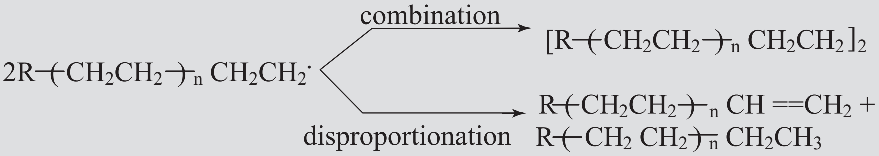
Step 3



Chain propagate by adding successive ethylene units, until their growth is stopped by combination or disproportionation.

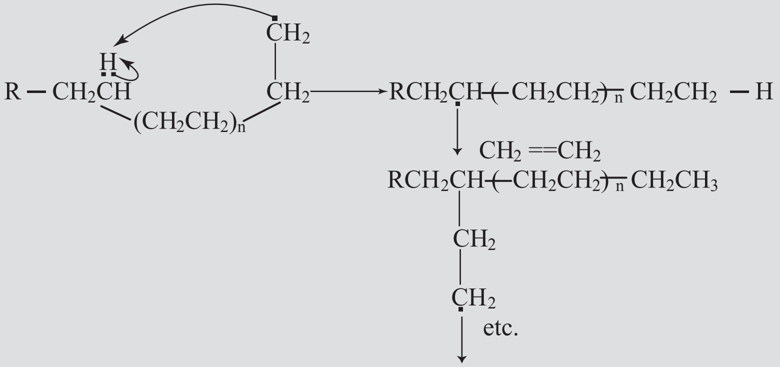
Chain Termination

Step 4

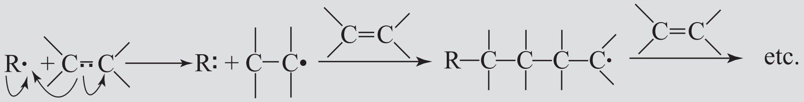


The radical at the end of the growing polymer chain can also abstract a hydrogen atom from itself by what is called "back biting". This leads to chain branching.

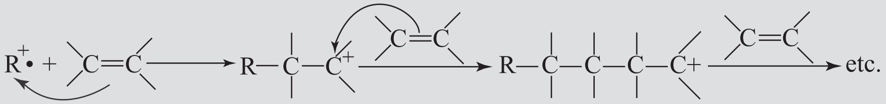
Chain Branching



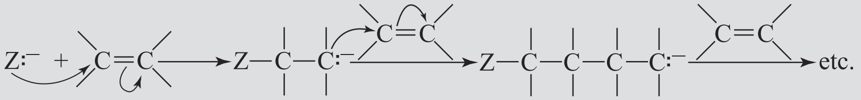
Radical Polymerization



Cationic Polymerization



Anionic Polymerization



BIOMOLECULES

- Living systems are composed of organic chemicals for example, Carbohydrates, Proteins, fats or lipid and nucleic acids.Biomolecules are the organic compounds present as essential constituents in different cells of living organisms.

CARBOHYDRATES

- Carbohydrates are optically active compounds that include polyhydroxy aldehydes or ketones with a general formula Cn.(H_2O)x. Here n or x can be 3 or 5 etc.
- These large polymeric molecules can be broken down into polyhydroxy aldehydes or ketones on hydrolysis.
- These compounds include sugars, glycogen, starchs, cellulose, dextrins and gums.

THEIR MAIN FUNCTIONS ARE

- To support the plant structure (cellulose), and
- To store chemical energy (sugars and starch).

CLASSIFICATION OF CARBOHYDRATES

Mono Saccharides These are not hydrolysed into smaller units and have a general formula $(CH_2O)_n$.

- All are sweet and show reducing properties.
- Monosaccharides are of two types Aldoses (having –CHO group) and Ketoses (having >CO group).
- There are about 20 mono saccharides occur in nature. The simplest are trioses (n = 3) for example, Glyceraldehyde, Dihydroxy acetone.
- A common pentose (n = 5) is Ribose.
- Two common hexoses (n = 6) are glucose (aldose) and fructose (ketose).
- Monosaccharides exist in the form of hemiacetals as cyclic structures (two stereomeric forms). For example, α–glucose and β–glucose also called Anomers

  $$\underset{(36\,\%)}{\alpha\text{-Glucose}} \leftrightarrow \underset{(0.02\,\%)}{\text{Open chain form}} \leftrightarrow \underset{(64\,\%)}{\beta\text{-Glucose}}$$

- Monosaccharides which differ in configuration at C_1 in aldoses while at C_2 in ketoses are known as Anomers. For example, α-D-glucose and β-D-glucose.
- These C_1 and C_2 carbon atom are called anomeric and glycosidic carbon atoms.
- The conversion of fructose into a mixture of glucose and mannose in basic conditions is given by Lobry deBruyn, van Eikenstein rearrangement.

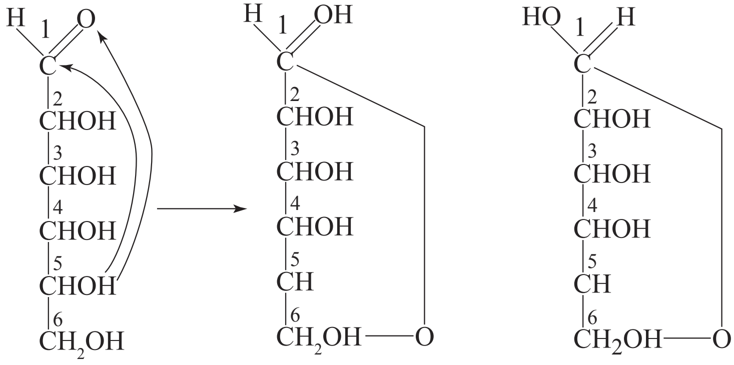
Glucose or Grape sugar or Dextrose

- Its molecular formula is $C_6H_{12}O_6$ and it is present in many fruits like grapes etc., up to 20 per cent.
- Naturally occruing glucose is dextro rotatory in nature so it is called dextrose.
- There are two form of glucose α-glucose and β-glucose and these are called anomers.
- α-glucose has a melting point of 146°C and specific optical rotation value 111° while β-glucose has a melting point 150°C and specific optical rotation 19.2°.
- When these α and β glucose are allowed to stand in water they give a rotation value of +52.5°. This spontaneous change in rotation is called muta rotation.

  $$\underset{[\alpha]_D = +112^o}{\alpha\text{-Glucose}} \leftrightarrow \underset{[\alpha]_D = +52.7^o}{\text{(equilibrium mixture)}} \leftrightarrow \underset{[\alpha]_D = +19^o}{\beta\text{-Glucose}}$$

- Glucose is prepared by the hydrolysis of sucrose with dilute H_2SO_4 in alcoholic solution.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Invertase enzyme in yeast}} \underset{\substack{\text{D-(+)-glucose} \\ +52.5^o}}{C_6H_{12}O_6} + \underset{\substack{\text{D-(–)-fructose} \\ -92.4^o}}{C_6H_{12}O_6}$$



D- Glucose
$[\alpha]_D = +53^o$

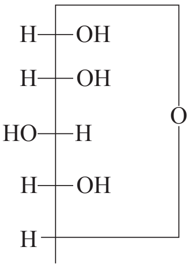
α-D- Glucose (I)
$[\alpha]_D = +112^o$

β-D- Glucose (II)
$[\alpha]_D = +19^o$

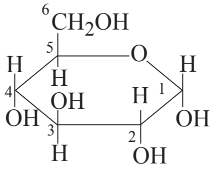
α-Glucose 36% ⇌ Open Chain form 0.02% ⇌ β-Glucose 64%

Cyclic Structures of D- glucose The open chain structure of glucose was given by Baeyer and the open chain structure can not explain following properties of D- glucose.

- It does not gives Schiff's test and also does not react with $NaHSO_3$ and NH_3.
- Pentaacetate of glucose does not react with NH_2OH indicating the absence of -CHO group.
- When acetals are formed by treating D- glucose with alcohol in the presence of dry Cl gas it adds only one molecule of alcohol.
- In crystalline from D- glucose has two different type of optical rotation.
- Howorth introduced cyclic structure of glucose which confirms the existence of α, β forms of glucose, mutarotation etc.

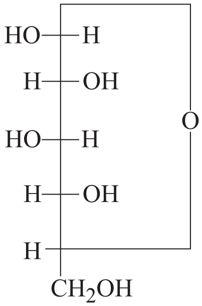


Fischer projection

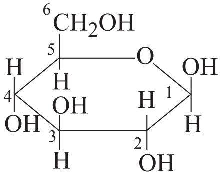


Howorth structure

α-D- glucose
Specific rotation = +111°



Fischer projection



Howorth structure

β -D- glucose
Specific rotation = + 19.2°

Mutarotation When crystal of either α- D- glucose or β- D- glucose are dissolved in water they from equilibrium mixture of both and their specific rotation is changed to a constant of + 52.5°. This phenomenon is known as mutatotation.

α - D- glucose ⇌ Equilibrium mixture ⇌ β- D- glucose
+111° + 52.5° + 19.2°

In a sample of D- glucose in solution followng equilibrium composition is found.

α - glucose ⇌ Open chain form ⇌ β- glucose
36 % 0.02 % 67 %

Anomers Molecules having same structure , same configuration everywhere except that at the first carbon are known as Anomers. e.g., α and β- glucose.

Epimers Molecules having same structure, same configuration except that at one of the chiral carbon (But not at first carbon) are known epimers of each other. For example, glucose and galactose are C_4 epimers while glucose and mannose are C_2 epimers.

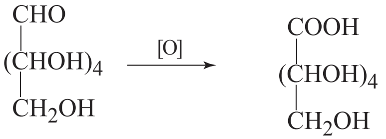
Lobry de Bruyn Van Ekenstein rearrangement In dilutre alkaline solution D- glucose , D- fructose and D-mannos are in equilibrium with each other. This reaction is known as Lobry de Bruyn Van Ekenstein rearrangement.

D-fructose which is ketose, due to this reaction can reduce Fehling solution or Tollen's reagent , as it's equilibrium mixture contain D- gluose and D- mannose which are Aldoses. Hence one can not use tollen's reagent or Fehling solution to distinguish glucose and frutose however Br_2/H_2O can be used for this purpose.

Important Reactions of Glucose

With Bromine Water Mild oxidizing agents like bromine water oxidize the aldose to the corresponding aldonic acid.

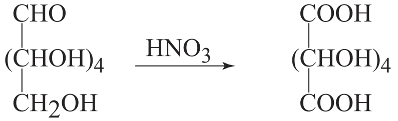
For example,



$$\begin{array}{c} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array} \xrightarrow{[O]} \begin{array}{c} COOH \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array}$$

Glucose Gluconic acid

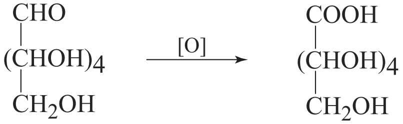
With Nitric Acid It gives a dicarboxylic acid as follows:



$$\begin{array}{c} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array} \xrightarrow{HNO_3} \begin{array}{c} COOH \\ | \\ (CHOH)_4 \\ | \\ COOH \end{array}$$

Glucose Saccharic acid

With Benedict's or Tollen's Reagents Benedict's or Tollen's reagents are mild oxidizing agents. They oxidize the aldoses to the corresponding aldonic acid as follows



$$\begin{array}{c} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array} \xrightarrow{[O]} \begin{array}{c} COOH \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array}$$

Glucose Gluconic acid

- **Reduction** Glucose is reduced to sorbitol (a hexahydric alcohol) on reaction with hydrogen in the presence of nickel as catalyst or on reaction with sodium amalgam in aqueous solution as follows:

$$HOH_2C(CHOH)_4\ CHO + H_2 \xrightarrow{Ni} HOH_2C(CHOH)_4CH_2OH$$

Sorbital

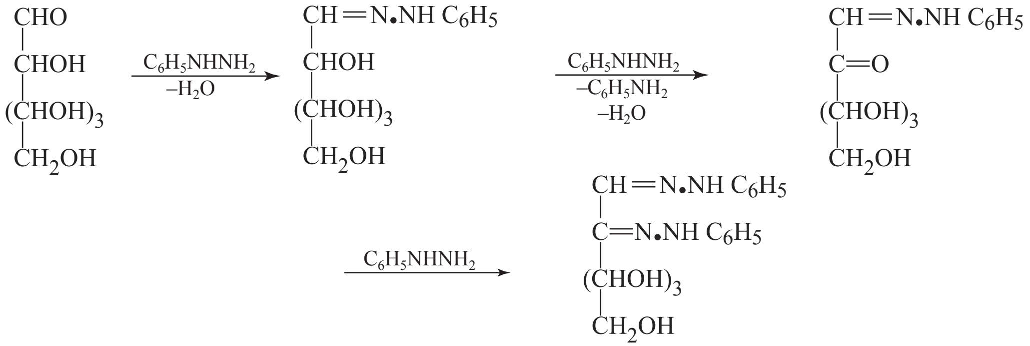
- **Ester Formation** When glucose reacts with acetic anhydride in presence of H_2SO_4, a pentacetyl derivative of glucose is obtained. It confirms glucose has 5 –OH groups.

$$\mathrm{HOH_2C.(CHOH)_4.CHO + 5\,Ac_2O \longrightarrow CH_2OAc.(CHOAc)_4.CHO + 5AcOH}$$

- **Ether Formation** Glucose reacts with dimethyl sulphate in presence of alkali to form penta-o-methyl derivative.

$$\mathrm{HOH_2C.(CHOH)_4.CHO + (CH_3)_2SO_4 \longrightarrow H_3COCH_2.(CHOCH_3)_4.CHO + 5CH_3HSO_4}$$

- **Osazone Formation** Glucose on reaction with phenyl hydrazine forms phenyl hydrazone. However, when warmed with excess of phenyl hydrazine, each glucose molecule reacts with three molecules of phenyl hydrazine and gives osazone.



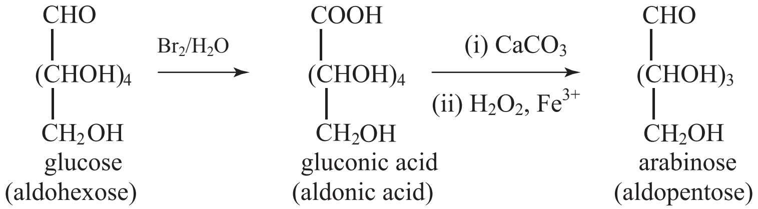
$$\begin{array}{l}\mathrm{CHO}\\ |\\ \mathrm{CHOH}\\ |\\ \mathrm{(CHOH)_3}\\ |\\ \mathrm{CH_2OH}\end{array} \xrightarrow[-\mathrm{H_2O}]{\mathrm{C_6H_5NHNH_2}} \begin{array}{l}\mathrm{CH{=}N.NH\,C_6H_5}\\ |\\ \mathrm{CHOH}\\ |\\ \mathrm{(CHOH)_3}\\ |\\ \mathrm{CH_2OH}\end{array} \xrightarrow[\substack{-\mathrm{C_6H_5NH_2}\\ -\mathrm{H_2O}}]{\mathrm{C_6H_5NHNH_2}} \begin{array}{l}\mathrm{CH{=}N.NH\,C_6H_5}\\ |\\ \mathrm{C{=}O}\\ |\\ \mathrm{(CHOH)_3}\\ |\\ \mathrm{CH_2OH}\end{array} \xrightarrow{\mathrm{C_6H_5NHNH_2}} \begin{array}{l}\mathrm{CH{=}N.NH\,C_6H_5}\\ |\\ \mathrm{C{=}N.NH\,C_6H_5}\\ |\\ \mathrm{(CHOH)_3}\\ |\\ \mathrm{CH_2OH}\end{array}$$

Glucosazone

Fructose also forms some osazone on reaction with phenyl hydrazine.

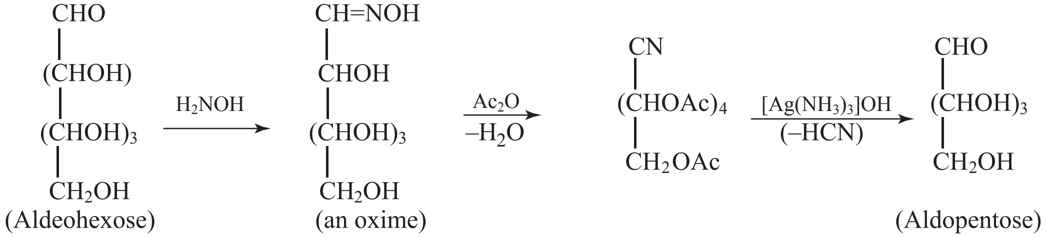
Chain shorting and lengthening

(i) Ruff Degradation In this method, the glucose (aldohexose) is converted to arabinose (aldopentose).



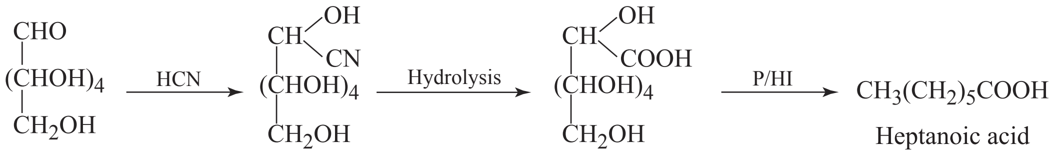
$$\begin{array}{c}\mathrm{CHO}\\ |\\ \mathrm{(CHOH)_4}\\ |\\ \mathrm{CH_2OH}\\ \text{glucose}\\ \text{(aldohexose)}\end{array} \xrightarrow{\mathrm{Br_2/H_2O}} \begin{array}{c}\mathrm{COOH}\\ |\\ \mathrm{(CHOH)_4}\\ |\\ \mathrm{CH_2OH}\\ \text{gluconic acid}\\ \text{(aldonic acid)}\end{array} \xrightarrow[\text{(ii) } \mathrm{H_2O_2,\ Fe^{3+}}]{\text{(i) } \mathrm{CaCO_3}} \begin{array}{c}\mathrm{CHO}\\ |\\ \mathrm{(CHOH)_3}\\ |\\ \mathrm{CH_2OH}\\ \text{arabinose}\\ \text{(aldopentose)}\end{array}$$

(ii) Wohl degradation This method involves the treatment with H_2NOH, $(CH_3CO)_2O$, $Ag(NH_3)_2^+/OH^-$.



$$\begin{array}{c}\mathrm{CHO}\\ |\\ \mathrm{(CHOH)}\\ |\\ \mathrm{(CHOH)_3}\\ |\\ \mathrm{CH_2OH}\\ \text{(Aldeohexose)}\end{array} \xrightarrow{\mathrm{H_2NOH}} \begin{array}{c}\mathrm{CH{=}NOH}\\ |\\ \mathrm{CHOH}\\ |\\ \mathrm{(CHOH)_3}\\ |\\ \mathrm{CH_2OH}\\ \text{(an oxime)}\end{array} \xrightarrow[-\mathrm{H_2O}]{\mathrm{Ac_2O}} \begin{array}{c}\mathrm{CN}\\ |\\ \mathrm{(CHOAc)_4}\\ |\\ \mathrm{CH_2OAc}\end{array} \xrightarrow[(-\mathrm{HCN})]{\mathrm{[Ag(NH_3)_3]OH}} \begin{array}{c}\mathrm{CHO}\\ |\\ \mathrm{(CHOH)_3}\\ |\\ \mathrm{CH_2OH}\\ \text{(Aldopentose)}\end{array}$$

- **Formation of Cyanohydrin** Glucose on reaction with hydrogen cyanide gives cyanohydrin. Hydrolysis of the cyanohydrin and reduction of the acid obtained with P/HI yields heptanoic acid as follows



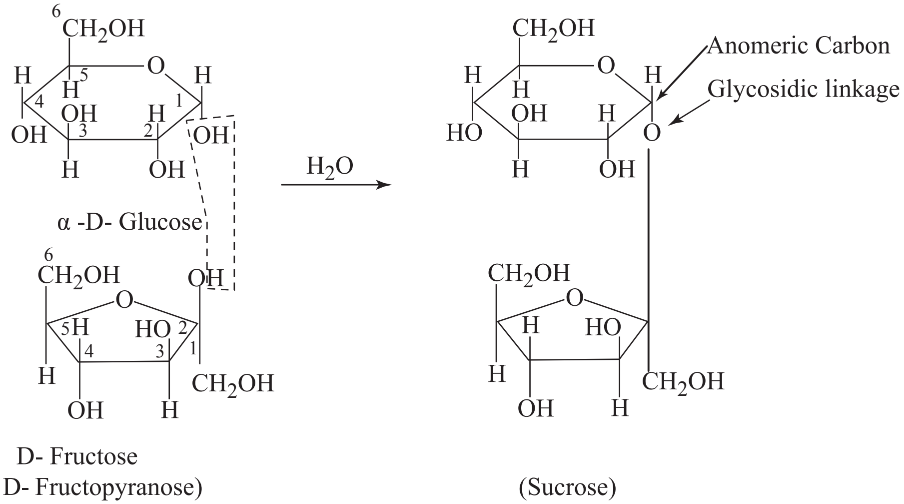
Oligosaccharides These on hydrolysis give 2-10 molecules of monosaccharides and are of following types

Disaccharides These form two mono saccharides molecules (same or different) on hydrolysis and have a general formula $C_{12}H_{22}O_{11}$.

- These are formed by a condensation reaction between two mono saccharides.
  For example, Sucrose is made up of one unit of glucose and one unit of fructose, while lactose is made of one unit of each glucose and galactose.
- These also show reducing properties except sucrose.
- **Sucrose or Cane Sugar** It is dextro rotatory and on hydrolysis it gives dextro rotatory glucose and laevorotatory fructose. It is called invert sugar and the reaction is called inversion.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Invertase enzyme in yeast}} \underset{\substack{\text{D-(+)-glucose} \\ +52.5^\circ}}{C_6H_{12}O_6} + \underset{\substack{\text{D-(–)-fructose} \\ -92.4^\circ}}{C_6H_{12}O_6}$$

- Here, overall mixture is laevorotatory.
- It is mainly obtained from sugar cane or beet root. It is a specific rotation of +66.5°.

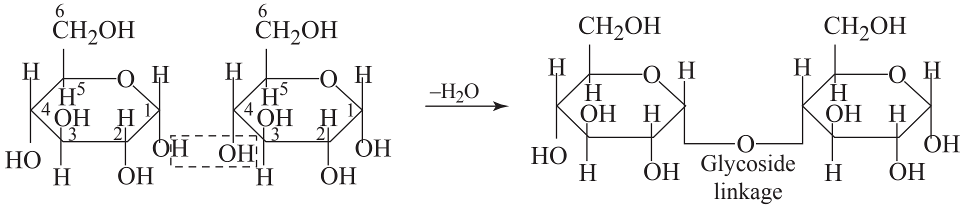


D- Fructose
(β- D- Fructopyranose)
(a)

(Sucrose)
(b)

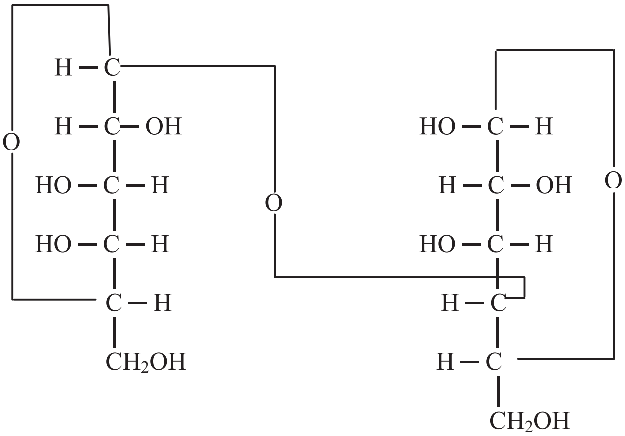
- **Maltose or Malt Sugar** It is a reducing sugar which is obtained by the hydrolysis of starch carried out by diastase enzyme.
- It has C_1 to C_4 linkage α-glucosidic linkages.
- On hydrolysis gives two moles of dextro rotatory glucose.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Maltase enzyme in yeast}} \underset{\underset{+52.5^{o}}{\text{D-(+)-glucose}}}{2C_6H_{12}O_6}$$



α -D- Glucose α -D- Glucose Maltose

- **Lactose or Milk Sugar** It is present in milk however mainly obtained from Whey (left after coagulation and separation of milk protein).
- On hydrolysis gives one molecule of each D-(+)-glucose and D-(+)-galactose.



β -(D) galactose β -(D) glucose

Lactose

Polysaccharides These produce large number of mono saccharides on hydrolysis and these are most common carbohydrates in nature. These are formed by linking together a large number of monosaccharide units through glycosidic linkage.

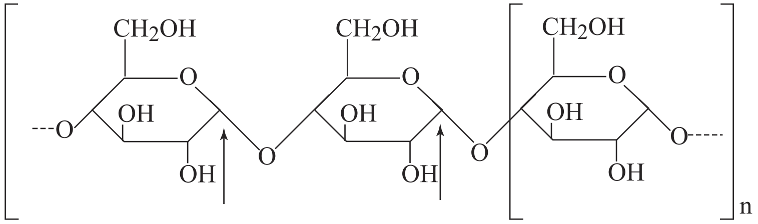
- Polysaccharides are amorphous, tasteless and insoluble in water and called non-sugars.
- Polysaccharides have mainly one of the two functions food storage or structural role.
  For example, Starch, Cellulose, glycogen etc.

Starch $(C_6H_{10}O_5)n$

Starch is the main storage polysaccharides of plants and present in seeds, tubers, roots etc. Some major sources of starch are wheat, rice, corn potato etc.

- It is a polymer of α–glucose and consists of two components amylose (20%) and amylopectin (80%).
- Molecular weight of amylose is in between 10000–1000000 while amylopectin 50000–10,0000000 Amylose, the water soluble fraction, is a linear polymer of α–glucose. It gives violet colouration with iodine solution as an inclusion complex is formed.

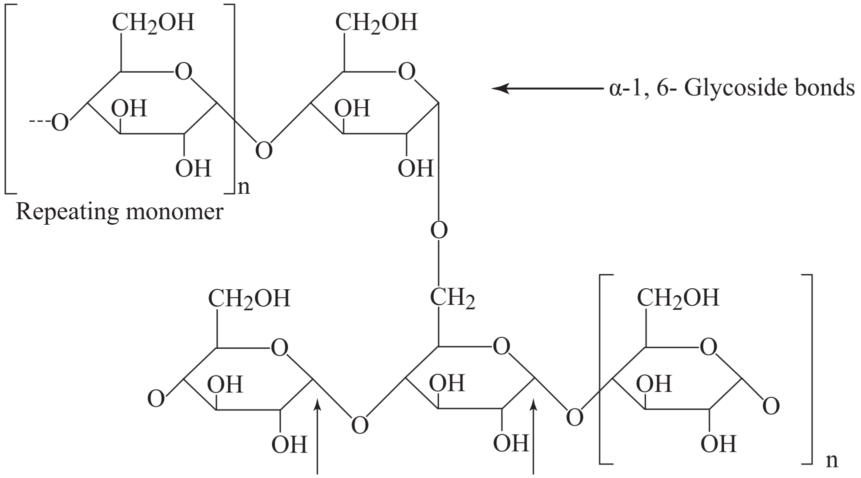
- Amylopectin, the water insoluble fraction, consists of branched chains of α–glucose.
- Starch is a food reserve in plants but food reserve in animals is glycogen.



α-1, 4-Glycoside bonds

Repeating monomer

Structure of amylose



α-1, 6- Glycoside bonds

Repeating monomer

α-1,4- Glycoside bonds

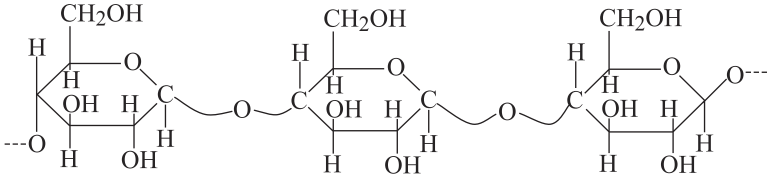
Repeating monomer

Structure of Amylopectin

Cellulose ($C_6H_{10}O_5$)n

- Cellulose is the major structural polysaccharide in higher plants. Cellulose is a linear polymer of β–glucose.
- Wood is a combination of cellulose (50 per cent) and lignins and resins (50 per cent).
- Cotton is pure cellulose (90 per cent) and rest is fats and waxes.

Cellulose can be easily converted into fibers due to its linear structure.



Structure of Cellulose

REMEMBER

- In human digestive system cellulose is undigestable as enzymes are not present to hydrolyse cellulose into glucose however it is possible in grazing animals.
- Collodion used in the manufacture lacquers is a solution that is pyroxylin (cellulose dinitrate and cellulose mononitrate) in alcohol and ether.
- Gun cotton (cellulose trinitrate) is a binder for solid rocket propellant and also used in making smoke less powders.
- Cellulose fibers are called Rayon.
  For example, Acetate rayon is cellulose diacetate.
- Viscose is an alkali solution of cellulose xenthate in NaOH.

Glycogen ($C_6H_{10}O_5$) It is reserved carbohydrates of animals which is stored in their liver and muscles. It is a branched condensation polymer of α-glucose.

Gum and Pectins

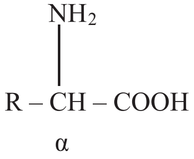
- Gum and pectins are also polysaccharides, gum arabic is exerted by trees while pectins are found in fruit skins and are extracted by boiling. Citrus rends contain 30 per cent pectin.

Test of Carbohydrates

- **Molisch's Test** It is used to detect all kind of carbohydrates. When molisch reagent (1 per cent alcoholic solution α-naphthol) is added in the aqueous solution of carbohydrate and then conc. H_2SO_4 is added a violet ring is formed at the junction of the two layers.

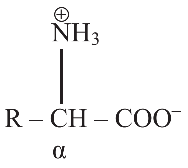
AMINO ACIDS

- Amino acids are carboxylic acids having an $-NH_2$ group also when it is at α-position these are called α-amino acids.



$$R-\underset{\alpha}{\overset{\overset{NH_2}{|}}{C}}H-COOH$$

- Except glycine all other α-amino acids are optically active. All naturally occurring α –amino acids are L-type and 26 in number.
- α-amino acids are the building blocks of proteins and 20 amino acids are present in nearly all proteins.
- α-amino acids are crystalline solids fairly soluble in water and having high melting points.
- α-amino acids can exist as Zwitter ions or dipolar ions.



$$R-\underset{\alpha}{\overset{\overset{\oplus}{N}H_3}{\overset{|}{C}}}H-COO^-$$

Isoelectric Point It is the pH value at which an amino acid exists as a neutral zwitter ion and has minimum solubility.

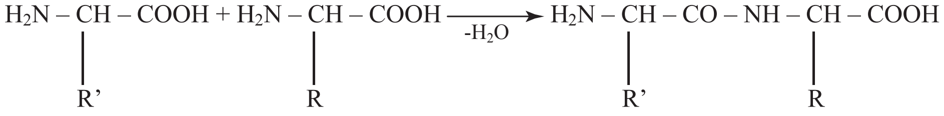
Non-Essential Amino Acids or Dispensable Amino Acids These can be synthesized in body, these are ten in number.

Essential Amino Acids These cannot be synthesized in the body and also known as indispensable amino acids. Their deficiency causes Kwashiorkor disease.

For example, Valine, Lucine, , Isolucine, Lysine, Threonil, Phenyl alanine Metionyl, tryptophan, histidine and Arginine.

Peptide Bond or Peptide Linkage Peptides are those amides which are formed due to condensation between $-NH_2$ group and –COOH group of two different amino acids.

- The –CO– NH- bond is called peptide linkage or bond.



$$H_2N-\underset{\underset{R'}{|}}{CH}-COOH+H_2N-\underset{\underset{R}{|}}{CH}-COOH\xrightarrow[-H_2O]{}H_2N-\underset{\underset{R'}{|}}{CH}-CO-NH-\underset{\underset{R}{|}}{CH}-COOH$$

Dipeptide

- An amino acid unit having free NH_2 group is known as N-terminal end while an amino acid with a free –COOH group is known as C-terminal end.
- N-terminal amino acid residue in a protein is determined by Sanger (1-fluoro-2, 4-dinitrobenzne) or DNP (2, 4-nitrophenyl).
- C-terminal amino acid residue in a protein is determined by hydrazinolysis.
- During writing the structures of peptides N-terminal end is taken on LHS while C-terminal end is at RHS side.

Rama Chandaran Angles It is possible to explain the conformatin of a protein molecule that is, polypeptide chain in the form of angle ψ between R_1 CH – CO– bonds and angle Φ between R_1 CH – NH – bonds. These two angles are called Ramachandaran angles.

PROTEINS

- Proteins are complex nitrogenous compounds present in living cells of plants and animals which are essential for the growth and maintenance of life.
- Proteins are polyamides formed from condensation of α-amino acids with a molecular weight greater than 10,000.
- The α-carbon atom of the amino acids is asymmetric and shows optical isomerism.
- Proteins mainly consist of *l* isomers of amino acids.
- There are 20 commonly occuring amino acids in proteins. Amino acids form zwitter ions.
- Lack of essential amino acids in diet can cause diseases such as Kwashiorkar.

Classification of Proteins Proteins are of two types:

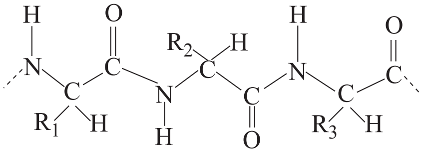
- **Fibrous Proteins** These are liner thread like molecules in which polypeptide chains are held together by hydrogen bonding.
- Such proteins are insoluble in water and quite stable to moderate change in temperature and pH value.

  For example, Keratin in skin, nails, hair. Myosin in muscles, fibroin in silk.

- **Globular Proteins** In such proteins the polypeptide chains get folded to give a spheroidal shape due to hydrogen bonding, van der Waal forces, dipolar interaction and disulphide bridging.
- Such proteins are soluble in water and change with a change of temperature and pH.
  For example, enzyme, haemoglobin, antibodies, insulin etc.

STRUCTURE OF PROTEINS

- Amino acids are joined together by an amide linkage called peptide bond.
- Proteins are long polymers of amino acids linked by peptide bonds (polypeptides).
- The sequence in which the amino acids are arranged in a protein is called the primary structure.



Primary structure of proteins

- **The Secondary Structure** arises due to the regular folding of the backbone of the polypeptide chain due to intramolecular hydrogen bonding between the carboxyl and amino groups.
- **α-Helix** When the size of the 'R' is large , intramolecular Hydrogen bonds are formed between C = O of one molecule and -NH of the fourth amino acid in the polypeptide chain to give right handed α-helix structure to the protein molecule. For example, α-keratin in skin, nails etc. Myosin in muscles, fibroin in silk.
- **β-Helix or β-Pleated Sheet Structure** When the size of the groups R is small, intermolecular Hydrogen bonds are formed between C = O of one polypeptide chain with -NH of the other chain to give a β-flat sheet structure to the protein molecule.
- When the size of the groups is moderate, the polypeptide chains contract a little to give a β-pleated sheet structure to protein molecule, that is, silk protein fibroin.
- **The Tertiary Structure** is the three-dimensional structure of globular proteins it arises due to the folding and superimposition of various secondary structural elements.
- **Denaturation** Various changes in the surroundings of a protein such as pH, temperature, presence of salts or certain chemical agents can disrupt the complex three-dimensional structure (conformation) of the proteins.
- Disruption of the native conformation of a protein will cause the protein to loose its biological activity. For example, On boiling an egg the albumins get coagulated.
- During formation of cheese from milk the globular protein lactalbumin becomes fibrous.
- The function of protein is to act as structural material of animal tissues, metabolic regulator, enzymes and antibodies.

DETECTION OF PROTEIN

- **Biuret Test** Alkaline solution of proteins gives violet colouration with 1 per cent copper sulphate solution due to formation of complex between Cu^{2+} peptide linkage.

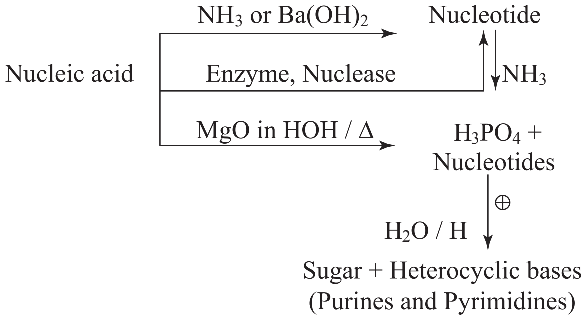
- **Millon's Test** Aqueous solution of protein (except tyrosine) gives a white precipitate with millon's reagent (Mercurous nitrate and mercuric nitrate in HNO_2).
- **Nin-Hydrin Test** Protein on boiling with dilute aqueous solution of nin-hydrin (2, 4-dihydroxy indane-1, 3-dione) gives blue violet colouration.
- **Xantho Protein Test** Here protein having tyrosine, phenyl alanine amino acids gives yellow colour with conc. HNO_3.

NUCLEIC ACID

- These are biomolecules present in the nuclei of all living cells in the form of nucleoproteins. Nucleic acids play an essential role in transmission of the hereditary characteristics and in the biosynthesis of proteins.
- Nucleic acids are the long polymers in which the monomeric units are nucleotides. The nucleotides are made up of three chemical components; a nitrogen containing heterocyclic base, a five-carbon sugar and a phosphoric acid. In nucleic acids, the individual nucleotides are linked through phosphate groups to give rise to long polynucleotide structures.

NUCLEIC ACID

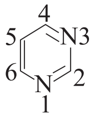
- There are two classes of nucleic acids DNA (deoxyribonucleic acid) and RNA (ribonucleic acid).
- Nucleic acids contain the element carbon, oxygen, nitrogen, hydrogen and phosphorus.
- They are bipolymers with molecular weight ranging from 10^6 to 10^8.
- They are polymers of nucleotides.
- All nucleic acids can undergo stepwise degradation to three fundamentals units:
  a heterocyclic base, a pentose sugar and phosphoric acid.



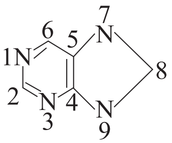
SUGARS Two sugars present in nucleic acids are: Ribose and Deoxy ribose.

- Ribose is present in RNA and Deoxyribose is present in DNA. These sugars are present in furanose form.

BASES The bases that occur in nucleic acids are derivatives of pyrimidine and purine.

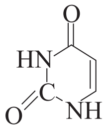


Pyrimidine

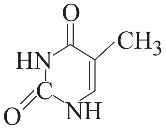


Purine

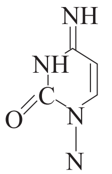
- Pyrimidine bases are uracil, thymine and cytosine.



Uracil

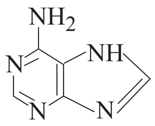


Thymine

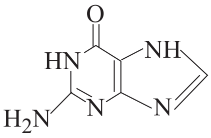


Cytosine

- The purine bases found in nucleic acids are adenine and guanine.



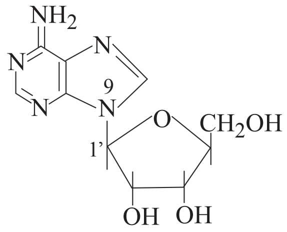
Adenine



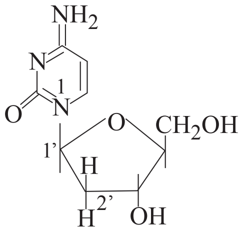
Guanine

NUCLEOSIDES These are β - glycosides of D-ribose or D-deoxyribose whose aglycones are pyrimidine of purine bases.

In purine nucleosides the C-1 of sugar is attached to N-9 of purines and in pyrimidine nucleosides, the C-1 of sugar is attached to N-1 of pyrimidines.

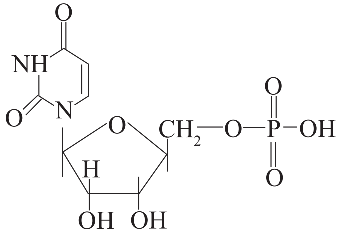


Adenosine



Adenosine 2'-Deoxy-cytosine

NUCLEOTIDES It is phosphoric ester of nuceloside. Esterfication always takes place between– OH of sugar and– OH of phosphoric acid.



Uridine monophosphate (UMP)

Abbreviated Names of Nucleotides Number of phosphate groups are indicated as follows

MP → monophosphate

DP → Diphosphate

TP → Triphosphate

AMP → Adenosine monophosphate

ADP → Adenosine diphosphate
ATP → Adenosine triphosphate
Bases are abbreviated as follows
A → Adenine
G → Guanine
C → Cytosine
U → Uracil

STRUCTURE OF RNA AND DNA

- The sequence of bases along the DNA or RNA chain shows primary structures of these and it controls the specific properties of nucleic acids.
- An RNA molecule is usually a single chain of ribose containing nucleotides.
- DNA consists of two long strands of polynucleotides coiled around each other in the form of a double helix (Watson and Crick model) ladder like structure joint together by hydrogen bonding.
- Here Hydrogen bonding is in between the nitrogenous base molecules of the nucleotide monomer.

  For example, Adenine with thymine forms two hydrogen bonds while guanine forms three hydrogen bonds with cytosine.
- Here thymine combines only with deoxyribose sugar while uracil combines with only ribose sugar.

Differences Between DNA and RNA

- DNA has D-2-deoxy ribose sugar while RNA has D-ribose sugar.
- DNA has Cytocine and Thymine (pyrimidine bases) and Guanine and Adenine (purine bases) while RNA has Uracil in place of Thymine.
- DNA is a double chain of polynucleotides while RNA is a single chain of polynucleotide.
- DNA can undergo replication but not RNA.
- DNA controls structure metabolism and genetic information while RNA regulates protein synthesis.

Functions of Nucleic Acids Nucleic acid has mainly these two functions.

- **Replication** The genetic information for the cell is contained in the sequence of the bases A, T, G and C in the DNA molecule.
- When a cell divides, DNA molecules replicate to make exactly same copies of themselves so that each daughter cell will have DNA identical to that of the parent cell.
- **Protein Synthesis** The genetic information coded in DNA in the form of specific base sequences has to be translated and expressed in the form of synthesis of specific proteins, that perform various functions in the cell.
- It involves two functions, that is, Transcription and Translation.

- The DNA sequence that codes for a specific protein or polypeptide is called a GENE and thus every protein in a cell has a corresponding gene.
- The relation between the nucleotide triplets and the amino acids is called the genetic code (introduced by NirenBerg, Hollay and Khorana 1968).
- **Mutations** It is a chemical change in a DNA molecule that could lead to synthesis of proteins with an altered amino acid sequence.
- Changes of DNA molecule may be caused by radiation, chemical agents or viruses.
- The majority of changes in DNA are repaired by special enzymes in the cell. Failures in repair by enzyme system can cause a mutation.

ENHANCE YOUR KNOWLEDGE

ENZYME

- Enzymes are biological catalysts which increase the rate of biochemical reactions even under mild conditions of temperature and pH of living organisms.
- Enzymes are chemically globular proteins.

PROPERTIES OF ENZYMES

THEY SPEED UP REACTIONS UP TO TEN MILLION TIMES (UPTO 10^{20} TIMES) AS COMPARED TO THE UNCATALYZED REACTIONS SO THEY ARE EFFICIENT CATALYSTS.

- Even small amounts of enzymes can be highly efficient. This is because the enzyme molecules are regenerated during their catalytic activity a million times in one minute.
- Enzymes function by lowering the energy of activation of a particular reaction.
- They are very specific in their action on substrates and each enzyme catalyzes only a specific type of reaction.
- They are active at moderate temperature (310 K) and pH (7) and 1 atmospheric pressure.
- The action of enzymes are inhibited by various organic and inorganic molecules called inhibitors.
- The activity of enzymes can be increased by metal ions and smaller organic molecules called coenzymes or cofactors.

  For example, Inorganic ions, Mg^{2+} Mn^{2+}, Fe^{2+}, Co^{2+}, Cu^{2+} etc.
  Organic molecules like vitamins (Thiamine, riboflavin etc.),
- Protein co-factor complex is called holoenzyme while the inactive protein part is apoenzyme.
- **Enzymes and Diseases** Certain diseases are caused by enzyme deficiencies.
- The congenital disease phenylketone urea, is due to deficiency of the enzyme phenylamine hydroxylase.
- Albinim is another disease caused due to deficiency of an enzyme Tyrosinase.
- Many heart attacks are due to blood clot formation in a coronary artery.
- The enzyme streptokinase is used to dissolve the clot.

Some Common Examples of Enzyme Catalysed Reactions

- Invertase enzyme is used to convert sucrose into glucose and fructose.
- Maltase enzyme is used to convert maltose into glucose.

- α-amylase enzyme is used to convert starch into glucose while emulsion enzyme is used in case of cellulose.
- Pepsin, trypsin enzyme are used to convert protein into amino acids.
  Some Valuable Facts:
- Killiani synthesis is used to convert an aldose into next higher aldose,

  [For example, arabinose (5C) to glucose (6C)] On the otherhand Ruff's degradation is used to convert an aldose into next lower aldose.
- Total number of possible optical isomers of glucose are 16 and of fructose are 8.
- Waston, Crick and Wilkins were awarded Noble prize in 1962 for suggesting the strucutre of DNA.
- Starch is also called Amylum.
- Insulin is a peptide hormone having 51 amino acids which are arranged in two chains one having 21 and the other having 30 amino acids.
- Haemoglobin is a globular protein present in red blood cells.
- The red colour of haemoglobin is due to the presence of non-proteinaseous part called heme.
- Plasma maintains the constant body temperature by carrying heat from the muscle and glands to the other parts of the body.
- The oxidation of carbohydrates in the presence of oxygen is termed as aerobic respiration.
- The degradation of carbohydrates in the absence of oxygen is referred to as anaerobic respiration.
- Anaerobic degradation of glucose into two molecules of pyruvic acid is termed as glycolysis.
- Antiferments are the substances like chloroform, mercury etc., which act as poisons
- for enzymes Saccharification is the process in the manufacture of alcohol in which starch is converted into fermentable sugar.
- British gum. Dextrin is prepared by heating starch to about 200ºC and is used as adhesive under the name British gum.
- Interferon is a protein substance produced by virus invaded cells that prevents reproduction of virus.

MULTIPLE-CHOICE QUESTIONS

Straight Objective Type Questions (Single Choice only)

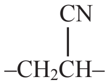
1. On the basis of mode of formation, polymers can be classified?

(a) as addition polymers only
(b) as condensation polymers only
(c) as copolymers
(d) both as addition and condensation polymers

2. Peroxide-initiated polymerisations occur via

(a) hydrocarbon combustion
(b) natural process synthesis
(c) isomeric saponification
(d) free radical chain propagation

3. Polyacrylonitrile, characterized by the



$-CH_2\overset{\overset{CN}{|}}{C}H-$ repeating unit is made from which of the following monomer?

(a) $CH_2 = CHCN$
(b) CH_3CH_2CN
(c) $HOCH_2CH_2CH_3$
(d) $CH_3CH = CHCN$

4. Polymer formation from monomers starts by
(a) Coordination reaction between monomers.
(b) Condensation reaction between monomers.
(c) Hydrolysis of monomers.
(d) Conversion of monomer to monomer ions by protons.

5. Synthetic rubber (neoprene) is
(a) Polyamide (b) Polyester
(c) Poly halodiene (d) Polysaccharide

6. Synthetic human hair wigs are made from a copolymer of vinyl chloride and acrylonitrile and is called
(a) Dynel (b) Cellulose
(c) PVC (d) Polyacrylonitrile

7. The compound used in the manufacture of terylene is
(a) ethylene (b) vinyl chloride
(c) ethylene glycol (d) adipic acid

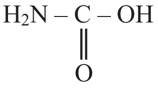
8. Which pair of species given below produce bakelite?
(a) phenol, methanol
(b) phenol, NaOH
(c) phenol, urea
(d) phenol, formaldehyde

9. Which one of the following pairs of monomers is used in the manufacture of 'Dacron'?
(a) Acrylonitrile and vinyl acetate
(b) Tetephthalic acid and ethylene glycol
(c) Phthalic acid and ethylene glycol
(d) Adipic acid and hexamethylene diamine

10. Which one of the following is used to make nonstick cookware?
(a) PVC
(b) polyestyrene
(c) polythene (terephthalate)
(d) polytetrafluoroethylene.

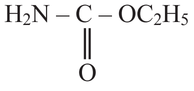
11. Ebonite is
(a) natural rubber (b) synthetic rubber
(c) highly vulcanized rubber (d) polypropene

12. Urethane is
(a) $H_2N-C\equiv N$ (b)



$$H_2N-\underset{\underset{O}{\|}}{C}-OH$$

(c) $HO-C\equiv N$ (d)



$$H_2N-\underset{\underset{O}{\|}}{C}-OC_2H_5$$

13. Glyptal polymer is obtained from glycerol by reacting with:
(a) malonic acid (b) phthalic acid
(c) maleic acid (d) acetic acid

14. The monomer unit of polyvinyl chloride has the formula:
(a) CH_3-CH_2Cl (b) $CH_2=CH_2$
(c) $CHCl=CHCl$ (d) $CH_2=CHCl$

15. P.V.C. is formed by polymerization of
(a) 1-chloroethene (b) ethane
(c) propene (d) 1-chloropropane

16. Which of the following contains isoprene units?
(a) Natural rubber (b) Nylon-66
(c) Polyethylene (d) Dacron

17. Terylene is a condensation polymer of ethylene glycol and
(a) benzoic acid (b) phthalic acid
(c) salicylic acid (d) terephthalic acid

18. Ziegler-Natta catalyst is
(a) $K[PtCl_3(C_2H_4)]$ (b) $(Ph_3P)_3RhCl$
(c) $Al_2(C_2H_5)_6+TiCl_4$ (d) $Fe(C_5H_5)_2$

19. Nylon-66 is made by using:
(a) phenol (b) benzaldehyde
(c) adipic acid (d) succinic acid

20. $F_2C=CF_2$ is monomer of
(a) Teflon (b) glyptal
(c) nylon-6 (d) buna-S.

21. Polymer used in bullet proof glass is
(a) PMMA (b) Lexan
(c) Nomex (d) Kevlar

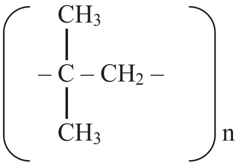
22. Nylon-6 is made from
(a) 1, 3-butadiene (b) chloroprene
(c) caprolactam (d) adipic acid

23. Which of the following is used in paints?
(a) chloroprene (b) nylon
(c) terylene (d) glyptal

24. Which of the following is a polyamide molecule?
(a) Rayon (b) nylon-6
(c) terylene (d) polystyrene

25. Teflon is a polymer of:
(a) tetrafluorethylene (b) tetraiodoethylene
(c) tetrabromoethylene (d) tetrachloroethylene

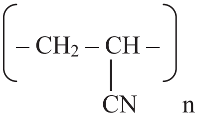
26. Monomer of

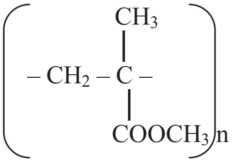


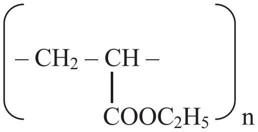
$$\left(-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\right)_n$$

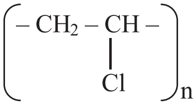
is
(a) 2-methylpropene (b) styrene
(c) propylene (d) ethene

27. Acrilan is a hard, horny and a high melting material. Which one of the following represents its structure?

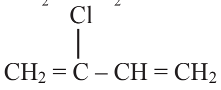
(a) 
$\left(-CH_2-\underset{CN}{CH}-\right)_n$

(b) 
$\left(-CH_2-\underset{COOCH_3}{\overset{CH_3}{C}}-\right)_n$

(c) 
$\left(-CH_2-\underset{COOC_2H_5}{CH}-\right)_n$

(d) 
$\left(-CH_2-\underset{Cl}{CH}-\right)_n$

28. Which one of the following monomers gives the polymer neoprene on polymerization?

(a) $CH_2 = CH - Cl$
(b) $CCl_2 = CCl_2$
(c) 
$CH_2 = \overset{Cl}{C} - CH = CH_2$
(d) $CF_2 = CF_2$

29. Nylon threads are made of:

(a) Polyester polymer
(b) Polyamide polymer
(c) Polyethylene polymer
(d) Polyvinyl polymer

30. Which of the following is a chain growth polymer?

(a) proteins (b) starch
(c) nucleic acid (d) polystyrene

31. Which of the following is a biodegradable polymer?

(a) cellulose (b) nylon-6
(c) polythene (d) polyvinyl chloride

32. Polymerization using Zeigler-Natta catalysis is advantages over free radical polymerization because:

(a) it gives highly branched polymer with a high degree of crystallinity
(b) it gives linear polymer molecules permitting stereochemical control.
(c) it can lead to living polymers via anionic polymerization
(d) it permits step reaction polymerization resulting in a highly cross linked polymer

33. Which of the following is a copolymer:

(a) Nylon 66 (b) polyethylene
(c) polyvinyl chloride (d) natural rubber

34. Which of the following is a polyamide?

(a) Teflon (b) nylon-66
(c) terylene (d) bakelite

35. Which percentage of sulphur is used in the vulcanization of rubber?

(a) 3% (b) 5%
(c) 30% (d) 55%

36. Which reagent is used for converting propylene to polypropylene?

(a) $TiCl_3$ + K/THF
(b) $TiCl_3 + (C_2H_5)_4Pb$
(c) $TiCl_3 + (CH_3)_2Mg$
(d) $TiCl_3 + CH_3\,(CH_2)_3$ Li

37. Which is not a polymer?

(a) sucrose (b) enzyme
(c) starch (d) Teflon

38. Which of the following polymers can be used for lubrication and as an insulator?

(a) PTFE (b) SBR
(c) PAN (d) PVC

39. Which of the following is biodegradable polymer of polyamide class?

(a) Nylon-66 (b) PHBV
(c) Dextran (d) Nylon-2-nylon-6

40. Which of the following is an addition polymer?

(a) High density polythene
(b) Nylon-6
(c) Dacron
(d) Nylon-66

41. Which one of the following polymers is prepared by condensation polymerization?

(a) Nylon-66 (b) Teflon
(c) Rubber (d) Styrene

42. Which of the following is one of the monomers of synthetic rubber?

(a) Acrolein
(b) 2-methylbuta-1,3-diene
(c) 4-chlorobuta-1,3-diene
(d) 2-chlorobuta-1,3-diene

43. Bakelite is manufactured by using a mixture of:

(a) Ethanol and phenol
(b) Ethanol and Formaldehyde
(c) Phenol and acetaldehyde
(d) Phenol and formaldehyde

44. Which of the following is fully fluorinated polymer?
(a) neoprene (b) Teflon
(c) Thiokol (d) PVC

45. Chain transfer reagent is
(a) O_2 (b) H_2
(c) CCl_4 (d) CH_4

46. Choose the correct relationship for α-D-glucose (A) and β-D-glucose (B)
(a) A and B are crystal modification
(b) A and B are epimers
(c) A is an aldose and B is a ketose
(d) A is a pyranose sugar and B is a furanose sugar

47. Galactose is converted into glucose in
(a) liver (b) stomach
(c) mouth (d) anintestine

48. The structure of DNA is
(a) triple helix (b) double helix
(c) single helix (d) linear.

49. Iodine test is shown by:
(a) starch (b) glycogen
(c) polypeptides (d) glucose

50. α–D–(+)–glucose and β–D–(+)–glucose are
(a) enantiomers (b) epimers
(c) conformers (d) anomers

51. Which of the following reagents cannot distinguished between glucose and fructose?
(a) Tollen's reagent (b) Fehling's solution
(c) Benedict's solution (d) All of these

52. Glucose gives silver mirror test with Tollen's reagent. It shows the presence of
(a) Ketonic group (b) aldehydic group
(c) alcoholic group (d) acidic group

53. Which substance chars when heated with conc. H_2SO_4?
(a) protein (b) hydrocarbon
(c) fat (d) carbohydrate

54. Cellulose is a polymer of
(a) glucose (b) fructose
(c) ribose (d) sucrose

55. Enzymes are made up of
(a) edible proteins
(b) carbohydrates
(c) nitrogen containing carbohydrates
(d) proteins with specific structures

56. RNA contains
(a) ribose sugar and thymine
(b) ribose sugar and uracil
(c) deoxyribose sugar and uracil
(d) deoxyribose sugar and thymine

57. The protein of the haemoglobin converts CO_2 of the tissues into
(a) O_2 and C (b) HCO_3^- and Fe^{2+}
(c) O_2 and CO (d) HCO_3^- and H^+

58. Glucose reacts with bromine water to produce
(a) glyceraldehydes (b) gluconic acid
(c) saccharic acid (d) glutaric acid

59. Phospholipids are esters of glycerol with:
(a) two carboxylic acid residues and one phosphate group.
(b) one carboxylic acid residue and two phosphate groups.
(c) three phosphate groups.
(d) three carboxylic acid residues.

60. The reason for double helical structure of DNA is operation of
(a) van der waals forces
(b) hydrogen bonding
(c) dipole–dipole moment
(d) electrostatic attractions

61. Subunits present in haemoglobin are
(a) 5 (b) 4
(c) 3 (d) 2

62. The number of chiral carbons in β–D (+)–glucose is
(a) 3 (b) 4
(c) 5 (d) 6

63. Carbohydrates are stored in human body as the polysaccharide
(a) glycogen (b) glucose
(c) starch (d) galactase

64. α– and β–Glucose differ in the orientation of –OH group around
(a) C_1 (b) C_2
(c) C_3 (d) C_4

65. The helical structure of protein is stabilized by
(a) ether bonds (b) peptide bonds
(c) dipeptide bonds (d) hydrogen bonds

66. The enzyme which hydrolysis triglycerides to fatty acids and glycerol is called
(a) pepsin (b) zymase
(c) maltose (d) lipase

67. A sequence of how many nucleotides in messenger RNA makes a codon for an amino acid
(a) one (b) two
(c) three (d) four

68. Insulin production and its action in human body are responsible for the level of diabetes. This compound belongs to which of the following categories

(a) an enzyme (b) an antibiotic
(c) a hormone (d) a co–enzyme

69. The carbohydrate which cannot be hydrolysed by the human digestive system is

(a) starch (b) cellulose
(c) glycogen (d) all of these

70. A certain compound gives negative test with ninhydrin and positive test with Benedict's solution. The compound is

(a) a protein (b) a monosaccharide
(c) a lipid (d) an amino acid

71. Sucrose molecule in made up of

(a) a gluco pyranose an a fructo pyranose.
(b) a gluco pyranose an a fructo furanose.
(c) a gluco furanose an a fructo pyranose.
(d) a gluco furanose an a fructo furanose.

72. The conversion of maltose to glucose is possible by the enzyme

(a) zymase (b) lactase
(c) maltase (d) diastase.

73. In biological systems, the RNA molecules direct the synthesis of specific proteins which are characteristics of each kind of organism. This process is known as:

(a) transcription (b) mutation
(c) replication (d) translation

74. Which sugar is present in DNA?

(a) purine only (b) deoxyribose
(c) ribose (d) pyrimidine only

75. The α-amino acid which contains the aromatic side chain is

(a) praline (b) tyrosine
(c) valine (d) tryptophan

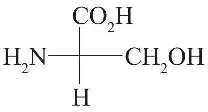
76. Which of the following compounds will not show mutarotation?

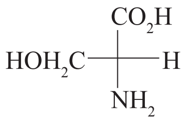
(a) β-D (+) glucopyranose
(b) α-D (+) glucospyranose
(c) β-D (+) galactopyranose
(d) Methyl-α-D-glucopyranoiside

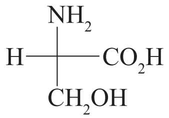
77. Methyl-α-D-glucoside and methyl-β-D-glucoside are

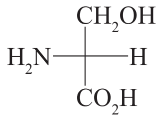
(a) epimers
(b) anomers
(c) enantiomers
(d) conformational diastereomers

78. Among the following L-serine is

(a)

$$\begin{array}{c} CO_2H \\ H_2N-\!\!\!\!\!+\!\!\!\!\!-CH_2OH \\ H \end{array}$$

(b)

$$\begin{array}{c} CO_2H \\ HOH_2C-\!\!\!\!\!+\!\!\!\!\!-H \\ NH_2 \end{array}$$

(c)

$$\begin{array}{c} NH_2 \\ H-\!\!\!\!\!+\!\!\!\!\!-CO_2H \\ CH_2OH \end{array}$$

(d)

$$\begin{array}{c} CH_2OH \\ H_2N-\!\!\!\!\!+\!\!\!\!\!-H \\ CO_2H \end{array}$$

79. The term anomers of glucose refers to

(a) isomers of glucose that differ in configurations at carbons one and four (C-1 and C-4).
(b) a mixture of (D) -glucose and (L)-glucose.
(c) enantiomers of glucose.
(d) isomers of glucose that differ in configuration at carbon one (C-1).

80. The pyrimidine bases present in DNA are

(a) cytosine and adenine
(b) cytosine and guanine
(c) cytosine and thymine
(d) cytosine and uracil

81. Which of the following hexoses will form the same osazone when treated with excess phenyl hydrazine?

(a) D-glucose, D-galactose and D-talose.
(b) D-fructose, D-mannose and D-galactose
(c) D-glucose, D-mannose and D-galactose
(d) D-glucose, D-fructose and D-mannose
(e) D-glucose, D-fructose and D-galactose

82. RNA and DNA are chiral molecules, their chirality is due to

(a) L-sugar component
(b) Chiral bases
(c) Chiral phosphate ester units
(d) D-sugar component

83. The secondary structure of a protein refers to

(a) hydrophobic interactions
(b) sequence of α-amino acids
(c) fixed configuration of the polypeptide backbone
(d) α-helical backbone

84. In DNA, the complementary bases are
(a) Adenine and guanine, thymine and cytosine.
(b) Uracil and adenine, Cytosine and guanine.
(c) Adenine and thymine, guanine and cytosine.
(d) Adenine and thymine, guanine and uracil.

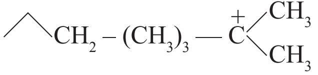
Brainteasers Objective Type Questions (Single choice only)

85. Which of the following is one of the monomers of synthetic rubber?
(a) Acrolein
(b) 2-methylbuta-1,3-diene
(c) 4-chlorobuta-1,3-diene
(d) 2-chlorobuta-1,3-diene

86. In a polymer sample, 30% of molecules have a molecular mass of 20,000, 40% have 30,000 and the rest 60,000. What is the weight average molecular mass of the polymer?
(a) 33,353 (b) 40,333
(c) 30,600 (d) 43,333

87. $[NH(CH_2)NHCO(CH_2)_4CO]n$ is a
(a) thermosetting polymer
(b) homopolymer
(c) copolymer
(d) addition polymer

88. The monomer of the polymer



$$\diagup\!\!\diagdown CH_2 - (CH_3)_3 - \overset{+}{C}(CH_3)_2$$

(a) $CH_3CH = CHCH_3$ (b) $CH_3CH = CH_2$
(c) $(CH_3)_2C = C(CH_3)_2$ (d) $H_2C = C(CH_3)_2$

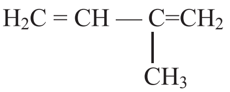
89. In the following reaction

$$\text{Cellulose} \xrightarrow[\text{(ii) HCl / HOH}]{\text{(i) CS}_2\text{ / NaOH}} [P]$$

Here the product [P] is
(a) Rayon (b) Cellulose acetate
(c) Gun cotton (d) Cellulose xanthate

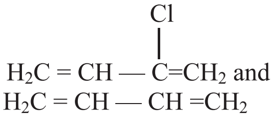
90. The number average molecular mass and mass average molecular mass of a polymer are respectively 30,000 and 40,000. The poly dispersity index of the polymer is
(a) < 1 (b) > 1
(c) 1 (d) 0

91. Buna - N synthetic rubber is a copolymer of
(a) $H_2C = CH —CH = CH_2$ and $H_5C_6 —CH = CH_2$
(b) $H_2C = CH — CN$ and $H_2C = CH —CH = CH_2$
(c)



$H_2C = CH —CN$ and
$H_2C = CH — \underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2$

(d)



$H_2C = CH — \overset{\displaystyle Cl}{\overset{|}{C}}=CH_2$ and
$H_2C = CH — CH =CH_2$

92. The monomers of Buna-S rubber are
(a) Styrene and butadiene
(b) Butadiene
(c) Isoprene and butadiene
(d) Vinyl chloride and sulphur

93. The free energy change is +13.8 kJ for the conversion of glucose to glucose-6-phoshate. This reaction
(a) Is spontaneous.
(b) Will occur spontaneously when coupled with the ATP = ADP reaction.
(c) Has a low activation energy and will occur rapidly.
(d) Will not occur spontaneously even when coupled with the ATP = ADP reaction.

94. Complete hydrolysis of cellulose gives:
(a) D–fructose
(b) D–glucose
(c) D–ribose
(d) L–glucose

95. During mutarotation of β-D-glucose in aqueous solution angle of optical rotation:
(a) Remains constant value of +19.2°C.
(b) Changes from an angle of +19.2° to a constant value of +52.5°.
(c) Remains constant value of +111°.
(d) Changes from an angle of +112° to a constant value of +52.5°.

96. At pH = 4, glycine exists as:
(a) $H_3\overset{+}{N} – CH_2 – COO^-$
(b) $H_3\overset{+}{N} – CH_2 – COOH$
(c) $H_2N – CH_2 – COOH$
(d) $H_2N – CH_2 – COO^-$

97. Chargaff's rule states that in an organism
(a) Amount of adenine (A) is equal to that of guanine (G) and the amount of thymine (T) is equal to that of cytosine (C).
(b) Amount of adenine (A) is equal to that of thymine (T) and the amount of guanine (G) is equal to that of cytosine (C).
(c) Amount of adenine (A) is equal to that of cytosine (C) and the amount of thymine (T) is equal to that of guanine (G).
(d) Amounts of all bases are equal

98. In the following reaction

Glucose + $3C_6H_5NH-NH_2 \xrightarrow{H^+/\Delta}$ Osazone + X + Y

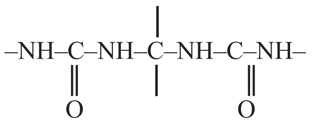
(X) and (Y) are

(a) $C_6H_5NH_2$ and NH_2OH
(b) $C_6H_5NH_2$ and NH_3
(c) NH_2OH and H_2O
(d) $C_6H_5NH-NHOH$ and NH_3

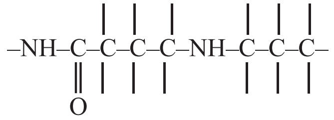
99. Among the following, the achiral amino acid is

(a) 2-methylglycine
(b) 2-ethylalanine
(c) Tryptophan
(d) 2-hydroxymethyl serine

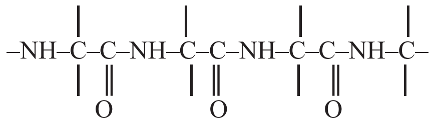
100. Which one of the following structures represents the peptide chain?

(a) 

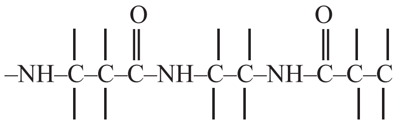
$$-NH-\underset{\underset{O}{\|}}{C}-NH-\overset{|}{\underset{|}{C}}-NH-\underset{\underset{O}{\|}}{C}-NH-$$

(b) 

$$-NH-\underset{\underset{O}{\|}}{C}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-NH-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-$$

(c) 

$$-NH-\overset{|}{\underset{|}{C}}-\underset{\underset{O}{\|}}{C}-NH-\overset{|}{\underset{|}{C}}-\underset{\underset{O}{\|}}{C}-NH-\overset{|}{\underset{|}{C}}-\underset{\underset{O}{\|}}{C}-NH-\overset{|}{\underset{|}{C}}-$$

(d) 

$$-NH-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{\overset{O}{\|}}{C}-NH-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-NH-\overset{\overset{O}{\|}}{C}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}$$

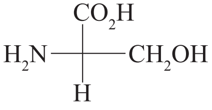
101. In both DNA and RNA heterocyclic base and phosphate ester linkages are at

(a) C_5' and C_2' respectively of the sugar molecule.
(b) C_2' and C_5' respectively of the sugar molecule.
(c) C_1' and C_5' respectively of the sugar molecule.
(d) C_5' and C_1' respectively of the sugar molecule.

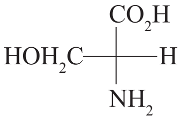
102. During the process of digestion, the proteins present in food materials are hydrolysed to amino acids. The two enzymes involved in the process Proteins $\xrightarrow{\text{enzyme (A)}}$ Polypeptides $\xrightarrow{\text{enzyme (B)}}$ amino acids are respectively:

(a) pepsin and trypsin
(b) invertase and zymase
(c) amylase and maltase
(d) diastase and lipase

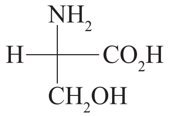
103. Among the following L-serine is

(a) 

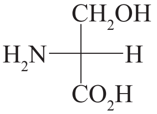
$$\begin{array}{ccc} & CO_2H & \\ H_2N & - \!\!+\!\! - & CH_2OH \\ & H & \end{array}$$

(b) 

$$\begin{array}{ccc} & CO_2H & \\ HOH_2C & - \!\!+\!\! - & H \\ & NH_2 & \end{array}$$

(c) 

$$\begin{array}{ccc} & NH_2 & \\ H & - \!\!+\!\! - & CO_2H \\ & CH_2OH & \end{array}$$

(d) 

$$\begin{array}{ccc} & CH_2OH & \\ H_2N & - \!\!+\!\! - & H \\ & CO_2H & \end{array}$$

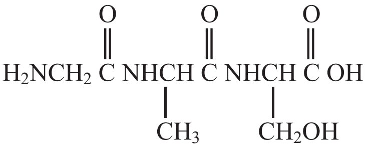
104. Hydrolysis of lactose with dilute acid yields

(a) equimolar mixture of D-glucose and D-glucose
(b) equimolar mixture of D-glucose and D-galactose
(c) equimolar mixture of D-glucose and D-fructose
(d) equimolar mixture of D-galactose and D-galactose

105. The two functional groups present in a typical carbohydrate are

(a) —CHO and —COOH
(b) >C=O and —OH
(c) —OH and —CHO
(d) —OH and —COOH

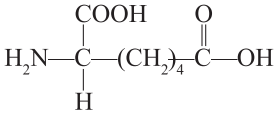
106. Which of the following notations represents the polypeptide?



$$H_2NCH_2\overset{\overset{O}{\|}}{C}NH\underset{\underset{CH_3}{|}}{CH}\overset{\overset{O}{\|}}{C}NH\underset{\underset{CH_2OH}{|}}{CH}\overset{\overset{O}{\|}}{C}OH$$

(a) Thr-Val-Gly (b) Ser-Ala-Gly
(c) Gly-Val-Thr (d) Gly-Ala-Ser

107. What would be the net charge on the given amino acid at pH = 14?



$$H_2N-\overset{\overset{COOH}{|}}{\underset{\underset{H}{|}}{C}}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-OH$$

(a) –1 (b) –2
(c) +1 (d) +2

108. Sucrose on hydrolysis gives:

(a) glucose + glucose (b) glucose + galactose
(c) glucose + fructose (d) glucose + lactose

109. Fructose is ketose sugar even then it gives red precipitate with Fehling solution because

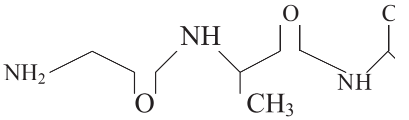
(a) Keto sugars undergo transformation into aldose sugars in the presence of Fehling's solution.
(b) Ketones are oxidized by Fehling solution.
(c) Both (a) and (b)
(d) None of these

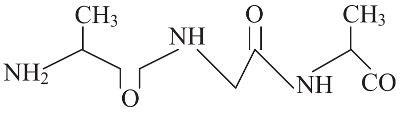
110. Which of the following is correct about isoelectric point of aminoacid?
(I) At this point amino acid is electrically neutral
(II) At this point amino acid is present in the form of zwitter ion
(III) If pH > isoelectric point amino acid will move towards cathode
(IV) If pH > isoelectric point amino acid will move towards anode
(a) I, II (b) I, II, III
(c) I, II, IV (d) II, III, IV

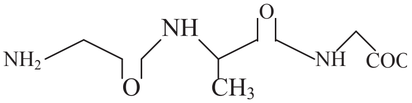
111. At pH = 4, glycine exists as:
(a) $H_3\overset{+}{N} - CH_2 - COO^-$
(b) $H_3\overset{+}{N} - CH_2 - COOH$
(c) $H_2N - CH_2 - COOH$
(d) $H_2N - CH_2 - COO^-$

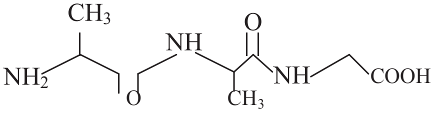
112. Which of the following set consists only of essential amino acids?
(a) Alanine, tyrosine, cystine
(b) Leucine, lysine, tryptophane
(c) Alanine, glutamine, lycine
(d) Leucine, praline, glycine

113. A tripe tide is written as Glycine- Alanine- Glycine, The correct structure of the tripe tide is

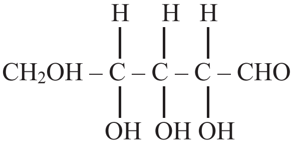
(a)


(b)


(c)


(d)


114. How many enantiomers are possible for the following sugar?



$$CH_2OH - \underset{OH}{\overset{H}{C}} - \underset{OH}{\overset{H}{C}} - \underset{OH}{\overset{H}{C}} - CHO$$

(a) 2 (b) 4
(c) 8 (d) 18

115. In DNA molecule, A + T/G + C ratio is 0.9 if the number of moles of cytosine in the molecule of DNA is 300, 000. The number of moles of thymine in the molecule is
(a) 240,000 (b) 150,000
(c) 120,000 (d) 270,000

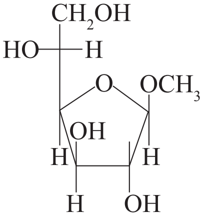
116. An aldose is oxidized separately by Br_2/H_2O (condition-A) and by HNO_3 (condition-B). Which of the following is the correct combination of the products formed?
(a) Condition-A gives aldaric acid while condition-B yields a mixture of aldonic and aldaric acids
(b) Condition-A gives aldonic acid while condition-B yields a mixture of aldonic and aldaric acids
(c) Condition-A gives aldaric acid while condition-B yields aldonic acid
(d) Condition-A gives aldonic acid while condition-B yields aldaric acid.

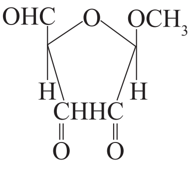
117. The efficiency of an enzyme to catalyse a reaction is due to its capacity to
(a) Decrease the bond energies of all the substrate molecules
(b) Increase the free energy of the catalyst substrate reaction
(c) Reduce the activation energy of the reaction
(d) Form strong enzyme substrate complex

118. The best solvent for removing butter stain from cloth is
(a) H_2O (b) C_2H_5OH
(c) $C_2H_5OC_2H_5$ (d) $CHCl_3$

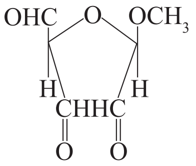
119. Mutarotation does not occur in
(a) L–glucose (b) D–glucose
(c) sucrose (d) none of these

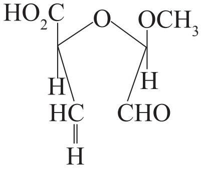
120. The products of periodic acid oxidation of the following compound are

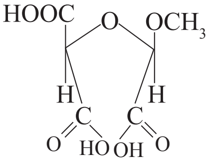


(a)


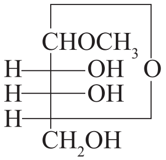
+ HCHO

(b)  + HCO_2H

(c)  + HCHO

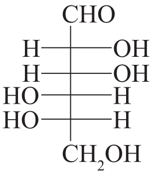
(d)  + HCHO

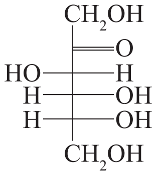
121. How many moles of HIO_4 is required to break down the given molecule here:

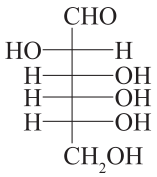


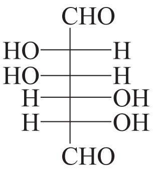
(a) 0 (b) 1
(c) 2 (d) 3

122. When D-glucose reacts with three moles of phenylhydrozine it forms glucosazone. Which of the following carbohydrates will give same osazone as that of D-glucose?

(I) 

(II) 

(III) 

(IV) 

(a) I, II (b) II, III
(c) III, IV (d) II, IV

123. Hemoglobin is a protein molecule which contains four iron atoms. If the mass percent of iron is 0.342%, what is the molar mass of hemoglobin?

(a) 1630 g/mol (b) 16,500 g/mol
(c) 65,300 g/mol (d) 73,500 g/mol

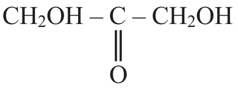
124. Which one of the following statements is/are true?

(I) Buna-S is a copolymer of butadiene and styrene
(II) Natural rubber is a 1,4-polymer of isoprene
(III) In vulcanization, the formation of sulphur bridges between different chains make rubber harder and stronger
(IV) Natural rubber has the trans-configuration at every double bond.

(a) I, II (b) I, II, III
(c) II, III, IV (d) I, II, III, IV

125. Which one of the following is first member of monosaccharides?

(a) $CH_2OH - CHOH - CHO$

(b) 

$CH_2OH - \underset{\underset{O}{\|}}{C} - CH_2OH$

(c) 

$CH_2OH - CHOH - \underset{\underset{O}{\|}}{C} - CH_2OH$

(d) $CH_2OH - CHOH - CHOH - CHO$

126. Choose the correct relationship for α-D-glucose (A) and β-D-glucose (B)

(a) A and B are crystal modification
(b) A and B are epimers
(c) A is an aldose and B is a ketose
(d) A is a pyranose sugar and B is a furanose sugar

127. Ring structure of glucose is due to formation of hemiacetal and ring formation between:

(a) C_1 and C_3 (b) C_1 and C_4
(c) C_1 and C_5 (d) C_2 and C_4

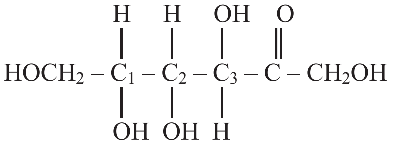
128. Consider the following statements about carbohydrates:

(1) Bromine water can be used to differentiate and aldose from a ketose.
(2) All monosaccharides, whether aldose or ketose, are reducing sugars.
(3) Osazone formation destroys the configuration about C-2 of an aldose, but does not affect the configuration of the rest of the molecule.
(4) A pair of diastereomeric aldoses which differ only in configuration about C-2 is termed as pair of anomers.

Which of the above statements are correct?

(a) 1 and 4 (b) 2 and 4
(c) 1, 2 and 3 (d) 2, 3 and 4

129. Which of the numbered carbon atoms in the monosaccharide show below are chiral?



$$HOCH_2-\underset{OH}{\overset{H}{C_1}}-\underset{OH}{\overset{H}{C_2}}-\underset{H}{\overset{OH}{C_3}}-\overset{O}{\overset{\|}{C}}-CH_2OH$$

(a) C_1 only
(b) C_2 and C_3
(c) C_1 and C_3
(d) C_1, C_2 and C_3

130. In secondary structures, what types of patterns do the segments of proteins chains form?
(I) α –helix (II) β-pleated sheet
(III) globular (IV) fibrous
(a) I and II (b) II and III
(c) I and IV (d) I, II and IV

Decisive Thinking Objective Type Questions (One or more than one choice)

131. Which is/are macromolecule here?
(a) DNA (b) Starch
(c) Palmitate (d) Insulin

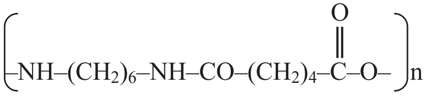
132. Which one of the following is/are example of chain growth polymer?
(a) Neoprene (b) Buna-S
(c) PMMA (d) Glyptal

133. Which of the following is/are example of addition polymer?
(a) polystyrene (b) Nylon
(c) PVC (d) Propylene

134. Which of the following polymers involves cross linkages?
(a) Melmac (b) Bakelite
(c) Polythene (d) Vulcanised rubber

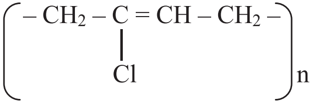
135. Which is/are true about polymers?
(a) polymers do not carry any charge
(b) polymers have high viscosity
(c) polymers scatter light
(d) polymers have low molecular weight

136. Which of the following is/are correctly matched?
(a) Nylon-66:



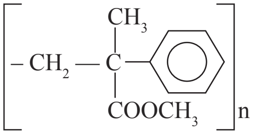
$$\left[-NH-(CH_2)_6-NH-CO-(CH_2)_4-\overset{O}{\overset{\|}{C}}-O-\right]_n$$

(b) Neoprene

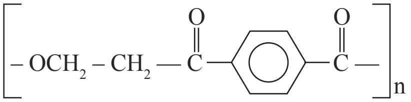


$$\left(-CH_2-\underset{Cl}{\underset{|}{C}}=CH-CH_2-\right)_n$$

(c) PMMA



(d) Terylene



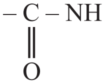
137. Which one of the following pairs is/are correctly matched?
(a) Taflon: Thermally stable cross linked polymer of phenol and formaldehyde
(b) Synthetic rubber: A copolymer of butadiene and styrene
(c) Terylene: Condensation polymer of terephthalic acid and ethylene glycol
(d) Perspex: A homopolymer of methyl methacrylate

138. Which of the following is/are correct regarding terylene?
(a) synthetic fibre
(b) thermosetting plastic
(c) step-growth polymer
(d) condensation polymer

139. Which one of the following is/are correctly match?
Polymer **Monomer(s)**
(a) Thiokol – Ethylene dichloride, sodium tetrasulphide
(b) Buna-S – Styrene, 1, 3-butadiene
(c) Orlon – Glycerol, phthalic anhydride
(d) Teflon – Tetrafluoroethylene

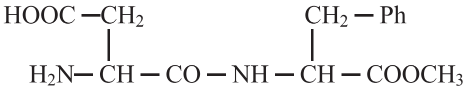
140. The incorrect statement in respect of protein haemoglobin is/are
(a) maintains blood sugar level
(b) acts as an oxygen carrier in the blood
(c) functions as a catalyst for biological reactions.
(d) forms antibodies and offers resistance to diseases

141. Which statement is/are correct about peptide bond?
(a) C – N bond length in proteins is smaller than usual bond length of C – N bond.
(b) spectroscopic analysis shows planar structure



$-\underset{O}{\underset{\|}{C}}-NH-$ bond

(c) C – N bond length in proteins is longer than usual bond length of C – N bond.
(d) none of these

142. 

$$\mathrm{H_2N-\overset{HOOC-CH_2}{\overset{|}{CH}}-CO-NH-\overset{CH_2-Ph}{\overset{|}{CH}}-COOCH_3}$$

(Aspartame)

Aspartame is nearly 160 times as sweet as sucrose and is used as α sugar substitute the correct statement about aspartame is/are

(a) It is tripeptide.
(b) It is having four functional groups.
(c) It can be named as aspartyl phenylalanine methyl ester.
(d) It is an ester derivative of dipeptide.

143. Which of the following is/are incorrect about enzymes?

(a) it reduces the activation energy.
(b) it increases the activation energy.
(c) it changes the equilibrium constant.
(d) none of these.

144. Which is/are incorrect statement?

(a) amylose is a component of cellulose.
(b) starch is a polymer of α–glucose.
(c) proteins are compounds of only one type of amino acids.
(d) in cyclic structure of fructose, there are four carbon atoms and one oxygen atom.

145. Which of the following is/are correct for glucose?

(a) It contains one ketone group
(b) It contains four >CHOH groups
(c) It contains one –CHO group
(d) It contains one CH_2OH group

146. Which is/are true?

(a) glucose is a disaccharide.
(b) starch is a polysaccharide .
(c) glucose and fructose are not anomers.
(d) invert sugar consists of glucose and fructose.

147. Which of the following statements is/are not correct?

(a) The metal ion present in vitamin B_{12} is Zn^{2+}.
(b) In photosynthesis CO_2 and H_2O are converted into carbohydrates in presence of sunlight.
(c) In haemoglobin the oxidation state of Fe is +6.
(d) Methyl salicylate is known as aspirin.

148. Which of the following is true?

(a) sucrose is a non reducing agent.
(b) glucose is oxidized by bromine water.
(c) glucose rotates plane polarized light in clockwise direction.
(d) fructose is oxidized by bromine water

Select the correct answer during the coded given below.

149. Which amino acids have asymmetric carbon atom?

(a) histidine (b) glycine
(c) alanine (d) phenylalanine.

150. Which of the following is/are present in a nucleotide?

(a) cytosine (b) guanine
(c) adenine (d) tyrosine.

151. Which of the following statements is/are not true for protein synthesis (translation)?

(a) amino acids are directly recognized by m–RNA.
(b) the third base of the codon is less specific.
(c) only one codon codes for an amino acid.
(d) every t–RNA molecule has more than one amino acid attachment.

152. Which of the following is/are correct?

(a) Acetyl salicyclic is acid is known as aspirin.
(b) The metal ion present in vitamin B_{12} is Mg^{2+}.
(c) Chlorophyll is responsible for the synthesis of carbohydrates in plants.
(d) The compound formed in the addition of oxygen to haemoglobin is called oxy haemoglobin.

153. Which of the following statement is/are not true?

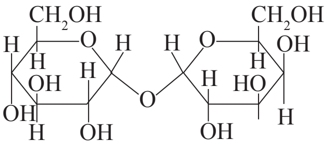
(a) Nucleotide + phosphate ester bond = nucleoside.
(b) DNA's are nucleotides and RNA are nucleosides.
(c) Nucleoside + phosphate ester bond = nucleotide.
(d) None of these.

154. Which of the following statements about aminoacids is/are true?

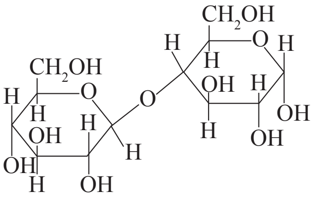
(a) They are all high melting solids.
(b) They are constituents of all proteins.
(c) Glycine is the only naturally occurring amino acid which is optically inactive.
(d) Most naturally occurring amino acids have D-configuration.

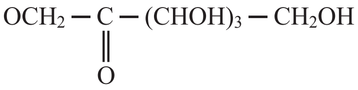
155. Which of the following is/are reducing sugar?

(a)

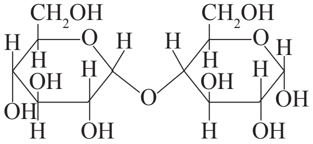


(b)



(c) 

$$OCH_2-\underset{\underset{O}{\|}}{C}-(CHOH)_3-CH_2OH$$

(d) 

Linked-Comprehension Type Questions

Comprehension 1

The phenomenon of formation of large molecules or polymers from monomers is called polymerization. Polymers can be formed by addition and condensation methods. Polydispersity index (PDI) is the ratio of weight average molecular mass and number average molecular mass it determines the homogeneity of a polymer.

156. Which of the following statements is correct about polymers?

(1) Polymers are substances made up of recurring structural units, each of which can be regarded as derived from a specific compound called a monomer.

(2) Polymers made from a single monomeric species are called homopolymers whereas those made up of two or more different monomeric species are called copolymers:

(3) Very often, polymers are macromolecules, and a sample of a given polymer is characteristically a mixture of molecules with different molecular weights.

(a) 1 and 2 only (b) 1 and 3 only
(c) 1, 2 and 3 (d) 2 only

157. Which of the following statements about polymers is correct?

(1) The ratio of the weight average and number average molecular masses, $\overline{M}_w / \overline{M}_n$, is called poly dispersion index (PDI.)

(2) The number average molecular mass, $\overline{M}_n$ and the weight average molecular mass M_w are expressed by the equations

$$\overline{M}_n = \frac{\Sigma N_i M_i}{\Sigma N_i} \quad \text{and} \quad \overline{M}_w = \frac{\Sigma N_i M_i^2}{\Sigma N_i M_i}$$

Here N_i is the number of molecules of molecular mass M_i of the species i.

(3) Some physical properties such as freezing point, vapour pressure and osmotic pressure are related directly to $\overline{M}_n$ whereas some other physical properties like light scattering, sedimentation and diffusion constant are related directly to $\overline{M}_w$.

(a) 1 and 2 (b) 2 and 3
(c) 1 and 3 (d) 1, 2 and 3

158. Which is correct about Gutta parcha rubber

(1) A very hard material.

(2) A synthetic polymer.

(3) A trans 1,4-polyisoprene polymer.

(a) 2 only (b) 3 only
(c) 1 and 3 only (d) 1, 2 and 3

159. What is the order of decreasing reactivity of the following monomers towards anionic polymerization?

(1) $CH_2 = CHCN$

(2) $CH_3CH = CH_2$

(3) $C_6H_5CH = CH_2$

(a) 1 > 2 > 3 (b) 3 > 2 > 1
(c) 2 > 3 > 1 (d) 3 > 1 > 2

Comprehension 2

Carbohydrates are polyhydroxyaldehydes or polyhydroxyketones and they are classified as Monosaccharides, Oligosaccharides and Polysaccharides. The most important naturally occurring monosaccharides are glucose and fructose. They are functional isomers and show optical activity. They can be distinguish by their chemical reactions.

160. Which one of the following pairs is incorrectly matched?

(A) Sucrose:	monosaccharide
(B) Fructose:	aldose sugar
(C) Glucose:	mutarotation
(D) Sucrose :	reducing sugar

(a) 2, 3 and 4 (b) 1, 2 and 3
(c) 1, 2 and 4 (d) 2 and 4 only

161. Glucose and fructose give the same osazone. One may, therefore, conclude that

(a) the structures of glucose and fructose have mirror image relationship.

(b) glucose and fructose have identical structures.

(c) the structures of glucose and fructose differ only in those carbon atoms which take part in osazone formation.

(d) glucose and fructose are anomers.

162. Consider the following statements about sucrose

(1) Hydrolysis of sucrose with dilute acid yields an equimolar mixture of D-glucose and D-fructose.

(2) Acid hydrolysis of sucrose is accompanied by a change in optical rotation.

(3) In sucrose, the glycosidic linkage is between C -1 of glucose and C-2 of fructose.

(4) Aqueous solution of sucrose exhibits mutarotation.

Which of the statements are correct?
(a) 1 and 2 only (b) 2 and 3 only
(c) 1, 2 and 3 (d) 1, 3 and 4

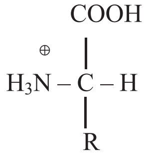
163. Consider the following statements:
(1) Monosaccharides are optically active polyhydroxy carbonyl compounds.
(2) Fructose does not reduce Fehling's solution because it is a ketose.
(3) α-D(+)-Glucose and β-D(+)-Glucose are anomers.
(4) D-glucose and D-mannose are C-2 epimers.
Which of the following statements are correct?
(a) 1, 2 and 3 (b) 1, 3 and 4
(c) 1, 2 and 4 (d) 2, 3 and 4

Comprehension 3

Protiens are nitrogenous organic compound having very high molecular masses. They are polyamides formed from α- amino acid. The bond formed between two amino acid is called a peptide bond(─CO ─NH─). The product obtained by this peptide bond formation are called peptides and they may be divided as di, tri, tetra , penta peptides.

164. Consider the following statements concerning proteins:
(1) All natural amino acids which are constituents of proteins are α-amino acids.
(2) α-amino acids are all optically active and have the L-configuration.
(3) An especially favourable conformation for the peptide linkage in proteins is the α-helix arrangement.
(4) α-amino acids are connected by ester linkages.
Which of the following statements are correct?
(a) 1 and 3 are correct (b) 1 and 2 are correct
(c) 2 and 3 are correct (d) 2, 3 and 4 are correct

165. The given structure of α-amino acid will exist at which pH?



$$H_3\overset{\oplus}{N}-\overset{\overset{COOH}{|}}{\underset{\underset{R}{|}}{C}}-H$$

(a) 0 (b) 2
(c) 4 (d) 7

166. Which statements are correct about peptide bond?
(1) –CONH– group is planar.
(2) C – N bond length in protein is longer than usual bond length of C – N bond.
(3) C – N bond length in protein is smaller than usual bond length of C – N bond.
(a) 2 and 3 (b) 1 and 2
(c) 2 only (d) 1 and 3

167. Sanger's reagent is used for the identification of:
(a) C–terminal of a peptide chain.
(b) N–terminal of a peptide chain.
(c) number of amino acids in a peptide chain.
(d) side chain of amino acids.

Comprehension 4

In case of disaccharides the two Monosaccharides are joined together by glycoside linkage. A glycoside bond is formed when the -OH group of the hamiactal carbon of one monosaccharides condensed with -OH group of another monosaccharide molecule leading to ─O─ bond. For example in sucrose α -D -glucopyranose and a β -D -fructofurnanose unit are joined together by α, β glycocydic linkage.

168. In which disaccharide glucosidic linkage is formed between anomeric –OH of glucose and anomeric –OH of fructose?
(a) Lactose (b) Maltose
(c) Cellobiose (d) Sucrose

169. In most of the cases glycosidic linkage is formed between:
(a) (1 → 4') (b) (4 → 4')
(c) (2 → 2') (d) (1 → 3')

170. Amylose and cellulose both are liner polymers of glucose. The difference between them is
(a) Amylose has β (1 → 4) linkage and cellulose has β (1 → 6) linkage
(b) Amylose has α (1 → 4) linkage and cellulose has α (1 → 6) linkage
(c) Amylose has α (1 → 4) linkage and cellulose has β (1 → 4) linkage
(d) Amylose has β (1 → 4) linkage and cellulose has α (1 → 4) linkage

Assertion-Reason Type Questions

In the following question two statements (Assertion) A and Reason (R) are given Mark.

(A) if A and R both are correct and R is the correct explanation of A;
(B) if A and R both are correct but R is not the correct explanation of A;
(C) A is true but R is false;
(D) A is false but R is true,

171. **(A):** D- Glucose and D- mannose are epimer
(R): Epimers are a pair of diasteramer that differ only the configuration about a single carbon atom(second carbon in this case)

172. **(A):** α-amino acids exist as dipolar ions or zwitter ions.
(R): α-amino acids are the building blocks of proteins.

173. **(A):** Proteins are made up of only α-amino acids.
(R): During denaturation, primary structure of proteins is not affected.

174. **(A):** Primary structure of proteins gives an idea about the conformation of the molecule.
(R): The differences in chemical and biological properties of various proteins arise due to the difference in primary structures.

175. **(A):** Glucose can be converted into its glycoside by its reaction with an alcohol in the presence of an acid (H^+). The remaining hydroxyl groups are unaffected by this process.
(R): Under the condition of the reaction, in addition to more stable oxonium ion which is involved in glycoside formation, less stable primary or secondary carbonium ions may be formed which are undesirable for the remaining hydroxyl groups to be converted into the corresponding ether derivative.

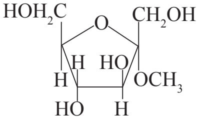
176. **(A):** Sequence of bases in DNA is TGAACCCTT and sequence of basesin m-RNA is CATTAAACC.
(R): In DNA nitrogenous bases have hydrogen bonds.

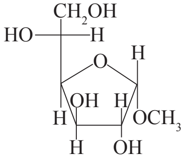
177. **(A):** Linseed oil is an important constituent of paints and varnishes.
(R): It is rich in trans-unsaturated fatty acids.

178. **(A):** D-glucose and D-Mannose are C-2 epimers.
(R): They only have different configuration at carbon number-2.

179. **(A):** The digestion of carbohydrates does not take place in stomach.
(R): Enzymes like salivary amylase become inactive in stomach where there is acidic pH.

180. **(A):** Methyl α -D- fructofuranoside (I) undergoes acid catalysed hydrolysis at faster rate than that of methyl α-D- glucofuranoside (II).





(R): The intermediate in glycoside is carbocation which 3° in case of I and 2° in case II.

181. **(A):** Millon's test is a test to identify carbohydrates.
(R): Millon's reagent is solution of mercurous nitrate and mercuric nitrate in nitric acid containing little nitrous acid.

182. **(A):** Natural rubber is a polymer of cis-isoprene.
(R): Polytrans isoprene is called Gutta Percha.

183. **(A):** Cellulose is not digested by humans.
(R): Cellulose is a branched polysaccharide of high molecular weight.

184. **(A):** Treatment of D-glucose with dilute alkali affords an equilibrium mixture consisting of D-mannose D-fructose and the starting substance D-glucose.

(B): The reaction involves an intermediate in which the hybridization of C_2 changes from sp^3 to sp^2.

185. **(A):** Styrene is more reactive than ethylene towards free radical polymerization.
(R): Polymerisation of styrene proceeds through more stable benzyl free radical.

186. **(A):** A solution of sucrose in water is dextro rotatory but on hydrolysis in presence of H^+, it becomes leavo rotatroy.
(R): Inversion of sugar follows first order kinetics.

187. **(A):** Reducing sugar give brick red ppt with Fehling's solution and show mutarotation.
(R): During mutarotation, one pure anomer is converted into mixture of two anomers.

188. **(A):** Glucose gives a reddish brown precipitate with Fehling's solution.
(R): Reaction of glucose with Fehling's solution gives CuO and gluconic acid.

[IIT 2007]

189. **(A):** Molecules that are not superimposable on their mirror images are chiral.
(R): All chiral molecules have chiral centers.

[IIT 2007]

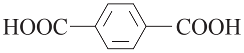
Matrix-Match Type Questions

190. Match list I (name of the vitamin) with list II (vitamin) and select the correct answer using the code given below the lists.

Column I (Name of the vitamin)
A. Cyanocobalamin B. Pyridoxine
C. Retinol D. Thiamine

Column II (Vitamin)
(p) Vitamin A (q) Vitamin B_1
(r) Vitamin B_6 (s) Vitamin B_{12}
(t) Vitamin C

(a) A-2, B-1, C-5, D-4
(b) A-4, B-3, C-1, D-2
(c) A-2, B-3, C-1, D-4
(d) A-4, B-1, C-5, D-2

191. Match the following:
Column I (Polymer)
(a) Orlon (b) Dacron
(c) Buna-N (d) SBR
Column II (Monomer units)
(p) $CH_2 = CH - CH = CH_2 + CH_2 = CH - CN$
(q) $PhCH = CH_2 + CH_2 = CH - CH = CH_2$
(r) $CH_2 = CH - CN$
(s) glycol + 

192. Match the following:
Column I
(a) Nylon (b) Terylene
(c) Teflon (d) Neoprene
Column II
(p) Polyester
(q) Polytetrafluoroethylene
(r) synthetic rubber
(s) polyamide

193. Match the following:
Column I
(a) α,-D-glucose and β,-D glucose
(b) D-glucose and D-galactose
(c) Erythrose and threose
(d) D(+)glyceraldehyde and L(-) glyceraldehydes
Column II
(p) enantiomers (q) anomers
(r) epimers (s) diastereomers

194. Match the following:
Column I
(a) α- and β-glucose
(b) (+)-and (–)-glucose
(c) D- and L-notations
(d) α –form ↔ open chain form ↔ β-form
Column II
(p) mutarotation
(q) enantiomers
(r) anomers
(s) configurational relationship

195. Match the following:
Column I (α-amino acids)
(a) Leucine
(b) phenylalanine
(c) Tyrosine
(d) Serine
Column II
(Rin R-CHNH$_2$ CO$_2$H)
(p) $P^{-}(OH)\,C_6H_4^{-}\,CH_2^{-}$
(q) $(CH_3)_2C^{-}$
(r) $HOCH_2^{-}$
(s) $C_6H_5CH_2^{-}$

196. Match the following:
Column I (Polymer)
(a) Bakelite
(b) Dacron
(c) Nylon-66
(d) Buna-S
Column II (Polymerizing units)
(p) Butadiene and styrene
(q) Phenol and methanal
(r) 1, 2-dihydrooxyethane and dimethyl terephthalate
(s) Urea and methanal
(t) 1, 6-hexanedioic acid and 1,6-diamino hexane

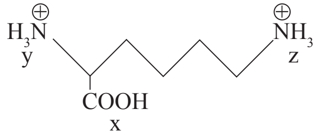
197. Match the following:
Column I
(a) Coordination polymerization
(b) Free radical polymerization
(c) Addition polymerization
(d) Natural rubber
Column II
(p) polypeptide
(q) Nylon-66
(r) Zeigler- Natta catalyst
(s) Azobisisobutyronitrile
(t) Cis-1, 4-polyisoprene

198. Match the following:
Column I
(a) Phenol + formaldehyde
(b) Terephthalic acid + ethylene glycol
(c) Caprolactam
(d) Butadiene + styrene
Column II
(p) Synthetic rubber (q) Bakelite
(r) Nylon-66 (s) Terylene

199. Match the following:
Column I (Chemical substances)
(a) Cellulose (b) Nylon-6, 6
(c) Protein (d) Sucrose
Column II (Type of polymers/Type of bonds)
(p) Natural polymer
(q) Synthetic polymer
(r) Amide linkage
(s) Glycoside linkage

The IIT-JEE Corner

200. In the compound given below



The correct order of acidity of the positions (X), (Y) and (Z) is

(a) X > Y > Z (b) Y > X > Z
(c) Z > X > Y (d) X > Z > Y

[IIT 2004]

201. The pair in which both the compounds give positive test with Tollen's reagent is

(a) fructose and sucrose
(b) acetophenone and hexanal
(c) glucose and sucrose
(d) glucose and fructose

[IIT 2004]

202. The two forms of D-glucopyranose obtained from the solution of D-glucose are called:

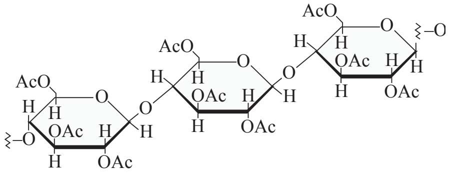
(a) Epimer (b) Isomer
(c) Anomer (d) Enantiomer

[IIT 2005]

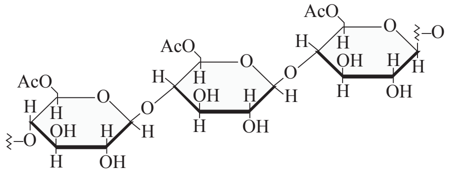
203. FCellulose upon acetylation with excess acetic anhydride/H_2SO_4 (catalytic) gives cellulose triacetate whose structure is.

[2008]

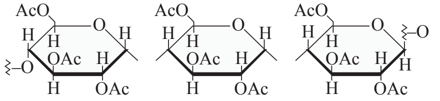
(a)



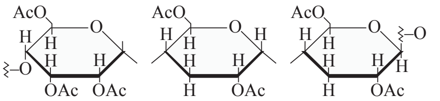
(b)



(c)



(d)



204. Among cellulose, poly (vinyl chloride), nylon and natural rubber, the polymer in which the intermolecular force at attraction is weakest is

[IIT 2009]

(a) Nylon
(b) Poly (vinyl chloride)
(c) Cellulose
(d) Natural Rubber

ANSWERS

Straight Objective Type Questions

1. (d)	**2.** (d)	**3.** (a)	**4.** (b)	**5.** (c)	**6.** (a)	**7.** (c)	**8.** (d)	**9.** (b)	**10.** (d)
11. (c)	**12.** (d)	**13.** (b)	**14.** (d)	**15.** (a)	**16.** (a)	**17.** (d)	**18.** (c)	**19.** (c)	**20.** (a)
21. (b)	**22.** (c)	**23.** (d)	**24.** (b)	**25.** (a)	**26.** (a)	**27.** (a)	**28.** (c)	**29.** (b)	**30.** (d)
31. (a)	**32.** (b)	**33.** (a)	**34.** (b)	**35.** (b)	**36.** (b)	**37.** (a)	**38.** (a)	**39.** (d)	**40.** (a)
41. (a)	**42.** (d)	**43.** (d)	**44.** (b)	**45.** (c)	**46.** (b)	**47.** (a)	**48.** (b)	**49.** (a)	**50.** (d)
51. (d)	**52.** (b)	**53.** (d)	**54.** (a)	**55.** (d)	**56.** (b)	**57.** (d)	**58.** (b)	**59.** (a)	**60.** (b)
61. (b)	**62.** (c)	**63.** (a)	**64.** (a)	**65.** (d)	**66.** (d)	**67.** (c)	**68.** (c)	**69.** (b)	**70.** (b)
71. (b)	**72.** (c)	**73.** (d)	**74.** (b)	**75.** (b)	**76.** (d)	**77.** (b)	**78.** (c)	**79.** (d)	**80.** (c)
81. (d)	**82.** (d)	**83.** (d)	**84.** (c)						

Brainteasers Objective Type Questions

85. (d)	**86.** (d)	**87.** (c)	**88.** (d)	**89.** (a)	**90.** (b)	**91.** (b)	**92.** (a)	**93.** (b)	**94.** (b)
95. (b)	**96.** (b)	**97.** (b)	**98.** (b)	**99.** (d)	**100.** (c)	**101.** (c)	**102.** (a)	**103.** (c)	**104.** (b)
105. (b)	**106.** (d)	**107.** (b)	**108.** (c)	**109.** (a)	**110.** (c)	**111.** (b)	**112.** (c)	**113.** (c)	**114.** (c)
115. (d)	**116.** (d)	**117.** (c)	**118.** (d)	**119.** (c)	**120.** (b)	**121.** (b)	**122.** (d)	**123.** (c)	**124.** (b)
125. (a)	**126.** (b)	**127.** (c)	**128.** (c)	**129.** (d)	**130.** (a)				

Decisive Thinking Objective Type Questions

131. (a), (b), (d) **132.** (a), (b), (c) **133.** (a), (c), (d) **134.** (a), (b), (d) **135.** (a), (b), (c)
136. (a), (b), (c) **137.** (b), (c), (d) **138.** (a), (c), (d) **139.** (a), (b), (d) **140.** (a), (c), (d)
141. (b), (c), (d) **142.** (b), (c), (d) **143.** (b), (c), (d) **144.** (a), (c), (d) **145.** (b), (c), (d)
146. (b), (c), (d) **147.** (a), (c), (d) **148.** (a), (b), (c) **149.** (a), (c), (d) **150.** (a), (b), (c)
151. (a), (c), (d) **152.** (a), (c), (d) **153.** (a), (b), (d) **154.** (a), (b), (c) **155.** (b), (c), (d)

Linked-Comprehension Type Questions

156. (c) **157.** (d) **158.** (d) **159.** (a) **160.** (c) **161.** (c) **162.** (c) **163.** (b) **164.** (a) **165.** (a)
166. (d) **167.** (b) **168.** (d) **169.** (a) **170.** (c)

Assertion-Reason Type Questions

171. (a) **172.** (b) **173.** (b) **174.** (d) **175.** (a) **176.** (d) **177.** (c) **178.** (a) **179.** (a) **180.** (a)
181. (d) **182.** (b) **183.** (b) **184.** (a) **185.** (a) **186.** (b) **187.** (a) **188.** (c) **189.** (c)

Matrix-Match Type Questions

190. (a) - (s), (b) - (r), (c) - (p), (d) - (q)
191. (a) - (r), (b) - (s), (c) - (p), (d) - (q)
192. (a) - (s), (b) - (p), (c) - (q), (d) - (r)
193. (a) - (q), (b) - (r), (c) - (s), (p) - (p)
194. (a) - (r), (b) - (q), (c) - (s), (d) - (p)
195. (a) - (q), (b) - (s), (c) - (p), (d) - (r)
196. (a) - (q), (b) - (r), (c) - (t), (d) - (p)
197. (a) - (r), (b) - (s), (c) - (q), (d) - (t)
198. (a) - (q), (b) - (s), (c) - (r), (d) - (p)
199. (a) - (p, s), (b) - (q, r), (c) –(p, r), (d) - (s)

The IIT-JEE Corner

200. (a) **201.** (d) **202.** (c) **203.** (a) **204.** (d)

HINTS AND EXPLANATIONS

Straight Objective Type Questions

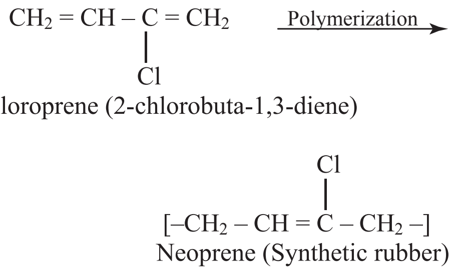
2. Peroxide initiated free radical mechanism in polymerization free radical mechanism also present.

21. Lexan is a polycarbonate and is obtained by condensation of diethyl carbonate and bisphenol A. It has unusually high impact strength and is used for making bullet-proof windows and safety or crash helmets.

37. Sucrose is a disaccharides which upon acid or enzymatic hydrolysis gives only two molecules of monosaccharides.

$$\text{Sucrose} \xrightarrow{H^+ \text{ or invertase}} \text{D(+)-glucose} + \text{D(–)-fructose}$$

42.



$$CH_2 = CH - \underset{\underset{Cl}{|}}{C} = CH_2 \xrightarrow{\text{Polymerization}}$$

Chloroprene (2-chlorobuta-1,3-diene)

$$[-CH_2 - CH = \overset{\overset{Cl}{|}}{C} - CH_2 -]$$

Neoprene (Synthetic rubber)

46. α-D-glucose and β-D-glucose are anomers, because they differ in the orientation of the hydroxyl group at only C_1. On the other hand, epimers have several chiral carbons (or centres) differing in configuration about any chiral centre, not necessarily at C_1. Thus, all anomers are epimers, but all epimers are not anomers.

47. Galactose is converted into glucose in liver.

48. DNA has double helix structure.

49. Starch gives blue colouration with iodine.

50. α–D–(+)–glucose and β–D–(+)–glucose have different configuration at C – 1 and are anomers

53. Carbohydrates undergo charring when heated with conc H_2SO_4 due to dehydration?

54. Cellulose is a polymer of β–(d)–glucose.

55. Enzymes are proteins with specific structure.

58. $CH_2OH-(CHOH)_4CHO \xrightarrow{[O],\ Br_2/H_2O} CH_2OH(CHOH)_4CH_2OH$

Gluconic acid

61. One molecule of haemoglobin has four haem groups and each of them can take up one molecule of oxygen.

69. Cellulose is insoluble in water and in most of the organic solvents.

70. As it gives a negative test with ninhydrin, it cannot be a protein or an amino acid. Since it gives a positive test with Benedict's solution, it must be a monosaccharide but not a lipid.

72. Maltose $\xrightarrow{\text{maltase}}$ glucose + glucose

74. Sugar constituent present in DNA is deoxyribose.

77. Methyl-α-D-glucoside and methyl-β-D glucoside differs at C-1, hence are called anomers.

82. DNA and RNA molecules are chiral in nature as in them the sugar present D(-)-2-deoxyribose and D(-)-ribose respectively are chiral molecules.

83. Secondary structure of proteins involves α-helical backbone and β-sheet structures. These structures are formed as a result of hydrogen bonding between different peptide groups.

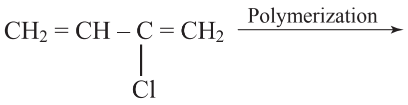
84. DNA contains two types of nitrogenous bases that is, Purine → Adenine (A), Guanine (G)

Pyrimidine → Cytosine (c), Thymine (T)

Adenine pairs with thymine (A : T) by two hydrogen bonds and guanine with cytosine (G : C) by three hydrogen bonds.

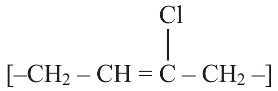
Brainteasers Objective Type Questions

85.



$$CH_2=CH-\underset{\displaystyle Cl}{\underset{|}{C}}=CH_2 \xrightarrow{\text{Polymerization}}$$

Chloroprene (2-chlorobuta-1,3-diene)



$$[-CH_2-CH=\overset{\displaystyle Cl}{\overset{|}{C}}-CH_2-]$$

Neoprene (Synthetic rubber)

87. $n_1H_2N-(CH_2)-NH_2 + n_2\ HOOC(CH_2)_4\ COOH$

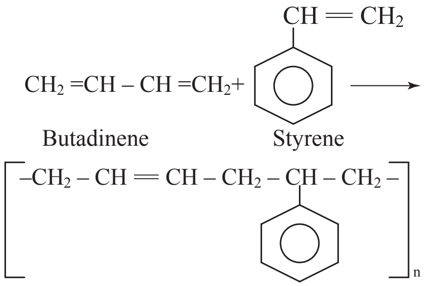
Methylene diamine Adipic acid

$\rightarrow [-NH(CH_2)NHCO(CH_2)_4CO-]_n$

88. The repeating structural unit of the polymer is $-CH_2-C(CH_3)_2-$ and hence the monomer is $CH_2=C(CH_3)_2$.

91. It is polymer of vinyl cyanide and Buta 1, 3 di- ene.

92. Buna – S is also known as Styrene Butadiene Rubber (SBR).



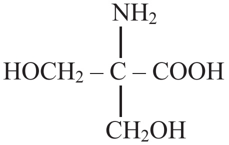
Buna – S

94. Cellulose is homopolysaccharide (polysaccharide with similar units) and it comes in the category of glucans.

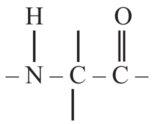
96. At pH = 4 (that is, acidic medium), an amphoteric Zwitter ion structure changes into cation when an acid is added to it.

97. According to Chargaff's rule, amount of adenine (A) is equal to that of thymine (T) and the amount of guanine (G) is equal to that of cytosine (C).

99. 2-hydroxymethyl serine is achiral as it has two $-CH_2OH$ groups so it has symmetry.



$$HOCH_2-\overset{\displaystyle NH_2}{\overset{|}{\underset{\displaystyle CH_2OH}{\underset{|}{C}}}}-COOH$$

100. As 

$$-\overset{\overset{\large H}{|}}{N}-\underset{|}{\overset{|}{C}}-\overset{\overset{\large O}{\|}}{C}-$$

repeating unit is characteristic of peptide chain.

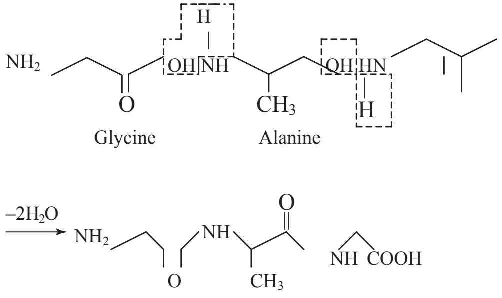
104. Lactose is hydrolyzed by dilute acids or by the enzyme lactase, to an equimolar mixture of D(+)-glucose and D(+)-galactose.

105. As carbohydrates are polyhydroxy carbonyl compounds (> C = O and —OH)

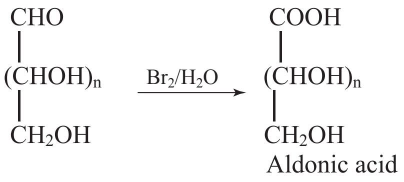
108. On hydrolysis with dilute acids, sucrose yields an equimolar mixture of D(+) glucose and D(–) fructose.

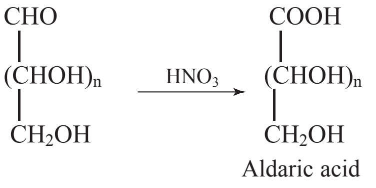
$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{HCl} C_6H_{12}O_6 + C_6H_{12}O_6$$

111. At pH = 4 (that is, acidic medium), an amphoteric Zwitter ion structure changes into cation when an acid is added to it.

113. 

Tripeptide structure

116. 



118. Lipids are soluble in $CHCl_3$.

119. On reducing sugars such as sucrose do not undergo mutarotation.

124. Natural rubber is cis-1,3 polyisoprene and has only cis-configuration at energy double bond.

126. α-D-glucose and β-D-glucose are anomers, because they differ in the orientation of the hydroxyl group at only C_1. On the other hand, epimers have several chiral carbons (or centres) differing in configuration about any chiral centre, not necessarily at C_1. Thus, all anomers are epimers, but all epimers are not anomers.

128. A pair of diastereomeric aldoses which differ only in configuration about C-2 is termed as pair of epimers.

Decisive Thinking Objective Type Questions

137. Taflon is thermally stable polymer of tetrafluoro ethylene ($CF_2 = CF_2$).

$$nF_2C = CF_2 \xrightarrow{\text{Polymerization}} [–F_2C – CF_2–]n$$

141. C – N bond in proteins has partial double bond character due to resonance.

143. Enzymes reduce the activation energy.

146. Glucose is a monosaccharide having chemical composition $C_6H_{12}O_{6.}$

149. Glycine (α-amino acetic acid) is the only α-amino acid which is achiral.

150. Nucleotide contains nitrogenous bases like adenine, guanine, thymine , cytosine and uracil.

Linked-Comprehension Type Questions

161. Glucose and fructose give the osazone, but they differ from each other only in configuration at C_1 and C_2

167. 1–Fluoro–2, 4–dinitrobenzene is called Sanger's reagent and is used for determination of N–terminal amino acid is a polypeptide chain.

Assertion-Reason Type Questions

174. The primary structure of a protein gives only the nature of linkages of α-amino acids in a protein chain.

181. Millon's test is a test for proteins. When millon's reagent is added to the aqueous solution of a protein, a white precipitate is formed.

183. Cellulose is not digested by humans due to lack of suitable enzymes.

188. $C_6H_{12}O_6$ + Fehling solution $\longrightarrow$

$(C_6H_{11}O_7)^- + Cu_2O$
Red ppt.

Matrix-Match Type Questions

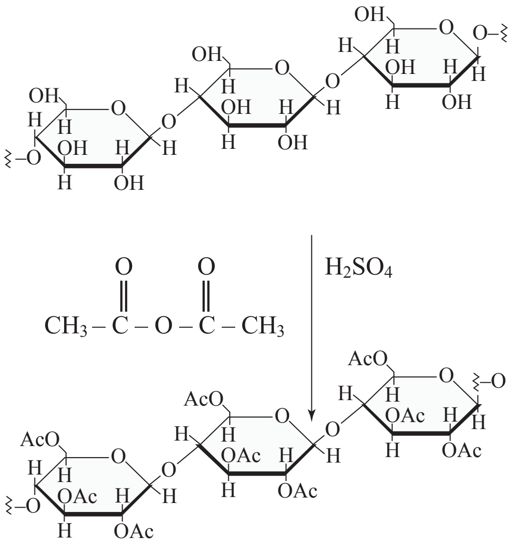
190. Cyanocobalamine → Vitamin (B_{12})
Pyridoxin → Vitamin (B_6)
Retinol → Vitamin (A)
Thiamine → Vitamin (B_1)

The IIT-JEE Corner

200. Carboxylic acids are stronger acids than N^+H_3, therefore, X is the strongest acid. since –COOH has –I effect which decreases with distance, therefore, effect is more pronounced on Y than on Z. As a result, Y is more acidic than Z. therefore, correct order of acidity of the positions is X > Y > Z.

202. Two form of D-glucopyranose are α-D-(+)-glucopyranose and β-D-(+)-glucopyranose. These are anomers (a pair of stereoisomers which differ in configuration only around first-carbon atom are called anomers).

203. Cellulose is a straight chain polysaccharide composed of D –glucose units which are joined by β – glycosidic linkages between C -1 of one glucose unit and C – 4 of the next glucose unit.

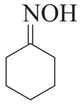


204. As chain of natural rubber involves weak van der Waal forces of interaction.

SUBJECTIVE SOLVED EXAMPLES

1. Give the structures of the products in each of the following reactions.

(i) Sucrose $\xrightarrow{H^+}$ A + B

(ii)  $\xrightarrow{H^+}$ (C) $\xrightarrow{\text{Polymerization}}$ $[-D-]_n$

Solution

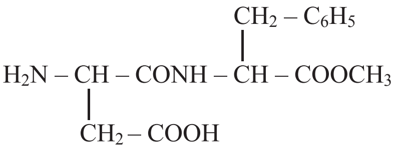
Sucrose on hydrolysis gives one molecule each of glucose (A) and fructose (B)

2. What type of bonding helps in stabilizing the α-helix structure of proteins ?

Solution

The α- helix structure of proteins is stabilized by intramolecular H- bonding between C= O of one amino acid residue and the N- H of the fourth amino acid residue in the chain Refer fig. in text part

3. Aspartame, an artificial sweetener, is a peptide and has the following structure:



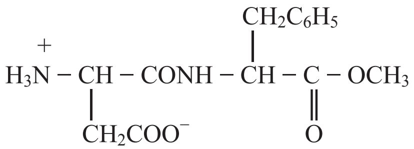
$$H_2N-\underset{\displaystyle CH_2-COOH}{\underset{|}{CH}}-CONH-\overset{\displaystyle CH_2-C_6H_5}{\overset{|}{CH}}-COOCH_3$$

(i) Identify the four functional groups.
(ii) Write the Zwitter ionic structure.
(iii) Write the structures of the amino acids obtained from the hydrolysis of aspartame.
(iv) Which of the two amino acids is more hydrophobic?

Solution

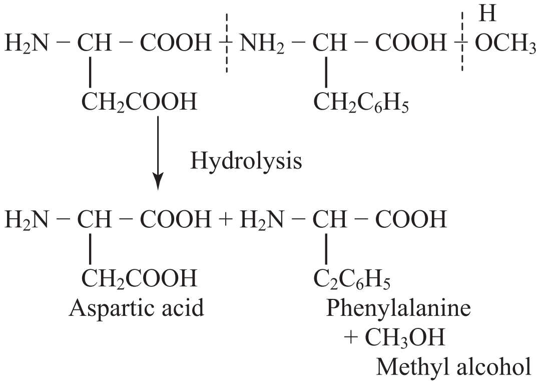
(i) The four functional groups in aspartame are: $-NH_2$ (amino group), −COOH (carboxyl group), $\overset{O}{\overset{\|}{-C}}-NH-$ (amide group) and $\overset{O}{\overset{\|}{-C}}-O-$ (ester group)

(ii) The zwitter ionic structure of aspartame is



$$\overset{+}{H_3N}-\underset{\underset{CH_2COO^-}{|}}{CH}-CONH-\overset{\overset{CH_2C_6H_5}{|}}{CH}-\underset{\underset{O}{\|}}{C}-OCH_3$$

(iii) The hydrolysis of aspartame gives following two amino acids:



$$H_2N-\underset{\underset{CH_2COOH}{|}}{CH}-COOH\ \vdots\ NH_2-\underset{\underset{CH_2C_6H_5}{|}}{CH}-COOH\ \vdots\ \overset{H}{OCH_3}$$

$$\Big\downarrow\ \text{Hydrolysis}$$

$$H_2N-\underset{\underset{CH_2COOH}{|}}{CH}-COOH+H_2N-\underset{\underset{C_2C_6H_5}{|}}{CH}-COOH$$

Aspartic acid

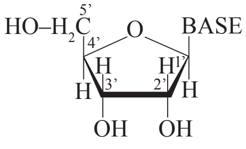
Phenylalanine + CH_3OH Methyl alcohol

(iv) Because of the presence of a large hydrocarbon part, i.e., phenyl group, phenylalanine is more hydrophobic than aspartic acid.

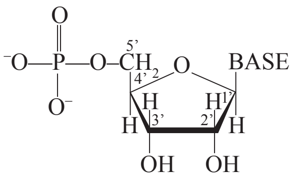
4. What is the difference between a nucleoside and a nucleotide?

Solution

A nucleoside is formed when 1- position of a pyrimidine (cytosine, thiamine or uracil) or 9- position of a purine (guanine or adenine) base is attached to C- 1 of sugar (ribose or deoxyribose) by a β- linkage. Thus, in general, nucleosides may be represented as: sugar -Base. For example, structure (I) represents a nucleoside.



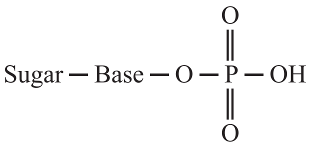
Nucleoside



Nucleotide

A nucleotide contains all the three components of nucleic acids, that is, a phosphoric acid group, a pentose sugar and a nitrogenous base. These are obtained by esterification of C5' — OH group of the pentose sugar by phosphoric acid.

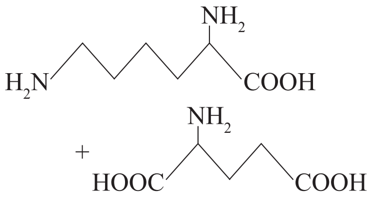
Thus, in general, a nucleotide is represented as



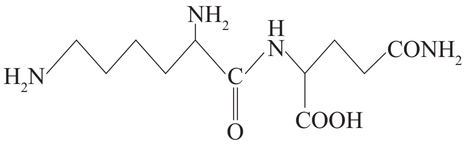
$$\text{Sugar}-\text{Base}-O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{P}}-OH$$

For example, structure (II) represents a nucleotide.

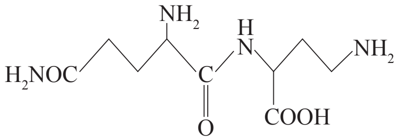
5. Following two amino acids liyosine and glutamine form dipeptide linkage. What are two possible dipeptides?



Solution

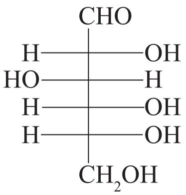


Lysylglutamine
(Lys -Gin or K -Q)



Glnyllysine
(Gln -Lys or Q -K)

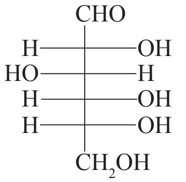
6. The Fisher projection of D-glucose is drawn below:



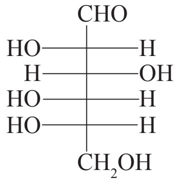
(i) Draw the Fisher projection of L-glucose.
(ii) Give the reaction of L-glucose with Tollen's reagent.

Solution

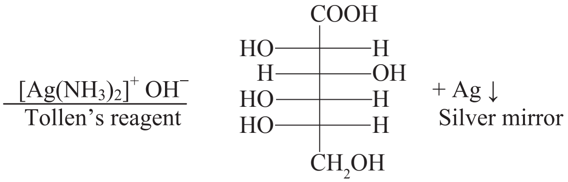
The fischer projection of L- glucose is the mirror image (or enantiomer) of D- glucose.



D- Glucose



L- Glucose

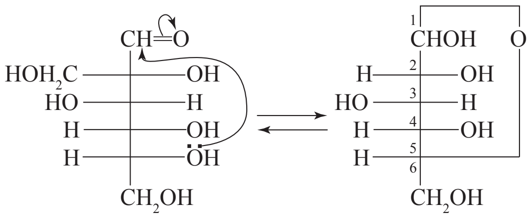


L- Gluconic acid

7. **7.** How do you explain the absence of aldehyde group in the pentaacetate of D- glucose?

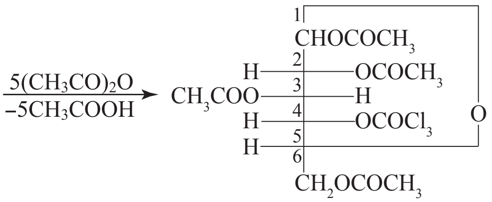
Solution

The cyclic hemiacetal form of glucose contains an OH group at C-1 which gets hydrolysed in the aqueous solution to produce the open chain aldehydic form which then with NH_2OH to form the

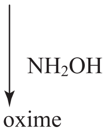


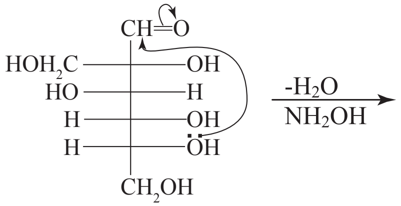
Glucose (Open chain form)

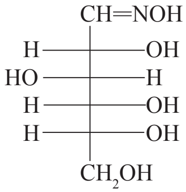
α- Glucose + β- Glucose



α- Glucose pentaacetate
+
β- Glucose pentaacetate







Glucose oxime

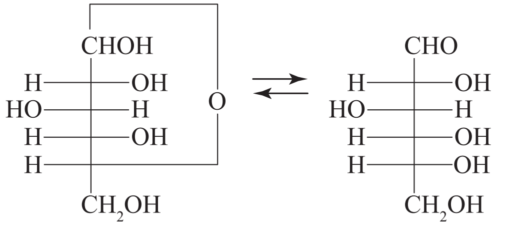
Corresponding oxime. Thus, glucose contains an aldehydic group. In contrast, when glucose is reacted with acetic anhydride, the OH group at C–1, along with the four other OH groups at C–2 , C–3 C–4 and C -6 form a pentaacetate. Since the pentaacetate of glucose does not contain a free OH group at C-1 it cannot get hydrolysed in aqueous solution to produce the open chain aldehydic form and hence glucose pentaacetate does not react with NH_2OH to form glucose form glucose oxime.

Thus, Glucose pentaacetate does not contain the aldehyde group.

8. **8.** What happens when D- glucose is treated with the following reagents?

(i) HI (ii) Bromine water (iii) HNO_3.

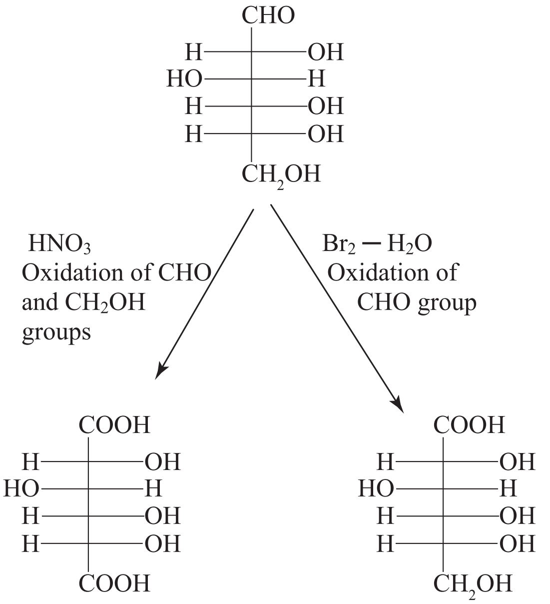
Solution



D- (+)- Glucopyranose (Hemiacetal form)

Glucose (open chain form)

$$\xrightarrow[\text{Reduction}]{HI} \underset{\text{n- Hexane}}{CH_3(CH_2)_4CH_3} + \underset{\text{2- Iodohexane}}{CH_3(CH_2)_2-CHI-CH_3}$$

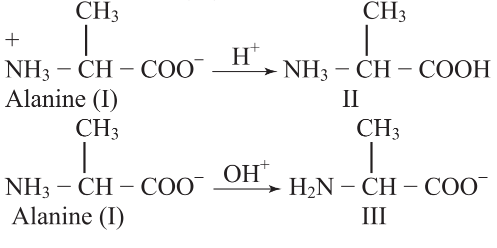


D- Saccharic acid D- Gluconic acid

9. Write the structure of alanine at pH = 2 and pH = 10.

Solution

Amino acids exists as zwitter ions (I) in aqueous solution. In presence of acid (pH = 2), the basic COO^- group accepts a proton to give cation (II) but in presence of a base (pH = 10), the acidic $\overset{+}{N}H_3$ group donates a proton to the base and thus exists as an anion (III).



$$\overset{+}{N}H_3 - \underset{\text{Alanine (I)}}{\overset{CH_3}{\overset{|}{C}H}} - COO^- \xrightarrow{H^+} NH_3 - \overset{CH_3}{\overset{|}{C}H} - COOH \quad \text{II}$$

$$NH_3 - \overset{CH_3}{\overset{|}{C}H} - COO^- \xrightarrow{OH^+} H_2N - \overset{CH_3}{\overset{|}{C}H} - COO^-$$

Alanine (I) III

10. Which of the following will reduce Tollen's reagent? Explain.

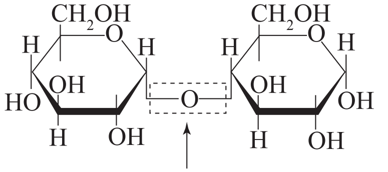
Solution

In disaccharide (Q), both the monosaccharides are linked through their centres (C_1), therefore, it is not a reducing disaccharide. In disaccharide (P), the reducing end (C_1) of one monosaccharide is linked to non-reducing end (C_4) of the other monosaccharide. In other words, reducing end of one monosaccharide is free. Therefore, it is a reducing disaccharide.

11. What do you understand by the term glycoside linkage?

Solution

The ethereal or oxygen linkage through which two monosaccharides are joined together by the loss of a water molecule to form a molecule of disaccharide is called the glycosidic linkage. The glycosidic linkage in maltose molecule is shown below :



α-D- Glucose Glycosidic linkage α-D- Glucose

12. What forces are responsible for the stability of α-helix? Why it is named as 3.6_{13} helix?

Solution

The stability of α-helix structure is due to intramolecular H- bonding between − NH− and −CO− groups of the same polypeptide chain. The α-helix is termed as 3.6_{13} helix as each turn of the helix has nearly 3.6 amino acids and the hydrogen bonding leads to the formation of a 13- membered ring.

13. How do starch (amylose) and glycogen differ in bonding?

Solution

Both amylose and glycogen are polymers of α- D-glucose. Amylose has linear structure in which C_1 of one glucose unit is connected to C_4 of the other by α glycosidic linkage. Glycogen, on the other hand, has highly branched structure. It consists of a large number of short chains each containing 10 -14 glucose units which are joined together through α- glycosidic linkage involving C_1 of one glucose unit to C_4 of the other. The C_1 of terminal glucose unit in each chain is further linked to C_6 of any other glucose unit in the next chain through C_1 -C_6 α- glycosidic linkage.

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PRACTICAL ORGANIC CHEMISTRY

CHAPTER 10

CHAPTER CONTENTS

Detection of elements (halogens); Detection and identification of the following functional groups: hydroxyl (alcoholic and phenolic), carbonyl (aldehyde and ketone), carboxyl, amino and nitro; Chemical methods of separation of mono-functional organic compounds from binary mixture and various level of multiple-choice questions.

DETECTION OF ELEMENTS (QUALITATIVE ANALYSIS)

DETECTION OF CARBON AND HYDROGEN

It is possible by heating the organic compound with dry CuO. Here, carbon is oxidized into CO_2 which turns lime water milky. Hydrogen is oxidized into water which turns anhydrous copper sulphate into blue colour.

LASSAIGNE'S TEST

Preparation of Lassaigne's Extract or Sodium Extract

The given organic compound (in small quantity) is fused with a small piece of sodium in an ignition tube. The tube is first heated gently and then strongly till it becomes red hot. It is then poured in the distilled water in a beaker. The solution is boiled and filtered. The filtrate is known as sodium extract.

- When an organic compound is fused with Na, a covalent organic compound is converted into an ionic compound. These N, S and halogens of the organic compound are converted into NaCN, Na_2S and NaX respectively. When N and S both are present NaCNS is also formed.

  $Na + C + N \longrightarrow NaCN$

  $2Na + S \longrightarrow Na_2S$

  $Na + X \longrightarrow NaX$

  $Na + C + N + S \longrightarrow NaCNS$

- Lithium is not used in Lassaigne test as it reacts slowly moreover its compounds are covalent. Potassium can not be used in this test as it's reaction is violent.

Test For Nitrogen

- Take sodium extract and add one drop NaOH and 1 ml $FeSO_4$ solution (fresh). Now boil it. After cooling add aqueous $FeCl_3$ and acidified it, A deep blue colour is formed which is of ferriferrocyanide.

$$FeSO_4 + 2NaOH \longrightarrow Fe(OH)_2 + Na_2SO_4$$

$$6NaCN + Fe(OH)_2 \longrightarrow Na_4Fe(CN)_6 + 2NaOH$$

$$3Na_4Fe(CN)_6 + 4FeCl_3 \longrightarrow \underset{\text{Ferri ferro cyanide 'Prussian blue'}}{Fe_4[Fe(CN)_6]_3} + 12NaCl$$

- It is not given by NH_4Cl, $NaNO_3$, NH_2NH_2 that is, without carbon compounds
- It is given by urea , aniline, acetamide, benzamide, azobenzene, glycine etc.

Test For Sulphur

(a) When lead acetate is added in sodium extract a black precipitate of lead sulphide is obtained.

$$Na_2S + (CH_3COO)_2Pb \longrightarrow \underset{\text{Black pp.t}}{PbS} + 2CH_3COONa$$

(b) When sodium nitro pruside solution is added in sodium extract a violet colour is formed.

$$Na_2S + Na_2[Fe(CN)_5NO] \longrightarrow \underset{\text{Sodium thio nitro prusside (Violet)}}{Na_4[Fe(CN)_5NOS]}$$

Nitrogen and Sulphur In the detection of nitrogen, if a red colour is formed it means both Nitrogen and Sulphur are present which is confirmed as follows:

$$3NaCNS + FeCl_3 \longrightarrow \underset{\substack{\text{(Red)} \\ \text{Ferric sulphocyanide}}}{Fe(CNS)_3} + 3NaCl$$

$$\text{Silver coin + Sod. ext.} \longrightarrow \text{Black coin}$$

$$NaCNS + HCl \longrightarrow HSCN + NaCl$$

$$4\,HSCN + Co(NO_3)_2 \longrightarrow \underset{\text{Blue colour}}{H_2[Co(SCN)_4]} + 2HNO_3$$

Middleten's Test $Na_2CO_3 + ZnO$

NaCNS is not formed in this test but ZnS is formed. (test of sulphur)

Test of Halogens

- Sodium extract is first boiled with few drops of HNO_3 (to decompose NaCN to HCN gas, Na_2S to H_2S gas and to neutralized free alkali) the solution is cooled and silver nitrate solution is added where a ppt. of AgX is formed.

$$NaCN + AgNO_3 \longrightarrow AgCN\downarrow + NaNO_3$$

$$Na_2S + 2AgNO_3 \longrightarrow Ag_2S + 2NaNO_3$$

$$NaCN + HNO_3 \xrightarrow{\Delta} 2NaNO_3 + HCN\uparrow$$

$$Na_2S + 2HNO_3 \xrightarrow{\Delta} 2NaNO_3 + H_2S\uparrow$$

$$Na + AgNO_3 \longrightarrow AgX + NaNO_3$$

- If a white precipitate, soluble in NH_4OH and in soluble in dil. HNO_3 is formed chlorine is confirmed.

  $NaCl + AgNO_3 \rightarrow \underset{\text{White ppt.}}{AgCl} + NaNO_3$

  $AgCl + 2NH_4OH \rightarrow \underset{\text{Diammine silver chloride}}{Ag(NH_3)_2\,Cl} + 2H_2O$

- If a light yellow precipitate, partially soluble in NH_4OH is formed bromine is confirmed.

  $NaBr + AgNO_3 \rightarrow \underset{\text{Light yellow ppt.}}{AgBr} + NaNO_3$

- If a dark yellow precipitate, insoluble in NH_4OH is formed iodine is confirmed.

  $NaI + AgNO_3 \rightarrow \underset{\text{Dark yellow ppt.}}{AgI} + NaNO_3$

Beilstein's Test By this test, we can confirm the absence or presence of halogens by heating the organic compound on copper wire

- If Cu wire with the compound gives no green flame again halogens are absent.
- If a bluish green flame (due to vapours of CuX_2) is observed halogens may or may not be present.
- Pyridine, thiourea also give green colour in this test.
- Beilstein Test is not given by 'fluorine' as CuF_2 is non volatile.

$CHCl_3$ or CCl_4 Layer Test (for Br and I)

- Take 2,3 ml sodium extract, H_2SO_4, 1ml $CHCl_3$ in a test tube and add excess of chlorine water, shake thoroughly and observe that
  - If the colour of the CCl_4 layer becomes brown Br is present.
  - If the colour of the CCl_4 layer turns violet iodine is present.

$2NaBr + Cl_2 \longrightarrow 2NaCl + Br_2$

$2NaI + Cl_2 \longrightarrow 2NaCl + I_2$

Test for Phosphorus

- First fuse organic compound with sodium peroxide so that phosphorous is converted into sodium phosphate which is extracted with water and boiled with concentrated HNO_3 and finally add ammonium molybdate to get a yellow precipitate of ammonium phospho molybdate.

  $2P + 5Na_2O_2 \rightarrow 2Na_3PO_4 + 2Na_2O$

  $Na_3PO_4 + 3HNO_3 \xrightarrow{\Delta} H_3PO_4 + 3NaNO_3$

  $H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 \rightarrow$

  $(NH_4)_3PO_4.12MoO_3 + 21\,NH_4NO_3 + 12H_2O$

  Ammonium Phosphomolybdate
  (yellow ppt.)

Detection and Identification of Functional Groups

(1) Detection and Identification of –OH Group

There are three tests which can be used to detect the presence of a hydroxyl group in an unknown organic compound. For these tests, we can use the liquid substance or a solution of the solid substance in dry ether or benzene.

(i) Take this solution and add small pieces of sodium metal in it. If bubbles of hydrogen are given off, it confirms the presence of –OH group.

$$2ROH + 2Na \rightarrow 2RONa + H_2$$

(ii) Take this solution and add phosphorous pentachloride in it. If the mixture becomes warm with liberation of HCl gas, it confirms the given substance is a hydroxyl compound.

$$ROH + PCl_5 \rightarrow RCl + POCl_3 + HCl \uparrow$$

(iii) Add acetyl chloride or benzoyl chloride to the substance. The liberation of HCl gas with separation of an oily layer shows the presence of an –OH group.

If the substance was taken in an organic solvent the oily ester may dissolve in it and the liberation of HCl gas indicates the presence of –OH group.

(iv) **Ester Test** When the aqueous solution of substance is heated with acetic acid in presence of H_2SO_4. A characteristic fruity smell indicates the formation of an ester.

$$CH_3COOH + HOR \xrightarrow{H_2SO_4} CH_3COOR + H_2O$$

(v) **Ceric Ammonium Nitrate Test** Take a small amount of organic compound and few drops of ceric ammonium nitrate is added into it, after shaking, a red colour is obtained. This test is useful only when compound contains less than 10 carbon atoms per molecule.

$$2ROH + (NH_4)_2\,[Ce(NO_3)_6] \rightarrow [Ce(NO_3)_4\,(ROH)_2] + 2NH_4NO_3$$

(2) Detection and Identification of Phenols

Following tests can be used to detect the presence of a phenolic group.

(i) **Litmus Test** It turns blue litmus paper into red.

(ii) **Ferric Chloride Test** Add 2-3 drops of neutral ferric chloride solution to a very dilute aqueous solution of the compound. The appearance of violet, blue green or red colouration indicates the presence of phenol.

$$3C_6H_5OH + FeCl_3 \rightarrow \underset{\text{(violet colour)}}{\underset{\text{Ferric phenoxide}}{(C_6H_5O)_3Fe}} + 3HCl$$

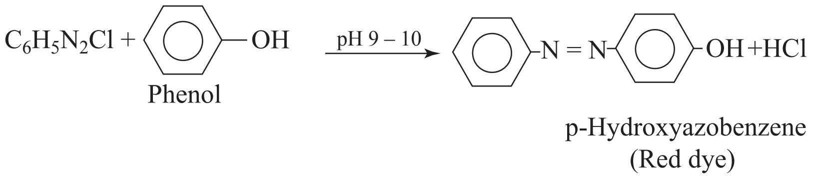
REMEMBER

- α-Naphthy glamine gives a blue colour with ferric chloride solution even though it does not contain a phenolic group.
- α –Nαphthol and β-naththol do not give any colour with $FeCl_3$ in aqueous solutions but they give characteristic colours in alcoholic solutions.

(iii) Azo-dye Test Dissolve a little of the compound in aqueous sodium hydroxide solution and cool it in ice-cold water. In another tube, take 2-3 ml of aniline, dissolve it in dil. HCl and cool in ice cold water. Add solid $NaNO_2$ to the solution of aniline in HCl and mix the two solutions. Formation of an orange or red dye indicates the presence of a phenol group.

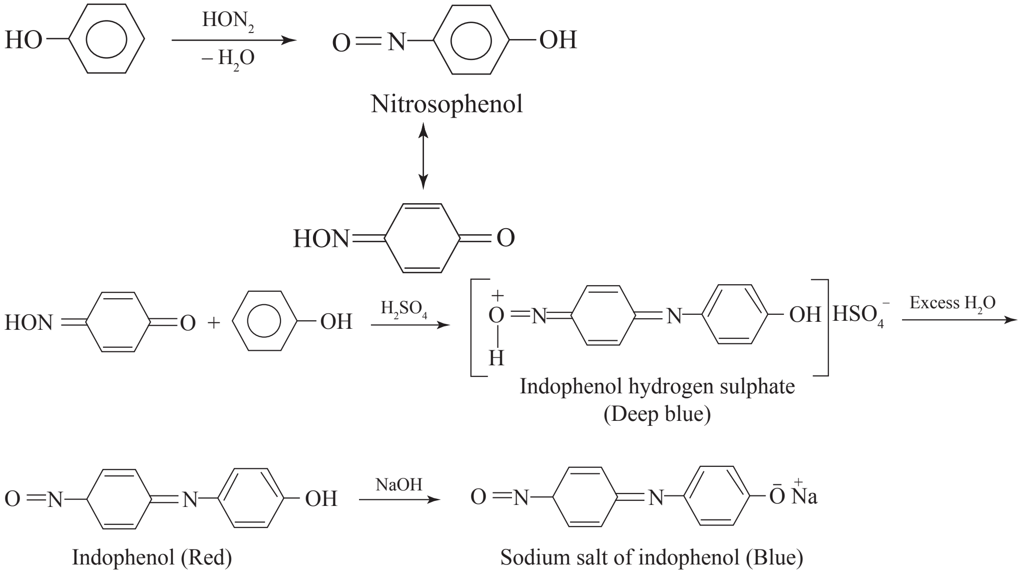
$$NaNO_2 + HCl \rightarrow HNO_2 + NaCL$$

$$\underset{}{C_6H_5NH_2 + HNO_2} \xrightarrow{\text{Ice cold}} \underset{\substack{\text{Benzene}\\ \text{diazonium chloride}}}{C_6H_5N_2Cl} + 2H_2O$$



(iv) Libermann's Reaction Dissolve about 0.1 g of the organic compound in 1 ml of conc. H_2SO_4. Add a pinch of sodium nitrite and shake. A blue green or blue violet colour is formed. Dilute the contents with water, the colour changes to red. Addition of NaOH to this solution changes the colour to blue, green or violet.

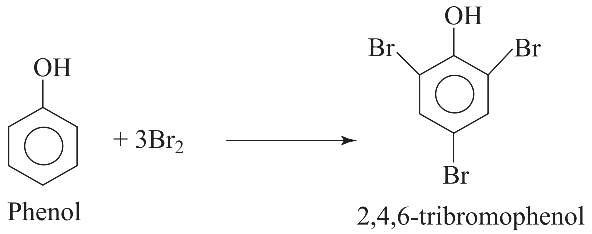
$$NaNO_2 + H_2SO_4 \rightarrow HNO_2 + NaHSO_4$$



- Only phenols possessing a free para position respond to this test. Nitrophenols and p-substituted phenols do not give the test.

(v) Bromine Water Test

Aqueous or alcoholic solution of the organic compound is mixed with bromine water A yellowish white precipitate is formed.



(vi) Ceric Ammonium Nitrate Test Take hot aqueous solution of the organic compound in a test tube and add few drops of ceric ammonium nitrate. A green or brown coloured precipitate is formed.

$$\underset{}{(NH_4)_2[Ce(NO_3)_6]} + \underset{\text{Phenol}}{2C_6H_5OH} \rightarrow \underset{\text{Green or brown ppt.}}{[Ce(NO_3)_4\,(C_6H_5OH)_2]} + 2NH_4NO_3$$

(vii) Phthalein Test (Fluorescein Test) This is specific test for different phenols. Heat 0.2 g each of given organic compound and phthalic anhydride with 2 drops of conc. H_2SO_4 in a test tube for one minute. Cool and then add to 10 per cent NaOH solution in excess taken in a beaker. Note the characteristic colour obtained.

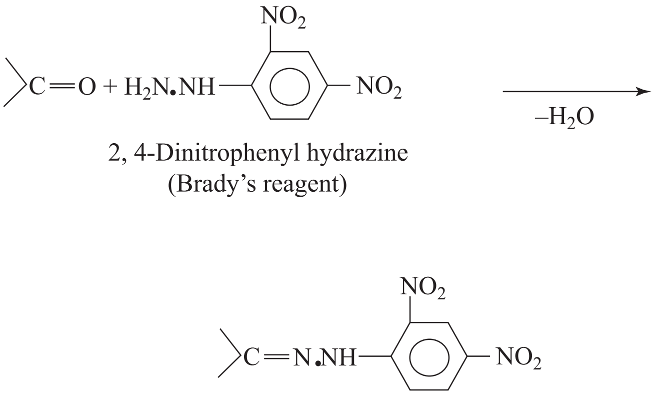
Colour	Compound
Red	Phenol, o-Cresol
Bluish-purple	m-Cresol
No colour	p-Cresol
Blue	Catechol
Green	α-Naphthol
Green fluorescent solution	Resorcinol
Deep purple	Hydroquinone (quinol)

(3) DETECTION AND IDENTIFICATION OF ALDEHYDIC (–CHO) AND KETONIC (–COR) GROUPS

In order of detect the presence of an aldehyde or a ketonic group we can use these tests.

(a) Common Tests (Test of Carbonyl Groups) Due to the presence of carbonyl group in aldehydes as well as ketones they respond to the following test:

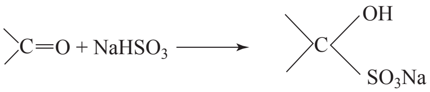
(i) 2, 4-Dinitrophenyl Hydrazine Test or Brady's Test Add a small amount of the given organic compound to about 3 ml of 2, 4-dinitrophenyl hydrazine reagent and shake. If no precipitate forms immediately, allow it to stand for 5-10 minutes or scratch the sides of the test tubes with a glass rod. A crystalline yellow, orange or red precipitate indicates the presence of a carbonyl group.



2, 4-Dinitrophenyl hydrazine
(Brady's reagent)

2, 4-Dinitrophenyl hydrazine
(Yellow, Orange or red ppt.)

(ii) Sodium Bisulphite Test Take a little of the compound in a test tube and add about 1 ml of a saturated solution of sodium bisulphite to it and stir the contents vigorously. A crystalline white precipitate indicates the presence of an aldehydic or ketonic group.



$$>C{=}O + NaHSO_3 \longrightarrow >C\begin{matrix}OH \\ SO_3Na\end{matrix}$$

Bisulphite Compound
Crystalline white ppt.)

- This test is not given by aromatic ketones like acetophenone and benzophenone. This test is also not given by Pentan-3-one.

DIFFERENTIATION TESTS BETWEEN ALDEHYDES AND KETONES

(b) Test given by Aldehydes only

(i) Tollen's Test Take 1 ml of freshly prepared 10 per cent silver nitrate solution in a test tube and add 1 ml of 10 per cent NaOH and shake. To the resulting mixture add dilute NH_4OH with constant shaking till the precipitate formed just dissolves. Now add a small amount of the unknown organic compound and shake well. A silver mirror along the sides of the test tube due to the reduction of silver ions to metallic silver in the cold or on warming indicates the presence of an aldehydic group.

$$AgNO_3 + NaOH \longrightarrow AgOH + NaNO_3$$

$$AgOH + 2NH_4OH \longrightarrow \underset{\text{Tollen's reagent}}{[Ag(NH_3)_2]OH} + 2H_2O$$

$$RCHO + 2[Ag(NH_3)_2]OH \longrightarrow RCOONH_4 + \underset{\text{Silver mirror}}{2Ag} + 3NH_3 + 2H_2O$$

- Both aliphatic and aromatic aldehydes give this test but ketones do not respond to this test because like aldehydes they are not good reducing agent.

(ii) Schiff's Reagent Test Add a little of the organic compound to 2 ml of Schiff's reagent (p-rosaniline hydrochloride solution whose pink colour is discharged by passing SO_2) and shake the mixture in cold. Appearance of pink colour indicates the presence of an aldehyde.

(iii) Fehling Solution Test Add a little of the compound to 2-3 ml of freshly prepared Fehling's solution. Heat on a water bath for 3-4 minutes. A red ppt. of Cu_2O indicates the presence of an aldehyde.

- This test is given only by aliphatic aldehydes but not by aromatic aldehydes like benzaldehyde as being weat reductant it can not reduce the reagent.

$$CuSO_4 + 2NaOH \rightarrow Cu(OH)_2 + Na_2SO_4$$

$$Cu(OH)_2 \rightarrow CuO + H_2O$$

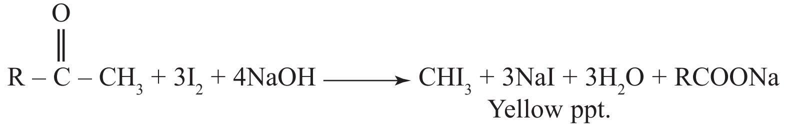
$$RCHO + 2CuO \rightarrow RCOOH + \underset{\text{Red. ppt.}}{Cu_2O}$$

(iv) Benedict's Solution Test This is a modification of Fehling's solution test and consists of alkaline cupric ions complexed with citrate ions. Add a few drops of organic compound or a solution of solid in water or ethanol to 4 ml of Benedict's solution taken in a test tube. Heat the mixture of boiling. A red precipitate (due to Cu_2O) indicates the presence of an aldehyde.

TEST GIVEN BY KETONES ONLY

(i) Sodium Nitroprusside Test Add a little of the organic compound to about 1 ml of sodium nitroprusside solution. Now make the solution alkaline by adding a few drops of sodium hydroxide. Red or purple colour indicates the presence of ketonic group.

(ii) Iodoform Test (for methyl ketones that is, ketones containing $-COCH_3$ grouping only) Dissolve 0.1 g or 4-5 drops of the compound in 2 ml of water (methanol or dioxane for water insoluble compounds). Now add 1 ml of 10 per cent NaOH solution followed by addition of a solution of iodine in potassium iodide drop wise. Yellow precipitate of iodoform indicates the presence of a methyl ketone.



$$R - \overset{\overset{\displaystyle O}{\|}}{C} - CH_3 + 3I_2 + 4NaOH \longrightarrow \underset{\text{Yellow ppt.}}{CHI_3} + 3NaI + 3H_2O + RCOONa$$

(4) DETECTION AND IDENTIFICATION –COOH GROUP

Detection Test For it following tests are generally used.

(i) Litmus Paper Test Here a pinch of the organic compound is shaken with 2-3 ml of distilled water followed by the addition of 2-3 drops of blue litmus solution.

If the blue litmus turns red, then an acidic group that is, -COOH or phenol groups may be present.

(ii) Sodium Bicarbonate Test Add a pinch of the substance (if solid) or a few drops of it (if liquid) to about 5 ml of cold saturated solution of sodium bicarbonate. Vigorous evolution of carbon dioxide with brisk effervescence in the presence of carboxylic group in the compound and absence of phenolic group.

$$RCOOH + NaHCO_3 \rightarrow RCOONa + H_2O + CO_2\uparrow$$

REMEMBER

- Besides carboxylic acids some nitrophenols like 2, 4-dinitrophenol and picric acid also evolve CO_2 on reaction with $NaHCO_3$ solution. However this test is not given by simple phenols. Nitrophenols on treatment with $NaHCO_3$ gives yellow coloured solutions.

CONFIRMATORY TESTS FOR CARBOXYLIC ACIDS

(iii) Ester Test or Fruity Smell Test Add about 2 ml of ethyl alcohol and 2-3 drops of conc. H_2SO_4 to a little of the compound in a test tube and heat the contents gently. A pleasant fruity smell ester formation confirms carboxylic group.

$$\mathrm{RCOOH} + \mathrm{C_2H_5OH} \xrightarrow{\text{conc. } H_2SO_4 . \Delta} \underset{\text{Ester}}{\mathrm{RCOOC_2H_5}} + \mathrm{H_2O}$$

(iv) $FeCl_3$ Test Shake a pinch of the compound with about 5 ml of distilled water and add ammonium hydroxide dropwise to get a clear solution. Heat to remove excess of NH_3 if any, cool and add 2-3 drops of neutral ferric chloride solution. Note the colour of the resulting solution or the precipitate.

Observation	Inference
Red colour changing to brown ppt. on heating.	Acetic acid, Formic acid
Light yellow colour	Oxalic acid
Buff-coloured ppt. which dissolves on adding dil. H_2SO_4	Succinic acid
Buff coloured ppt. in the cold which dissolves on adding dil. H_2SO_4 but a white ppt. is formed	Benzoic acid
Violet colouration	Salicylic acid
Brownish buff coloured ppt.	Phthalic acid
Light yellow coloured ppt.	Cinnamic acid

$$\mathrm{RCOOH} + \mathrm{NH_4OH} \rightarrow \underset{\substack{\text{Ammonium salt}\\ \text{(soluble)}}}{\mathrm{RCOONH_4}} + \mathrm{H_2O}$$

$$3\mathrm{RCOONH_4} + \mathrm{FeCl_3.H_2O} \rightarrow \underset{\text{Basic iron salt}}{\mathrm{Fe(OH)(OOCR)_2}} + 3\mathrm{NH_4Cl} + \mathrm{RCOOH}$$

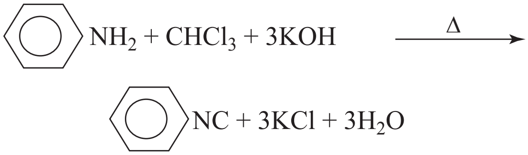
TEST FOR AMINES (-NH_2)

(i) Solubility Test Amines are the organic compounds that have appreciable basicity and so they dissolve in mineral acids.

(ii) Litmus Test Amides have appreciable basicity due to their basic nature amines turn red litmus blue.

$$\mathrm{CH_3CH_2NH_2} + \mathrm{H_2O} \rightleftharpoons \mathrm{CH_3CH_2\,{}^{+}NH_3} + \mathrm{OH^-}$$

(iii) Carbylamine Reaction It is a test of primary amines and chloroform here pungent bad smelling isocyanides are formed. Here dichlorocarbene is reaction intermediate.



Phenyl Isocyanide

(iv) Nitrous Acid Test

Primary Aliphatic Amines It reacts with nitrous acid to give bubbles of gas.

$RNH_2 + HONO \rightarrow ROH + H_2O + N_2$

Primary Amine Alcohol

Secondary Amines It reacts with nitrous acid to form a yellow oily nitrosoamine.

$R_2NH + HONO \rightarrow R_2N - NO + H_2O$

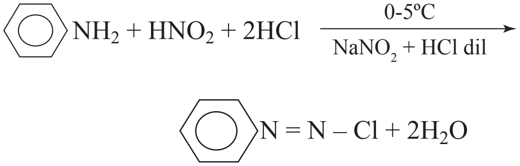
Sec-amine Nitrosoamine

Tertiary Amines It reacts with nitrous acid to form soluble nitrite salts as follows

$R_3N + HONO \rightarrow R_3NH^+ ONO^-$

Tert-amine Trialkyl ammonium nitrite

(v) Azo Dye Test A small amount of organic compound is dissolved in dilute HCl then cooled in ice-cold water bath and add cold solution of sodium nitrite with constant stirring followed by β-naphthol solution. An orange-red dye is obtained.



Benzene di azonium chloride

β-naphthol

Phenyl azo β-naphthol
(orange red dye) [Scarlet]

- Formation of an orange red dye with alk. Solution of β– naphthol confirms the presence of aromatic p-amino group.
- If a compound reacts with HNO_2 but does not form a dye with β– naphthol compound may contain NH_2 group in the side chain.

ESTIMATION OF ELEMENTS OR QUANTITATIVE ANALYSIS

ESTIMATION OF CARBON AND HYDROGEN

- The estimation of carbon and hydrogen is made by **Liebig's Combustion Method.**

$$\text{Org. Compound} + \underset{\text{Dry}}{2\mathrm{CuO}} \xrightarrow[\text{Sparingly}]{\Delta} \mathrm{CO_2 + H_2O}$$

$$\mathrm{C + 2CuO \xrightarrow{\Delta} CO_2 + 2Cu}$$

$$\mathrm{CO_2 + Ca(OH)_2 \longrightarrow \underset{\text{Milky}}{CaCO_3\downarrow} + H_2O}$$

$$\begin{tikzcd} \mathrm{CaCO_3} \arrow[d, "\mathrm{H_2O + CO_2}\ \text{excess}"] \\ \mathrm{Ca(HCO_3)_2}\ \text{(soluble)} \end{tikzcd}$$

$$\mathrm{H_2 + CuO \xrightarrow{\Delta} Cu + H_2O}$$

$$\mathrm{CuSO_4 + 5H_2O \longrightarrow \underset{\text{Blue}}{CuSO_4.5H_2O}}$$

$$\mathrm{C}\ \% = \frac{12}{44} \times \frac{\text{wt. of } \mathrm{CO_2}}{\text{wt. of org. compound}} \times 100$$

$$\mathrm{H}\ \% = \frac{2}{18} \times \frac{\text{wt. of } \mathrm{H_2O}}{\text{wt. of org. compound}} \times 100$$

- Oxygen can not be detected by a chemical test.

ESTIMATION OF NITROGEN Many methods are used to find out the percentage of nitrogen but the following two methods are commonly used.

- **Duma's Method** This method can be used for the estimation of nitrogen in all the types of organic compounds. Nitrogen of the compound is estimated as N_2 gas.

$$\mathrm{N}\ \% = \frac{28}{22400} \times \frac{\text{Volume of } \mathrm{N_2} \text{ at S.T.P}}{\text{wt. of org. compound}} \times 100$$

OR

$$\mathrm{N}\ \% = \frac{\text{Vol of } \mathrm{N_2} \text{ at S.T.P}}{8 \times \text{wt. of org. compound}}$$

- **Kjeldahl's Method** The method is applicable only for those compounds in which nitrogen is attached directly to either carbon or hydrogen.

Method It is based on the fact that an organic compound on heating with conc. H_2SO_4 in the presence of $CuSO_4$ and K_2SO_4 gives ammonium sulphate if it has nitrogen. Ammonium sulphate on heating with KOH or NaOH liberates ammonia which is utilized by H_2SO_4

$$\mathrm{(NH_4)_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O + 2NH_3}$$
$$\mathrm{2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4}$$

- This method is generally used to find out the percentage of nitrogen in organic compounds used as food stuffs, fertilizers etc. It is a very simple method.

$$N\ \% = \frac{1.4 \times N \times V}{\text{wt. of org. compound}}$$

Here N = normality of the acid used to neutralize ammonia

V = volume of the acid used to neutralize ammonia

Estimation of Halogens

- ***Carius Method*** The method is suitable for those organic compounds which decompose easily.
- Here the organic compound is heated with fuming HNO_3 and few crystals of $AgNO_3$ in a sealed tube as a result the precipitate of AgX is formed.

$$\text{Organic compound} + HNO_3 \rightarrow HX$$
$$HX + AgNO_3 \rightarrow HNO_3 + \underset{\text{ppt.}}{AgX}$$

$$X\ \% = \frac{\text{At. wt of X}}{\text{Mol. wt. of AgX}} \times \frac{\text{wt. of AgX}}{\text{wt. of org. compound}} \times 100$$

Atomic weight of chlorine = 35.5,
Atomic weight of bromine = 80
Atomic weight of iodine = 127
Atomic weight of silver = 108

- It is also estimated by piria and schiff's method.

Estimation of Phosphorous

- When a known mass of given organic compound is heated with fuming HNO_3 in a Carius tube, phosphorous is oxidized into H_3PO_4. Phosphoric acid thus formed is precipitated as magnesium ammonium phosphate by adding magnesia mixture (a solution containing $MgCl_2$, NH_4Cl and NH_4OH).

$$MgCl_2 + NH_4Cl + H_3PO_4 \rightarrow \underset{\text{Magnesium ammonium phosphate}}{MgNH_4PO_4} + 3HCl$$

- This precipitate is filtered, washed, dried and then ignited to get magnesium pyrophosphate.

$$2MgNH_4PO_4 \xrightarrow{\Delta} \underset{\text{Magnesium pyrophosphate}}{Mg_2P_2O_7} + 2NH_3 + H_2O$$

- It is weighed and the percentage of phosphorous is find out by using the relation.

$$P\ \% = \frac{62}{222} \times \frac{\text{Mass of } Mg_2P_2O_7 \text{ formed}}{\text{Mass of substance taken}} \times 100$$

Estimation of Sulphur It is estimated by Carius method.

- Organic compound with C, H, S + $HNO_3 \xrightarrow{\text{heat}} CO_2 + H_2O + H_2SO_4$

  $H_2SO_4 + BaCl_2 \rightarrow 2HCl + \underset{\text{White ppt.}}{BaSO_4}$

  $$S\ \% = \frac{32}{233} \times \frac{\text{Wt. of } BaSO_4}{\text{wt. of org. compound}} \times 100$$

Molecular Weight Determination

- ***Silver Salt Method***

  Molecular weight of acid = equivalent weight x basicity

  = E × n

  = n [W/w × 108 – 107]

  Here n = basicity.

- ***Platinichloride Method***

  Molecular weight of base = equivalent weight of base × acidity

  = B × n

  $$= n\left[\frac{W}{w} \times \frac{195}{2} - 205\right]$$

  Volumetric Method

  Molecular weight of acid = equivalent weight x basicity

  $$= n\left[\frac{m}{v} \times 1000\right]$$

- ***Victor Mayer Method***

  $$\text{Vapour Density} = \frac{\text{wt. of certain vol. of vapour at NTP}}{\text{wt. of same vol. of } H_2 \text{ at NTP}}$$

EMPIRICAL AND MOLECULAR FORMULAS

Empirical Formula It gives the simplest ratio of the number of atoms of different elements present in one molecule of a compound.

- It does not represent the actual number of atoms of different elements present in one molecule of the compound.
- **Calculation of the empirical formula** involves these steps one by one
  - I. First determine the percentage composition by weight of each element present in the compound.
  - II. Now the percentage of each element is divided by its atomic weight to get the relative number of atoms of each element.

III. These relative numbers obtained are divided by smallest number to get the simplest ratio numbers.
IV. If the simplest ratio number is not a whole number it should be multiplied by a suitable integer to get a whole number.
V. The ratio of these simple whole numbers give the empirical formula of the compound.

MOLECULAR FORMULA It shows the actual number of atoms of different elements present in one molecule of the compound.

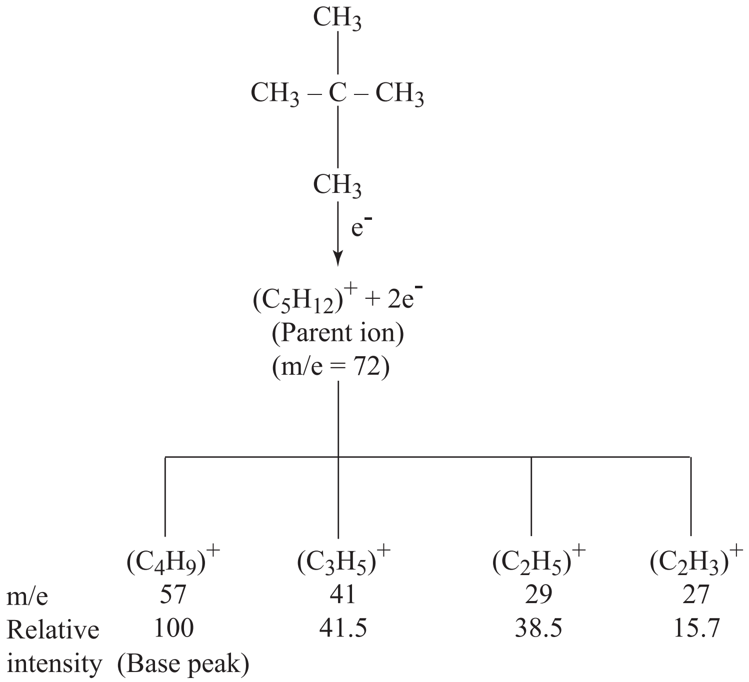
- $n = \dfrac{\text{Molecular weight}}{\text{Empirical formula weight}}$
- Molecular formula = empirical formula x n.
- Molecular weight of a substance can be determined by following methods like Vapour density method, Elevation in boiling point method, Depression in freezing point methods etc.
- The molecular weight of volatile compounds are determined by Victor Mayer's method.

  Molecular Weight = 2 x Vapour density
- Molecular weight = empirical formula weight x n.
- For some compounds the molecular formula and empirical formula may be same also.

MODERN METHODS OF STRUCTURE ELUCIDATION

- Due to the rapid development in the field of scientific instrumentation, it is now quite easy to find the complete structure of an organic compound with maximum accuracy.
- In these methods, only a small amount of the organic compound is needed.
- Molecular weight and molecular formulae can be readily determined with the help of mass spectrometry.
- The nature and type of functional groups present in a particular molecule can be easily find out from nuclear magnetic resonance (N.M.R), electronic (U.V), infra-red (I.R.) spectroscopies.
- At last the complete three dimensional structure of a molecule, including its bond lengths and bond angles can be determined by X-rays diffraction technique.
- This kind of formula which gives the three dimension arrangement its atoms including functional groups, bond length, bond angles etc., is known as structural formula.
- **Mass Spectroscopy** In a mass spectrometer, the molecules are bombarded with a stream of high energy electrons. As a result these molecules get ionized and cleaved into a number of fragments, a few of which may positive ions.
- Each type of a ion has a particular ratio of mass to charge that is, m/e value as for most of the ions, the charge is one so m/e ratio simply represents the mass of the ions.

  For example, In case of 2, 2-dimethylpropane (that is, neo-pentane), m/e values for different ions can be given as:



- These set of ions can be analysed by using a mass spectrometer in such a way that a specific signal is achieved for each value of m/e and the intensity of each specific signal corresponds to relative abundance of the ion producing that specific signal.
- The largest peak in this spectrum is known as base peak. Its intensity is assumed to be 100 and the intensities of other peaks can be expressed relative to it.
- When a graph is plotted between different value of m/e and relative intensities of the signal it is known as mass spectrum.
- This spectrum helps in finding the exact molecular weight of the compound.
- When one electron is removed from the parent molecule (A), then the parent ion (or molecular ion) A^+ is formed.

$$A + e^- \rightarrow \underset{\substack{\text{Molecular ion} \\ \text{(Parent ion)}}}{A^+} + 2e^-$$

- Its m/e value gives the molecular weight of this compound.
- Sometimes, the A^+ peak is the base peak and it can be easily recognized.
- In other cases, if it is not the base peak and has to be identified or located. Once identified, it gives the most accurate mass of the compound.

MULTIPLE-CHOICE QUESTIONS

Straight Objective Type Questions (Single Choice only)

1. To sodium fusion extract, Cl_2 water and CCl_4 were added and shaken wel. There is violet colour in the organic layer. This indicates the presence of

(a) Fluorine (b) Chlorine
(c) Bromine (d) Iodine

2. In Carius tube, the compound $ClCH_2COOH$ was heated with fuming HNO_3 and $AgNO_3$. After filtration and washing, a white ppt. was formed. The ppt. is

(a) Ag_2SO_4 (b) $AgNO_3$
(c) AgCl (d) $ClCH_2COOAg$

3. A mixture of acetone and CCl_4 can be separated by

(a) Steam distillation
(b) Azeotropic distillation
(c) Vacuum distillation
(d) Fractional distillation

4. MIC (which is responsible for Bhopal gas tragedy) can be produced by which of the following test

(a) Mulliken test
(b) Carbylamine test
(c) Victor - Meyer test
(d) Libermann Nitrose test

5. When pieces of human hair are heated strongly with soda-lime, smell of ammonia can be detected. Which one of the following conclusion can be drawn from this observation?

(a) hair contains amino acids
(b) ammonium salt is present in hair
(c) ammonia is present in the human hair
(d) none of the above

6. A mixture of benzene and chloroform is separated by

(a) sublimation (b) separation funnel
(c) crystallization (d) distillation.

7. During ninhydrin test of amino acid the precipitate formed is of

(a) Voilet colour (b) Red colour
(c) Blue colour (d) Orange colour

8. Absolute alcohol cannot be obtained by simple fractional distillation since:

(a) Boiling point of C_2H_5OH is very close to that of water
(b) Pure C_2H_5OH is unstable
(c) C_2H_5OH forms hydrogen bonds with water
(d) Constant boiling azeotropic mixture is formed with water.

9. Prussian blue is obtained by mixing together aqueous solution of Fe^{3+} salt with

(a) Ferrocyanide
(b) Ferricyanide
(c) Sodium cyanide
(d) Hydrogen cyanide

10. A compound on reaction with NaOH, phenolphphalein first gives pink colour which disappears on heating. The compound can be

(a) An aldehyde
(b) Ester
(c) Acid
(d) Ketone

11. HCOOH and HCHO may not be distinguished by:

(a) Tollen's test
(b) 2, 4 -DNP test
(c) Benedict's test
(d) Sodium bicarbonate test

12. Which of the following test is not suitable for alkenes?

(a) With 1% alkaline $KMnO_4$
(b) With 1% Bromine water
(c) Ozonolysis
(d) With Ammonical silver nitrate

13. To separate a mixture of amines from each other one should follow

(a) Hinsberg's method
(b) Beckmann's method
(c) Victor Meyer's method
(d) Zeisel method

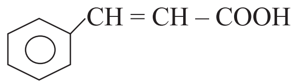
14. Phenol can be distinguished from ethanol by:

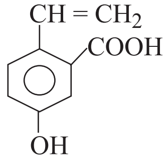
(a) Schiff's base
(b) Benedict's reagent
(c) Tollen's reagent
(d) $FeCl_3$

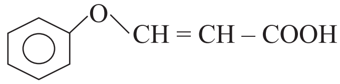
15. The Beilstein test for organic compounds is used to detect

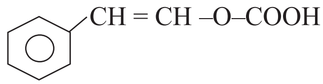
(a) nitrogen
(b) sulphur
(c) carbon
(d) halogens

16. A mono carboxylic acid decolourizes Br_2 water, on heating with soda lime derivatives of styrene formed, with neutral $FeCl_3$, a buff coloured precipitate is formed. This acid can be shown as:

(a) 

(b) 

(c) 

(d) 

17. Which of the following can give white a precipitate with ammonical silver nitrate?

(a) Ethene
(b) Propyne
(c) But- 2- yne
(d) Both (b) and (c)

18. Absolute alcohol is prepared by

(a) fractional distillation
(b) Kolbe's method
(c) Vaccum distillation
(d) Azeotropic distillation

19. p-Cl- $C_6H_4NH_2$ and $PhNH_3^+Cl^-$ can be distinguished by

(a) $AgNO_3$
(b) NaOH
(c) Zn
(d) $LiAlH_4$

20. Which of the following is the best scientific method to test presence of water in a liquid?

(a) taste
(b) smell
(c) use of litmus paper
(d) use of anhydrous copper sulphate

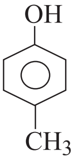
21. Which of the following test can be used for ketones?

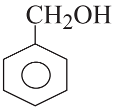
(a) DNP test
(b) Haloform test
(c) Fehling solution test
(d) Both (b) and (c)

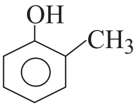
22. Sodium nitroprusside reacts with sulphide ion to give a purple colour due to the formation of

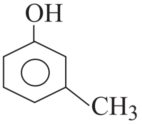
(a) $[Fe(CN)_5\ NOS]^{3-}$
(b) $[Fe(CN)_5\ NOS]^{4-}$
(c) $[Fe(CN)_5\ NO]^{3-}$
(d) $[Fe(NO)_5\ CN]^{+}$

23. Compound (P), C_7H_8O gives positive test with neutral $FeCl_3$ and can be nitrated to form three types of nitro compounds the compound (P) can be

(a) 

(b) 

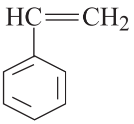
(c) 

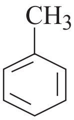
(d) 

24. Which of the following can not react with Fehling solution?

(a) HCHO
(b) C_6H_5CHO
(c) Glucose
(d) CH_3CHO

25. (P) and (Q) given below can be chemically distinguished using





(a) Alkaline $KMnO_4$
(b) Br_2 water
(c) both of these
(d) none of these

26. Which one of the following is correct?
The colour of solution is violet when iodine is dissolved in:

(a) C_6H_6
(b) $(CH_3)_2CO$
(c) C_6H_5N
(d) CCl_4

27. $CH_3C \equiv CCH_3$ and $CH_3CH = CHCH_3$ can be distinguished by

(a) reacting with ozone followed by hydrolysis with Zn and then treatment with Tollen's reagent.
(b) reacting with ammonical $AgNO_3$.
(c) reacting with bromine – water.
(d) reacting with acidified $KMnO_4$ and heating.

28. Which of the following do not responed towards Lassaigne's test?
(a) Benzene dizonium salts
(b) Hydrazine
(c) Borazine
(d) All of these

29. Which of the following is not correctly matched for ferric chloride test?

	Compound	Colour of precipitate
(a)	Aromatic Acid	Buff colour
(b)	Quinols	Green colour
(c)	Amino acid	Blue colour
(d)	Phenols	Intense purple green

30. Which is not correct about Molisch test?
(a) In it 1% alc. solution of α naphthol is used.
(b) Here a deep violet ring is formed.
(c) Here a stable condensation product of α naphthol and furfural is formed.
(d) It is a test for carbohydrate.

Brainteasers Objective Type Questions (Single choice only)

31. A compound with empirical formula CH_2O has a vapour density of 30. its molecular formula is
(a) $C_3H_6O_3$ (b) $C_2H_4O_2$
(c) $C_2H_2O_2$ (d) $C_6H_{12}O_6$

32. An organic compound is heated with HNO_2 at 0°C and then the resulting solution is added to a solution of β- naphthol whereby a brilliant red dye is produced. The observations indicate that the compound possesses.
(a) $-CONH_2$ group (b) $-NO_2$ group
(c) aliphatic NH_2 group (d) aromatic NH_2 group

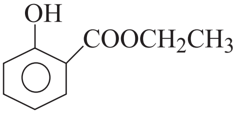
33. If a compound on analysis was found to contain C = 18.5%, H = 1.55%, Cl = 55.04% and O – 24.81% then its empirical formula is
(a) CHClO (b) CH_2ClO
(c) C_2H_5OCl (d) ClC_2H_5O

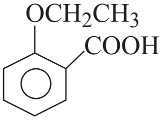
34. A gaseous hydrocarbon has 85% carbon and vapour density of 28. The possible formula of the hydrocarbon will be:
(a) C_4H_8 (b) C_2H_4
(c) C_2H_2 (d) C_3H_6

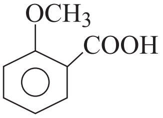
35. An organic compound having molecular mass 60 is found to contain C = 20%, H = 6.67% and N = 46.67% while rest is oxygen. On heating it gives NH_3 along with a solid residue. The solid residue gives violet colour with alkaline copper sulphate solution. The compound is
(a) CH_3NCO (b) CH_3CONH_2
(c) $(NH_2)_2CO$ (d) $CH_3CH_2CONH_2$

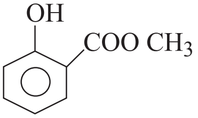
36. Which of the following compounds does not show Lassaigne's test for nitrogen?
(a) urea (b) azobenzene
(c) hydrazine (d) phenylhydrazine

37. A compound (X) on hydrolysis gave an acid and alcohol. Acid gave violet colour with neutral $FeCl_3$ while alcohol gave yellow precipitate on boiling with I_2 and NaOH, X can be:

(a) 

(b) 

(c) 

(d) 

38. An organic compound contains C, H, N, S and Cl. for the detection of chlorine, the sodium extract of the compound is first heated with a few drops of concentrated HNO_3 and then $AgNO_3$ is added to get a white ppt of AgCl. The digestion with HNO_3 before the addition of $AgNO_3$ is
(a) To create a common ion effect.
(b) To prevent the formation of NO_2.
(c) To prevent the hydrolysis of NaCN and Na_2S.
(d) To convert CN^- and S^{2-} volatite HCN and H_2S, or else they will interfere with the test forming AgCN or Ag_2S.

39. If 0.2 gram of an organic compound containing carbon, hydrogen and oxygen on combustion, yielded 0.147 gram carbon dioxide and 0.12 gram water. What will be the content of oxygen in the substance?
(a) 73.29% (b) 68.45%
(c) 85.23% (d) 89.50%

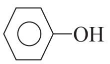
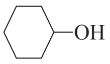
40. The ammonia evolved from the treatment of 0.30 g of an organic compound for the estimation of nitrogen was passed in 100 ml of 0.1 M sulphuric acid. The excess of acid required 20 ml of 0.5 M sodium hydroxide solution for complete neutralization. The organic compound is

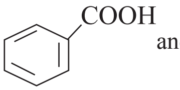
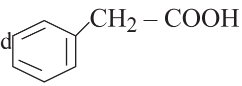
(a) Benzamide (b) Acetamide
(c) Thiourea (d) Urea

41. Which of the following reagent can be used to separate a mixture of aniline and phenol?
(a) H_2O (b) NaOH
(b) $NaHCO_3$ (d) HCl
(a) I and IV (b) II and III
(c) I and IIII (d) II and IV

42. In an organic compound of molar mass 108 g mol^{-1} C, H and N atoms are present in 9 : 1 : 3.5 by weight. Molecular formula can be
(a) $C_3H_6N_2$ (b) $C_6H_8N_2$
(c) $C_5H_6N_3$ (d) $C_4H_{12}N_2$

43. Each pair has been matched with the suitable reagent used for making distinction. Which pair has been matched wrongly?

Pair	**Reagent**
(a) $CH_3CH_2C = CH,. CH_3C = CCH_3$	Br_2 water
(b) $CH_2 = CH_2, CH_3 - CH_3$	MnO_4^-/OH^-
(c) $CH_3CH_2C = CH,. CH_3C = CCH_3$	$AgNO_3/NH_4OH$
(d)  ,  FeCl$_3$	$FeCI_3$

44.  and 

give positive test with
(I) $NaHCO_3$
(II) Na metal
(III) NaOH
(IV) Sodalime decarboxylation followed by oxidation with chromyl chloride vapours followed by treatment with Tollen's reagent.
(a) I, II (b) II, III
(c) I, II, III (d) I, III, IV

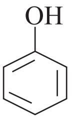
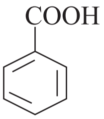
45. Which of the following is not correctly matched here?

	Column I	**Column II**
(a)	Nitrobenzene	Mulliken's test
(b)	Amino acid	Ninhydrin's test
(c)	Phenol	Conc. $NaHCO_3$
(d)	Carbohydrate in ethanol	10 % β- naphthol

46. An organic compound contains 49.3% carbon, 6.84% hydrogen and its vapour density is 73. Molecular formula of the compound is
(a) $C_3H_{10}O_2$
(b) $C_3H_5O_2$
(c) $C_6H_{10}O_4$
(d) $C_4H_{10}O_2$

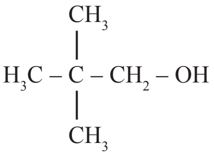
[MP PET 2000]

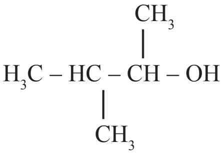
47. Which of these can not be distuinguished by adding HCl or Na_2CO_3?
(I) CH_3CH_2OH and $CH_3CHOHCH_3$
(II) CH_3COCH_3 and CH_3CH_2CHO
(III)

 and 

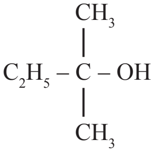
(IV) $R-NH_2$ and $R-Cl$
(a) I, II (b) II, III
(c) III, IV (d) I, IV

48. An organic compound with the molecular formula $C_5H_{12}O$, gives turbidity with Lucas reagent immediately. The compound is

(a) 
$H_3C-C(CH_3)_2-CH_2-OH$

(b) 
$H_3C-HC(CH_3)-CH(CH_3)-OH$

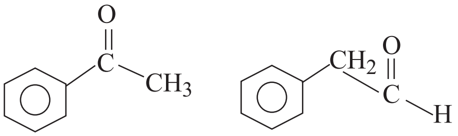
(c) $CH_3-CH_2-CH_2-CH_2-CH_2-OH$

(d) 
$C_2H_5-C(CH_3)_2-OH$

49. An organic compound contains carbon, hydrogen and oxygen. Its elemental analysis gave C, 38.71% and H, 9.67%. The empirical formula of the compound would be
(a) CHO (b) CH_4O
(c) CH_3O (d) CH_2O

50. The compound formed in the positive test for nitrogen with the Lassaigne solution of an organic compound is
(a) $Fe(CN)_3$
(b) $Fe_4[Fe(CN)_6]_3$
(c) $Na_4[Fe(CN)_5 NOS]$
(d) $Na_3[Fe(CN)_6]$

51. Consider the following pairs of organic compounds

(I) 

(II) CH_3OH CH_3CH_2OH

(III) CH_3COCH_3 HCHO

A test that can make distinction between each pair is

(a) Silver-mirror test
(b) Victor-Meyer's test
(c) Iodoform test
(d) Lucas test

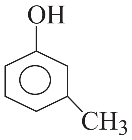
52. 0.765 g of an acid gives 0.535 g of CO_2 and 0.14 g of H_2O. Then the ratio of the percentage of carbon and hydrogen is

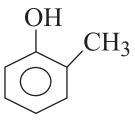
(a) 1 : 9 (b) 20 : 16
(c) 18 : 11 (d) 19 : 2

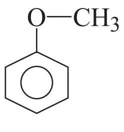
53. An organic compound containing carbon, hydrogen and oxygen contains 52.2% carbon and 13.04% hydrogen. Vapour density of the compound is 23. Its molecular formula will be

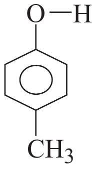
(a) C_4H_8O (b) C_3H_8O
(c) C_2H_6O (d) $C_5H_{10}O$

54. A compound P, C_7H_8O is insoluble in water, dil. HCl and aqueous $NaHCO_3$. It dissolves in dilute NaOH. When P is treated with bromine water it is converted rapidly into a compound of formula $C_7H_5OBr_3$. Identify the structure of P:

(a) 

(b) 

(c) 

(d) 

Decisive Thinking Objective Type Questions (One or more than one choice)

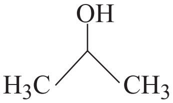
55. The amine mixture that reacts with Hinsberg's reagent in a alkaline medium are

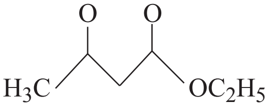
(a) $C_2H_5 - CO - NH_2$
(b) $C_6H_5N(C_2H_5)_2$
(c) p- $CH_3C_6H_5NH_2$
(d) $C_6H_5NHC_2H_5$

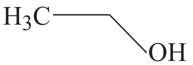
56. Which of the following statements is/are correct?

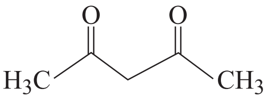
(a) in the estimation of carbon, an organic compound is heated with CaO in a combustion tube.
(b) using Lassaigne's test nitrogen and sulphur present in an organic compound can be tested.
(c) using Beilstein's test the presence of halogen in a compound can be tested.
(d) Lassaigne's tests fails to identify nitrogen in diazo compound.

57. Among the following which will respond to iodoform test

(a) 

(b) 

(c) 

(d) 

58. Which of the following will evolve CO_2 on reaction with $NaHCO_3$?

(a) Picric acid
(b) Salicylic acid
(c) 4- Nitrobenzoic acid
(d) Benzoic acid

59. The presence of -NO_2 group can not be confirmed by

(a) Bellstein's test
(b) AzO dye test
(c) Mulliken's test
(d) $AgNO_3$ test

60. What is/are correct avout p- amine, s- amine, t- amine?

(a) All react with $CS_2 + HgCl_2$
(b) All react with dil. HCl
(c) All react with dil H_2SO_4
(d) All react with HNO_2

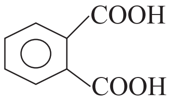
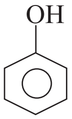
61. Bottles containing C_6H_5I and $C_6H_5CH_2I$ lost their original labels. They were labeled A and B for testing. A and B were separately taken in test tubes and boiled with NaOH solution. The end solution in each tube was made acidic with dilute HNO_3 and some $AgNO_3$. solution added. Solution B gave a yellow precipitate. Which one of the following statements is/are not true for the experiment?

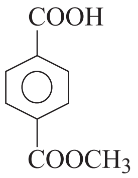
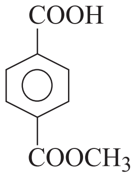
(a) A was $C_6H_5CH_2I$
(b) A was C_6H_5I
(c) B was C_6H_5I
(d) Addition of HNO_3 was unnecessary?

62. Among the following which statement is/are correct?
(a) $CH_3 - CO - OH$ will not respond to haloform test.
(b) Schiff's reagent and Schiff's base are different compound.
(c) Both aldehyde and ketone can react with 2, 4 - dinitrophenylhydrazise reagent.
(d) Fehling solution is a good reagent to detect aromatic aldehydes.

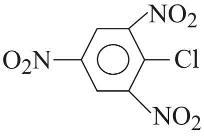
63. Which of the following can be purified by steam distillation?
(a) Bromobenzene
(b) Salicylaldehyde
(c) Nitrobenzene
(d) p-Hydroxybenzaldehyde

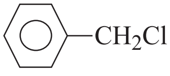
64. Fluorescein test is positive with

(a) 
(b) 

(c) 
(d) 

65. Detection of the chlorine is/are possible without preparing sodium extract in:

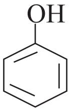
(a) 

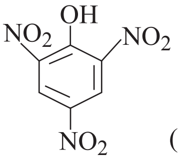
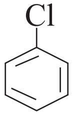
(b) 

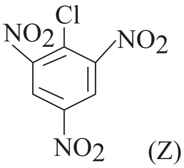
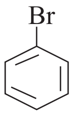
(c) $CHCl_3$
(d) $CH_2 = CHCH_2Cl$

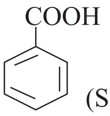
66. Choose the correct statement from the following:
(a) Lucas test can be used to distinguish 1°, 2° and 3° alcohols.
(b) Anhydrous $ZnCl_2$ and conc. HCl is used as Lucas reagent.
(c) 1° and 2° amines can be also be distinguished by using Lucas test.
(d) Alcohols with Lucas reagent gives insoluble alkyl chlorides.

67. The most reactive among the following pairs towards NaOH is

(I)  (X) CH3CH2OH (Y)

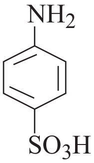
(II)  (P)  (Q)

(III)  (Z)  (R)

(IV)  (S) HCOOH (T)

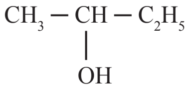
(a) In I -X
(b) In IV -T
(c) In III -Z
(d) In II -Q

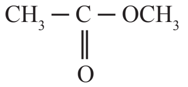
68. Select the incorrect statement
(a) the presence of nitrogen in diazonium salts can be detected by Lassaigne's test.
(b) Beilstein test is a reliable test for detection of halogens in organic compound.
(c) Lassiagne's test for the detection of sulphur fails if organic compound is volatile.
(d) Potassium can be used in place of sodium in the preparation of Lassaigne's extract.

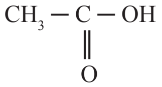
69. Which of the following will give test for N in sodium extract?
(a) NH_2 -NH_2
(b) $C_6H_5NHNH_2$
(c) 
(d) NH_2CONH_2

70. Which of the following can be distinguished by iodoform test?

(a) $Ph-CO-CH_3$

(b) 
$CH_3-CH(OH)-C_2H_5$

(c) 
$CH_3-C(=O)-OCH_3$

(d) 
$CH_3-C(=O)-OH$

71. The Beilstein's test confirms the presence of
(a) Fluorine (b) Iodine
(c) Bromine (d) Chlorine

72. Which of the following reactions occur during the detection of nitrogen in organic substances by Lassaigne's test?
(a) $FeSO_4 + 6NaCN \rightarrow NaCN$
(b) $3Na_4[Fe(CN)_6] + 2Fe(SO_4)_3 \rightarrow Fe[Fe(CN)_6]_3 + 6Na_2SO_4$
(c) $Na + C + N \rightarrow NaCN$
(d) none of these

73. In Lassaigne's test the organic compound is fused with Na followed by extraction with distilled water. Which of the following is possible fusion product?
(a) NaCN (b) NaNC
(c) NaCNS (d) Na_2S

74. Select the correct statement
(a) an organic liquid vaporizes at a temperature below its boiling point in steam distillation.
(b) Lassaigne's test for the detection of sulphur fails if organic compound is volatile.
(c) naphthalene can be separated from ammonium chloride by sublimation method.
(d) CCl_4 does not give a white precipitate with silver nitrate solution.

75. Compound (P) $C_8H_{10}O$ reacts with sodium to give colourless and odour less gas and upon vigorous oxidation using $KMnO_4$ gives terephthalic acid, the compound contains
(a) phenilic-OH
(b) Alkyl substitution at para position
(c) alkyl substitution at metaposition
(d) Benzene ring

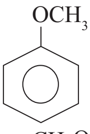
Linked-Comprehension Type Questions

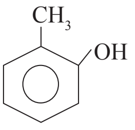
Comprehension 1

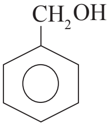
An organic (P) compound having C = 81.6 % H = 4.8 %, N = 13.6 % has a vapour density of 57.5. It gives off ammonia on heating with KOH. Reaction of (P) with Na and ethanol gives a basic compound (Q) which gives off N_2 and forms a compound (R) when reacted with HNO_2. This compound (R) can be oxidized into benzoic acid.

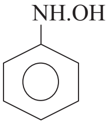
76. Here the compound (P), (Q) can be respectively?
(a) $C_6H_5NC, C_6H_5NHCH_3$
(b) $C_6H_5CN, C_6H_5CH_2NH_2$
(c) $C_6H_5CH_2CN, C_6H_5CH_2NH_2$
(d) $C_6H_5CN, C_6H_5NH_2$

77. Here the compound (R) cab be ?

(a) 

(b) 

(c) 

(d) 

78. Which of these test can be used to distinguish (R) from P, Q here ?
(I) Liebermann's test
(II) Phthalein test
(III) Can test
(IV) ester test.
(a) II, III only (b) I, IV only
(c) II, IV (d) III, IV only

Comprehension 2

An Organic compound containing C, H, O exists in two isomeric forms A and B. An amount of 0.108 g of one of the isomers gives on combustion 0.308 g of CO_2, and 0.072 g of H_2O. A in insoluble in NaOH and $NaHCO_3$, while B is soluble in NaOH. A reacts with concentrated HI to give compounds C and D, C can be separated from D by the ethanolic $AgNO_3$ solution and D is soluble in NaOH. B reacts readily with bromine water to give compound E of molecular formula $C_7H_5OBr_3$.

79. The empirical formula and molecular formula of the compound A and B are respectively
(a) C_6H_6O, C_7H_8O (b) $C_8H_{10}O, C_8H_{10}O$
(c) $C_7H_8O, C_8H_{10}O$ (d) C_7H_8O, C_7H_8O

80. Here the compound A and B are respectively
(a) Benzyl alcohol and para- cresol
(b) Meta- cresol and anisole
(c) Anisole and meta- cresol
(d) Anisole and para cresol

81. Which of the following test can not be used to distinguish compound D here
(a) Ferric chloride solution test
(b) Acidic $K_2Cr_2O_7$
(c) Leibermall nitroso test
(d) Oxidation in air

Comprehension 3

An organic acid (A), $C_5H_{10}O_2$ reacts with Br_2 in the presence of phosphorus to give (B). Compound (B) contains on asymmetric carbon atom and yields (C) on dehydrobromination. Compound (C) does not show geometric isomerism and on decarboxylation gives an alkene (D) which on ozonolysis gives (E) and (F). Compound (E) gives a positive Schiff's test but (F) does not.

82. Here the organic acid (A) and compound B are respectively
(a) 2- methyl butanoic acid, 3- bromo 2- methyl butanoic acid
(b) 3 - methyl butanoic acid, 2- bromo 3- mehtyl butanoic acid
(c) 2, 2- dimethyl propanoic acid, 3- bromo 2- methyl butanoic acid
(d) pentanoic acid, 3- bromo pentanoic acid

83. Here compound C can be given as
(a) 3- methyl but -2- en- 1- oic acid
(b) 2- methyl but -2- en- 1- oic acid
(c) pent 2- en- 1- oic acid
(d) pent 3- en- 1- oic acid

84. Here the compound D can be given as
(a) But -2- ene
(b) 2- methyl propene
(c) Butene -1
(d) But -2- yne

85. Here the compounds E and F are respectively?
(a) Acetone and formaldehyde
(b) Formaldehyde and acetone
(c) Acetaldehyde and acetone
(d) Acetone and acetaldehyde

Assertion-Reason Type Questions

In the following question two statements (Assertion) A and Reason (R) are given Mark.
(a) if A and R both are correct and R is the correct explanation of A.
(b) if A and R both are correct but R is not thecorrect explanation of A.
(c) A is true but R is false.
(d) A is false but R is true.

86. (A): 1^o, 2^o, 3^o Amine's can be distinguished by diethyl oxalate.
(R): 1^o amines form N- alkyl oxamide solid product, 2^o amine form oxamic ester which is liquid, 3^o amine do not react.

87. (A): Al alkyl halide of the molecular formula, C_5H_9X adds to one mole of Br_2/CCl_4 but does not give Beilstein's test.
(R): Alkyl halide must be alkyl iodide .

88. (A): Halogen free amides also give green colouration with Beilstein's reagent.
(R): They form volatile copper cynadies.

89. (A): Lassaigne's test is not shown by diazonium salts .
(R): Diazonium salts lose N_2 on heating much before they have a chance to react with fused sodium metal.

90. (A): During digestion with conc. H2SO4, nitrogen of the compound is converted to $(NH_4)_2SO_4$.
(R): $(NH_4)_2SO_4$ on heating with alkali gives NH_3 gas.

91. (A): During test for nitrogen with Lassaigne extract on adding $FeCl_3$ solution, sometimes a red precipitate is formed.
(R): This indicated that sulphur is also present.

92. (A): An organic compound on diazotization followed by reaction with alkaline solution of β- naphthol gives orange dye.
(R): An organic compound is aromatic amino compound which forms diazonium salts and undergoes coupling reaction to form azo dye.

93. (A): A mixture of p- methylbenzoic acid and picric acid can be separated by $NaHCO_3$ solution.
(R): p- Methylbenzoic acid is soluble in $NaHCO_3$ and it gives effervescence of CO_2.

94. (A): Only p- amine benzoic acid forms azo dye with phenols and naphthols, but not o- aminobenzoic acid.
(R): Diazotization of o- aminobenzoic acid forms benzyne.

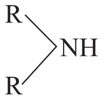
95. (A): Thiophence present in commercial benzene as an impurity can be removed by shaking the mixture with cold conc. H_2SO_4.
(R): Thiophence is a heterocyclic aromatic compound.

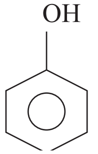
Matrix-Match Type Questions

96. Match the following:
Column I (Tests)
(a) CAN test
(b) Leiber mann's test
(c) Benedict's test
(d) Iodoform test
Column II (Final colour)
(p) Blue colour
(q) Yellow colour
(r) Red colour
(s) Green colour

97. Match the following:

Column I

(a) 

(b) 

(c) Carbohydrate (d) Nitrobenzene

Column II

(p) Molisch test

(q) Mulliken's test

(r) Phthalein test

(s) Leibermann's nitroso test

(t) Hoffmann's method

98. Match the following:

Column I

(a) Presence of 'S' (b) Presence of'N'

(c) Presence of 'Br' (d) Presence of N, S

Column II

(p) $HNO_3/AgNO_3$ (q) $FeCl_3$

(r) $Co(NO_3)_2$ (s) $Na_2[Fe(CN)_5NO]$

(t) $Pb(CH_3COO)_2$

99. Match the following:

Column I

(a) But -1- yne (b) But 2- ene

(c) CH_3COCH_3 (d) HCOOH

Column II

(p) Baeyer's reagent (q) Ammonical Cu_2Cl_2

(r) $I_2/NaOH$ (s) $HgCl_2$

100. Match the following:

Column I

(a) Primary amines (b) Aldehydes

(c) Phenol (d) Alcohols

Column II

(p) Ceric Ammonium nitrate

(q) Braddy's reagent

(r) Neutral $FeCl_3$

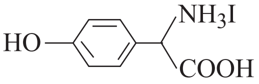
(s) Benzene sulphonyl chloride

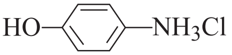
(t) Schiff base

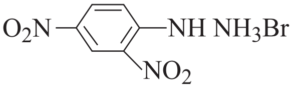
101. Match the following:

Column I

(a) $H_2N - NH_3Cl$

(b) 

(c) 

(d) 

Column II

(p) sodium fusion extract of the compound gives Prussian blue colour with $FeSO_4$.

(q) gives positive $FeCl_3$ test.

(r) gives white precipitate with $AgNO_3$.

(s) reacts with aldehyde to form the corresponding hydrazone derivatives. **[IIT 2008]**

ANSWERS

Straight Objective Type Questions

1. (a) **2.** (c) **3.** (d) **4.** (b) **5.** (a) **6.** (d) **7.** (c) **8.** (d) **9.** (a) **10.** (b)
11. (a) **12.** (d) **13.** (a) **14.** (d) **15.** (d) **16.** (b) **17.** (b) **18.** (d) **19.** (a) **20.** (d)
21. (d) **22.** (b) **23.** (d) **24.** (b) **25.** (b) **26.** (d) **27.** (a) **28.** (d) **29.** (c) **30.** (c)

Brainteasers Objective Type Questions

31. (b) **32.** (d) **33.** (a) **34.** (a) **35.** (c) **36.** (c) **37.** (a) **38.** (d) **39.** (a) **40.** (d)
41. (d) **42.** (b) **43.** (a) **44.** (c) **45.** (c) **46.** (c) **47.** (a) **48.** (d) **49.** (c) **50.** (b)
51. (c) **52.** (d) **53.** (c) **54.** (a)

Decisive Thinking Objective Type Questions

55. (c), (d) **56.** (b), (c), (d) **57.** (a), (c), (d) **58.** (a), (b), (c), (d) **59.** (a), (d)
60. (b), (c), (d) **61.** (a), (c), (d) **62.** (a), (b), (c) **63.** (a), (b), (c) **64.** (b), (c)
65. (a), (b), (d) **66.** (a), (b), (d) **67.** (a), (b), (d) **68.** (a), (b), (d) **69.** (b), (c), (d)
70. (a), (b) **71.** (b), (d) **72.** (a), (b), (c) **73.** (a), (c), (d) **74.** (a), (b), (d)
75. (b), (d)

Linked-Comprehension Type Questons

76. (d) **77.** (c) **78.** (d) **79.** (d) **80.** (c) **81.** (b) **82.** (b) **83.** (a) **84.** (b) **85.** (b)

Assertion-Reason Type Questions

86. (a) **87.** (c) **88.** (a) **89.** (a) **90.** (b) **91.** (a) **92.** (a) **93.** (d) **94.** (a) **95.** (b)

Matrix-Match Type Questions

96. (a) - (r), (b) - (p), (c) - (r), (d) - (q)
97. (a) - (s, t), (b) - (r, s), (c) - (p), (d) - (q)
98. (a) - (s, t), (b) - (q), (c) - (p), (d) - (q, r)
99. (a) - (q), (b) - (p), (c) - (s), (d) - (r)
100. (a) - (s), (b) - (q, t), (c) - (p, r), (d) - (p)
101. (a) – (r, s), (b) - (p, q), (c) - (p, q), (d) - (p, s)

HINTS AND EXPLANATION

Straight Objective Type Questions

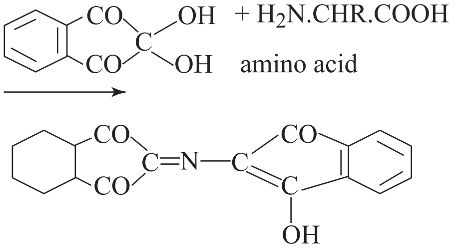
2. In carius method, Cl is converted into AgCl.

3. CCl_4 and acetone differ in their boiling point.

5. Hair contains amino acids which upon fusion with soda-lime (NaOH + CaO) evolve NH_3.

6. Distillation particularly fractional distillation because the boiling point of benzene (80°C) and chloroform (61.5°C) are close.

7.

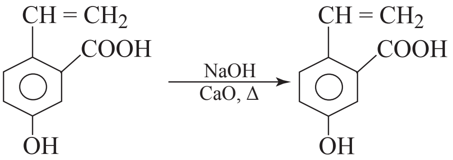


9. $4Fe^{3+} + 3K_4Fe(CN)_6 \rightarrow$
$Fe_4[Fe(CN)_6]_3 + 12\ K^+$
Prussian blue

10. RCOOR' + NaOH + Phenolphthalein
$\xrightarrow{\Delta}$ RCOOH + R'OH (colourless solution)

12. As ammonical silver nitrate is used for distinguishing a terminal alkyne from other alkynes.

16.

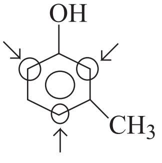


18. Azeotropic distillation since alcohol and water form a constant boiling mixture (azeotrope).

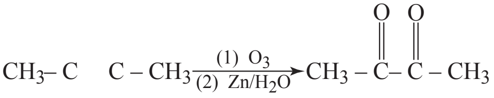
20. Anhydrous $CuSO_4$ turns blue in presence of water.

$$\underset{\text{White}}{CuSO_4} + 5H_2O \longrightarrow \underset{\text{Blue}}{CuSO_4 + 5H_2O}$$

23. Here three distinct possibilities of attack by any electrophile can be shown as



26. I_2 in $CHCl_3$ or CCl_4 layer gives violet colour.



$$CH_3-C\quad C-CH_3 \xrightarrow[(2)\ Zn/H_2O]{(1)\ O_3} CH_3-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-CH_3$$

The resulting product will not give Tollen's test while $CH_3-CH=CH-CH_3 \xrightarrow[(2)\ Zn/H_2O]{(1)\ O_3}$ $2CH_3CHO$; CH_3CHO formed will give Tollen's test

29. As in case of amino acid red colour ppt. is formed.

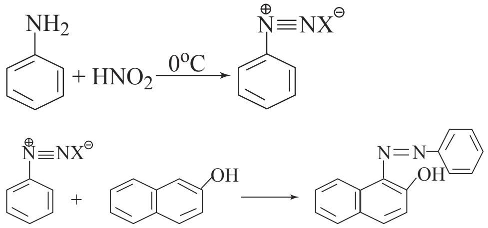
Brainteasers Objective Type Questions

31. Mol. wt. = 2 x V.D = 2 x 30 = 60

$$\frac{\text{mol. wt.} \times \text{empirical formula}}{\text{Emprirical formula wt}}$$

$$= \frac{60}{30} \times CH_2O = C_2H_4O_2$$

32.



33. C : H : Cl : O

$$= \frac{18.5}{12} : \frac{1.55}{1} : \frac{55.04}{35.5} : \frac{24.81}{16}$$

= 1 : 1 : 1 : 1

so empirical formula = CHClO

34. $C : H = \frac{85}{12} : \frac{15}{1} = 1 : 2$

Empirical formula = CH_2

So empirical formula weight

= 12 + 2 x 1 = 14

mol. wt. = 2 x V. D = 2 x 28 = 56

as $n = \frac{56}{14} = 4$

so molecular formula

= n x empirical formula

= 4 x CH_2 = C_4H_8

35.

Element	%	relative no. of atom	simplest ratio
C	20	1.67	1
H	6.67	6.67	4
N	46.67	3.33	2
O	26.66	1.67	1

The molecular formula is CH_4N_2O. So the compound is H_2NCONH_2.

$$2NH_2CONH_2 \xrightarrow{\Delta} \underset{\text{biuret}}{NH_2CONHCONH_2} + NH_3\uparrow$$

Biuret gives violet colour with alkaline copper sulphate solution.

36. Hydrazine (NH_2NH_2) does not contain C and on fusion with Na metal, it cannot form NaCN. So hydrazine does not show Lassaigne's test.

38. $Na + C + N \xrightarrow{\Delta} NaCN$

$2Na + S \xrightarrow{\Delta} Na_2S$

Both NaCN and Na_2S will react with $AgNO_3$ to form AgCN and Ag_2S.

They must be removed before performing $AgNO_3$ test for halogens.

So, On adding HNO_3, NaCN and Na_2S

$NaCN + HNO_3 \rightarrow NaNO_2 + HCN\uparrow$

$Na_2S + 2HNO_3 \rightarrow 2NaNO_3 + H_2S\uparrow$

Hence, CN^- and S^{2-} are removed as HCN and H_2S, by adding HNO_3

39. $\%C = \frac{12}{44} \times \frac{0.147}{0.2} \times 100 = 20.045$

$\% H = \frac{2}{18} \times \frac{0.12}{0.2} \times 100 = 6.666$

%O = (100 – 20.045 – 0.6666)

= 73.289 = 73.29 (approx)

42. Ratio of masses : C : H : N = 9 : 1 : 3.5

Ratio of atom =

$$\frac{9}{12} : \frac{1}{1} : \frac{3.5}{14}$$

$$= 1 : \frac{1}{1} \times \frac{12}{9} \times \frac{3.5}{14} \times \frac{12}{9}$$

= 1 : 1.33 : 0.33 = 3 : 4 : 1

Empirical formula of the compound C_3H_4N

Empirical mass = 12 x 3 + 4 x 1 + 14 x 1

= 36 + 4 + 14 = 54

But molecular mass = 108

$$n = \frac{\text{Mol.mass}}{\text{E.F.mass}} = \frac{108}{54} = 2$$

So molecular formula = $(C_3H_4N)_2$

= $C_6H_8N_2$

46. Percentage of O = 100 – 49.3 – 6.84

= 43.86

$$C : H : O = \frac{49.3}{12} : \frac{6.84}{1} : \frac{43.86}{16}$$

= 3 : 5 : 2

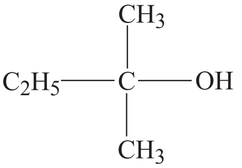
so empirical formula = $C_2H_5O_2$

and weight = 73

molecular weight = 2 x V.D. = 2 × 73 = 146

so molecular formula = $\frac{146}{73}$ $(C_3H_5O_2)$ = $C_6H_{10}O_4$

48. According to the given conditions $C_5H_{12}O$ must be a 3° alcohol.



2-methyl-2-butanol

2-methyl-2-butanol

49. Atomic mass of C = 12, H = 1 and O = 16.

Element	% composition	Mole ratio	Simple ratio
C	38.71	38.71/12 = 3.22	3.22/3.22 = 1
H	9.67	9.67/1 = 9.67	9.67/3.22 = 3
O	51.62	51.62/16 = 3.22	3.22/3.22 = 1

Thus empirical formula of the compound is CH_3O.

50. If nitrogen is present in organic compound then sodium extract contains $Na_4[Fe(CN)_6]$

Na + C + N fuse NaCN

$FeSO_4 + 6NaCN \rightarrow \underset{(A)}{Na_4[Fe(CN)_6]} + Na_2SO_4$

(A) changes to Prussian blue $Fe_4[Fe(CN)_6]_3$ on reaction with $FeCl_3$.

$4FeCl_3 + 3Na_4\,[Fe(CN)_6] \rightarrow$
$Fe_4\,[Fe(CN)_6]_3 + 12NaCl$

52. $\% \text{ C} = \frac{12}{44} \times \frac{0.535}{0.765} \times 100 = 19.07$

$\% \text{ H} = \frac{2}{18} \times \frac{0.138}{0.765} \times 100 =- 2.004$

C : H = 19 : 2

53. %O = 100 – (52.2 + 13.04) = 34.76

$\text{C : H : O} = \frac{52.2}{12} : \frac{13.04}{1} : \frac{34.76}{16} = 2 : 6 : 1$

empirical formula = C_2H_6O
empirical formula wt.

= 2 x 12 + 6 × 1 + 1 × 16 = 46

mol. wt. = 2 × V. D = 2 × 23 = 46

mol. formula = empirical formula = C_2H_6O

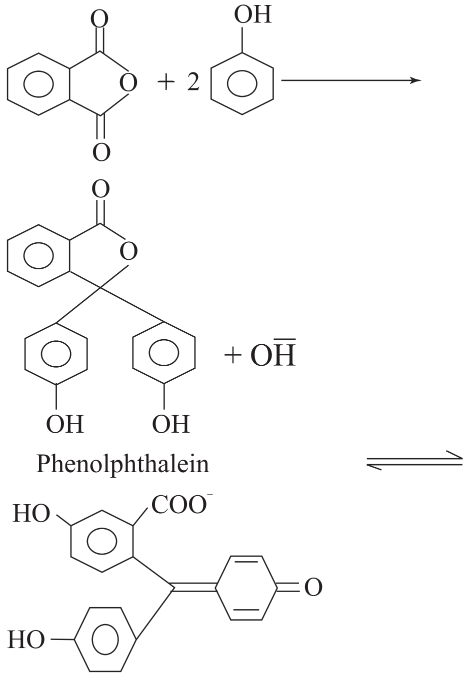
Decisive Thinking Objective Type Questions

56. In estimation of C, organic compound is heated with CuO
$2CuO + C \rightarrow 2Cu + CO_2$

61. As B gives yellow precipitate with $AgNO_3/HNO_3$, B must be $C_6H_5CH_2I$ and hence A is C_6H_5I.

63. Bromobenzene, Salicylaldehyde and Nitrobenzene are steam volatile and immiscible with water, therefore, can be purified by steam distillation. p- Hydroxybenzaldehyde is not steam volatile.

64. Phenols react with phthalic anhydride to give condensed product .



68. A volatile compound vapourises during fusion with sodium metal and Na_2S is not produced. Hence, Lassiagne's extract shows the absence of S^{2-} ions.

72. The varius reactions taking place in Lassaigne's test for nitrogen are

$Na + C + N \rightarrow NaCN$

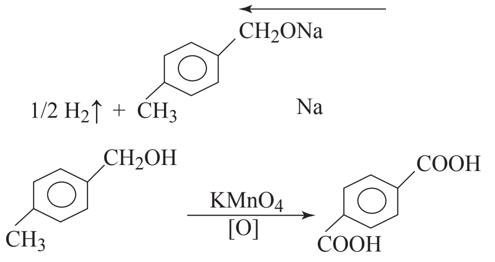
$FeSO_4 + 6NaCN \rightarrow Na_4[Fe(CN_6] + Na_2SO_4$

$3Na_4\,[Fe(CN)_6] + 2Fe(SO_4)_3 \rightarrow$

$Fe_4Fe(CN)_6]_3 + 6\,Na_2SO_4$
prussion blue colour

73. $Na + C + N \rightarrow NaCN$;
$Na + 2S \rightarrow Na_2S$;
$Na + C + N + S \rightarrow NaCNS$

75.



terephthalic acid

Linked-Comprehension Type Questions

76.

$$P \xrightarrow[C_2H_5OH]{Na} Q \xrightarrow{HNO_2} R \xrightarrow{\text{oxidation}} C_6H_5COOH$$

Benzoic acid

So compound R is an alcohol and on oxidation gives benzoic acid, therefore, (R) must be benzyl alcohol, and (Q) must be benzylamine hence (A) must be Benzenenitrile.

$$\underset{(P)}{C_6H_5COOH \equiv N} \xrightarrow[-NH_3]{2H_2O/H^+} \underset{\text{Benzoic acid}}{C_6H_5-COOH}$$

$$C_6H_5COOH \xrightarrow{KOH} C_6H_5COOK + H_2O$$

77. $\underset{(A)}{C_6H_5CH_2 \equiv NH_2} + \xrightarrow{4[H]} Na/alc. \underset{\text{Benzyl amine (B)}}{C_6H_5-CH_2-NH_2}$

$$\xrightarrow[-N_2, -H_2O]{HNO_2} \underset{\text{Benzyl alcohol (C)}}{C_6H_5-CH_2-OH} \xrightarrow{[O]} \underset{\text{Benzoic acid}}{C_6H_5COOH}$$

78. As being an alcohol (R) gives positive tests with them.

79. Calculation of ephirical formula

$$\% \text{ of C} = \frac{12}{44} \times \frac{0.308}{0.108} \times 100 = 77.77$$

$$\% \text{ of H} = \frac{2}{18} \times \frac{0.072}{0.108} \times 100 = 7.40$$

$$\% \text{ of O} = 100 - [77.77 + 7.40] = 14.83.$$

$$C = \frac{77.77}{12} \text{ or } \frac{6.46}{0.928}$$

$$= 7 : H = \frac{7.40}{1} \text{ or } \frac{7.40}{0.928} = 8$$

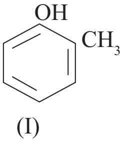
$$O = \frac{14.83}{16} \text{ or } \frac{0.928}{0.928} = 1$$

Empirical formula C_7H_8O.

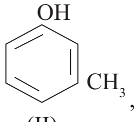
Since B gives on bromination $C_7H_5OBr_3$, it means that 3H- atoms are replaced by 3Br- atoms.

Hence, molecular formula of A and B is C_7H_8O.

80. C_7H_8O represents five isomers :

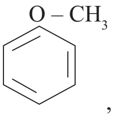


(I),

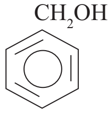


(II),

,

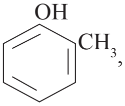


(IV),



(V)

As A is insoluble in both $NaHCO_3$ and NaOH it can only be

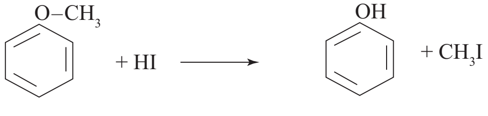


, i.e., Anisole (A).

As B is soluble in NaOH, it must be one of the cresols .

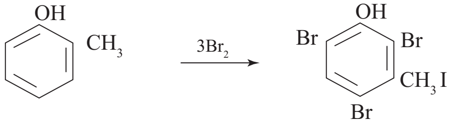
As it gives $C_2H_5OBr_3$ on bromination, it can only be m- cresol.

As A reacts with HI to give C and D it must be an ether, i.e., anisole.



Anisole (A) Phenol (D)

As C can be separated from D by ethanolic $AgNO_3$, so C must be CH_3I, i.e., methyl iodide. As D is soluble in NaOH, it must be phenol.



C_3H_3O (B) 2, 4, 6,- Tribromo -m- cresol

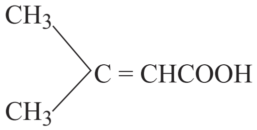
Hints for Questions no. **82–85.**

(i) (A) is an acid showing HVZ reaction in presence of $P + Br_2$. It suggests that (A) is $R.CH_2COOH$.
Br_2/P

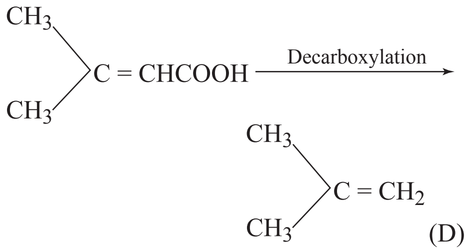
(ii) $R-CH_2.COOH \longrightarrow RCHBr.COOH$ where R is C_3H_7.

(iii) RCHBrCOOH has asymmetric C atom represented by C*. $\xrightarrow{\quad}$ –HBr

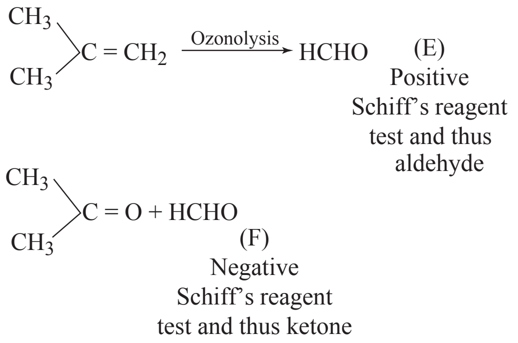
(iv) RCHBr.COOH $\xrightarrow{\quad}$ (C); since C has not geometrical isomers and thus, (C) may be



(v)

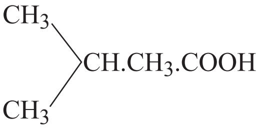


(vi)



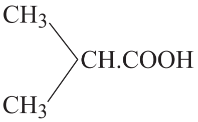
(vii) Hence the compound can be identified as follows:

(a)

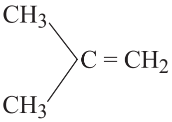


(b)

(c)

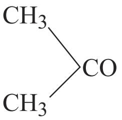


(d)



(e) HCHO

(f)

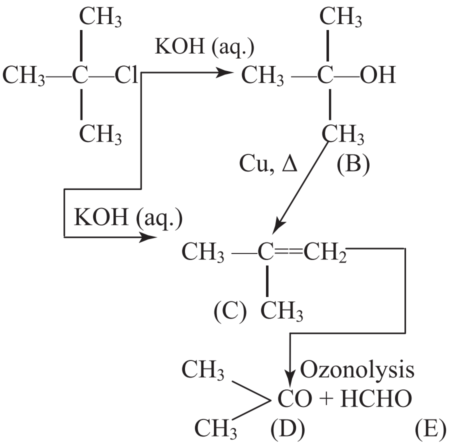


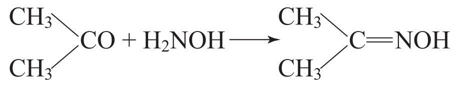
SUBJECTIVE SOLVED EXAMPLES

1. An organic compound (A), C_4H_9Cl on reacting with aqueous KOH gives (B) and on reaction with alcoholic KOH gives (C) which is also formed on passing the vapours of (B) over heated copper. The compound (C) readily decolorizes bromine water. Ozonolysis of (C) gives two compound (D) and (E). Compound (D) reacts with NH_2OH to give (F) and the compound (E) reacts with NaOH to give an alcohol (G) and sodium salt (H) of an acid. (D) can also be prepared from propyne on treatment with water in presence of Hg^{2+} and H_2SO_4. Identify (A) to (H) with proper reasoning.

Solution

The reactions suggest that (A) is $(CH_3)_3CCl$





$$(CH_3)_2CO + H_2NOH \longrightarrow (CH_3)_2C{=}NOH$$

(D) (F)

$$\underset{(E)}{2HCHO} + NaOH \rightarrow \underset{(H)}{HCOONa} + \underset{(G)}{CH_3OH}$$

(Cannizzaro's reaction)

(i) (D) is obtained from propyne as

$$CH_3—C{\equiv}CH \xrightarrow[Hg^{2+},\ H_2SO_4]{H_2O} CH_3COCH_3$$

and thus (D) is acetone.

(ii) (E) undergoes Cannizzaro's reaction and thus HCHO [as (D) and (E) are formed from ozonolysis of (C)].

(iii) the alkene (C) formed by the action of KOH (alc.) on (A), on ozonolysis gives (D) and (E). Thus, (C) is $(CH_3)_2\ C{=}{=}CH_2$ and (A) is $(CH_3)_3.CCl$.

2. A hydrocarbon (A)of molecular weight 54 reacts with an excess of Br_2 in CCl_4 to give a compound (B) whose molecular weight is 593% more than that of (A). However, on catalytic hydrogenation with excess of hydrogen, (A) forms (C) whose molecular weight is only 7.4% more than that of (A). (A) reacts with CH_3CH_2Br in the presence of $NaNH_2$ to give another hydrocarbon (D) which on ozonolysis yields diketone (E). (E) on oxidation gives propanoic acid. Give structures of (A) to (E) with reason.

Solution

(i) Mol. wt. of (a) suggest it to be C_4H_6, i.e., mol. wt. = 54

(ii) C_4H_6 has terminal triple bond as it reacts with CH_3CH_2Br in presence of $NaNH_2$

(iii) $$\underset{(A)}{CH_3.CH_2.C{\equiv}CH} \xrightarrow{Br_2} \underset{(B)}{CH_3.CH_2.CBr_2.CHBr_2}$$

Mol. wt. = 54 Mol. wt. = 374

$$\text{Thus, mol. wt. of (B)} = \frac{593 \times 54}{100} + 54$$

$$= 320 + 54$$

$$= 374$$

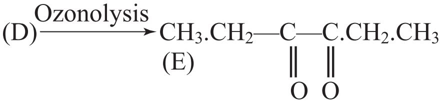
(iv) $$CH_3—CH_2.C{\equiv}CH \rightarrow \underset{(C)}{CH_3.CH_2.CH_2.CH_3}$$

Mol. wt. = 58

$$\text{Thus,}\quad \text{Mol. wt. of (C)} = \frac{7.4}{100} \times 54 + 54$$

$$= 58$$

(v) $$CH_3.CH_2.C{\equiv}CH \xrightarrow{NaNH_2} \underset{(D)}{CH_3.CH_2.C{\equiv}C.CH_2.CH_3}\ CH_3.CH_2Br$$



$$(D) \xrightarrow{Ozonolysis} \underset{(E)}{CH_3.CH_2—\underset{\|}{\overset{}{C}}—\underset{\|}{C}.CH_2.CH_3}$$

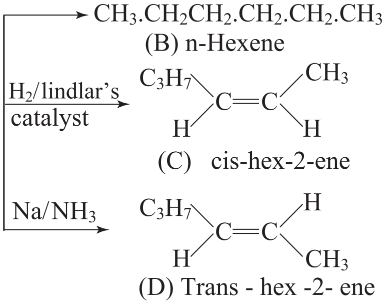
$$\xrightarrow{[O]} \underset{(F)}{CH_3.CH_2COOH}$$

3. Hydrocarbon (A). C_6H_{10} on treatment with H_2/Ni, H_2/Lindlar's catalyst and Na/liquid ammonia forms three different reduction products (B), (C) and (D) respectively. (A) does not form any salt with ammoniacal $AgNO_3$ solution, but forms a salt (E) on heating with $NaNH_2$ in an inert solvent. Compound (E) reacts with CH_3I to give (F). Compound (D) on oxidative ozonolysis gives n- butanoic acid along with other product. Give structures of (A) to (F) with proper reasoning.

Solution

The given compound (A) is $CH_3.CH_2CH_2.C{\equiv}C.CH_3$. This is confirmed by the following findings.

(i) $CH_3.CH_2.CH_2.C{\equiv}C.CH_3$

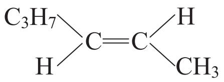


(ii) (A) is non - terminal alkyne as it does not give white salt with ammoniacal $AgNO_3$

(iii) (A) forms (E) with $NaNH_2$ which reacts with CH_3I to give (F).

$$CH_3.CH_2.Ch_2C{\equiv}C.CH_3 \xrightarrow[\Delta]{NaNH_2}$$

$$\underset{(E)}{CH_3.Ch_2.CH_2CH_2.C \equiv CNa} \xrightarrow{CH_3I} \underset{(F)}{CH_3.CH_2.CH_2.CH_2.C{\equiv}C.CH_3}$$

(iv) 

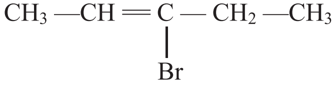
$$\xrightarrow[\text{Oxidation}]{\text{Ozonolysis}} \underset{\substack{\text{(n-Butanoic acid)}\\(D)}}{C_3H_7COOH} + CH_3COOH$$

4. An organic compound (A), C_5H_9Br which readily decolorizes bromine water and $KMnO_4$ solution, gives (B), $C_5H_{11}BR$ on treatment with Sn/ HCl. The reaction of (A) with $NaNH_2$ produces (C) with evolution of ammonia. (C) neither reacts with sodium nor forms any metal acetylide but reacts with Lindlar's catalyst to give (D) and on reaction with Na/ NH_3 (liq.) produces (E). Both the compounds (D) and (E) are isomeric. Give structures of (A) to (E) with proper reasoning.

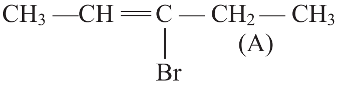
Solution

(i) (A) Decolorsis bromine water and $KMNO_4$, thus it has unsaturation.

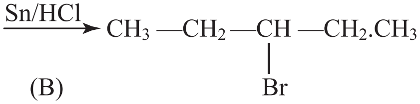
(ii) The reactions suggest (A) to be



$$CH_3—CH{=}\underset{Br}{\underset{|}{C}}—CH_2—CH_3$$

(iii) 

$$CH_3—CH{=}\underset{Br}{\underset{|}{C}}—CH_2—CH_3 \quad (A)$$



$$\xrightarrow{Sn/HCl} CH_3—CH_2—\underset{Br}{\underset{|}{CH}}—CH_2.CH_3 \quad (B)$$

$$(A) \xrightarrow{NaNH_2} \underset{(C)}{CH_3—C{\equiv}C—CH_2—CH_3}$$

$$CH_3—C{\equiv}C—CH_2—CH_3$$

$$\xrightarrow{\text{Lindlar's catalyst}} \underset{\substack{\text{(cis form)}\\(D)}}{CH_3—CH{=}CH.CH_2.CH_3}$$

$$\xrightarrow{Na/NH_3(l)} \underset{\substack{\text{(Trans -forms)}\\(E)}}{CH_3—CH{=}CH.CH_2.CH_3}$$

(iv) (C) being non terminal alkyne and thus neither reacts with sodium nor forms any metal acetylide.

(v) (D) and (E) are geometrical isomers.

5. Dehydrobromination of compounds (A) and (B) yield the same alkene (C). Alkene (C) can regenerate (A) and (B) by the addition of HBr in the presence and absence of peroxide respectively. Hudrolysis of (A) and (B) give isomeric products, (D) and (E) respectively, 1, 1-diphenyl ethane is obtained on reaction of (C) with benzene in presence of H^+. Give structures of (A) to (E) with reasons.

Solution

The given reactions suggest that.

(i) (B) is $C_6H_5CHBr.CH_3$

$$\xrightarrow[\text{KOH (alc.)}]{-HBr} \underset{(C)}{C_6H_5CH{=}CH_2}$$

$$\xrightarrow{HBr} \underset{(B)}{C_6H_5CHBrCH_3} \xrightarrow{HOH} \underset{(E)}{C_6H_5CHOH.CH_3}$$

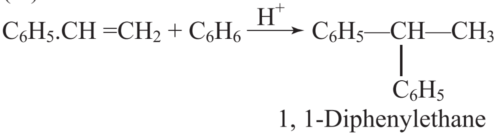
And(A) is

$$C_6H_5.CH_2.CH_2Br \xrightarrow[\text{KOH(alc.)}]{-HBr} \underset{(C)}{C_6H_5CH{=}CH_2}$$

$$\xrightarrow[\text{Peroxide}]{HBr} \underset{(A)}{C_6H_5CH_2—CH_2Br} \xrightarrow{HOH} \underset{(D)}{C_6H_5CH_2CH_2OH}$$

(ii) (D) and (E) are isomeric alcohols

(iii)



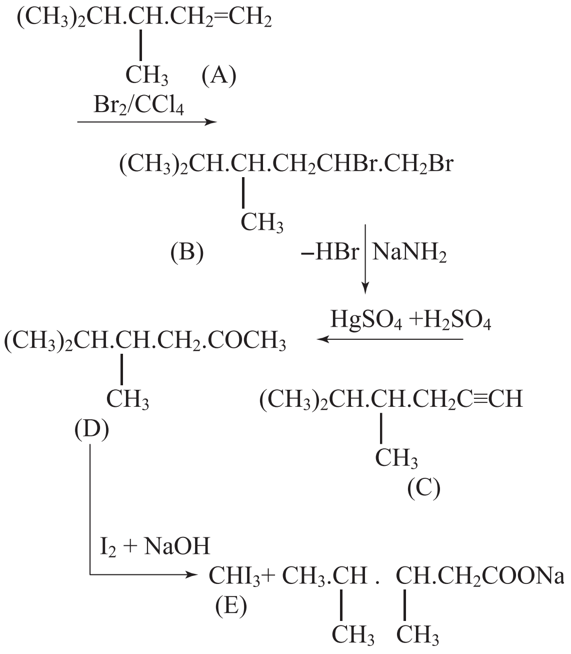
$$C_6H_5.CH{=}CH_2 + C_6H_6 \xrightarrow{H^+} C_6H_5—\underset{C_6H_5}{\underset{|}{CH}}—CH_3$$

1, 1-Diphenylethane

6. An alkene (A) on passing through Br_2 /CCl_4 gives a compound (B), which on dehydrobromination in the presence of $NaNH_2$ gives a hydrocarbon (C). Compound (C) yield (D) when warmed with dilute H_2SO_4 in the presence of $HgSO_4$. (D) gives a yellow precipitate of (E on treatment with I_2 and NaOH and alos forms sodium salt of 3, 4- Dimethylpentanoic acid. Give structures of (A) to (E) with reasons.

Solution

The given reaction suggest the following :



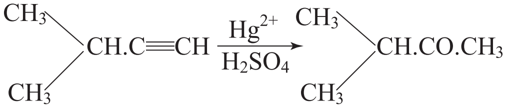
$$(CH_3)_2CH.\underset{CH_3}{\underset{|}{CH}}.CH_2{=}CH_2 \quad (A) \xrightarrow{Br_2/CCl_4} (CH_3)_2CH.\underset{CH_3}{\underset{|}{CH}}.CH_2CHBr.CH_2Br \quad (B)$$

$$(B) \xrightarrow[NaNH_2]{-HBr} (CH_3)_2CH.\underset{CH_3}{\underset{|}{CH}}.CH_2C{\equiv}CH \quad (C) \xrightarrow{HgSO_4 + H_2SO_4} (CH_3)_2CH.\underset{CH_3}{\underset{|}{CH}}.CH_2.COCH_3 \quad (D)$$

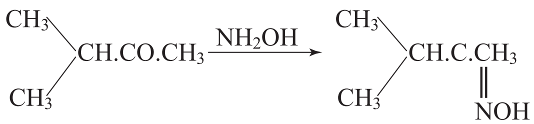
$$(D) \xrightarrow{I_2 + NaOH} \underset{(E)}{CHI_3} + CH_3.\underset{CH_3}{\underset{|}{CH}}\ .\ \underset{CH_3}{\underset{|}{CH}}.CH_2COONa$$

7. An alkyne with 5 carbon atoms per molecule when passed through dilute sulphuric acid containing mercuric sulphate given a compound which forms an oxime, but has no effect on Fehling's solution. The compound on oxidation gives dimethyl acetic acid. It reacts with sodamide to form a hydrocarbon. What is the structure of the alkyne?

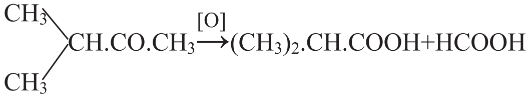
Solution



(3- Methylbutyne)



(Oxime)



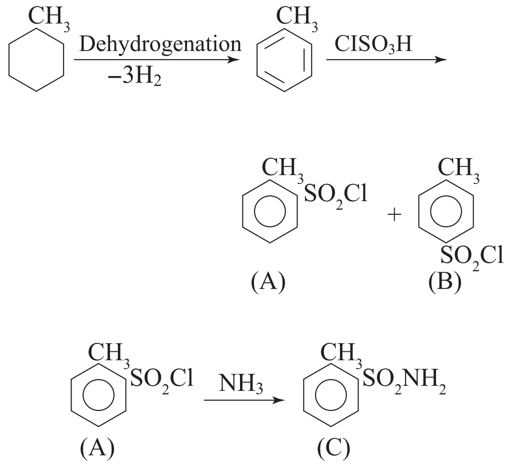
8. (a) Catalytic dehydrogenation of methylcyclohexane, obtained from petroleum, gives a liquid which on treatment with chlorosulphonic acid at 370 K yields a mixture of two isomers (A) and (B), $C_7H_7SO_2Cl$. The major isomer (A) reacts with ammonia to form (C), which on oxidation with permanganate gives compound (D). On heating compound (D) gives a well known sweetening agent (E). The minor isomer (B) also reacts with ammonia to give a compound (F) which on treatment with NaClO /NaOH gives an antiseptic (G). Identify (A) to (G) with proper reasoning.

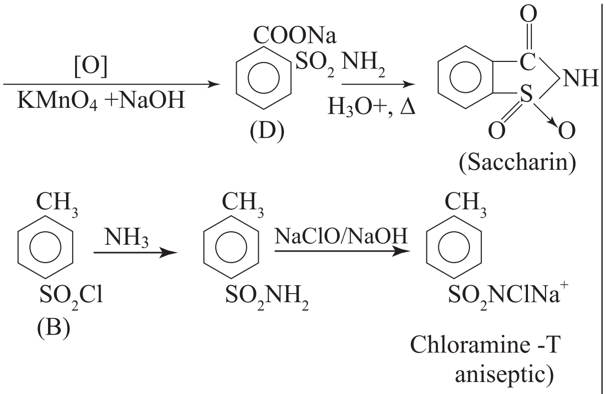
(b) Which of the following has larger dipole moment? Explain.

1-Butyne or 1- Butene

Solution

(a) The given statements suggest that following reactions are possible:





(b) 1- Butne has more dipole moment because sp-hybridized carbon has more electronegative in comparison to 1- butene (sp^2 -hybridised carbon). It is evidences by acidic nature of butyne -1

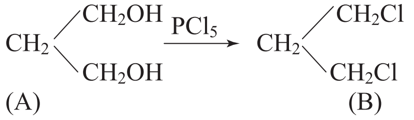
$\underset{}{CH_3CH_2}\underset{sp}{C}\equiv\underset{sp}{CH}$ $\quad$ $CH_3CH_2\underset{sp^2}{CH}=\underset{sp^2}{CH_2}$

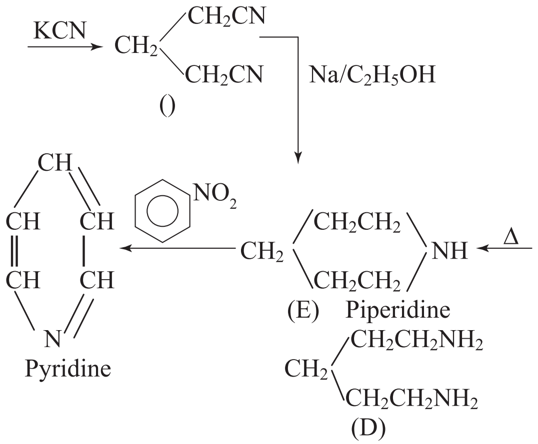
9. An organic compound (A) composed of C, H and O givers characteristic colour with ceric ammonium nitrate. Treatment of (A) with PCl_5 gives (B) which reacts with KCN to form (C). The reduction of (C) with warm Na/ C_2H_5OH produces (D) which on heating gives (E) with evolution of ammonia. Pyridine is obtained on treatment of (E) with nitrobenz3ene. Give structure of (A) to (E) with proper reasoning.

Solution

(i) (A) gives characteristic colour with ceric ammonium nitrate and thus, it has OH group.

(ii) Reactions suggest that (A) is

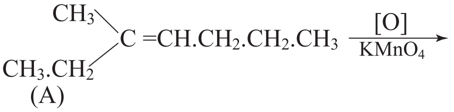




10. Alkenes (A) and (B) yield the same alcohol (C) on hydration. On vigorous oxidation with $KMnO_4$ (A) gives a carbonyl compound (D) and an acid (E), each containing four carbon atoms. On the other hand (B) gives an acid (F) and a carbonyl compound (G). In (G) no two identical groups are attached to the same carbon atom. Give structure of (A) to (G) with proper reasoning.

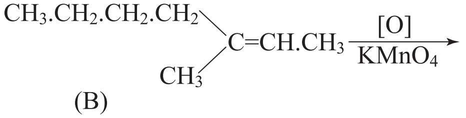
Solution

(i) Since alkene (A) on oxidation gives a carbonyl compound (D) and acid (E) of four carbon atoms each and thus



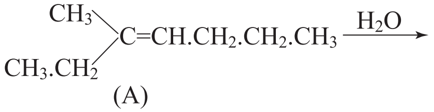
$\underset{\text{Butanone}}{\underset{(D)}{CH_3.CO.CH_2.CH_3}} + \underset{\text{Butanoic acid}}{\underset{(E)}{CH_3.CH_2.CH_2.COOH}}$

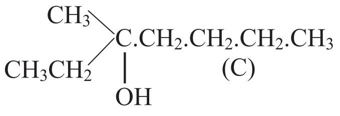
(ii) Alkene (A) and (B) give same alcohol on hydration and thus , (B) can only be (Also no two groups on same carbon atom).

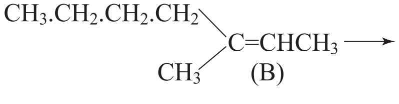


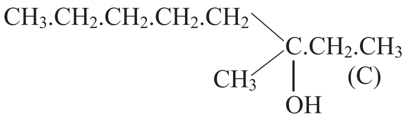
$\underset{\text{Hexanone- 2}}{\underset{(G)}{CH_3COCH_2.CH_2.CH_2CH_3}} + \underset{\text{Acetic acid}}{\underset{(F)}{CH_3COOH}}$

(iii) The hydration of(A) and (B) give same alcohol









(3- Methylheptan -3- ol)

11. Compound (A) contains only carbon and hydrogen. It decolorises bromine in CCl_4 solution and reacts slowly with concentrate H_2SO_4. Compound (A) reacts with HBr to form (B). (B) reacts with NaOH to form (C). On oxidation (C) gives hexanone -3. Write the structures of (A), (B) and (C) and give reactions.

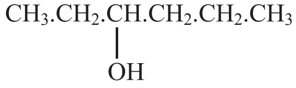
Solution

(1) (A) contains carbon and hydrogen, decolorizes Br_2 in CCl_4 and so (A) is unsaturated hydrocarbon.

$$(A) \xrightarrow{HBr} \underset{\text{Bromide}}{(B)} \xrightarrow{NaOH} \underset{\text{Alcohol}}{(C)} \xrightarrow{Oxidation} \text{Hexanone-3}$$

(2) Since oxidation of (C) gives ketone and thus, (C) should be secondary alcohol.

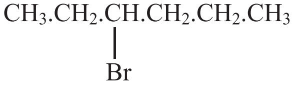
(3) The position of OH in (C) should be at '3' because hexan -3-one is formed.

(C) is 

$$CH_3.CH_2.\underset{\substack{|\\ OH}}{CH}.CH_2.CH_2.CH_3$$

Hexan -3-ol

(4) (C) is obtained by hydrolysis of (B) and thus, () is



$$CH_3.CH_2.\underset{\substack{|\\ Br}}{CH}.CH_2.CH_2.CH_3$$

3-Bromohexane

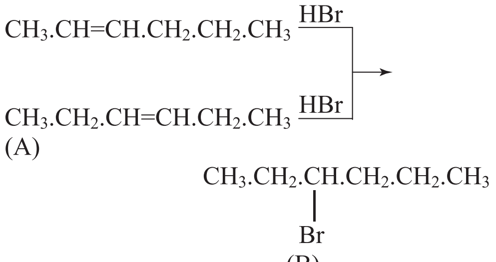
(5) (B) is formed be the action of HBr on (A and thus, (A) can be

$CH_3.CH= CH.CH_2.CH_2.CH_3$
(A) Hex -2- ene

or

$CH_3.CH_2.CH=CH.CH_2.CH_3$
(A) Hex -3- ene

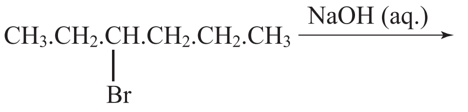
Reactions:



$$\left.\begin{array}{l} CH_3.CH=CH.CH_2.CH_2.CH_3 \xrightarrow{HBr} \\ CH_3.CH_2.CH=CH.CH_2.CH_3 \xrightarrow{HBr} \end{array}\right] \rightarrow CH_3.CH_2.\underset{\substack{|\\ Br}}{CH}.CH_2.CH_2.CH_3$$

(A)

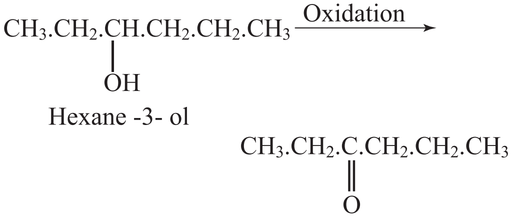
(B)



$$CH_3.CH_2.\underset{\substack{|\\ Br}}{CH}.CH_2.CH_2.CH_3 \xrightarrow{NaOH\ (aq.)} CH_3.CH_2.\underset{\substack{|\\ OH}}{CH}.CH_2.CH_2.CH_3$$

3- Bromohexane (B)

Hexane -3- ol (C)



$$CH_3.CH_2.\underset{\substack{|\\ OH}}{CH}.CH_2.CH_2.CH_3 \xrightarrow{Oxidation} CH_3.CH_2.\underset{\substack{\|\\ O}}{C}.CH_2.CH_2.CH_3$$

Hexane -3- ol

Hexan -3- one

12. It requires 0.7 g of a hydrocarbon (A) to react completely with Br_2 (2.0 g). On treatment of (A) with HBr it yielded monobromo alkane (B). The same compound (B) was obtained when (A) was treated with HBr in presence of peroxide. Write down the structure formulae of (A) and (B) and explain the reactions involved.

Solution

(i) (A) reacts with HBr to give mono bromo alkane (B), so (A) is alkene.

(ii) (A) gives same product on addition of HBr in absence and presence of peroxide and thus, (A) is symmetrical alkene.

(iii) Now 2 g Br_2 reacts with 0.7 g of (A)

$$160 \text{ g } Br_2 \text{ reacts with } \frac{0.7\times160}{2}$$

$$= 56 \text{ g of (A)}$$

M. w. of alkene = 56

$C_nH_{2n} = 56$

$n = 4$

(iv) Thus , alkene is C_4H_8 having structure $CH_3.CH=CH.CH_3$
But -2- ene
(A)

Reactions:

$$\underset{(A)}{CH_3—CH=CH—CH_3} \xrightarrow[HBr]{\text{Presence or absence of peroxide}} \underset{\substack{\text{2- Bromobutane}\\ (B)}}{CH_3CHBr.CH_2.CH_3}$$

13. A chloro compound (A) showed the following properties:

i. Decolorised bromine in CCl_4
ii. Absorbed hydrogen catalytically.
iii. Gave a precipitate with ammonical cuprous chloride.
iv. When vapourised 1.4g of (A) 448 mL of vapours at STP.
Identify (A) and write down the equations of reactions

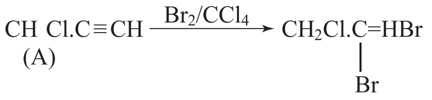
Solution

(i) (A) decolorsises Br_2 in CCl_4 and absorbs H_2 and thus, (A) is unsaturated molecule having double o triple bond.
(ii) (A) gives a precipitate with ammonical Cu_2Cl_2 and thus, it has terminal alkyne linkage, i.e., triple bond at corner.
(iii) Since (A) has Cl and one ≡ bond at terminal so (A) may be

$$RCl.C \equiv CH$$
$$R + 35.5 + 12 + 12 + 1 = 74.5$$
$$R = 14$$
$$R \text{ is } CH_2$$

(iv) Thus, (A) is $CH_2Cl.C{\equiv}CH$, i.e., 3 -Chloropropyne

Reactions:



$$\underset{(A)}{CH\ Cl.C{\equiv}CH} \xrightarrow{Br_2/CCl_4} \underset{\displaystyle Br}{CH_2Cl.C{=}HBr}$$

1,2 -dibromo, 3- chloroprop -1- ene

$$\underset{(A)}{CH_2Cl.C{\equiv}CH} \xrightarrow{H_2} \underset{\text{1-Chloropropane}}{CH_2Cl.CH_2—CH_3}$$

$$\underset{(A)}{2CH_2Cl.C{\equiv}CH} \xrightarrow[\text{or Am. } Cu_2Cl_2]{Cu_2O} \underset{\text{Red ppt.}}{2CH_2Cl.C{\equiv}C.Cu + H_2O}$$

14. An organic compound (A), C_6H_{10} on reduction first gives (B), C_6H_{12} and finally (C) C_6H_{14}. (A) on ozonolysis followed by hydrolysis gives two aldehydes (D) C_2H_4O and (E) $C_2H_2O_2$. Oxidation of (B) with acidified $KMnO_4$ gives (F) $C_4H_8O_2$. Determine the structure of (A) to (F) with proper reasoning.

Solution

(i) (A), C_6H_{10} either has one triple bond or two double bonds.
(ii) Ozonolysis of (A) suggest that it has two double bonds.

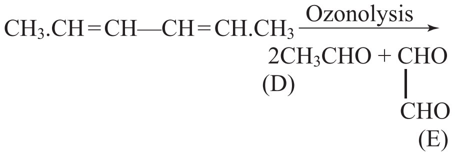
$$\underset{(A)}{C_6H_{10}} \xrightarrow{\text{Ozonolysis}} \underset{(D)}{C_2H_4O} + \underset{(E)}{C_2H_2O_2}$$

Since, (D) and (E) are aldehydes, i.e.,
CH_3CHO and
Ethanal (D)

$$\begin{array}{c} CHO \\ | \\ CHO \end{array}$$

Ethane -1, 2- dial (E)

(A) is $CH_3CH{=}CH—CH{=}CH.CH_3$
Hexa -2, 4- diene



$$CH_3.CH{=}CH—CH{=}CH.CH_3 \xrightarrow{\text{Ozonolysis}} \underset{(D)}{2CH_3CHO} + \underset{(E)}{\begin{array}{c} CHO \\ | \\ CHO \end{array}}$$

(iii) (A) gives (B) on reduction and finally gives (C).

$$CH_3.CH{=}CH—CH{=}CH—CH_3 \xrightarrow{H_2}$$

$$\underset{\text{(B) Hex -2-ene}}{CH_3.CH_2.CH_2\,CH{=}CH.CH_3} \Big\downarrow H_2$$

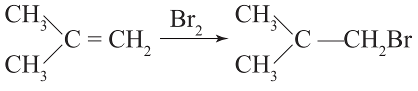
$$\underset{\text{Hexane}}{CH_3.CH_2.CH_2.CH_2.CH_2.CH_3}$$

$$CH_3.CH_2.CH_2CH{=}CH.CH_3 \xrightarrow{[O]} \underset{(F)}{CH_3.CH_2.CH_2.COOH} + CH_3COOH$$

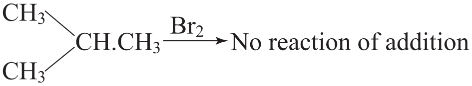
15. A 10 g mixture of isobutene and isobutene requires 20 g of Br_2 (in CCl_4) for complete addition. If 10 g of the mixture is catalytically hydrogenated and the entire alkane is monobrominated in the presence of light at 127°C, which exclusive product and how much of it would be formed? (Atomic weight of bromine = 80).

Solution

Let isobutane be a g and isobutene be b g. Thus, a+ b = 10



(isobutene)



(Isobutane)

Now, 160 g Br_2 is needed for 56 g isobutene

20 g Br_2 is needed for $\dfrac{56 \times 20}{160}$

$= 7$ g

Thus, isobutene, i.e., b = 7g

isobutane, i.e., a = 3 g

Now 7 g isobutene is converted to isobutene by reduction to give

$\dfrac{58 \times 7}{56}$g isobutene = 7.25 g.

Now isobutene reacts with Br_2 to give monobromo product in light

$C_4H_{10} + Br_2 \rightarrow C_4H_9Br + HBr$

58 g C_4H_{10} gives produc = 137 g C_4H_9 HBr

(7.25 + 3) g C_4H_{10} gives product

$= \dfrac{137 \times 10.25}{58}$g C_4H_9 Br

= 24 .21 g C_4H_9 Br

16. An organic acid (A), $C_5H_{10}O_2$ reacts with Br_2 in the presence of phosphorus to give (B). Compound (B) contains on asymmetric carbon atom and yields (C) on dehydrobromination. Compound (C) does not show geometric isomerism and on decarboxylation gives an alkene (D) which on ozonolysis gives (E) and (F). Compound (E) gives a positive Schiff's test but (F) does not. Give structures of (A) to (F) with reasons.

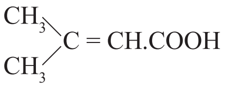
Solution

(i) (A) is an aicd showing HVZ reaction in presence of P + Br_2. It suggests that (A) is $R.CH_2COOH$.

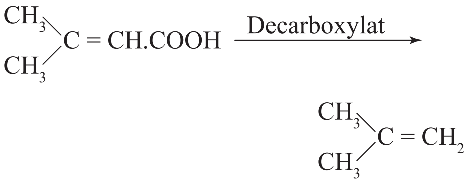
(ii) R- $CH_2.COOH \xrightarrow{Br_2/P}$ RCHBr.COOH where R is C_3H_7.

(iii) RCHBrCOOH has asymmetric C atom represented by C*. -HBr

(iv) RCHBr.COOH $\xrightarrow{-HBr}$ (C); since C has not geometrical isomers and thus, (C) may be

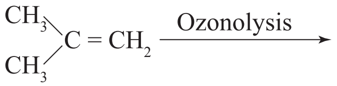


(v)

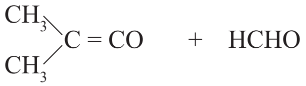


(D)

(vi)



(F)
Negative
Schiff's reagent
test and thus ketone

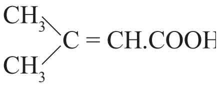


(E)
Positive
Schiff's reagent
test and thus aldehyde

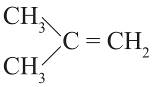
(vii) Thus,

(a)

(b)

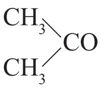


(c)



(d)

(e) hcho

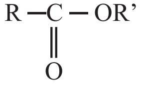


(f)

17. An ester has molecular weight 102. On aqueous hydrolysis it produces a monobasic acid an alcohol. If 0.185 gof the acid product completely neutralizes 25 mL of 0.1 N NaOH, find out the structure formulae of the produced alcohol, acid and the eater with proper reasoning.

Solution

(i) Ester is



$R-\underset{\underset{O}{\|}}{C}-OR'$

Molecular weight of ester = 102

Molecular weight of R + R' = 102 -44 = 58

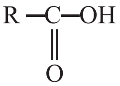
(ii)

Given $R - COOR' \xrightarrow{HOH} RCOOH + R'OH$

(A) acid Alcohol

mM of acid = mM of NaOH

$$\frac{0.185}{M/1} \times 1000 = 25 \times 0.1$$

Molecular weight of acid  $R-\overset{\overset{\displaystyle O}{\|}}{C}-OH$ = 74

Molecular weight of R

= 74 -(Molecular weight of COOH)

= 74 - 45 = 29

Molecular weight of R' = 58 - 29 = 29

Thus, R =R', also R may be C_nH_{2n+1} = 29

i.e., R' and R is C_2H_5

(iii) Thus, ester is $CH_3.CH_2COOCH_2.CH_3$

Reaction

$CH_3CH_2COOC_2H_5$ + H_2O

Ester

(Ethyl propanoate)

CH_3CH_2COOH + C_2H_5OH

Acid Alcohol

(Propanoic acid) (Ethyl alcohol)