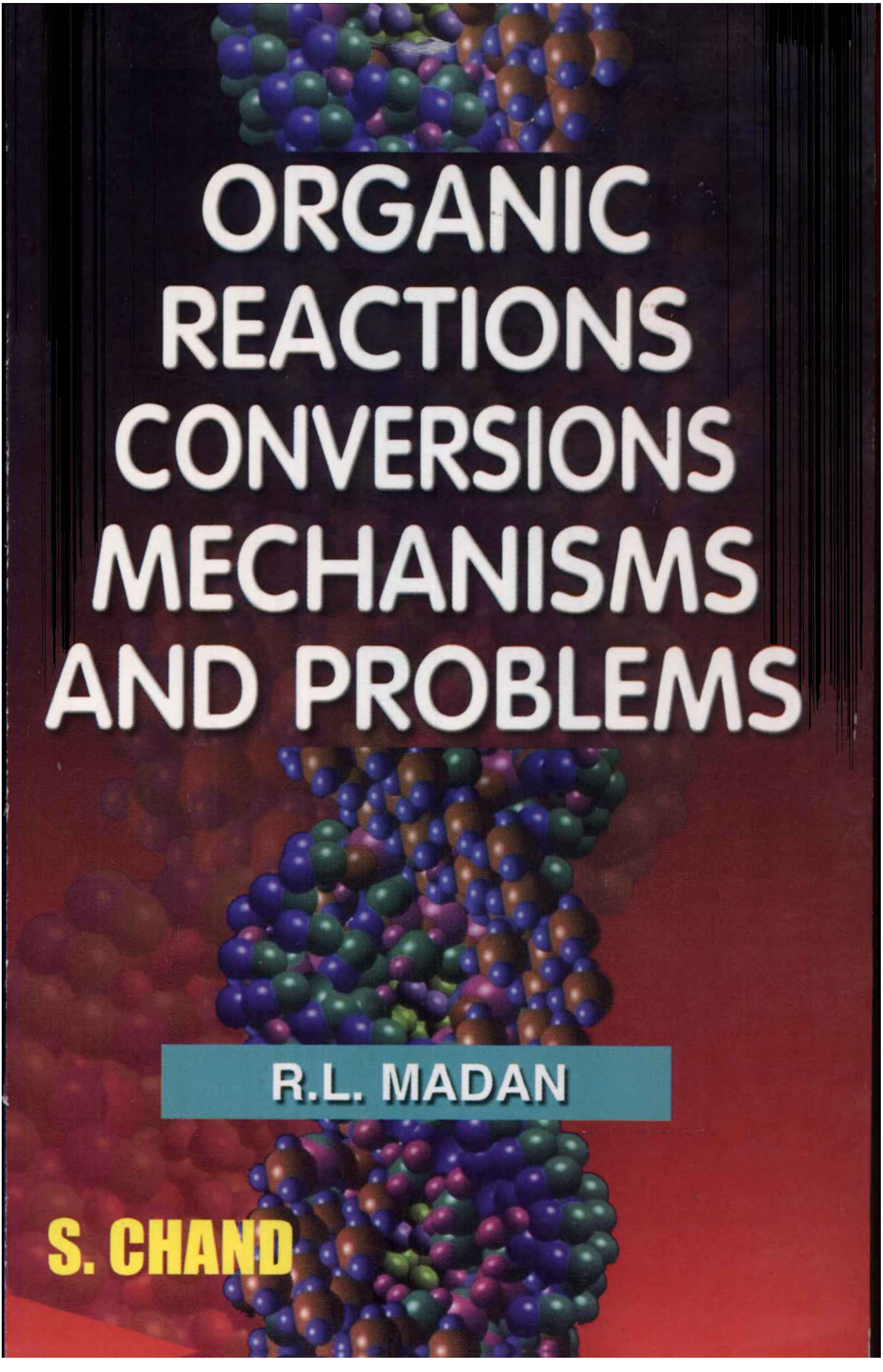

# ORGANIC REACTIONS CONVERSIONS MECHANISMS AND PROBLEMS

R.L. MADAN

S. CHAND

# ORGANIC
# REACTIONS, CONVERSIONS, MECHANISMS and PROBLEMS

**[For (CBSE and ISC) Classes XI and XII, IIT Entrance Examination, Medical Entrance Examinations, Delhi College of Engineering Entrance Examination and Other Engineering Colleges Entrance Examinations]**

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*First Edition 2001*
*Reprint with corrections 2002*
*Reprint with corrections 2005*

ISBN : 81-219-2038-8

PRINTED IN INDIA

*By Rajendra Ravindra Printers (Pvt.) Ltd., Ram Nagar, New Delhi-110 055*
*and published by S. Chand & Company Ltd.,*
*7361, Ram Nagar, New Delhi-110 055*

# PREFACE

The author feels pleasure in placing 'Organic Reactions, Conversions, Mechanisms and Problems' in the hands of students appearing for XI, XII examinations of CBSE, ISC and various state boards and also for engineering and medical entrance examinations.

It is author's feeling that normal textbooks for XI and XII classes do not give enough material to score handsome marks in organic chemistry in entrance examinations. Supplementary material is badly needed, apart from the textbooks, which can expose the students to different types of problems, and widen the horizon of students. The present book is an effort in this direction.

Subject-matter has been divided into ten chapters. It has been endeavoured to present all possible types of questions that can be set in the board or entrance examinations.

Questions on mechanism of reactions are increasingly being set in various examinations. No authentic book is available in the market to meet this requirement. Having understood the mechanism of reaction, a student can just play with the problems related with that reaction. The book deals with IUPAC nomenclature of organic compounds to start with and goes on to name reactions, conversions, identification of compounds, what happens when distinguishing between pairs of compounds, problems based on organic reactions, etc.

The author thanks Shri Ravindra Kumar Gupta, Managing Director, S. Chand & Company Ltd., Delhi and Shri Navin Joshi, Regional Manager, S. Chand & Company Ltd., Lucknow for their encouragement. The author also thanks the production and other staff of S. Chand & Company Ltd. for their cooperation in bringing out the book in a nice form

Suggestions for further improvement of the book will be thankfully acknowledged.

**R.L. MADAN**

# CONTENTS

## 1

# IUPAC Nomenclature of Organic Compounds

Nomenclature means giving name to a compound. We have the *old* or *trivial* or *common* system of nomenclature and IUPAC system of nomenclature. IUPAC system of nomenclature is more scientific and methodic and provides names to compounds without any flow. IUPAC stands for International Union of Pure and Applied Chemists.

Trivial or common names of compounds particularly simple compounds are still prevalent and find wide usage even now.

In this chapter, we give the IUPAC system of nomenclature of organic compounds. There are certain rules to be followed in IUPAC nomenclature. But before that we shall learn certain terms.

(*i*) **Word root.** The word root represents the number of carbon atoms in the *parent chain*. The parent chain in the compound is selected by following certain rules as discussed later. For the chains upto four carbon atoms special word roots are used, but for he chains containing more than four carbon atoms, Greek numerals are used. The general word root for different aliphatic compounds is ALK. The word roots for carbon chains of different lengths are given below.

**Table Word Roots for Carbon Chains of Different Lengths**

| *Chain Length* | *Word root* | *Chain Length* | *Word root* |
|---|---|---|---|
| $C_1$ | Meth- | $C_9$ | Non- |
| $C_2$ | Eth- | $C_{10}$ | Dec- |
| $C_3$ | Prop- | $C_{11}$ | Unidec- |
| $C_4$ | But- | $C_{12}$ | Dodec- |
| $C_5$ | Pent- | $C_{13}$ | Tridec- |
| $C_6$ | Hex- | $C_{18}$ | Octadec- |
| $C_7$ | Hept- | $C_{20}$ | Icos- |
| $C_8$ | Oct- | $C_{30}$ | Tricont- |

(*ii*) **Primary suffix.** Primary suffix is used to represent saturation or unsaturation in the carbon chain. While writing the name, primary suffix is added to the word root. Some of the primary suffixes are given below.

**Table. Some Primary Suffixes.**

| *Nature of Carbon Chain* | *Primary Suffix* |
|---|---|
| Saturated Carbon Chain | *ane* |
| Unstaturated Carbon Chains: | |
| one $C=C$ bond | *ene* |
| two $C=C$ bonds | *adiene* |
| three $C=C$ bonds | *atriene* |
| one $C\equiv C$ bonds | *yne* |
| two $C\equiv C$ bonds | *adiyne* |

(*iii*) **Secondary suffix.** Secondary suffix is used to indicate the functional group in the organic compound. It is added to the primary suffix by dropping its terminal *e*. Secondary suffixes for various functional groups are given below.

**Table. Some Organic Families and Secondary Suffixes.**

| *Class of organic compound* | *General formula* | *Functional Group* | *Suffix* | *IUPAC name of the family* $\left(\textit{Word root} + \textit{Prim. suffix} + \textit{Sec. suffix}\right)$ |
|---|---|---|---|---|
| Alcohols | R—OH | —OH | -ol | Alkanol |
| Thioalcohols | R—SH | —SH | -thiol | Alkanethiol |
| Amines | $\text{R—NH}_2$ | $\text{—NH}_2$ | -amine | Alkanamine |
| Aldehydes | R—CHO | —CHO | -al | Alkanal |
| Ketones | R—COR | $>CO$ | -one | Alkanone |
| Carboxylic acids | R-COOH | —COOH | -oic acid | Alkanoic acid |
| Amides | $\text{R—CONH}_2$ | $\text{—CONH}_2$ | -amide | Alkanamide |
| Acid chlorides | R—COCl | —COCl | -oylchloride | Alkanoyl chloride |
| Esters | R—COOR | —COOR | -oate | Alkyl alknoate |
| Nitriles | $\text{R—C}\equiv\text{N}$ | $\text{—C}\equiv\text{N}$ | -nitrile | Alkane nitrile |

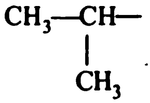
*If the name of the secondary suffix begins with a consonant, then the terminal 'e' of the primary suffix is no dropped while adding secondary suffix to it.*

*The terminal 'e' of primary suffix is retained if some numerical prefix like di, tri, etc., is used before the secondary suffix.*

(*iv*) **Prefix.** Prefix is a part of the name which appears before the word root. Prefixes are used to represent the names of alkyl groups or some functional groups as discussed below.

(*a*) **Alkyl groups.** These are formed by the removal of H atom from the alkanes. These are represented by the general formula $C_nH_{2n+1}$— or R—. Some alkyl groups along with their prefixes are given in the table below.

**Table. Some Alkyl Groups along with their Prefixes**

| *Alkane* | *Alkyl Group* | *Prefix* |
|---|---|---|
| $CH_4$ | $CH_3$— | Methyl |
| $C_2H_6$ | $CH_3CH_2$ | Ethyl |
| $C_3H_8$ | $CH_3CH_2CH_2$— | *n*-Propyl |
| $C_3H_8$ |  $CH_3\text{—}\underset{\underset{CH_3}{|}}{CH}\text{—}$ | isopropyl or (1-Methyl ethyl) |

(*b*) **Some functional groups** are always indicated by the prefixes instead of secondary suffixes. These prefixes for various functional groups are given below.

**Table. Functional Groups which are always Represented by Prefixes**

| *Functional Group* | *Prefix* | *Family* | *IUPAC Name* |
|---|---|---|---|
| —$NO_2$ | Nitro | R—$NO_2$ | Nitroalkane |
| —OR | Alkoxy | R—OR | Alkoxyalkane |
| —Cl | Chloro | R—Cl | Chloroalkane |
| —Br | Bromo | R—Br | Bromoalkane |
| —I | Iodo | R—I | Iodoalkane |
| —F | Fluoro | R—F | Fluoroalkane |
| —NO | Nitroso | R—NO | Nitrosoalkane |

(*c*) **In poly functional compound,** *i.e.*, compound with more than one functional groups, one of the functional groups is treated as principal functional group and is indicated by the secondary suffix whereas other functional groups are treated as substituents and are indicated by the prefixes. The prefixes for various functional groups are given below.

**Table. Prefixes for Functional Groups in Poly Functional Compound**

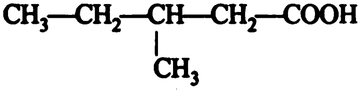
| *Functional Group* | *Prefix* | *Functional Group* | *Prefix* |
|---|---|---|---|
| —OH | Hydroxy | —COOR | Carbalkoxy |
| —CN | Cyano | —COCl | Chloroformyl |
| —NC | Isocyano | —$CONH_2$ | Carbamoyl |
| —CHO | Formyl | —$NH_2$ | Amino |
| —SH | Mereapto | = NH | Imino |
| —SR | Alkylthio | >CO | Keto or Oxo |
| —COOH | Carboxy | | |

**Arrangement of Prefixes, word root and suffixes in naming an organic compound arrangment.**

The prefixes, word root and suffixes are arranged as follows while writing the name

*Prefix(es) + Word root + prim. suffix + sec. suffix*

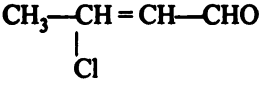
The following examples will illustrate



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

(3-Methyl pentanoic acid)

| Methyl.... | Pent..... | an......... | oicacid |
|---|---|---|---|
| prefix | word roof | primary suffix | secondary suffix |



$CH_3{-}\underset{\underset{\displaystyle Cl}{|}}{CH}=CH{-}CHO$

(3-Cholorobut-2 enal)

| Chloro....... | but....... | en........ | al |
|---|---|---|---|
| prefix | word root | primary suffix | secondary suffix |

**Notes. 1.** *The name of organic compound may or may not contain prefix or secondary suffix but it always contains word root and primary suffix. For example, the names of straight chain alkanes ; alkenes and alkymes do not contain any prefix and secondary suffix.*

$CH_3CH_2CH_2CH_3$

(Butane)

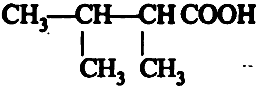
| But......... | ane........ |
|---|---|
| word root | primary suffix |

$CH_3{-}CH_2CH=CHCH_3$

(penttene-2)

| Pent........ | ene....... |
|---|---|
| word root | primary suffix |

**2.** *Numerical prefixes such as di, tri, etc., are used before the prefixes or secondary suffixes, if the compound contains more than one similar substituents or similar functional groups.*

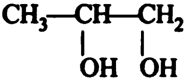


$CH_3{-}\underset{\underset{\displaystyle CH_3}{|}}{CH}{-}\underset{\underset{\displaystyle CH_3}{|}}{CH}\,COOH$

(2, 3-dimethyl butanoic acid)

| Di..... | methyl... | but...... | an...... | oic acid....... |
|---|---|---|---|---|
| Numercial prefix | Prefix | word root | prim. suffix | sec. suffix |

*While adding numerical prefix before the secondary suffix, the terminal 'e' of the primary suffix is not removed.*



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

(Propane 1, 2-diol)

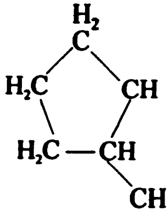
| Prop..... | ane... | di........ | ol |
|---|---|---|---|
| word root | prim. suffix | Numerical prefix | sec. suffix |

$\begin{array}{l} COOH \\ | \\ COOH \end{array}$

(Ethane dioic acid)

| Eth....... | ane......... | di....... | oic acid |
|---|---|---|---|
| word root | prim. suffix | Numerical prefix | sec. suffix |

**3.** *In case of alicyclic compounds, a separate secondary prefix cyclo is used immediately before the word root. Word root, here depends upon the number of carbon atoms in the ring.*



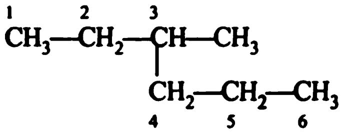
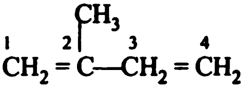
(2-Methyl cyclopentanol)

| Methyl | cyclo | pent | an | ol |
|---|---|---|---|---|
| prefix | sec.<br>prefix | word<br>root | p. suffix | sec.<br>suffix |

## Rules for IUPAC Nomenclature

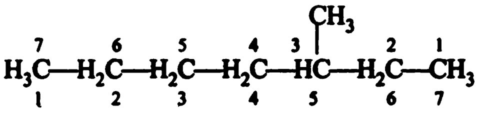
1. **Longest Possible Chain Rule.** The longest possible continuous chain of carbon atoms containing the main functional group and also as many of the carbon-carbon multiple bond(s) is selected. This chain is taken as the **parent chain**. The name of the compound is derived from the alkane having the same number of carbon atoms as the parent chain.

For example,

| *Structure* | *Parent chain* | *Alkane from which name of the compound is derived* |
|---|---|---|
|  $\overset{1}{CH_3}-\overset{2}{CH_2}-\overset{3}{CH}(\underset{4}{CH_2}-\underset{5}{CH_2}-\underset{6}{CH_3})-CH_3$ | Contains six carbon atoms | Hexane |
|  $\overset{1}{CH_2}=\overset{2}{C}(CH_3)-\overset{3}{CH_2}=\overset{4}{CH_2}$ | Contains four carbon atoms | Butane |

2. **Lowest possible number rule for Longest Chain containing only substituents/side chains.** (*a*) The longest chain selected is numbered from that end which gives lowest number to the carbon bearing the substituents or side chains.

(*b*) The location of the substituent is indicated by a numeral which precedes the suffix. The numeral is the number of the carbon atom to which the substituent/side chain is attached. For example,

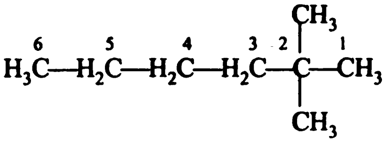


$\underset{1}{\overset{7}{H_3C}}-\underset{2}{\overset{6}{H_2C}}-\underset{3}{\overset{5}{H_2C}}-\underset{4}{\overset{4}{H_2C}}-\underset{5}{\overset{3}{HC}}(CH_3)-\underset{6}{\overset{2}{H_2C}}-\underset{7}{\overset{1}{CH_3}}$ (I)

3-Methyl heptane

The numbering is done from the right side as it gives lower number (number 3) to the carbon bearing methyl group.

(*c*) If the same substituents/side chains occur more than once, prefixes di, tri, tetra, etc., are used to indicate their number. They are preceded by a number (one number for each group present) to indicate the carbon atom bearing them. For example,

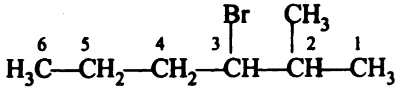


$$\overset{6}{H_3C}-\overset{5}{H_2C}-\overset{4}{H_2C}-\overset{3}{H_2C}-\underset{CH_3}{\overset{\overset{CH_3}{|}}{\overset{2}{C}}}-\overset{1}{CH_3}$$

(II)

2, 2-Dimethylhexane

(*d*) If there are more than one side chains/substituents, they should be arranged in alphabetical order. However, prefixes (di, tri, etc.) and any other that is hyphenated (*n*-, *sec*-, *tert*-, etc.) should be ignored while arranging the side chains/substituents alphabetically. But the prefixes like cyclo, iso, neo should not be ignored.



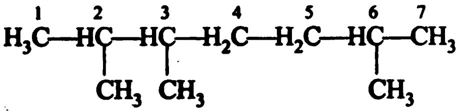
$$\overset{6}{H_3C}-\overset{5}{CH_2}-\overset{4}{CH_2}-\overset{\overset{Br}{|}}{\overset{3}{CH}}-\overset{\overset{CH_3}{|}}{\overset{2}{CH}}-\overset{1}{CH_3}$$

(III)

3-Bromo-2-methylhexane

The methyl is attached to carbon number 2 and bromine atom to carbon number 3. Since bromine comes first in alphabetical order, the exact name is 3-Bromo-2-methyl hexane and not 2-methyl-3-bromohexane. Thus, the substituents are written in alphabetical order.

(*e*) If identical alkyl groups (side chains), are at equal distances from both the ends, the chain is numbered from the end where there are more side chains/substituents. For example,

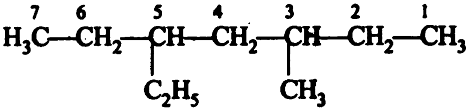


$$\overset{1}{H_3C}-\underset{CH_3}{\overset{2}{HC}}-\underset{CH_3}{\overset{3}{HC}}-\overset{4}{H_2C}-\overset{5}{H_2C}-\underset{CH_3}{\overset{6}{HC}}-\overset{7}{CH_3}$$

(IV)

2, 3, 6-Trimethylheptane and not 2, 5, 6-Trimethylheptane

(*f*) If different alkyl groups are in equal position w.r.t. the ends of the chain, the chain is numbered from the end which gives the smaller number to the smaller alkyl substituents. For example,



$$\overset{7}{H_3C}-\overset{6}{CH_2}-\underset{C_2H_5}{\overset{5}{CH}}-\overset{4}{CH_2}-\underset{CH_3}{\overset{3}{CH}}-\overset{2}{CH_2}-\overset{1}{CH_3}$$

(V)

5-Ethyl-3-methylheptane and not 3-Ethyl-5-methylheptane

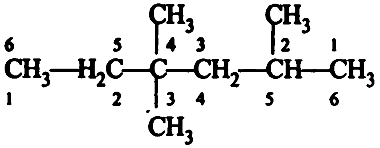
**Note :** A hyphen (-) is always put between the numeral and the side chain/substituent.

3. **Lowest Sum Rule.** The longest chain selected is numbered from that end which keeps the sum of numbers used to indicate the positions of the side chains/substituents and functional group(s) as small as possible.

In example IV, the lowest sum = 2 + 3 + 6 = 11.

The name 2, 5, 6-Trimethyl heptane is incorrect as the sum of the number = 2 + 5 + 6 = 13.

Similarly in the following example VI, the correct name is 2, 4, 4-Trimethyl hexane and not 3, 3, 5-Trimethyl hexane as the sum of the first set of numbers is 10 (2 + 4 + 4) and second set of numbers is 11 (3 + 3 + 5).

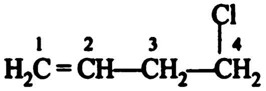


$$\overset{6}{\underset{1}{CH_3}}-\overset{5}{\underset{2}{H_2C}}-\overset{\overset{CH_3}{|}\,4}{\underset{3\,\underset{CH_3}{|}}{C}}-\overset{3}{\underset{4}{CH_2}}-\overset{\overset{CH_3}{|}\,2}{\underset{5}{CH}}-\overset{1}{\underset{6}{CH_3}}$$

(VI)

4. **Lowest Number for Largest Chain containing Functional Groups.** When a compound has a functional group including a multiple bond and one or more side chains/substituents, the lowest number should be given to the functional group even if it violates the lowest sum rule. For example,

(*i*)

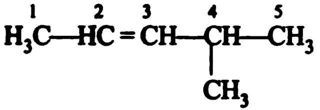


$$\overset{1}{H_2C}=\overset{2}{CH}-\overset{3}{CH_2}-\overset{\overset{Cl}{|}\,4}{CH_2}$$

(VII)

4-Chlorobut-1-ene

The chain is numbered from left side so as to give lowest number to the double bond.

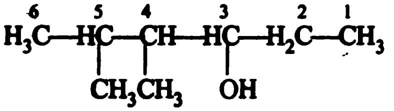


$$\overset{1}{H_3C}-\overset{2}{HC}=\overset{3}{CH}-\overset{4}{\underset{\underset{CH_3}{|}}{CH}}-\overset{5}{CH_3}$$

(VIII)

4-Methylpent-2-ene

(*ii*)

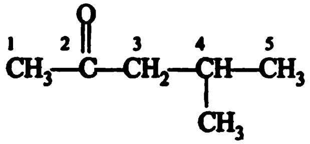


$$\overset{6}{H_3C}-\overset{5}{\underset{\underset{CH_3}{|}}{HC}}-\overset{4}{\underset{\underset{CH_3}{|}}{CH}}-\overset{3}{\underset{\underset{OH}{|}}{HC}}-\overset{2}{H_2C}-\overset{1}{CH_3}$$

(IX)

4, 5-Dimethylhexan-3-ol

(*iii*)

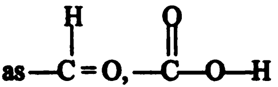


$$\overset{1}{CH_3}-\overset{\overset{O}{\|}\,2}{C}-\overset{3}{CH_2}-\overset{4}{\underset{\underset{CH_3}{|}}{CH}}-\overset{5}{CH_3}$$

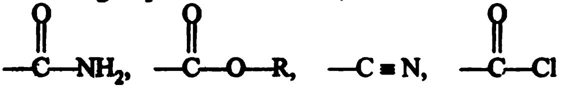
(X)

4-Methylpentan-2-one

If functional group such as

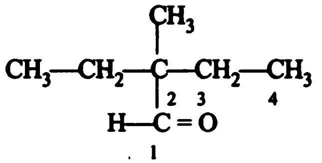


$-\overset{\overset{H}{|}}{C}=O,\ -\overset{\overset{O}{\|}}{C}-O-H$



$-\overset{\overset{O}{\|}}{C}-NH_2,\ -\overset{\overset{O}{\|}}{C}-O-R,\ -C\equiv N,\ -\overset{\overset{O}{\|}}{C}-Cl$ etc.,

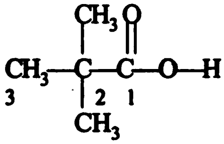
are present in the molecule, the numbering of the parent chain in such cases must start from the carbon atom of the functional group and the number 1 given to the carbon atom of the above functional groups. For example,

(*a*)


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

(XI)

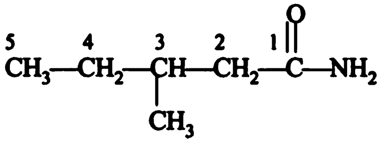
(2-Ethyl-2-Methylbutanal)

(*b*)


$$\mathrm{\underset{3}{CH_3}{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{\underset{2}{C}}}{-}\overset{\overset{O}{\|}}{\underset{1}{C}}{-}O{-}H}$$

(XII)

2, 2-Dimethylpropanoic acid

(c)


$$\mathrm{\overset{5}{CH_3}{-}\overset{4}{CH_2}{-}\underset{\underset{CH_3}{|}}{\overset{3}{CH}}{-}\overset{2}{CH_2}{-}\overset{\overset{O}{\|}}{\overset{1}{C}}{-}NH_2}$$

(XIII)

3-Methylpentanamide

**5. For Longest Chain containing Two or More Different Functional Groups (Poly Functional Compounds).** When a compound contains two or more different functional groups, one of the functional groups is chosen as the **Principal functional group** and the remaining functional groups (secondary functional groups) are considered as the substituents. The following rules should be noted down :

(*i*) When two or more functional groups are present in a compound, the principal functional group is chosen which has the highest priority.

**Functional groups are arranged in order of decreasing priority as given below :**

*Sulphonic acids > Carboxylic acids > acid anhydrides > esters > acid chlorides > amides > nitriles isocyanides > aldehydes > ketones > alcohols > amines > alkenes, alkynes > halo, nitro, alkoxy, alkyl.*

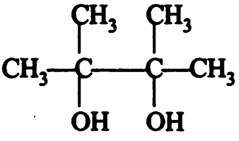
The prefixes for secondary functional groups are :

| *Group* | *Name* | *Group* | *Name* |
|---|---|---|---|
| —OH | Hydroxy | —COOH | Carboxy |
| —OR | Alkoxy | —CN | Cyno |
| $>C=O$ | Keto or oxo | | |
| | | —COOR | Caroboalkoxy |
| —CHO | Formyl | —CONH$_2$ | Carboxamide |
| —NH$_2$ | Amino | —COCl | Chloroformyl |
| —NHR | N-alkylamino | | |
| —NR$_2$ | N, N-dialkylamino | | |

**Examples**

(*i*) $H_3CO\overset{2}{CH_3}\overset{1}{CH_2}-OH$ 2-Methoxyethanol

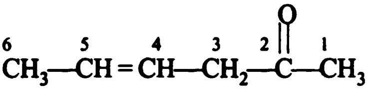
Prefix : Methoxy
Word Root : eth
Pri. suffix : an
Sec. suffix : ol

(*ii*) 

$CH_3-\underset{OH}{\overset{CH_3}{C}}-\underset{OH}{\overset{CH_3}{C}}-CH_3$

2, 3-Dimethylbutane-2, 3-diol

Numerical prefix : Di
Prefix : methyl
Word Root : but
Pri. suffix : ane
Numerical suffix : di
Sec. suffix : ol

(*iii*) 

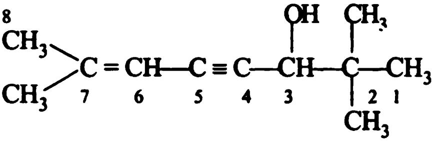
$\overset{6}{CH_3}-\overset{5}{CH}=\overset{4}{CH}-\overset{3}{CH_2}-\overset{\overset{O}{\|}}{\underset{2}{C}}-\overset{1}{CH_3}$

Hex-4-en-2-one

Word Root : Hex
Pri. suffix : ene
Sec. suffix : one

(*iv*) $HO\overset{3}{CH_2}\overset{2}{CH_2}-\overset{1}{COOH}$ 3-Hydroxypropanoic acid

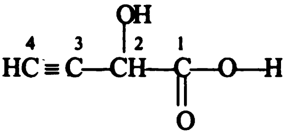
Prefix : Hydroxy
Word Root : prop
Pri. suffix : an
Sec. suffix : oic acid

(*v*) 

$\overset{8}{CH_3}\!\!>\!\overset{7}{C}=\overset{6}{CH}-\overset{5}{C}\equiv\overset{4}{C}-\underset{3}{\overset{OH}{CH}}-\underset{CH_3}{\overset{CH_3}{\underset{2}{C}}}-\underset{1}{CH_3}$ (with second $CH_3$ on C-7)

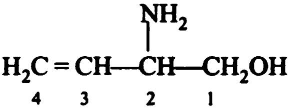
2, 2, 7-Trimethyloct-6-en-4-yn-3-ol

Prefix : Methyl
Word Root : oct
Pri. suffixes : ene, yne
Sec. suffix : ol

(*vi*) 

$\overset{4}{HC}\equiv\overset{3}{C}-\overset{OH}{\underset{2}{CH}}-\underset{\underset{O}{\|}}{\overset{1}{C}}-O-H$

2-Hydroxybut-3-ynoic acid

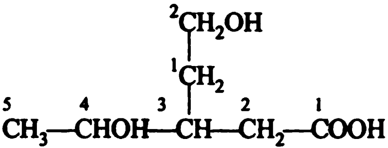
(*vii*) 

$\underset{4}{H_2C}=\underset{3}{CH}-\underset{2}{\overset{NH_2}{CH}}-\underset{1}{CH_2OH}$

2-Aminobut-3-en-1-ol

(*viii*) $\underset{3}{\text{CH}_2}=\underset{2}{\text{CH}}-\underset{1}{\text{CH}_2\text{OH}}$ Prop-2-en-1-ol

**6.** If the chain of the carbon atom selected as the branched chain also contains multiple bonds or functional groups, the branched chain is separately numbered. This is done in such a way that the carbon of the branched chain which is attached to the parent chain is assigned no. 1. Also, the name of such branched chains are written in brackets. For example :



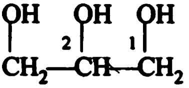
$$\overset{5}{\text{CH}_3}-\overset{4}{\text{CHOH}}-\overset{\overset{{}^{2}\text{CH}_2\text{OH}}{\overset{|}{\overset{{}^{1}\text{CH}_2}{|}}}}{{}^{3}\text{CH}}-\overset{2}{\text{CH}_2}-\overset{1}{\text{COOH}}$$

4-Hydroxy-3 (2-hydroxy ethyl)-pentanoic acid

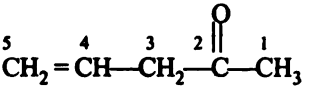
(*ii*) Select the chain of carbon atoms that includes the maximum number of functional groups.

It is numbered from that end which gives lowest number to the principal functional group.

**Examples**

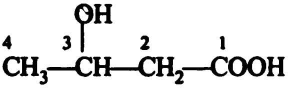
(*a*) 

$\overset{\overset{\text{OH}}{|}}{{}^{3}\text{CH}_2}-\overset{\overset{\text{OH}}{|}}{{}^{2}\text{CH}}-\overset{\overset{\text{OH}}{|}}{{}^{1}\text{CH}_2}$ 1, 2, 3-Propanetriol
or Propane-1, 2, 3-triol

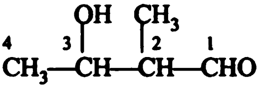
(*b*) 

$\overset{5}{\text{CH}_2}=\overset{4}{\text{CH}}-\overset{3}{\text{CH}_2}-\overset{\overset{\text{O}}{\|}}{{}^{2}\text{C}}-\overset{1}{\text{CH}_3}$ Pent-4-en-2-one

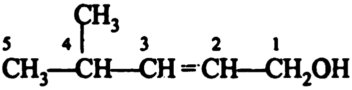
(*c*) $\overset{4}{\text{CH}_3}-\overset{3}{\text{CH}}=\overset{2}{\text{CH}}-\overset{1}{\text{COOH}}$ But-2-enoic acid
or 2-Butenoic acid

(*d*) 

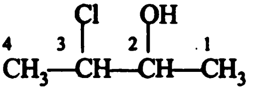
$\overset{4}{\text{CH}_3}-\overset{\overset{\text{OH}}{|}}{{}^{3}\text{CH}}-\overset{2}{\text{CH}_2}-\overset{1}{\text{COOH}}$ 3-Hydroxybutanoic acid

(*e*) 

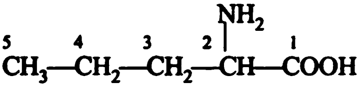
$\overset{4}{\text{CH}_3}-\overset{\overset{\text{OH}}{|}}{{}^{3}\text{CH}}-\overset{\overset{\text{CH}_3}{|}}{{}^{2}\text{CH}}-\overset{1}{\text{CHO}}$ 3-Hydroxy-2-methyl butanal-1

(*f*) 

$\overset{5}{\text{CH}_3}-\overset{\overset{\text{CH}_3}{|}}{{}^{4}\text{CH}}-\overset{3}{\text{CH}}=\overset{2}{\text{CH}}-\overset{1}{\text{CH}_2\text{OH}}$ 4-Methyl-pent-2-en-1-ol

(*g*) 

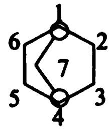
$\overset{4}{\text{CH}_3}-\overset{\overset{\text{Cl}}{|}}{{}^{3}\text{CH}}-\overset{\overset{\text{OH}}{|}}{{}^{2}\text{CH}}-\overset{1}{\text{CH}_3}$ 3-Chlorobutan-2-ol

(*h*) 

$\overset{5}{\text{CH}_3}-\overset{4}{\text{CH}_2}-\overset{3}{\text{CH}_2}-\overset{\overset{\text{NH}_2}{|}}{{}^{2}\text{CH}}-\overset{1}{\text{COOH}}$ 2-Amino pentanoic acid

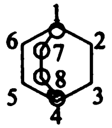
## NOMENCLATURE OF BICYCLIC HYDROCARBONS

We come across compounds, containing two or more rings fused together or having two carbon atoms in common. These common carbon atoms are called **bridgehead** carbons. Consider, for example, the following bicyclic compounds (containing two rings)



I

Bicyclo (2.2.1) Cycloheptane



II

Bicyclo (2.2.2) Cyclooctane

Both two compounds have two bridge head carbons (common carbons) at position 1 and 4. These common carbons have been shown as encircled.

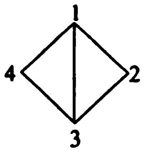
1. We number various carbon atoms in such structures starting from any common carbon and go on numbering all carbon atoms in one direction till the cyclic structure is complete.

2. Then, we number the left out carbon atoms, in one direction. Thus, in compound I, there are 7 carbon atoms and in compound II, there are 8 carbon atoms. Thus compound I is Bicycloheptane and compound II is Bicyclooctane.

3. To name, these compounds, we find out, what are the numbers of carbon atoms separating the common carbons, when seen through different routes. Thus, in compound I, there are two carbons through one route, two carbons through the second route and one carbon through the third route, separating the common carbons. This compound will be named as Bicyclo (2. 2. 1) heptane. Here, the numbers 2, 2, 1 represent the number of carbon atoms separating the common carbons in different directions. These numbers in decreasing order are written in *square brackets* after the word bicyclo.

4. Coming to compound II, we find that there are two carbons in one direction, 2 carbons in the second direction and 2 carbons in the third direction, separating the common carbon atoms. Thus, the name of the compound is Bicyclo (2. 2. 2) cyclooctane.

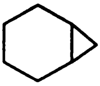
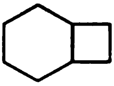
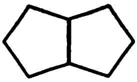
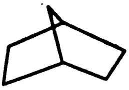
5. In the case of fused rings, there is no carbon in one of the directions, separating the common points consider the following compound :



Bicyclo (1.1.0) butane

There are 4 carbon atoms in all. Thus, it is bicyclobutane. No. 1 and 3 are common points. These common points are separated by one carbon in one direction one carbon in second direction and no (zero) carbon in the third direction (direct link between position 1 and 3). Thus, the name of the compound is Bicyclo (1.1,0) butane.

**Example.** Write name of the following bicyclic compounds

(i)

(ii)

(iii)

(iv)


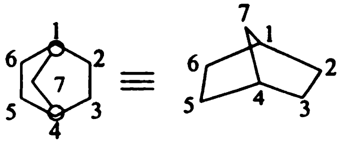
**Solution :**

(i) There are two common points. These points are separated by 4, 1 and 0 carbon atoms in different directions. Total no. of carbon atoms in the compound is 7. Thus, the name will be Bicyclo (4. 1. 0) heptane.

(ii) There are the two common carbons in the compound, which are separated by 4, 2 and 0 carbon atoms in different directions. There are a total of 8 carbon atoms. Therefore, it is named as Bicyclo (4. 2. 0) octane.

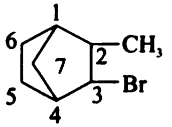
(iii) Following the same procedure, the name of compound (iii) is Bicyclo (3. 3. 0) octane.

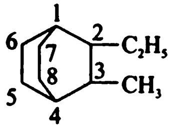
(iv) This compound is the same as compound I discussed earlier.



Position 1 and 4 are common points. These are seperated by 2, 2 and 1 carbon atoms in different directions. Therefore, the compound is named as Bicyclo (2. 2. 1) haptane.

**Example :** Name the following compounds:

(i)


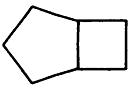
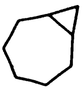
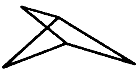
(ii)


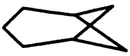
**Solution :** (i) There is a methyl group at the position 2 and the bromo group at the position 3. Therefore, the compound can be named as 3- Bromo-2-methyl bicyclo (2. 2. 1) heptane.

(ii) There is a methyl group at position 3 and ethyl group at position 2. Therefore, the name of the compound is 2- ethyl-3 methyl (2. 2. 2) octane.

## PROBLEMS FOR PRACTICE

Write the names of the following compounds:

(i)

(ii)

(iii)

(iv)

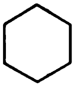
(v)


**Answers**

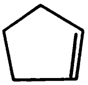
(i) Bicyclo (3. 2. 0) heptane (ii) Bicyclo (5. 1. 0) octane (iii) Bicyclo (1. 1. 1) pentane (iv) Bicyclo (2. 1. 1) hexane (v) Bicyclo (3. 1. 1) heptane

## Nomenclature of alicyclic organic compounds

Names of alicyclic compounds are derived by putting another prefix 'cyclo' before the word root which depends upon the number of carbon atoms in the ring. The suffixes *ane, ene* or *yne* are written depending upon saturation or unsaturation in the ring, as usual.

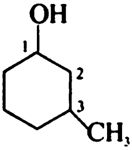


Cyclohexane

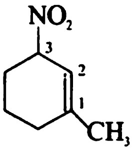


Cyclopentene

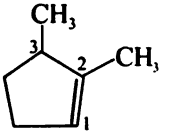
If some substituent or functional group is present, it is indicated by some appropriate prefix or suffix and its position is indicated by numbering the carbon atoms of the ring. The *numbering is done in such a way so as to assign least possible number to the functional group or substituent in accordance with the rules already discussed.* Some examples are :



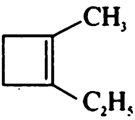
3-Methylcyclohexanol



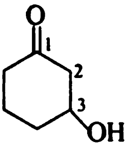
1-Methyl-3-nitrocyclohexane



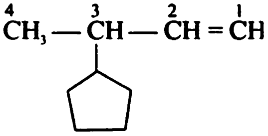
2, 3-Dimethylcyclopentene



1-Ethyl-2-Methylcyclobutene



3-Hydroxycyclo Hexanone



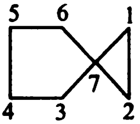
3-Cyclopentyl-1-Butene

## Nomenclature of spiro compounds

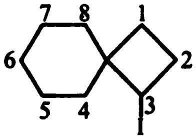
Compounds containing a carbon which is common to two different rings are called *spiro* compounds. Such compounds are named following the steps given below.

1. Total number of carbon atoms in the two rings are counted.
2. The number of carbon atoms in the two rings (excluding the common carbon at intersection) are counted separately.
3. The numbering of ring carbon atoms is done starting from the smaller ring and adjacent to the common carbon atom and then moving around the bigger ring, finally ending at the common carbon atom.
4. The position of the substituent is indicated by the number arrived at according to the above rules.

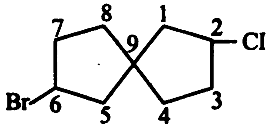
5. The name of the compound begins with the word spiro followed by the number of carbon atoms in the two rings within square brackets followed by the name of the hydrocarbon corresponding to the total number of ring carbon atoms in the compound.
6. The number of carbon atoms in the two rings are separated by dots instead of commas. The following examples will illustrate.



Spiro [2.4] heptane



3-Iodospiro [3.5] nonane



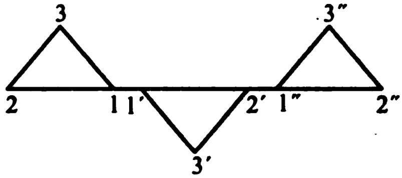
6-Bromo-2-Chlorospiro [4.4] nonane

**Nomenclature of two or more identical cyclic hydrocarbon units assembled together**

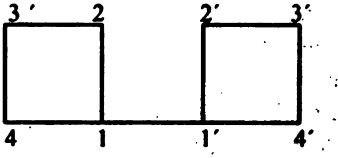
Sometimes, we come across compounds in which similar cyclic hydrocarbon units are assembled together. Such compounds are named by putting numerical prefixes such as *bi* for two, *ter* for three, *quater* for four, *quinque* for five, etc., before the name of the repeating units.

Carbon atoms of each unit are numbered with unprimed (like 1,2,3, ...) or primed like (1′, 2′, 3′, ... 1″, 2″, 3″. ...) Arabic numerals

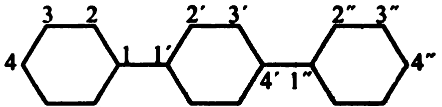
The points linking the different units are indicated by writing the locants before the name. The following examples will illustrate.



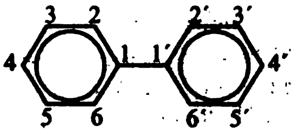
1, 1′, 2′, 1″-Quatercyclopropane



1, 1′-Bicyclobutane

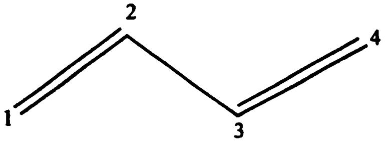


1, 1′, 4′, 1″-Tercyclohexane

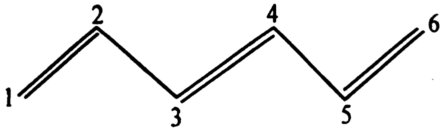


1, 1′-Biphenyl

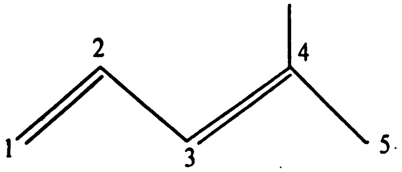
**Bond line notation of organic compounds.** It is a simple, brief and convenient method of representing organic molecules. In these notations, the bonds between the carbon atoms are represented by lines. A single line (–) represents a single bond, two parallel lines (=) represent a double bond and three parallel lines (≡) represent a triple bond. The intersection of lines represents carbon atoms carrying appropriate number of H atoms. For example, 1, 3-butadiene ($CH_2 = CH—CH = CH_2$) can be represented as follows :



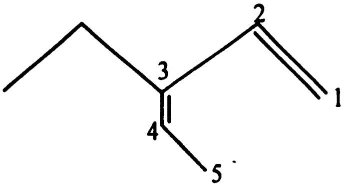
Some bond line structures along with their IUPAC names are given below :



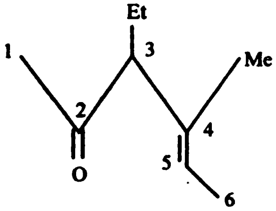
1, 3, 5-Hexatriene



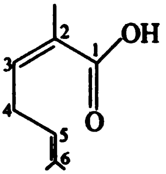
4-Methyl-1,3-pentadiene



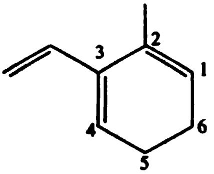
3-Ethyl-1,3-pentadiene



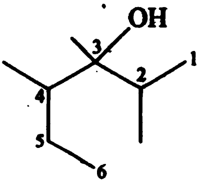
3-Ethyl-4 methylhex-4-en-2-one



2, 6-Dimethyl-2, 5-heptadienoic acid



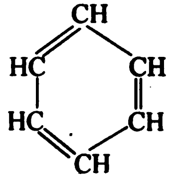
3-Ethenyl-2methyl-1, 3-hexadiene



2, 3, 4-Trimethylhex-1-en-3-ol

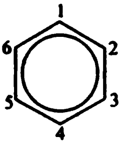
### Nomenclature of aromatic compounds

Aromatic compounds are cyclic compounds which contain one or more benzene type rings. Benzene is a simplest hydrocarbon of aromatic series which has a planar cyclic ring of six carbon atoms having three double bonds in alternate positions as shown below :

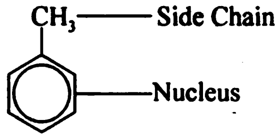


Benzene

or



The carbon atoms of benzene are numbered from 1 to 6 as shown above. The benzene ring is called the **nucleus** and alkyl groups attached to the ring are called **side chains.**

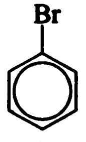


Benzene forms only one mono substituted derivative. However, it can form three disubstituted derivatives; namely 1, 2; 1, 3 and 1, 4 derivatives. These are respectively called *ortho* (or *o*-), *meta* (or *m*-) and *para* (or *p*-) derivatives.

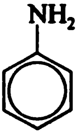
Tri and poly substituted derivatives are named by numbering the chain in such a way that the parent group gets the lowest number and sum of the positions of substituents is the smallest.

**Rule 1.** The word root for benzene derivatives is benzene.

**Rule 2.** The name of substituent group is added as a prefix to the word root in case of mono-substituted benzenes. For example,

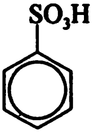


Bromobenzene



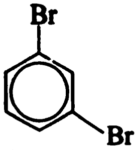
Aminobenzene

In some cases the name of the group is written as suffix. For example,

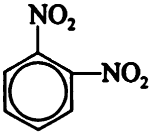


Benzene sulphonic acid

**Rule 3.** When two similar groups are attached to the benzene ring, numerical prefix *di* is placed before the name of the group, relative portion of the groups are indicated by suitable numbers or by the symbols *o, m* or *p*. For example,

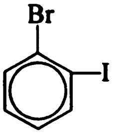


1, 3-Dibromobenzene
or *m*-Dibromobenzene



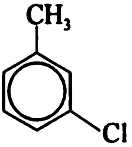
1, 2-Dinitrobenzene
or *o*-Dinitrobenzene

**Rule 4.** When two different groups are attached to the ring, the names of both groups are added as prefixes, in alphabetical order, to the word root and their relative positions are indicated. For example,

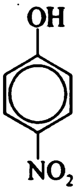


2-Bromoiodobenzene
or *o*-Bromoiodobenzene

If one of the groups gives a special name to the compound, than the name of the other group only is written as prefix. For example,

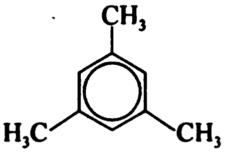


3-Chlorotoluene

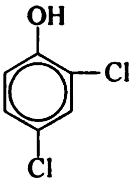


4-Nitrophenol

**Rule 5.** In case of tri-substituted or higher-substituted derivatives, the positions of groups are indicated by numbers.



1, 3, 5-Trimethylbenzene

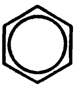


2, 4-Dichlorophenol

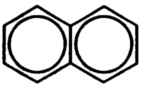
**Names of Some Aromatic Compounds**

**1. Hydrocarbons (Arenes)**

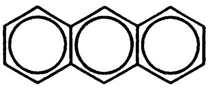
(*a*) *Hydrocarbons containing condensed rings*



Benzene

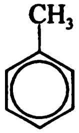


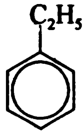
Naphthalene

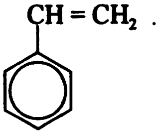


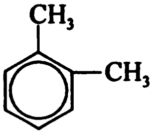
Anthracene

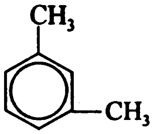
(*b*) *Hydrocarbons containing one ring only*

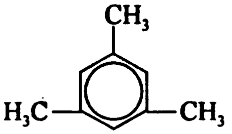

Methylbenzene
(Toluene)


Ethylbenzene

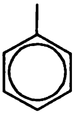

Phenylethene
(styrene)

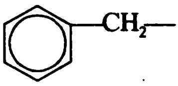

1, 2-Dimethyl
benzene
(*o*-Xylene)

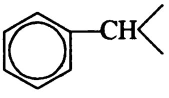

1, 3-Dimethyl
benzene
(*m*-Xylene)

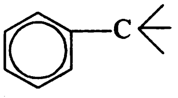

1, 3, 5-Trimethyl
benzene
(Mesitylene)

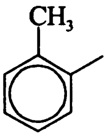
**2. Aromatic or Aryl radicals :**

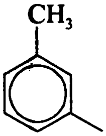

Phenyl radical

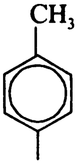

Benzyl (*monovalent*)


Benzal (*divalent*)

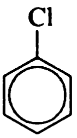

Benzo (*trivalent*)

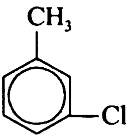

*o*-Tolyl

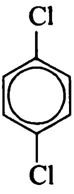

*m*-Tolyl

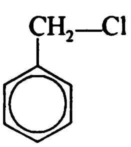

*p*-Tolyl

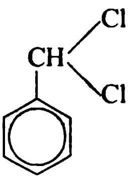
**3. Halogen Derivatives :**

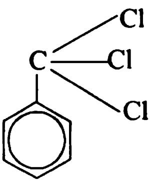

Chlorobenzene


3-Chlorotoluene

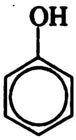

1, 4-Dichlorobenzene


Chloro phenyl
methane
(benzyl chloride)

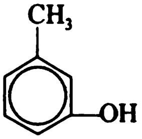

Dichloro phenyl
methane
(benzal chloride)


Trichloro phenyl
methane
(benzo trichloride)

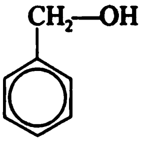
### 4. Phenols :



Hydroxy benzene
(Phenol)



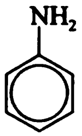
3-Hydroxy toluene
(*m*-Cresol)



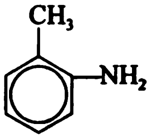
Phenylmethanol
(Benzyl alcohol)

Here benzyl alcohol is not phenol but an aromatic alcohol.

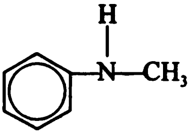
### 5. Amino Derivatives :



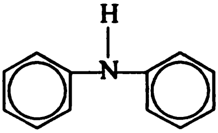
Benzenamine
(Aniline)



2-Methyl benzenamine
(2-Amino toluene)

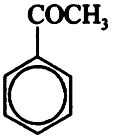


N-Methylaniline

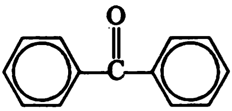


Diphenyl amine

### 6. Ketones :

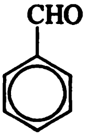


Methyl phenyl ketone
or
Acetophenone

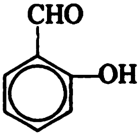


Diphenyl ketone
or
Benzophenone

### 7. Aldehydes :

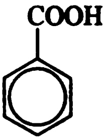


Benzaldehyde

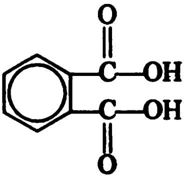


2-Hydroxy benzaldehyde
(Salicyladehyde)

### 8. Carboxylic acids :

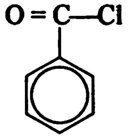


Benzoic acid

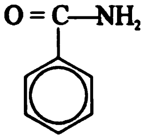


Phthalic acid
(1, 2-Benzene dicarboxylic acid)

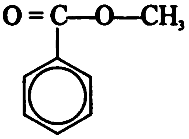
### 9. Acid derivatives :



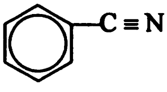
Benzoyl chloride



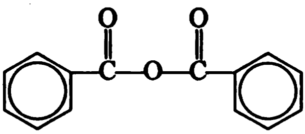
Benzamide



Methyl benzoate

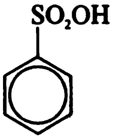


Benzonitrile
(phenyl cyanide)

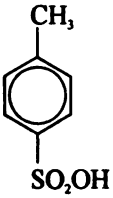


Benzoic anhydride

### 10. Sulphonic acids :

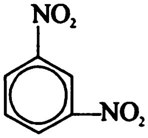


Benzene sulphonic acid

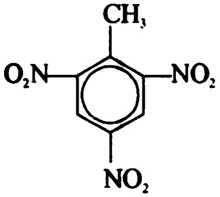


*p*-Toluene sulphonic acid (PTS)

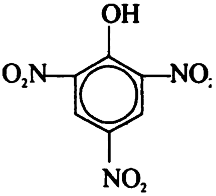
### 11. Nitro derivatives :



1, 3-Dinitro benzene

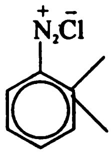


2, 4, 6-Trinitro toluene
(T.N.T.)

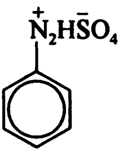


2, 4, 6-Trinitro phenol
(Picric acid)

### 12. Diazonium salts :

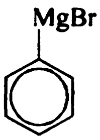


Benzene diazonium
chloride

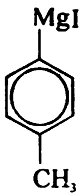


Benzene diazonium
hydrogen sulphate

### 13. Grignard reagents :

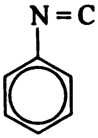


Phenyl magnesium
bromide

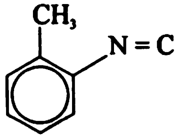


*p*-Tolyl magnesium iodide

**14. Isocyanides :**



Benzene carbylamine

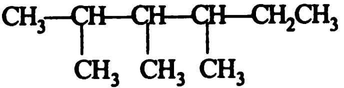


*o*-Toluene carbylamine

**Q. 1. Give the IUPAC names of the following compounds :**

(*i*) $(CH_3CH_2CH_2)_4C$

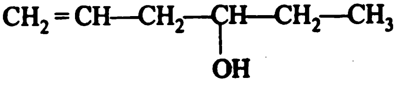
(*ii*) $CH_2{=}CH{-}CH_2{-}CH{=}CH_2$

(*iii*)


$$CH_3{-}\underset{CH_3}{\underset{|}{C}H}{-}\underset{CH_3}{\underset{|}{C}H}{-}\underset{CH_3}{\underset{|}{C}H}{-}CH_2CH_3$$

(*iv*) $OHCH_2{-}C{\equiv}C{-}CH_2OH$

(*v*) $(CH_3)_2CH{-}CH_2{-}COOH$

(*vi*)


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

**Ans.** (*i*) 4, 4-di *n*-propylheptane

(*ii*) 1, 4-pentadiene

(*iii*) 2, 3, 4-trimethylhexane

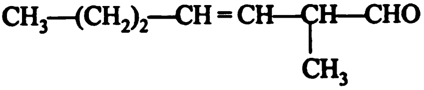
(*iv*) But-2-yne-1, 4-diol

(*v*) 3-methylbutanoic acid

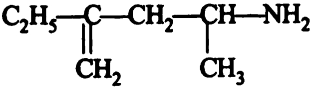
(*vi*) Hex-5-en-3-ol

**Q. 2. Give IUPAC names of the following :**

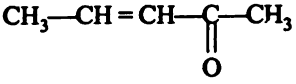
(*i*) $CH_3{-}CH_2{-}CH{=}CH{-}C{\equiv}CH$

(*ii*)


$$CH_3{-}(CH_2)_2{-}CH{=}CH{-}\underset{CH_3}{\underset{|}{C}H}{-}CHO$$

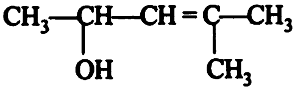
(*iii*)


$$C_2H_5{-}\underset{CH_2}{\underset{\|}{C}}{-}CH_2{-}\underset{CH_3}{\underset{|}{C}H}{-}NH_2$$

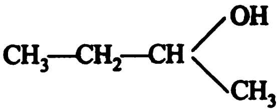
(*iv*)


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

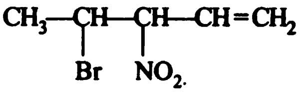
(*v*) $CH_3{-}CO{-}CH_2{-}CH_2{-}COOH$

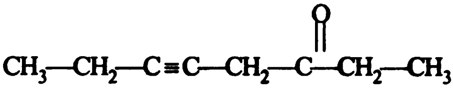
(*vi*)


$$CH_3{-}\underset{OH}{\underset{|}{C}H}{-}CH{=}\underset{CH_3}{\underset{|}{C}}{-}CH_3$$

(*vii*)


$$CH_3{-}CH_2{-}CH\begin{matrix}\diagup OH\\ \diagdown CH_3\end{matrix}$$

(*viii*) 
$CH_3—CH(Br)—CH(NO_2)—CH=CH_2$

(*ix*) 
$CH_3—CH_2—C \equiv C—CH_2—C(=O)—CH_2—CH_3$

**Ans.** (*i*) Hex-3-ene-5-yne

(*ii*) 2-Methyl hept-3-enal

(*iii*) 4-Amino-2-ethyl pent-1-ene

(*iv*) Pent-3-en-2-one

(*v*) 4-Keto pentanoic acid

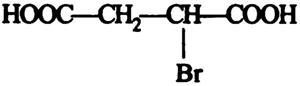
(*vi*) 4-Methyl pent-3-en-2-ol

(*vii*) 1-Methyl propan-1-ol

(*viii*) 4-Bromo-3-nitro pent-1-ene

(*ix*) Oct-5-yn-3-one

**Q. 3. Write IUPAC names of the following :**

(*i*) 
$HOOC—CH_2—CH(Br)—COOH$

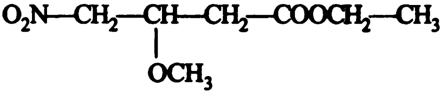
(*ii*) $HC \equiv C—CH_2—CH = CH$

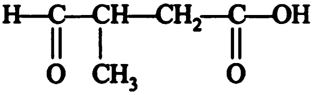
**Ans.** (*i*) 2-Bromo butane-1, 4-dioic acid

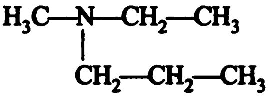
(*ii*) Pent-1-en-4-yne

**Q. 4. Write IUPAC names of the following :**

(*i*) $(CH_3)_2CH—N—(CH_3)_2$

(*ii*) 
$O_2N—CH_2—CH(OCH_3)—CH_2—COOCH_2—CH_3$

(*iii*) 
$H—C(=O)—CH(CH_3)—CH_2—C(=O)—OH$

(*iv*) 
$H_3C—N(CH_2—CH_2—CH_3)—CH_2—CH_3$

**Ans.** (*i*) Isopropyl dimethylamine

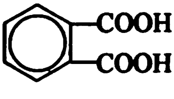
(*ii*) Ethyl 3-methoxy-4-nitrobutanoate

(*iii*) 4-oxo-3-methyl butanoic acid

(*iv*) N-Ethyl-N-methyl-1-aminopropane

**Q. 5. Write IUPAC names of the following :**

(*i*) $CH_2(COOH)CH(COOH)CH_2COOH$

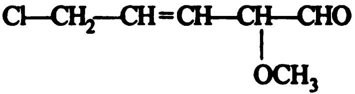
(*ii*) 

**Ans.** (*i*) 3-Carboxypentane-1, 5-dicarboxylic acid

(*ii*) Benzene 1, 2 dioic acid

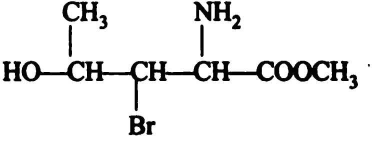
**Q. 6. Write IPUAC names of the following :**

(*i*)



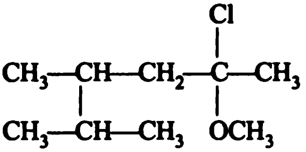
$Cl-CH_2-CH=CH-CH(OCH_3)-CHO$

(*ii*)

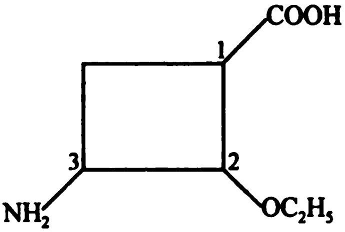


$HO-CH(CH_3)-CH(Br)-CH(NH_2)-COOCH_3$

(*iii*)



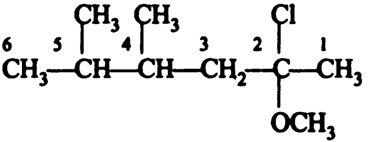
(*vi*)



**Ans.** (*i*) 5-Chloro-2-methoxy pent-3-enal

(*ii*) Methyl 2-amino-3-bromo-4-hydroxy pentanoate

(*iii*) The compound can be written as



$\overset{6}{CH_3}-\overset{5}{CH}(CH_3)-\overset{4}{CH}(CH_3)-\overset{3}{CH_2}-\overset{2}{C}(Cl)(OCH_3)-\overset{1}{CH_3}$

2-Chloro-2-methoxy-4, 5 dimethylhexane

(*iv*) 3-Amino-2-ethoxy cyclobutanoic acid

**Q. 7. Write the structural formulae of the following compounds :**

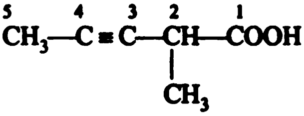
(*i*) 2-Methyl-3-pentynoic acid (*ii*) 3-Ethyl-5-hydroxy-3-hexenal

(*iii*) 2-Methyl-1, 3-butadiene (*iv*) Hept-1-en-4-yne

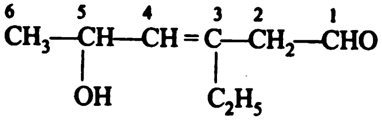
(*v*) Pent-3-enoic acid

(*vi*) 1-Amino-4-methyl pentan-2-one

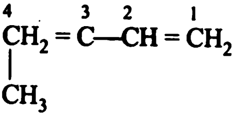
**Ans.** (*i*)



$\overset{5}{CH_3}-\overset{4}{C}\equiv\overset{3}{C}-\overset{2}{CH}(CH_3)-\overset{1}{COOH}$

(*ii*)


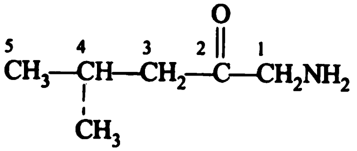
$$\overset{6}{CH_3}-\underset{OH}{\overset{5}{CH}}-\overset{4}{CH}=\underset{C_2H_5}{\overset{3}{C}}-\overset{2}{CH_2}-\overset{1}{CHO}$$

(*iii*)


$$\underset{CH_3}{\overset{4}{CH_2}}=\overset{3}{C}-\overset{2}{CH}=\overset{1}{CH_2}$$

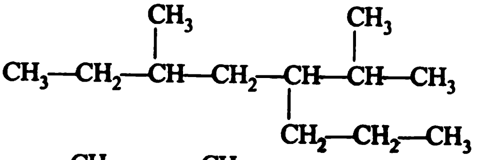
(*iv*) $\overset{7}{CH_3}-\overset{6}{CH_2}-\overset{5}{C}\equiv\overset{4}{C}-\overset{3}{CH_2}-\overset{2}{CH}=\overset{1}{CH_2}$

(*v*) $\overset{5}{CH_3}-\overset{4}{CH}=\overset{3}{CH}-\overset{2}{CH_2}-\overset{1}{COOH}$

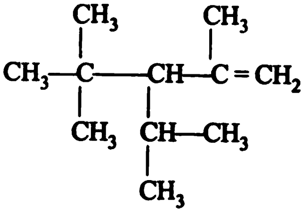
(*vi*)


$$\overset{5}{CH_3}-\underset{CH_3}{\overset{4}{CH}}-\overset{3}{CH_2}-\overset{O}{\overset{\|}{\overset{2}{C}}}-\overset{1}{CH_2NH_2}$$

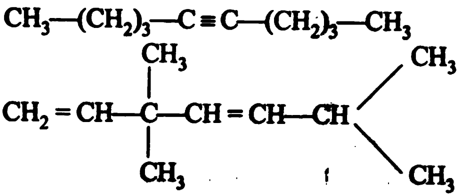
**Q. 8. Give the IUPAC names of :**

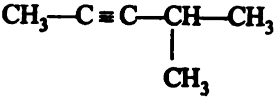
(*i*)


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

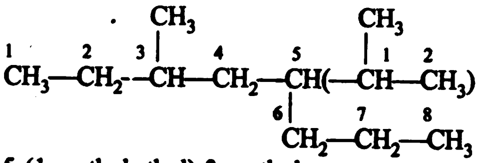
(*ii*)


(*iii*) $CH_3-(CH_2)_3-C\equiv C-(CH_2)_3-CH_3$

(*iv*)


(*v*)


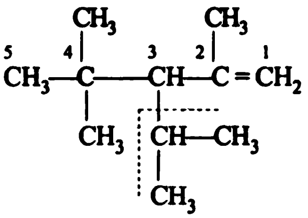
$$CH_3-C\equiv C-\underset{CH_3}{CH}-CH_3$$

**Ans.** (*i*)


$$\overset{1}{CH_3}-\overset{2}{CH_2}-\overset{CH_3}{\overset{3}{CH}}-\overset{4}{CH_2}-\underset{\overset{6}{CH_2}-\overset{7}{CH_2}-\overset{8}{CH_3}}{\overset{5}{CH}}(-\overset{CH_3}{\overset{1}{CH}}-\overset{2}{CH_3})$$

⟵ **Side chain**

**5-(1-methyl ethyl)-3-methyl octane**

(*ii*) 

$$\overset{5}{CH_3}-\overset{4}{\underset{CH_3}{\overset{CH_3}{C}}}-\overset{3}{\underset{CH(CH_3)-CH_3}{CH}}-\overset{2}{\overset{CH_3}{C}}=\overset{1}{CH_2}$$

Side Chain

3-(1-methyl ethyl)-2, 4, 4 Trimethyl-1-pentene

(*iii*) 5-Decyne

(*iv*) 3, 3, 6-Trimethyl-1, 4-heptadiene

(*v*) 4-Methyl-2-pentyne

**Q. 9. Write the structural formulae of the following compounds :**

(*i*) 2-Methyl pent-2-en-1-ol

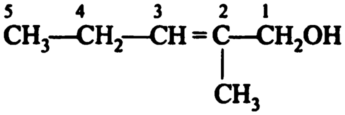
(*ii*) Hex-1-en-4-yne

(*iii*) 4-Cyano-3-methoxy butanoic acid

(*iv*) 4-Amino-2-ethyl-2-pentenal

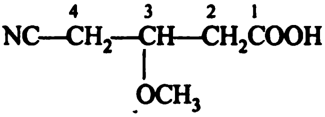
(*v*) 3, 5-Octadiene

(*vi*) 4-Chloro-2-Isoproyl-3-methyl cyclopentanone

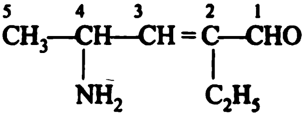
**Ans.** (*i*) 

$$\overset{5}{CH_3}-\overset{4}{CH_2}-\overset{3}{CH}=\overset{2}{\underset{CH_3}{C}}-\overset{1}{CH_2OH}$$

(*ii*) $\overset{6}{CH_3}-\overset{5}{C}\equiv\overset{4}{C}-\overset{3}{CH_2}-\overset{2}{CH}=\overset{1}{CH_2}$

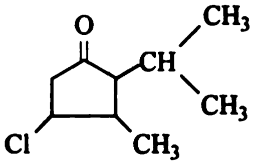
(*iii*) 

$$NC-\overset{4}{CH_2}-\overset{3}{\underset{OCH_3}{CH}}-\overset{2}{CH_2}\overset{1}{COOH}$$

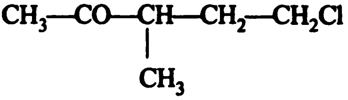
(*iv*) 

$$\overset{5}{CH_3}-\overset{4}{\underset{NH_2}{CH}}-\overset{3}{CH}=\overset{2}{\underset{C_2H_5}{C}}-\overset{1}{CHO}$$

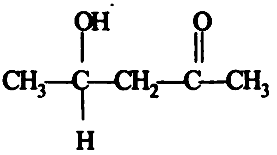
(*v*) $\overset{1}{CH_3}-\overset{2}{CH_2}-\overset{3}{CH}=\overset{4}{CH}-\overset{5}{CH}=\overset{6}{CH}-\overset{7}{CH_2}-\overset{8}{CH_3}$

(*vi*) 

**Q. 10. Write the IUPAC name of the following compound**

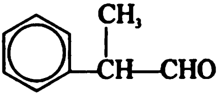
(*i*) 

$$CH_3-CO-\underset{CH_3}{CH}-CH_2-CH_2Cl$$

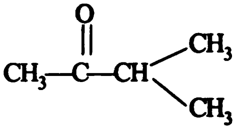
(*ii*) 

$CH_3-\underset{H}{\overset{OH}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$

(*D.S.B. 1998*)

(*iii*) 

(*A.I.S.B. 1998*)

(*iv*) 

(*A.I.S.B. 1998*)

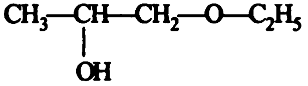
**Ans.** (*i*) 5-chloro-3-methyl-2-pentanone

(*ii*) 4-hydroxy-2-pentanone

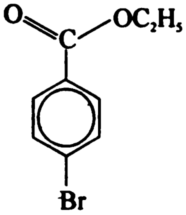
(*iii*) 2-methyl-2-phenyl propanal

(*iv*) 3-methyl-2-butanone

**Q. 11. Write IUPAC names of the following**

(*i*) 

$CH_3-\underset{OH}{CH}-CH_2-O-C_2H_5$

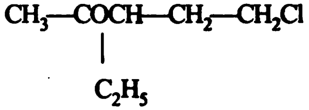
(*ii*) 

(*D.S.B. 1999*)

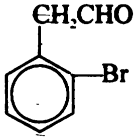
**Ans.** (*i*) 1-ethoxypropan-2-ol

(*ii*) ethyl 4-bromophenyl methamoate

**Q. 12. Write IUPAC names of the following compounds**

(*i*) 

$CH_3-\underset{C_2H_5}{COCH}-CH_2-CH_2Cl$

(*ii*) 

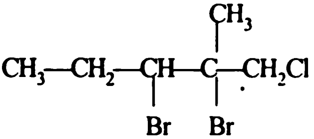
(*A.I.S.B. 1999*)

**Ans.** (*i*) 5-Chloro-3-ethyl-2-pentanone

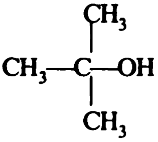
(*ii*) 2-bromophenyle ethanal

**Q. 13. Give IUPAC names of the following compounds :**

(*i*) $(CH_2)_3COH$

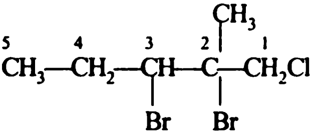
(*ii*) 

$CH_3-CH_2-\underset{Br}{CH}-\underset{Br}{\overset{CH_3}{C}}-CH_2Cl$ (*A.I.S.B. 2000*)

**Ans.** (*i*) 

$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH$

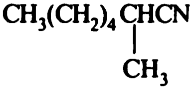
2-Methylpropan-2-ol

(*ii*) 

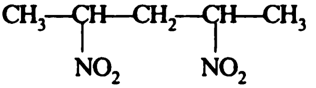
$\overset{5}{CH_3}-\overset{4}{CH_2}-\underset{Br}{\overset{3}{CH}}-\underset{Br}{\overset{CH_3}{\overset{2}{C}}}-\overset{1}{CH_2Cl}$

2, 3-Dibromo-1-chloro-2-methylpentane

**Q.14. Write IUPAC names of the following compounds**

(*i*) 

$CH_3(CH_2)_4\underset{CH_3}{CH}CN$

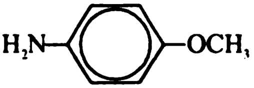
(*ii*) 

$CH_3-\underset{NO_2}{CH}-CH_2-\underset{NO_2}{CH}-CH_3$ (*A.I.S.B. 2002*)

**Ans.** (*i*) 2-Methylheptane nitrile

(*ii*) 2, 4-dinitropentane

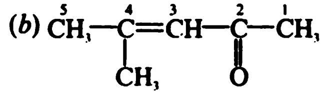
**Q.15. (*a*) Write IUPAC name of the following**



**(*b*) Draw the structure of 4-methylpent-3-en-2-one**

(*A.I.S.B. 2004*)

**Ans.** (*a*) 4-methoxy benzenamine

(*b*) 

$\overset{5}{CH_3}-\underset{CH_3}{\overset{4}{C}}=\overset{3}{CH}-\underset{O}{\overset{2}{\underset{\|}{C}}}-\overset{1}{CH_3}$

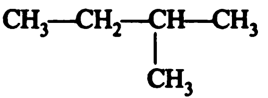
# 2

# Problems Based upon Isomerism and Physical Properties

**Q. 1. Write the structural formulae of n-pentane, isopentane and neopentane. Which of these has highest boiling point and why ?**

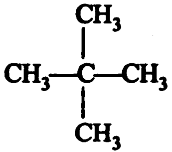
$CH_3-CH_2-CH_2-CH_2-CH_3$

*n*-Pentane



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

Isopentane



$CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_3$

Neopentane

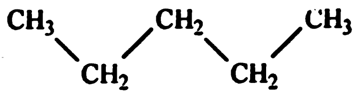
**Highest Boiling Point.** Of the three pentanes, *n*-pentane has the highest boiling point.

*Explanation.* All the three pentanes are non-polar compounds having only weak intermolecular forces of attraction (van der Wall's forces). The molecular weights of the three isomers are naturally the same but they have different surface areas. As the surface area of *n*-pentane is larger than those of the other two, it has strongest intermolecular forces of attraction. Therefore it has highest boiling point as compared to iso- and neo-pentanes.

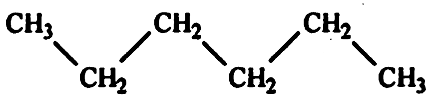
**Q. 2. As we move up from *n*-pentane to *n*-hexane, there is an increase of about 35° in the melting point but on moving from *n*-hexane to *n*-heptane the increase is only about 4°. How can you account for the observations ?**

**Ans.** Disproportionate variation in melting points of the three alkanes can be explained on the basis of their molecular weights and their ability to fit in the crystal structures as follows.

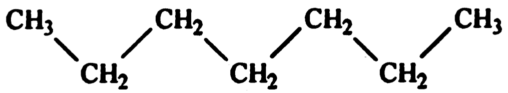
In alkanes, the carbon atoms form zig-zag chains as depicted below for *n*-pentane, *n*-hexane and *n*-heptane.



*n*-Pentane



*n*-Hexane



*n*-Heptane

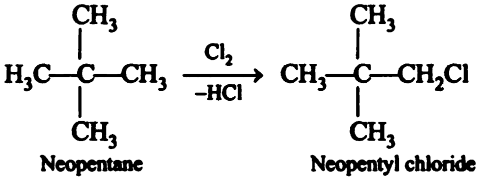
It is apparent that in *n*-hexane, the two terminal methyl groups lie on opposite sides of the zig-zag chain which enables this chain to fit in closely in the crystal structure. But in *n*-pentane and *n*-heptane, the two terminal groups lie on the same side so that the crystal structure is not so closely packed.

As we move from *n*-pentane to *n*-hexane, the molecular weight increases as well as the packing arrangement becomes more closed. Both these factors require greater energy to melt the solid. As such there is a large increase in melting point.

On the other hand, as we move from *n*-hexane to *n*-heptane, the molecular weight increases but the packing arrangement does not remain so close. While the melting point would tend to increase due to increase in molecular weight, the decrease in close packing would tend to have the opposite effect. The net result in that there is only a small increase in melting point in this case.

**Q. 3. An alkane with molecular weight 72 formed only one monochloro-substitution product. Suggest a structure for the alkane.**

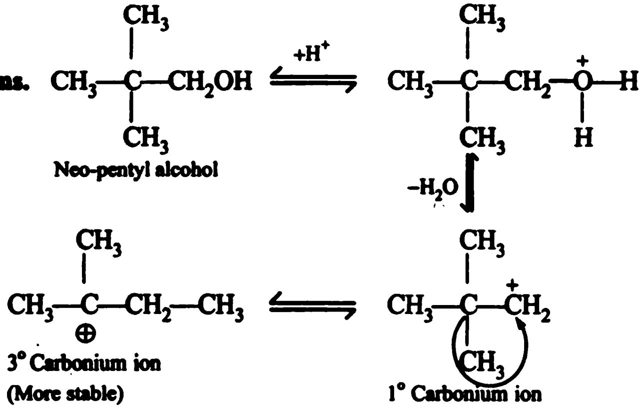
**Ans.** Molecular weight 72 suggests that the alkane has the molecular formula $C_5H_{12}$. Out of three isomeric pentanes viz. *n*-pentane, isopentane and neo-pentane, the last one is the answer to the question. This is because only neopentane has one type of hydrogen (primary) and hence would give one monochloro-substitution product.

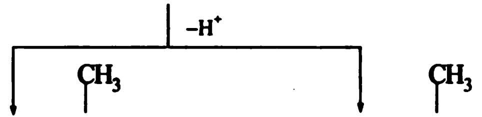


$$H_3C-C(CH_3)_2-CH_3 \xrightarrow[-HCl]{Cl_2} CH_3-C(CH_3)_2-CH_2Cl$$

**Q. 4. When neopentyl alcohol $(CH_3)_3C.CH_2OH$ is heated with acid, it is slowly converted into a mixture of two isomeric alkenes of the formula $C_5H_{10}$. Name these alkenes according to IUPAC system of nomenclature and also show how they are formed. Which one of them is the major product and why ?**

**Ans.**

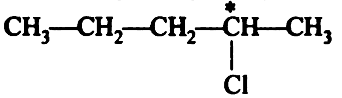
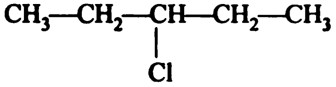
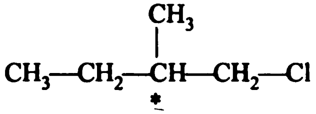
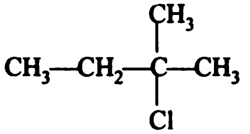
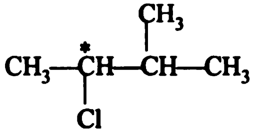
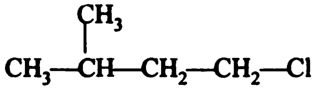
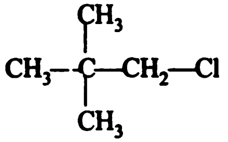



$\xrightarrow{-H^+}$ $CH_3-\overset{\overset{CH_3}{|}}{C}=CH-CH_3$ + $CH_2=\overset{\overset{CH_3}{|}}{C}-CH_2-CH_3$

2-Methyl but-2-ene
[Major product]

2-Methylbut-1-ene
[Minor]

**Q. 5. Write all the possible structures for a compound having molecular formula $C_5H_{11}Cl$. Name these according to IUPAC system. How many of them are optically active ?**

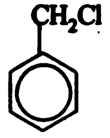
| **Ans.** | **Structural Formula** | **IUPAC Name** |
|---|---|---|
| (*a*) | $CH_3-CH_2-CH_2-CH_2-CH_2-Cl$ | 1-Chloropentane |
| (*b*) |  $CH_3-CH_2-CH_2-\underset{\underset{Cl}{\vert}}{\overset{*}{C}H}-CH_3$ | 2-Chloropentane |
| (*c*) |  $CH_3-CH_2-\underset{\underset{Cl}{\vert}}{CH}-CH_2-CH_3$ | 3-Chloropentane |
| (*d*) |  $CH_3-CH_2-\underset{*}{\overset{\overset{CH_3}{\vert}}{CH}}-CH_2-Cl$ | 1-Chloro-2-methylbutane |
| (*e*) |  $CH_3-CH_2-\underset{\underset{Cl}{\vert}}{\overset{\overset{CH_3}{\vert}}{C}}-CH_3$ | 2-Chloro-2-methylbutane |
| (*f*) |  $CH_3-\underset{\underset{Cl}{\vert}}{\overset{*}{C}H}-\overset{\overset{CH_3}{\vert}}{CH}-CH_3$ | 2-Chloro-3-methylbutane |
| (*g*) |  $CH_3-\overset{\overset{CH_3}{\vert}}{CH}-CH_2-CH_2-Cl$ | 1-Chloro-3-methylbutane |
| (*h*) |  $CH_3-\underset{\underset{CH_3}{\vert}}{\overset{\overset{CH_3}{\vert}}{C}}-CH_2-Cl$ | 1-Chloro-2, 2-dimethylpropane |

**Optically active forms.** The isomers (*b*), (*d*) and (*f*) are optically active due to the presence of **chirality** in their structures.

**Q. 6. Write the structures and names of all possible isomers of an aromatic compound with the mol. formula $C_7H_7Cl$.**

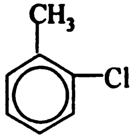
**Ans.** The structures and names of possible isomers of the compound with molecular formula $C_7H_7Cl$ are given below :

(*i*)



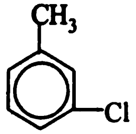
Benzyl chloride

(*ii*)



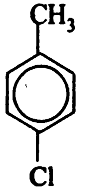
*o*-Chlorotoluene
(or *o*-Methyl chloro
benzene)

(*iii*)



*m*-Chlroro
toluene

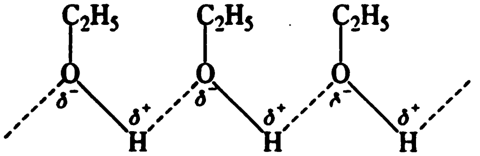
(*iv*)



*p*-Chloro
toluene

**Q. 7. Alcohol has higher boiling point than alkyl halide or alkane of comparable mol. wt. Why ?**

**Ans.** Since in alcohol (ROH), strongly electronegative oxygen atom is directly linked to hydrogen atom, its molecules get associated through intermolecular hydrogen bonding as shown above. This increases the molecular mass and hence the boiling point of alcohol rises.

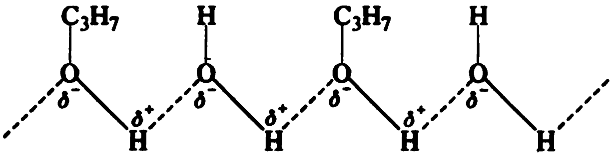


On the other hand, no such hydrogen bonding is possible in alkyl halide or alkane. Therefore such compounds have lower boiling points.

**Q. 8. Unlike propane or butane, propanol is soluble in water, why ?**

**Ans.** Propane molecules cannot join with water molecules through hydrogen bonding as propane has no oxygen-hydrogen bond in its molecule. Consequently, propane is not soluble in water.

On the other hand, propanol is soluble in water as its molecule contains —OH bond, which causes propanol molecules to form hydrogen bonds with water molecules as shown below :



Consequently propanol is soluble in water.

**Q. 9. Why is *n*-hexanol is insolube in water ?**

**Ans.** Alcohols have the general formula ROH. As the R group becomes larger, ROH resembles more closely with the hydrocarbon.

In *n*-hexanol molecule, the carbon content is quite high which causes it to resemble closely with hexane (which is not soluble in water). Moreover, the large hexyl ($C_6H_{15}$—) group obstructs the formation of hydrogen bonds between water and *n*-hexanol molecules. As a result, *n*-hexanol is not soluble in water.

**Q. 10. The boiling point of 1-propanol (molecular mass 60) is 370 K while the boiling point of 1, 2-ethanediol (molecular mass 62) is 470 K. Explain the reason for high boiling point of 1, 2-ethanediol.**

**Ans.** Since 1, 2-ethanediol molecule contains two —OH groups, it is capable of forming more intermolecular hydrogen bonds and hence is very highly associated substance. Therefore, its boiling point is very high.

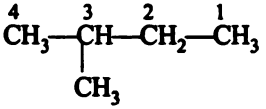
On the other hand, 1-propanol molecule has only one —OH group, its molecules are not much associated through hydrogen bonding. Consequently, its boiling point is lower than that of 1, 2-ethanediol.

**Q. 11. Give the structure of pentane that would be expected to produce the largest number of isomeric monochloro derivatives.**

**Ans.** There are three isomers of pentane.

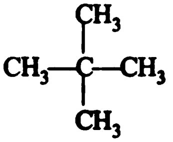
$CH_3CH_2CH_2CH_2CH_3$

*n*-pentane



$$\overset{4}{CH_3}-\underset{\displaystyle CH_3}{\overset{3}{CH}}-\overset{2}{CH_2}-\overset{1}{CH_3}$$

Isopentane



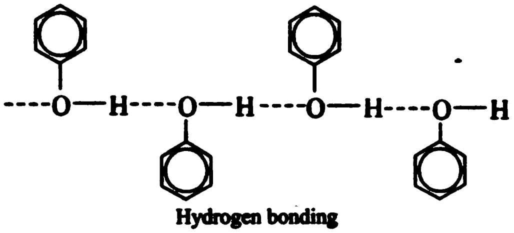
$$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}-CH_3$$

Neopentane

Out of the three pentanes, isopentane produces the largest number of isomeric monochloro derivatives corresponding to substitution at C-1, C-2, C-3 or C-4.

**Q. 12. Why has phenol higher boiling point than toluene ?**

**Ans.** Phenol (molecular mass 94) boils at 455 K while toluene (molecular mass 92) boils at 383 K only. The reason for higher boiling point of phenol as compared to toluene is that phenol forms intermolecular hydrogen bonds leading to association of its molecule. Consequently, its molecular mass increases manyfold and hence its boiling point is high. Additional energy is required to break the hydrogen bonds which raises its boiling point. Hydrogen bonding in phenol is depicted below :

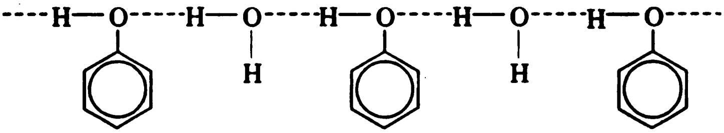


Hydrogen bonding

On the other hand, toluene does not contain any strong electronegative atom attached to hydrogen. Therefore, it does not form intermolecular hydrogen bonding. Hence, its boiling point is lower than that of phenol.

**Q. 13. Why is phenol more soluble in water than toluene ?**

**Ans.** Phenol is somewhat soluble in water as phenol molecules can form hydrogen bonds with water molecules as shown below :

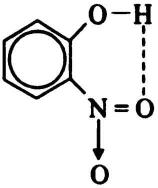


Intermolecular hydrogen bonding

On the other hand, toluene is not capable of forming hydrogen bonds with water molecules, hence toluene is not soluble in water. It can be said, in general, that a compound is soluble in water if it can form hydrogen bond with it.

**Q. 14. Account for the lower boiling point and decreased water solubility of *o*-nitrophenol as compared with their *m*- and *p*-isomers.**

**Ans.** *o*-Nitrophenol forms *intramolecular* hydrogen bonding resulting in the formation of a six membered ring.



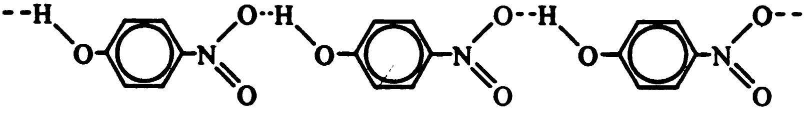
*o*-Nitrophenol

Intramolecular hydrogen bonding

Due to intramolecular hydrogen bonding, *o*-nitrophenol is incapable of forming hydrogen bonding with other *o*-nitrophenol molecules, *i.e.*, intermolecular hydrogen bonding. Hence, it does not exist as associated molecule. Moreover, the molecular size shrinks as a consequence of intramolecular bonding.Therefore, its boiling point is not high.

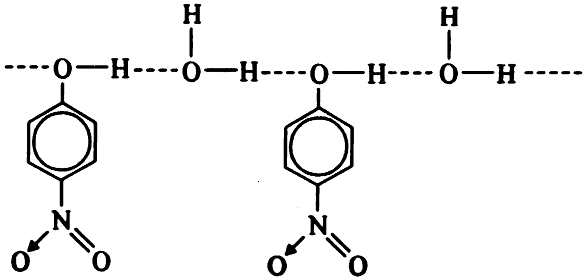
Similarly, due to intramolecular hydrogen bonding, *o*-nitrophenol does not form hydrogen bonds with water molecules also. Therefore, it is not very soluble in water.

*m*-nitrophenol as well as *p*-nitrophenol form intermolecular hydrogen bonding resulting in association of molecules. Consequently, they have high boiling points.



Intermolecular hydrogen bonding of *p*-nitrophenol.

Moreover, *m*- and *p*-nitrophenols can also form hydrogen bonds with water molecules. Consequently, they are more soluble in water than *o*-nitrophenol.



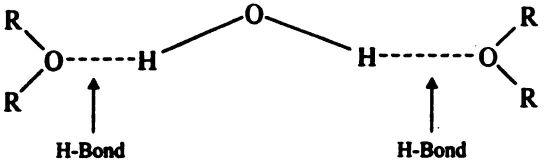
**Q. 15. Why do ethers have lower boiling points than isomeric alcohols?**

**Ans.** Ethers have lower boiling points than isomeric alcohols. For example, ethyl alcohol boils at 351 K while diethyl ether boils at 308 K. This is because in ether the oxygen atom is not directly linked with hydrogen atom. Therefore, hydrogen bonding is not possible between the ether molecules. Hence, their boiling points are not high.

On the other hand, alcohols such as ethyl alcohol exhibit hydrogen bonding as they contain oxygen atom which is directly linked with hydrogen atom. As a result, the molecules of alcohol get associated due to hydrogen bonding. Due to strong intermolecular interaction between the molecules of alcohol, they have high boiling points.

**Q. 16. Why do alcohols and isomeric ethers have comparable water solubilities ?**

**Ans.** Like alcohols, ethers can also form hydrogen bonds with water. Consequently, ethers have some solubility in water.

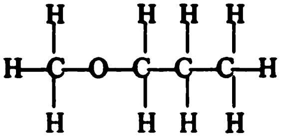


Moreover, ethers are weakly polar molecules. This is also the reason for their solubility in water. However, the solubility of ethers in water decreases as the size of alkyl group increases. Ethers are more soluble in alcohol due to hydrogen bonding and similarity of structure.

**Q. 17. How many isomeric ethers are possible for $C_4H_{10}O$ ? Give their structures and IUPAC names.**

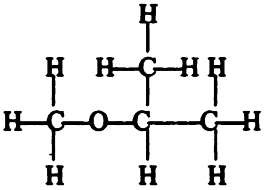
**Ans.** Three isomeric ethers are possible having the molecular formula $C_4H_{10}O$. Their structures and IUPAC names are given below :

1.



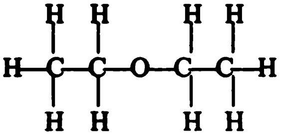
1-Methoxypropane

2.



2-Methoxypropane

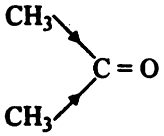
3.



Ethoxyethane

**Q. 18. The boiling point of acetone is 329 K while that of propanal is 322 K although both have the same molecular mass.**

**Ans.** Boiling point is a property which is related to the polarity in the molecule. Greater the polarity in the molecule, greater will be the intermolecular attraction and hence higher will be the boiling point. Acetone has a higher boiling point compared to propanal because of double inductive effect of two alkyl groups.

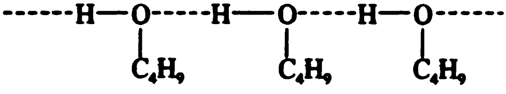


$CH_3 \rightarrow CH_2 \rightarrow CHO$

In propanal, there is inductive effect of only one alkyl group. Hence greater polarity will be induced in acetone.

**Q. 19. *n*-butyl alcohol boils at 391 K while *n*-butyraldehyde boils at 349 K though their molecular masses are 74 and 72 respectively. Account for the higher b.p. of the alcohol.**

**Ans.** There is hydrogen bonding in the case of *n*-butyl alcohol which results in association of *n*-butyl alcohol molecules.



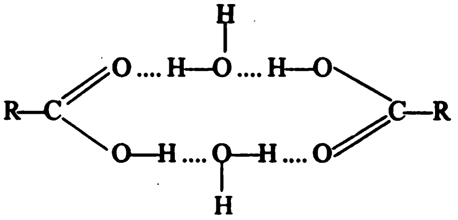
$$\cdots\cdots H-\underset{C_4H_9}{\underset{|}{O}}\cdots\cdots H-\underset{C_4H_9}{\underset{|}{O}}\cdots\cdots H-\underset{C_4H_9}{\underset{|}{O}}\cdots\cdots$$

No such hydrogen bonding takes place in *n*-butyraldehyde. Hence these molecules are not associated. As such, *n*-butyl alcohol boils at a higher temperature compared to *n*-butyraldehyde. Boiling point is a property which is dependent upon the size of the molecule. Associated molecules which become bigger and heavier require a higher temperature to boil.

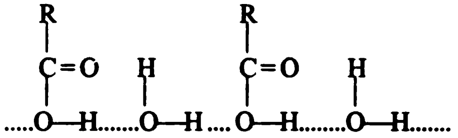
**Q. 20. Explain why the first few members of carboxylic acids are soluble and higher members insoluble in water ?**

**Ans.** Lower members from formic to butyric acid are soluble in water because of the formation of hydrogen bond between water and the acid. Because of electronegativity difference between oxygen and hydrogen, hydrogen bond is formed as shown below.

(*i*)



(*ii*)



As the size of the alkyl group increases, the solubility in water decreases because the strength of hydrogen bond decreases. This is because a long fatty chain hinders the formation of hydrogen bond. Hence higher fatty acids are insoluble in water. They are, however, soluble in organic solvents like benzene and ether.

**Q. 21. Explain why carboxylic acids show much higher boiling point compared to alcohols of comparable molecular masses ?**

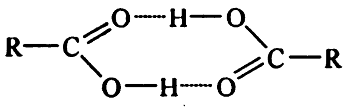
*Or*

**Most of the carboxy acids exist as dimers. Explain.**

*Or*

**Mol. wt. of acetic acid is double the calculated value. Explain.**

**Ans.** Carboxylic compounds exhibits hydrogen bonding between two acid molecules as shown below :



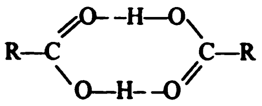
Thus the acid molecule exists as a dimer in which two molecules have been associated into one molecule. Thus, the size of the molecule is increased which accounts for the higher boiling point of carboxylic compounds. No such dimerisation takes place in between alcohol molecules. Hence carboxy compounds have higher boiling points compared to alcohols of comparable molecular weights.

**Q. 22. Explain the following: (i) Most aromatic acids are solids but the acids of acetic acid group are mostly liquids.**

**(ii) Amines have lower boiling points than those of the corresponding alcohols.**

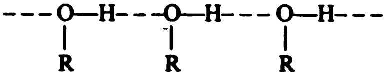
*(A.I.S.B. 2002)*

**Ans.** (i) Aromatic acids have planer benzene ring which pack tightly in the crystal lattice. There are strong binding forces between the molecules. Therefore most aromatic acids are solids. Acids of acetic acid group are mostly liquids because they don't pack themselves tightly. Also, There are no continuous hydrogen bonds between the acid molecules. They only form the dimers as given below



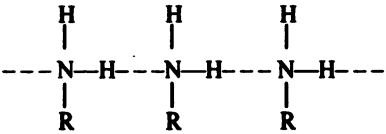
This dimerisation keeps their physical state to liquid without reaching the solid state.

(ii) There is a greater extent of hydrogen bonding in alcohols, because of considerable difference in the electronegativities of oxygen and hydrogen.



$$---\underset{\substack{|\\ R}}{O}\text{—}H---\underset{\substack{|\\ R}}{O}\text{—}H---\underset{\substack{|\\ R}}{O}\text{—}H---$$

Some amount of hydrogen bonding does take place in the case of amine. But it is not much due to insufficient difference between the electronegativities of nitrogen and hydrogen



$$\cdots\underset{R}{\overset{H}{N}}-H\cdots\underset{R}{\overset{H}{N}}-H\cdots\underset{R}{\overset{H}{N}}-H\cdots$$

Greater the extent of hydrogen bonding, greater is the association leading to higher boiling point.

**Q. 23. A racemic mixture of (±)2–phenyl propanoic acid on esterification with (–) 2-butanol gives two esters. Give stereochemistry of the esters obtained.** *(I.I.T. 2003)*

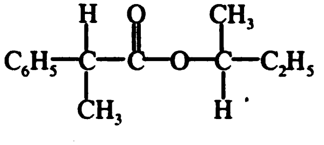
**Ans.** (+) 2–phenyl propanoic acid + (–) 2–butanol

→ (–) 2–butyl (+) 2– phenyl propanoate

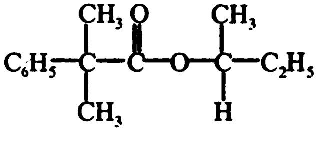
(–) 2–phenyl propanoic acid + (–) 2–butanol

→ (–) 2–butyl (–) 2– phenyl propanoate

Their structures may be represented as



$$C_6H_5-\underset{CH_3}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-O-\underset{H}{\overset{CH_3}{C}}-C_2H_5$$

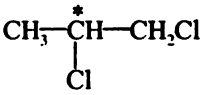


$$C_6H_5-\underset{CH_3}{\overset{CH_3}{C}}-\overset{O}{\overset{\|}{C}}-O-\underset{H}{\overset{CH_3}{C}}-C_2H_5$$

**Q. 24. Identify and indicate the presence of centre of chirality, if any in the following molecules. How many stereoisomers are possible for those containing chiral centre ?**

(*i*) 1, 2 – dichloropropane
(*ii*) 3 – bromopent –1–ene *(A.I.S.B. 2004)*

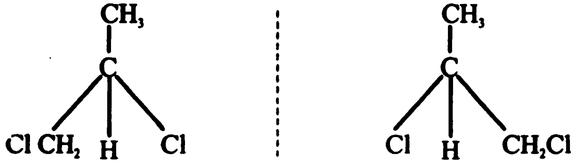
**Ans.** (*i*)



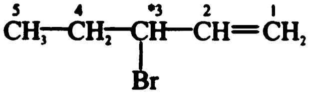
$$CH_3-\underset{Cl}{\overset{*}{C}}H-CH_2Cl$$

1, 2–dichloropropane

The carbon marked with asterisk (*) is chiral. This compound will exist in two optical forms as given below.



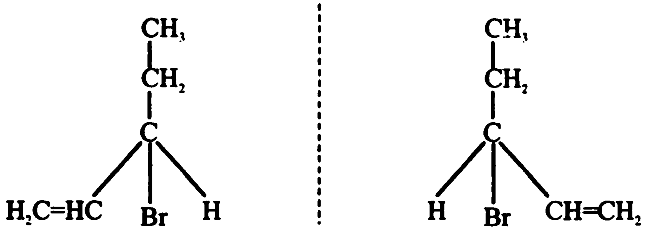
d-form Mirror l-form

(*ii*) 

$\overset{5}{C}H_3-\overset{4}{C}H_2-\underset{Br}{\overset{*3}{C}H}-\overset{2}{C}H=\overset{1}{C}H_2$

3-bromopent-1-ene

C-3 in the above compound is chiral. It will exist in two optical forms which are mirror images of each other



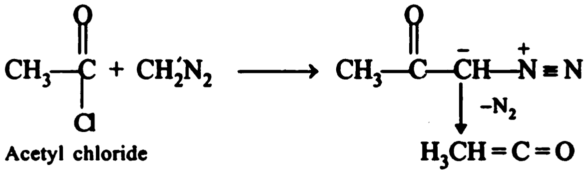
d-form Mirror l-form

# 3

# Organic Name Reactions

## 1. Arndt-Eistert Synthesis

This reaction is used to convert an acid (aliphatic or aromatic) into the next higher homologue. Acid chloride reacts with 2 molecules of diazomethane to give a diazoketone which loses nitrogen to form a keten when heated in the presence of silver oxide as a catalyst. The keten on hydrolysis with water produces a carboxylic acid. The synthesis is explained with the help of following reactions.



$$CH_3-\underset{Cl}{\overset{O}{\overset{\|}{C}}} + CH_2N_2 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-\overset{-}{C}H-\overset{+}{N}\equiv N \xrightarrow{-N_2} H_3CH=C=O$$

Acetyl chloride

Keten

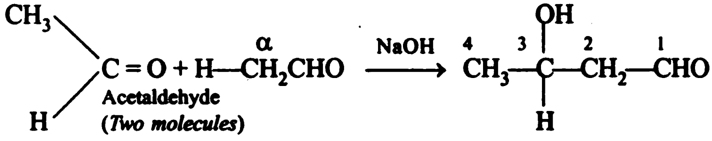
$$CH_3.CH=C=O + H_2O \longrightarrow CH_3CH_2COOH$$

Propionic acid

## 2. Aldol Condensation

(*A.I.S.B. 1993, 2000 ; D.S.B. 1993 ; C.B.S.E. Sample Paper 1997*)

Two molecules of aldehydes or ketones containing α-hydrogen atoms on treatment with a dilute base undergo condensation to form *β-hydroxyaldehydes* or *β-hydroxyketones*. This reaction is called *aldol condensation*. Following reactions illustrate this condensation.



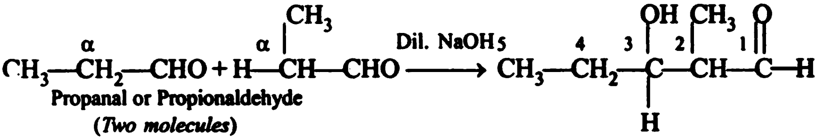
$$\begin{matrix}CH_3\\ H\end{matrix}\!\!>C=O + H-\overset{\alpha}{C}H_2CHO \xrightarrow{NaOH} \overset{4}{C}H_3-\overset{3}{\underset{H}{\overset{OH}{\overset{|}{\underset{|}{C}}}}}-\overset{2}{C}H_2-\overset{1}{C}HO$$

Acetaldehyde

(*Two molecules*)

3-Hydroxybutanal

(*Aldol*)

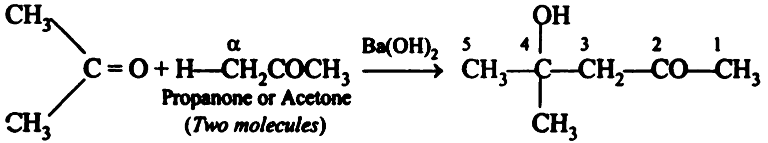


$$CH_3-\overset{\alpha}{C}H_2-CHO + H-\overset{CH_3}{\overset{|}{\overset{\alpha}{C}H}}-CHO \xrightarrow{Dil.\ NaOH5} \overset{4}{C}H_3-CH_2-\overset{3}{\underset{H}{\overset{OH}{\overset{|}{\underset{|}{C}}}}}-\overset{2}{\overset{CH_3}{\overset{|}{C}H}}-\overset{1}{\overset{O}{\overset{\|}{C}}}-H$$

Propanal or Propionaldehyde

(*Two molecules*)

3-Hydroxy-2-methylpentanal

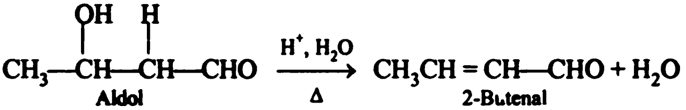


Propanone or Acetone (*Two molecules*)

4-Hydroxy-4-methyl-2-pentanone (*Diacetone* alcohol)

The products of aldol condensation on heating with dilute acids undergo dehydration leading to the formation of α, β-unsaturated aldehydes or ketones.

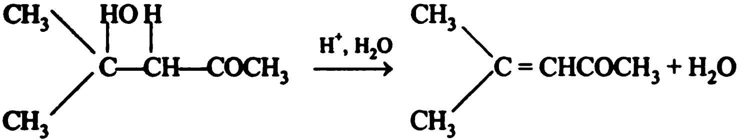
**Example :**



$$CH_3-\overset{OH}{\overset{|}{C}H}-\overset{H}{\overset{|}{C}H}-CHO \xrightarrow[\Delta]{H^+,\, H_2O} CH_3CH=CH-CHO+H_2O$$

Aldol

2-Butenal (*Crotonaldehyde*)



Diacetone alcohol

4-Methyl-3-penten-2-one (*Mesityl oxide*)

Aldehydes such as formaldehyde, benzaldehyde etc. which do not contain α-hydrogen do not undergo aldol condensation.

### 3. Bouveault-Blanc reduction

The reduction of esters to alcohols by nascent hydrogen generated by the action of sodium and alcohol is known as *Bouvault-Blanc reduction.*

$$\underset{\text{Ester}}{RCOOR'} + 4[H] \xrightarrow{Na/C_2H_5OH} \underbrace{RCH_2OH + R'OH}_{\text{Alcohols}}$$

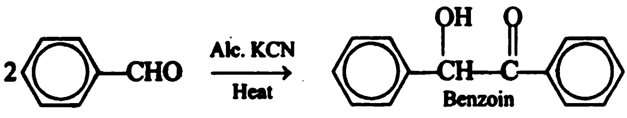
**Example :**

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + 4[H] \xrightarrow{Na/C_2H_5OH} \underset{\text{Ethanol}}{2C_2H_5OH}$$

### 4. Benzoin condensation

Two molecules of aromatic aldehydes on heating with an ethanolic solution of KNC undergo condensation to form *benzoins*. This reaction is called *benzoin condensation.*

**Example :**

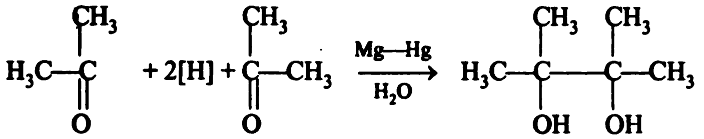


Benzaldehyde (2 molecules)

Benzoin

### 5. Bimolecular reduction

Reduction of acetone to pinacol by magnesium amalgam and water is called *bimolecular reduction.*

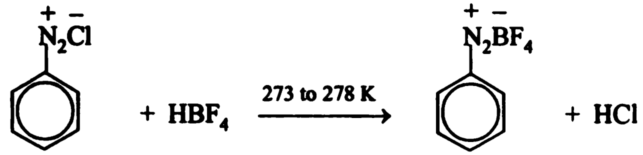


Acetone Acetone

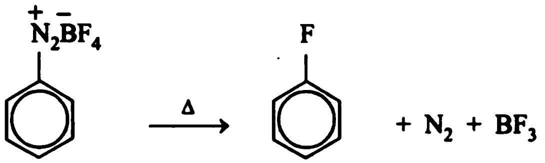
Tetramethyl ethylene glycol
or
2, 3-Dimethyl-2, 3-butanediol
(*Pinacol*)

### 6. Balz-Schiemann reaction

This reaction involves the decomposition of diazonium fluoroborate to aryl fluorides.



Benzene-diazonium chloride | Fluoroboric acid | Benzenediazonium fluoroborate

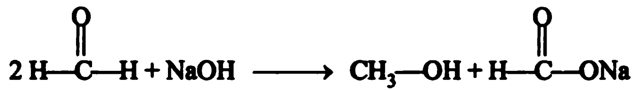


Fluorobenzene

### 7. Cannizzaro reaction (*D.S.B. 1993*)

Aldehydes not containing an α-hydrogen atom, when treated with concentrated alkali solution undergo *disproportionation i.e.*, self oxidation-reduction. As a result, one molecule of the aldehyde is reduced to the corresponding alcohol and the second one is oxidised to the corresponding carboxylic acid. This reaction is called *Cannizzaro reaction.* For example, formaldehyde on treatment with conc. NaOH solution gives methyl alcohol and sodium formate whereas benzaldehyde gives benzyl alcohol and sodium benzoate.

**Examples :**



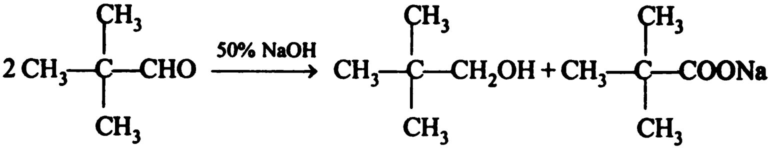
$$2\,H{-}\overset{O}{\overset{\|}{C}}{-}H + NaOH \longrightarrow CH_3{-}OH + H{-}\overset{O}{\overset{\|}{C}}{-}ONa$$

Formaldehyde (50%) Methyl alcohol Sod. formate

$$2\,C_6H_5CHO + NaOH \longrightarrow C_6H_5CH_2OH + C_6H_5COONa$$

Benzaldehyde (50%) Benzyl alcohol Sod. benzoate

2, 2-Dimethylpropanal which does not contain α-hydrogen undergoes the reaction as follows :



$$2\,CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CHO \xrightarrow{50\%\ NaOH} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2OH + CH_3-\underset{CH_3}{\overset{CH_3}{C}}-COONa$$

2, 2-Dimethylpropanal 2, 2-Dimethylpropanol Sod. 2, 2-dimethylpropanoate

### 8. Claisen-Schmidt reaction

The condensation of benzaldehyde with aliphatic aldehyde or ketone having α-hydrogen in the presence of dilute alkali to form α, β-unsaturated carbonyl compound is known as *Claisen-Schmidt reaction* or *Claisen reaction.*

**Examples :**

$$\underset{\text{Benzaldehye}}{C_6H_5CH}\ \boxed{O + H_2}\ \underset{\text{Acetaldehyde}}{CH.CHO} \xrightarrow[373\ K]{NaOH} \underset{\text{Cinnardealdehyde}}{C_6H_5CH = CH.CHO} + H_2O$$

$$\underset{\text{Benzaldehyde}}{C_6H_5CH}\ \boxed{O + H_2}\ \underset{\text{Acetone}}{CH.CO.CH_3} \xrightarrow[373\ K]{NaOH} \underset{\text{Benzalacetone}}{C_6H_5CH = CH.CO.CH_3} + H_2O$$

(*4-Phenyl-3-buten-2-one*)

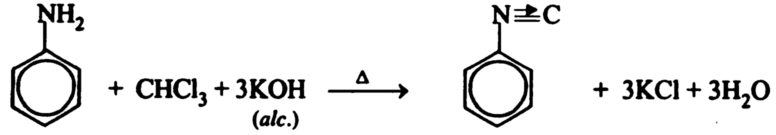
### 9. Carbylamine reaction (*A.I.S.B. 1996*)

When a primary amine is warmed with chloroform and alcoholic KOH, it forms an isocyanide or carbylamine having offensive smell. This reaction is called *carbylamine reaction.* Both aliphatic and aromatic amines give this reaction.

**Examples :**

$$\underset{\text{Ethylamine}}{CH_3CH_2NH_2} + CHCl_3 + \underset{(alc.)}{3KOH} \xrightarrow{\Delta} CH_3CH_2N \rightleftarrows C + 3KCl + 3H_2O$$

Ethyl isocyanide
or Ethyl carbylamine



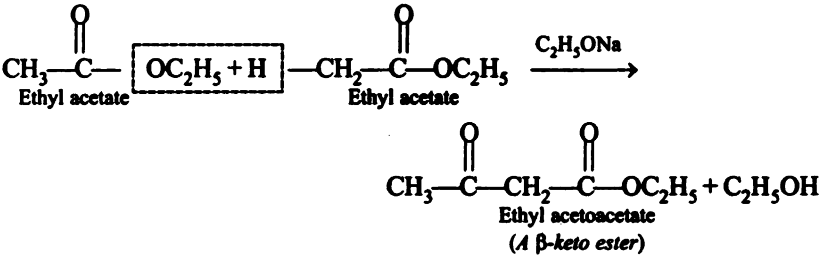
Aniline Phenyl isocyanide
or Phenyl carbylamine

Secondary and tertiary amines do not give this reaction. Hence, it is used as a test for the distinction of primary amines from secondary and tertiary amines.

### 10. Clasien condensation

The self condensation of two molecules of an ester containing α-hydrogens in presence of a strong base such as sodium ethoxide to form a β-keto ester is called *Claisen condensation.*

**Example :**

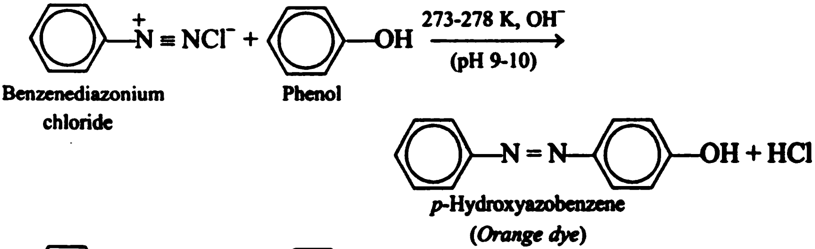


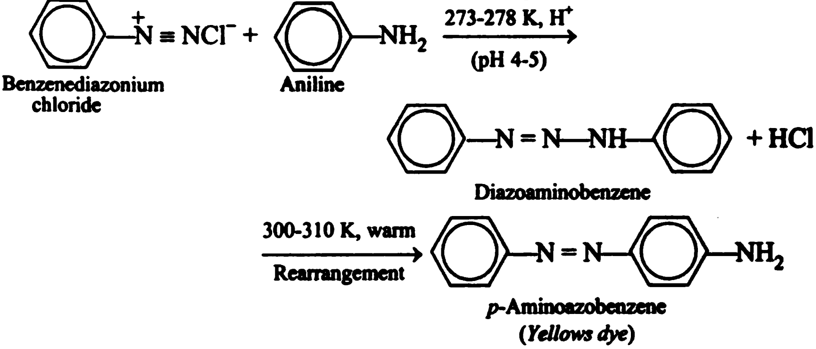
$$CH_3-\overset{O}{\overset{\|}{C}}-\boxed{OC_2H_5 + H}-CH_2-\overset{O}{\overset{\|}{C}}-OC_2H_5 \xrightarrow{C_2H_5ONa} CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OC_2H_5 + C_2H_5OH$$

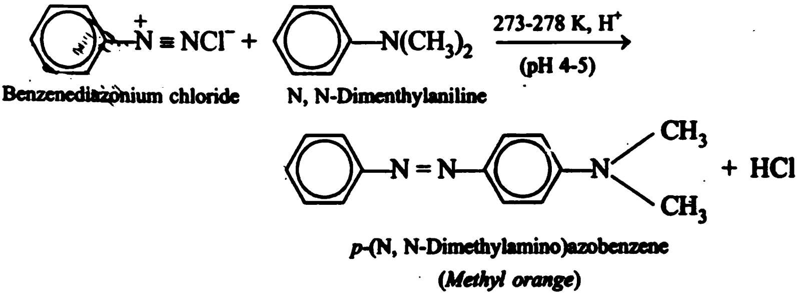
## 11. Coupling reaction

The reaction of diazonium salts with phenols or aromatic amines to form *azo* compounds of the general formula, Ar—N = N—Ar is called *coupling reaction*. The coupling with phenols takes place in *mildly alkaline* medium while with amines it occurs under *faintly acidic conditions*.

**Examples :**







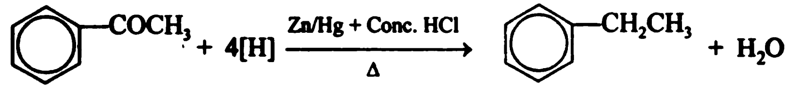
## 12. Clemmensen reduction

The reduction of aldehydes and ketones with amalgamated zinc and concentrated hydrochloric acid to give corresponding hydrocarbons is called *Clemmensen reduction.*

**Examples :**

$$CH_3COCH_3 + 4[H] \xrightarrow[\Delta]{Zn/Hg + Conc.\ HCl} CH_3CH_2CH_3 + H_2O$$

Acetone Propane



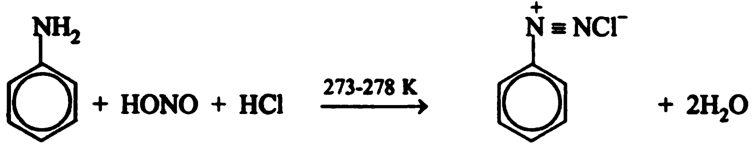
Acetophenone Ethylbenzene

## 13. Diazotisation reaction

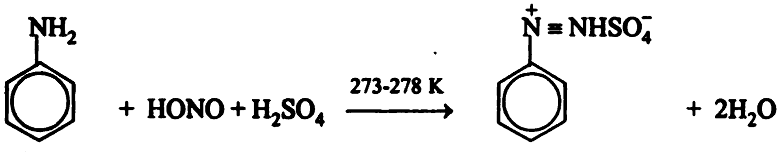
When a cold solution of a primary aromatic amine in a dilute mineral acid (HCl or $H_2SO_4$) is treated with a cold solution of nitrous acid at 273-278 K, arenediazonium salt is formed. This reaction is called *diazotisation reaction.*

**Example :**

$$NaNO_2 + HCl \longrightarrow HONO + NaCl$$



Aniline (1° *Aromatic amine*) Benzenediazonium chloride

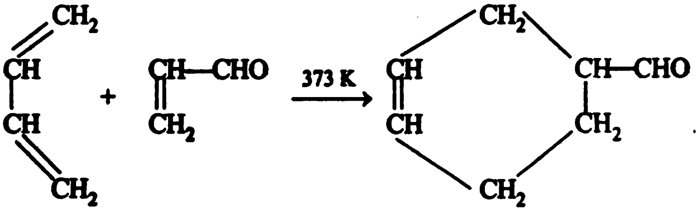


Aniline Benzenediazonium hydrogen sulphate

## 14. Diels-Alder reaction

The reaction between α, β-unsaturated carbonyl compound (dienophile) and a conjugated diene to form an addition product (adduct) is known as *Diels-Alder reaction.*

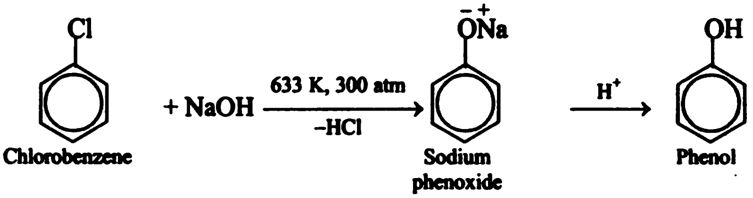
**Example :**



1, 3-Butadiene (*Conjugated diene*) Acrolein (*Dienophile*) 1, 2, 3, 6-tetrahydrobenzaldehyde (*Adduct*)

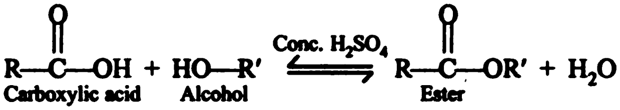
### 15. Dow process

This process involves the treatment of chlorobenzene with aqueous sodium hydroxide solution at 633 K under 300 atmospheres to form sodium phenoxide, which on acidification gives phenol.

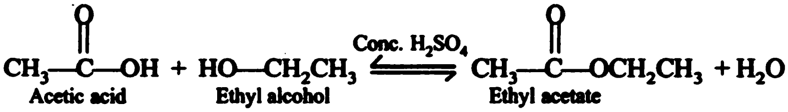


### 16. Esterification reaction (Fischer-Speiar Esterification)

Carboxylic acids react with alcohols in presence of dry HCl gas or a few drops of conc. $H_2SO_4$ as catalyst to form esters. For example,



$$\underset{\text{Carboxylic acid}}{R-\overset{O}{\overset{\|}{C}}-OH} + \underset{\text{Alcohol}}{HO-R'} \xrightleftharpoons{\text{Conc. } H_2SO_4} \underset{\text{Ester}}{R-\overset{O}{\overset{\|}{C}}-OR'} + H_2O$$



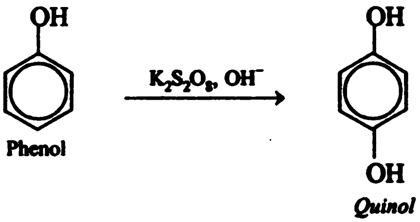
$$\underset{\text{Acetic acid}}{CH_3-\overset{O}{\overset{\|}{C}}-OH} + \underset{\text{Ethyl alcohol}}{HO-CH_2CH_3} \xrightleftharpoons{\text{Conc. } H_2SO_4} \underset{\text{Ethyl acetate}}{CH_3-\overset{O}{\overset{\|}{C}}-OCH_2CH_3} + H_2O$$

*This reaction which is slow and reversible is called* **esterification reaction**. When dry HCl gas is used as a catalyst, the reaction is known as *Fischer-speier esterification.*

### 17. Elbs persulphate oxidation

In this reaction, monohydric phenols are oxidised to dihydric phenols by alkaline potassium persulphate. Hydroxylation normally occurs in the *p*-position but, if this is not free then the *o*-position is attacked.

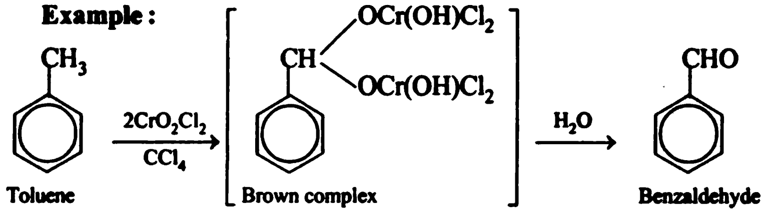
**Example :**



### 18. Etard reaction

The oxidation of toluene with chromyl chloride ($CrO_2Cl_2$) in $CCl_4$ or $CS_2$ to give benzaldehyde is called *Etard reaction*. In this reacton, chromyl chloride first forms a brown complex with toluene which is decomposed by $H_2O$ to give benzaldehyde.

**Example :**



## 19. Fittig reaction

This reaction is a type of Wurtz reaction. It involves the reaction between two molecules of an aryl halide with sodium in presence of dry ether to form a diaryl. For example,

## 20. Finkelstein reaction or Conant-Finkelstein reaction

This reaction involves the treatment of alkyl chloride or bromide with sodium iodide in acetone or methanol solution to form alkyl iodide.

$$\underset{\text{Alkyl chloride}}{R{-}Cl} + NaI \longrightarrow \underset{\text{Alkyl iodide}}{R{-}I} + NaCl$$

$$\underset{\text{Ethyl chloride}}{C_2H_5{-}Cl} + NaI \longrightarrow \underset{\text{Ethyl iodide}}{C_2H_5{-}I} + NaCl$$

$$CH_3Br + NaI \longrightarrow CH_3I + NaBr$$

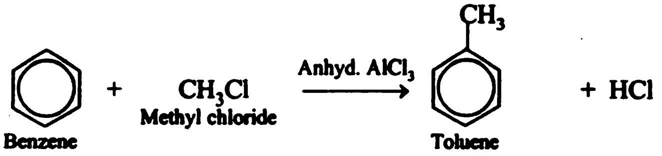
## 21. Friedel-Crafts reaction

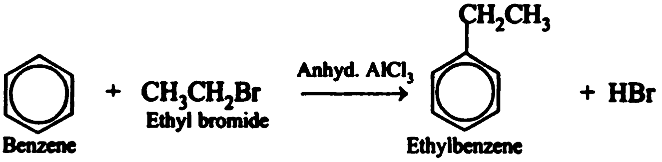
(*A.I.S.B. 1987 ; D.S.B. 1992*)

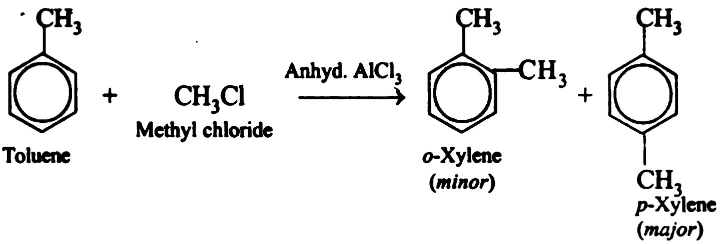
This reaction is used for introducing an alkyl or an acyl group into an aromatic compound in presence of a Lewis acid catalyst like $AlCl_3$. Substances like $BF_3$, $FeCl_3$, $SnCl_4$ etc. can also be used as catalysts.

(*a*) **Friedel-Crafts alkylation.** Benzene reacts with alkyl halides in presence of anhydrous aluminium chloride to form alkylbenzenes.

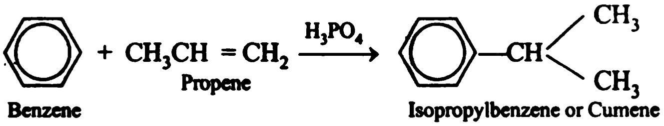
**Examples :**





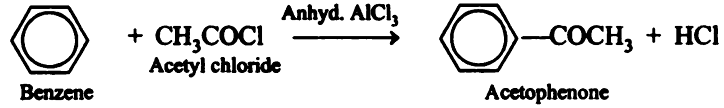


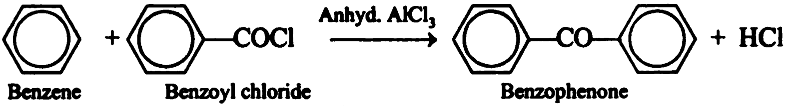
In case of substituted benzenes, the incoming alkyl group takes up preferably para position w.r.t. the substituent already present to avoid steric hinderance.

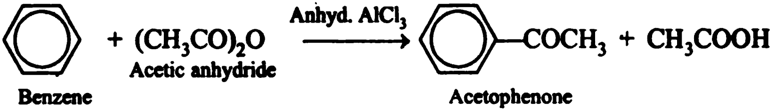


(*b*) **Friedel-Crafts acylation.** Benzene reacts with acid chlorides or anhydrides in presence of anhyd. $AlCl_3$ to form ketones.

**Examples :**

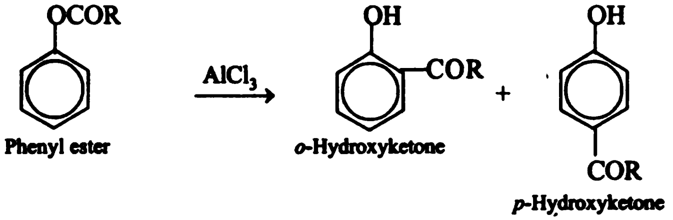


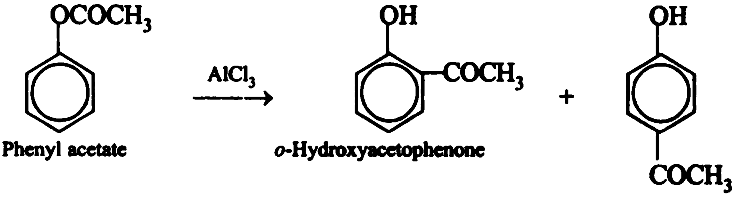




## 22. Fries rearrangment

Phenyl ester undergoes rearrangement in the presence of anhydrous aluminium chloride to form *o*- or *p*-hydroxyketone, or a mixture of both. This rearrangement in which acyl group migrates from phenolic oxygen to ortho or para position is known as *Fries rearrangement.*





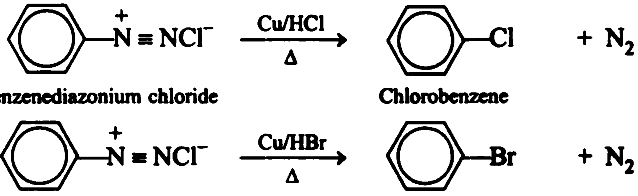
Phenyl acetate o-Hydroxyacetophenone p-Hydroxyacetophenone

Low temperature (333 K or less) favours the formation of *p*-isomer, whereas high temperature (above 433 K) favours the *o*-isomer.

### 23. Gattermann reaction

This is a modification of *Sandmeyer reaction*. In this reaction benzenediazonium chloride is treated with copper powder and a halogen acid to form aryl halides.

**Examples :**



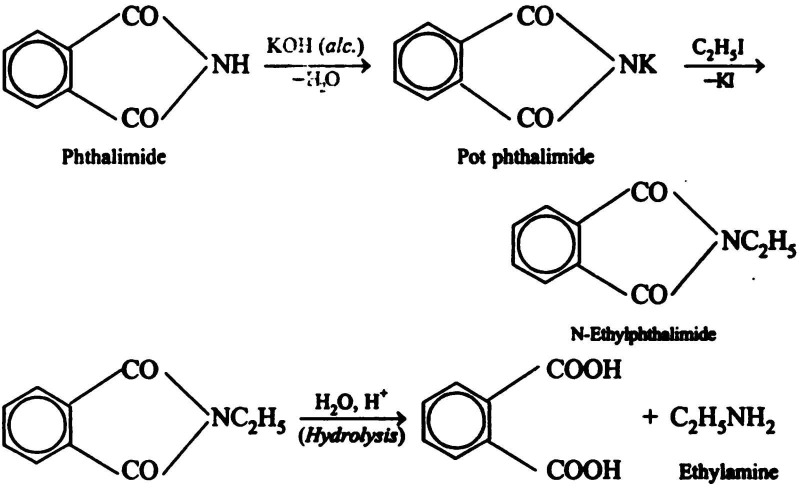
Benzenediazonium chloride Chlorobenzene

Benzenediazonium chloride Bromobenzene

### 24. Garbriel phthalimide synthesis

In this reaction phthalimide is converted into its potassium salt on treatment with alcoholic potassium hydroxide. Potassium phthalimide is then heated with an alkyl halide to yield an N-alkylphthalimide which is hydrolysed to phthalic acid and a primary amine by heating with HCl or KOH solution.

**Example :**



Phthalimide Pot phthalimide

N-Ethylphthalimide

N-Ethylphthalimide Phthalic acid Ethylamine

This synthesis is very useful for the preparation of pure aralkyl and aliphatic primary amines. However aromatic primary amines cannot be prepared by this method.

### 25. Haloform reaction (Iodoform reaction)

Compounds containing the grouping $CH_3CHOH$— or $CH_3CO$— on treatment with a halogen and excess of alkali (*i.e.* sodium hypohalite, NaOX) form haloforms. If the halogen used is iodine, yellow precipitates of iodoform are formed and the reaction is called *iodoform reaction.*

**Examples :**

$$\underset{\text{Ethanol}}{CH_2CH_2OH} + 4I_2 + 6NaOH \longrightarrow \underset{\text{Iodoform}}{CHI_3} + HCOONa + 5NaI + 5H_2O$$

$$\underset{\text{2-Propanol}}{CH_3CHOHCH_3} + 4I_2 + 6NaOH \longrightarrow \underset{\text{Iodoform}}{CHI_3} + CH_3COONa + 5NaI + 5H_2O$$

$$\underset{\text{Propanone}}{CH_3COCH_3} + 3I_2 + 4NaOH \longrightarrow \underset{\text{Iodoform}}{CHI_3} + CH_3COONa + 3NaI + 3H_2O$$

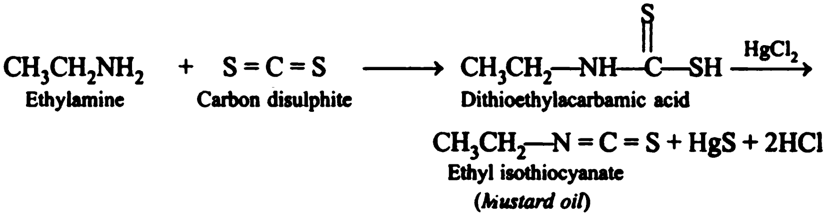
$$\underset{\text{Acetophenone}}{C_6H_5COCH_3} + 3I_2 + 4NaOH \longrightarrow \underset{\text{Iodoform}}{CHI_3} + C_6H_5COONa + 3NaI + 3H_2O$$

*Iodoform reaction may be used for the distinction of methylcarbinols and methyl ketones from other alcohols and ketones.*

### 26. Hofmann mustard oil reaction

A mixture of a primary aliphatic amine, carbon disulphide and mercuric chloride on heating gives alkyl isothiocyanate which has a characteristic smell like that of mustard oil. This reaction is called *Hofmann mustard oil reaction.*

**Example :**



$$\underset{\text{Ethylamine}}{CH_3CH_2NH_2} + \underset{\text{Carbon disulphite}}{S=C=S} \longrightarrow \underset{\text{Dithioethylacarbamic acid}}{CH_3CH_2{-}NH{-}\overset{\overset{\displaystyle S}{\|}}{C}{-}SH} \xrightarrow{HgCl_2}$$

$$\underset{\substack{\text{Ethyl isothiocyanate}\\ \textit{(Mustard oil)}}}{CH_3CH_2{-}N=C=S} + HgS + 2HCl$$

In this reaction, dithiocarbamic acid is first formed which decomposes on heating with $HgCl_2$ to give alkyl isothiocyanate.

### 27. Hell-Volhard Zelinsky reaction (*A.I.S.B. 1987 ; D.S.B. 1988*)

Aliphatic carboxylic acids containing α-hydrogens react with $Cl_2$ or $Br_2$ in presence of a small amount of red phosphorus to give α-haloacids. This is called *Hell-Volhard-Zelinsky* (*H.V.Z.*) *reaction.* With excess of halogen, all the α-hydrogen atoms of an aliphatic carboxylic acid are replaced by halogen atoms.

**Examples :**

$$\underset{\text{Acetic acid}}{CH_2COOH} \xrightarrow[-HCl]{Cl_2,\,P} \underset{\text{Monochloroacetic acid}}{\overset{\alpha}{ClCH_2COOH}} \xrightarrow[-HCl]{Cl_2,\,P} \underset{\text{Dichloroacetic acid}}{\overset{\alpha}{Cl_2CHCOOH}}$$

$$\xrightarrow[-HCl]{Cl_2,\,P} \underset{\text{Trichloroacetic acid}}{Cl_3CCOOH}$$

$$\underset{\text{Propionic acid}}{\overset{\beta\quad\alpha}{CH_3CH_2COOH}} \xrightarrow[-HBr]{Br_2,\,P} \underset{a\text{-Bromopropionic acid}}{\overset{\alpha}{CH_3CHBrCOOH}} \xrightarrow[-HBr]{Br_2,\,P} \underset{\alpha,\,\alpha\text{-Dibromopropionic acid}}{CH_3CBr_2COOH}$$

$$\Big\downarrow \; Br_2,\,P$$

No further reaction.

### 28. Hunsdiecker or Borodine-Hunsdiecker reaction

The decomposition of the silver salt of a carboxylic acid with $Br_2$ in refluxing $CCl_4$ to form an alkyl or aryl bromide with one carbon less than the original aicd is called *Hunsdiecker reaction.*

**Examples :**

$$RCOOAg + Br_2 \xrightarrow[\text{Reflux}]{CCl_4,\,350\text{ K}} R{-}Br + CO_2 + AgBr$$

$$\underset{\text{Silver propionate}}{CH_3CH_2COOAg} + Br_2 \xrightarrow[\text{Reflux}]{CCl_4,\,350\text{ K}} \underset{\text{Ethyl bromide}}{CH_3CH_2{-}Br} + CO_2 + AgBr$$

$$\underset{\text{Silver benzoate}}{C_6H_5COOAg} + Br_2 \xrightarrow[\text{Reflux}]{CCl_4,\,350\text{ K}} \underset{\text{Bromobenzene}}{C_6H_5{-}Br} + CO_2 + AgBr$$

Hunsdiecker reaction may also be used for stepping down the homologous series.

### 29. Hofmann bromamide reaction or Hofmann degradation of amides

*(A.I.S.B. 1992 ; D.S.B. 1992)*

A primary amide is converted to a primary amine containing one carbon atom less than the original amide on heating with a $Br_2$ in presence of NaOH or KOH. This reaction is *called Hofmann bromamide reaction or Hofmann degradation of amidcs.*

**Examples :**

$$\underset{\text{Acetamide}}{CH_3CONH_2} + Br_2 + 4NaOH \xrightarrow{\Delta} \underset{\text{Methlamine}}{CH_3NH_2} + 2NaBr + Na_2CO_3 + 2H_2O$$

$$\underset{\text{Propionamide}}{CH_3CH_2CONH_2} + Br_2 + 4KOH \xrightarrow{\Delta} \underset{\text{Ethylamine}}{CH_3CH_2NH_2} + 2KBr + K_2CO_3 + 2H_2O$$

$$\underset{\text{Benzamide}}{C_6H_5CONH_2} + Br_2 + 4KOH \xrightarrow{\Delta} \underset{\text{Aniline}}{C_6H_5NH_2} + 2\,KBr + K_2CO_3 + 2H_2O$$

This reaction is extremely useful for stepping down or descending a homologous series.

### 30. Knoevenagel reaction

On treating aldehydes with compounds containing active methylene group in the presence of an organic base, α, β-unsaturated acids are formed. This reaction is known as *Knoevenagel reaction.*

**Examples :**

(*i*) On treating benzaldehyde with malonic acid (compound containing active methylene group) in the presence of pyridine (base), cinnamic acid is formed.

$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} + \underset{\text{Malonic acid}}{CH_2(COOH)_2} \xrightarrow{\text{Pyridine, }\Delta} \underset{\text{Cinnamic acid}}{C_6H_5CH=CH.COOH} + CO_2 + H_2O$$

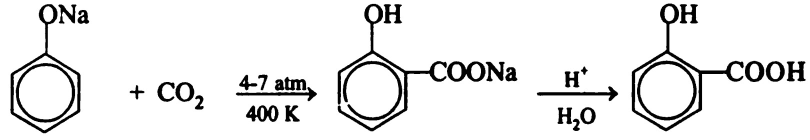
(*ii*) $\underset{\text{Acetaldehyde}}{CH_3CHO} + \underset{\text{Malonic acid}}{CH_2(COOH)_2}$

$$\xrightarrow{\text{Pyridine, }\Delta} \underset{\text{Crotonic acid}}{CH_3CH=CH.COOH} + CO_2 + H_2O$$

### 31. Kolbe reaction or Kolbe-Schmidt reaction

(*A.I.S.B. 1987 ; D.S.B. 1993*)

Sodium phenoxide reacts with carbon dioxide under pressure (4–7 atmospheres) at 400 K to form sodium salicylate which upon acidification with mineral acids gives salicyclic acid. This reaction is called *Koble reaction* or *Kolbe-Schmidt reaction.*



Sod. phenoxide Sod. salicylate Salicylic acid

### 32. Kolbe electrolytic reaction (*A.I.S.B. 1988 ; D.S.B. 1993*)

This reaction is used to prepare alkanes and alkynes by electrolysis of aqueous solution of sodium or potassium salt of suitable acids.

**Examples :**

(*a*) **Ethane** is produced when an aqueous solution of potassium acetate is electrolysed.

$$\underset{\text{Pot. acetate}}{2CH_3COOK} \longrightarrow 2CH_3COO^- + 2K^+ \quad (\textit{Ionization})$$

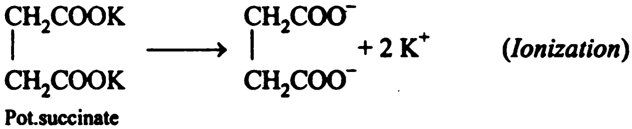
$$2H_2O \rightleftharpoons 2OH^- + 2H^+ \quad (\textit{Ionization})$$

*At anode* : $2CH_3COO^- - 2e^- \longrightarrow \underset{\text{Ethane}}{CH_3\text{—}CH_3} + 2CO_2$

*At cathode* : Both $K^+$ and $H^+$ are present but $H^+$ ions are preferentially discharched due to their lower discharge potential.

$$2H^+ + 2e^- \longrightarrow 2H^{\cdot} \longrightarrow H_2$$

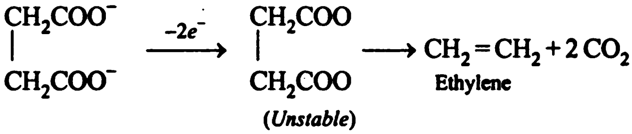
(*b*) **Ethylene** is produced when potassium salt of succinic acid is electrolysed.



$$\underset{\text{Pot.succinate}}{\begin{array}{l}CH_2COOK\\ |\\ CH_2COOK\end{array}} \longrightarrow \begin{array}{l}CH_2COO^-\\ |\\ CH_2COO^-\end{array} + 2\,K^+ \qquad (\textit{Ionization})$$

$$2H_2O \rightleftharpoons 2OH^- + 2H^+ \qquad (\textit{Ionization})$$

*At anode* :

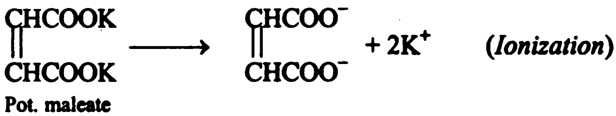


$$\begin{array}{l}CH_2COO^-\\ |\\ CH_2COO^-\end{array} \xrightarrow{-2e^-} \underset{(\textit{Unstable})}{\begin{array}{l}CH_2COO\\ |\\ CH_2COO\end{array}} \longrightarrow \underset{\text{Ethylene}}{CH_2=CH_2} + 2\,CO_2$$

*At cathode* : $H_2$ is produced as above

$$2H^+ + 2e^- \longrightarrow H_2$$

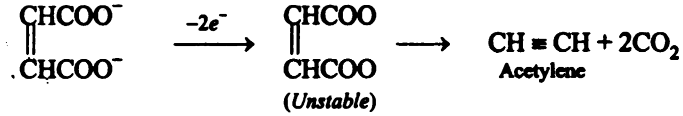
(*c*) **Acetylene** is produced when potassium maleate or fumarate is electrolysed.



$$\underset{\text{Pot. maleate}}{\begin{array}{l}CHCOOK\\ \|\\ CHCOOK\end{array}} \longrightarrow \begin{array}{l}CHCOO^-\\ \|\\ CHCOO^-\end{array} + 2K^+ \qquad (\textit{Ionization})$$

$$2H_2O \rightleftharpoons 2OH^- + 2H^+ \qquad (\textit{Ionization})$$

*At anode* ·



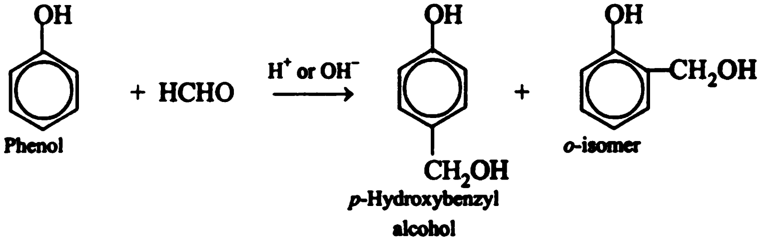
$$\begin{array}{l}CHCOO^-\\ \|\\ CHCOO^-\end{array} \xrightarrow{-2e^-} \underset{(\textit{Unstable})}{\begin{array}{l}CHCOO\\ \|\\ CHCOO\end{array}} \longrightarrow \underset{\text{Acetylene}}{CH\equiv CH} + 2CO_2$$

*At cathode* : $H_2$ is produced as above

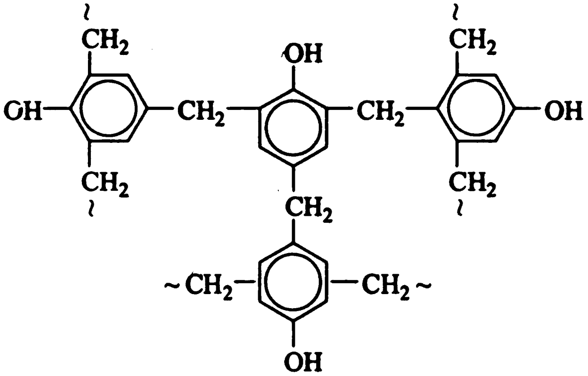
$$2H^+ + 2e^- \longrightarrow H_2$$

### 33. Lederer-Manasse reaction

This reaction involves the condensation of phenol with aliphatic or aromatic aldehyde at *o*- or *p*-position. Phenol undergoes condensation with formalin (40% aqueous formaldehyde) at low temperature to form *p*-hydroxybenzyl alcohol along with a small amount of *o*-isomer.



This reaction forms the basis of the preparation of *Bakelite* (phenol-formaldehyde resin), a cross linked polymer. Structure of bakelite is as follows :



### 34. Libermann nitroso reaction

Both aliphatic and aromatic secondary amines react with nitrous acid (or a mixture of $NaNO_2$ and HCl) to give N-nitrosoamines which are generally *yellow neutral oily compounds* and are insoluble in dilute mineral acids.

$$\underset{\text{Secondary amine}}{R_2NH} + HO{-}N=O \longrightarrow \underset{\text{N-Nitrosodilkylamine}}{R_2N{-}N=O} + H_2O$$

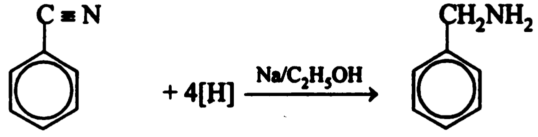
Nitrosoamines on warming with a crystal of phenol and conc. $H_2SO_4$ form a green solution which on adding aqueous alkali turns deep blue and then red on dilution. This reaction is called *Liebermann nitroso reaction* and is used as a test for secondary amines.

### 35. Mendius reaction

The reduction of alkyl and aryl amides to primay amines with nascent hydrogen, produced by the action of sodium amalgam on alcohol is called *Mendius reaction.*

**Examples :**

$$\underset{\text{Acetonitrile}}{CH_3C\equiv N + 4[H]} \xrightarrow{Na/C_2H_5OH} \underset{\text{Ethylamine}}{CH_3CH_2NH_2}$$

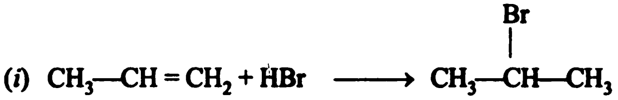


Benzonitrile Benzylamine

### 36. Markovnikov's rule

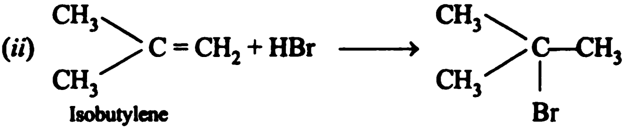
This rule states that when addition across an unsymmetrical alkene takes place, the positive part of the addendum (the molecule to be added) goes to that carbon atom of the double bond which holds the greater number of hydrogen atoms.

**Examples :**



$$\text{(i)}\quad CH_3-CH=CH_2 + HBr \longrightarrow CH_3-\underset{}{\overset{Br}{\overset{|}{C}H}}-CH_3$$

Propene 2-Bromopropane



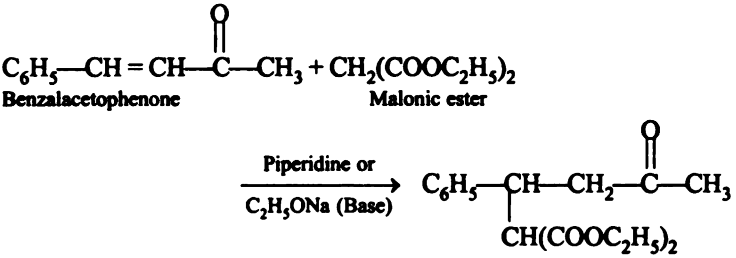
$$\text{(ii)}\quad (CH_3)_2C=CH_2 + HBr \longrightarrow (CH_3)_2\underset{\underset{Br}{|}}{C}-CH_3$$

Isobutylene (Methylpropene) tert-Butyl bromide (2-Bromo-2-methylpropane)

### 37. Michael condensation

The addition reaction between α, β-unsaturated carbonyl compound and a compound containing active methylene group such as malonic ester, acetoacetic ester is known as *Michael condensation.*

**Example :**

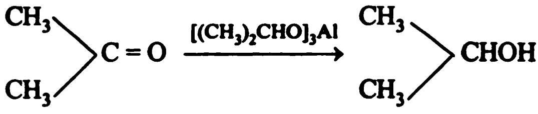


$$C_6H_5-CH=CH-\overset{\overset{O}{\|}}{C}-CH_3 + CH_2(COOC_2H_5)_2 \xrightarrow[C_2H_5ONa\ (Base)]{Piperidine\ or} C_6H_5-\underset{\underset{CH(COOC_2H_5)_2}{|}}{C}H-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$$

Benzalacetophenone Malonic ester Addition product

### 38. Meerwein—Ponndorf—Verley reduction

The reduction of carbonyl compounds (aldehydes or ketones) to alcohols by aluminium isopropoxide in isopropyl alcohol is known as Meerwein-Ponndorf-Verley reduction. The reagent aluminium isopropoxide is specific as it does not affect the reducible groups such as double bond or a nitro group.

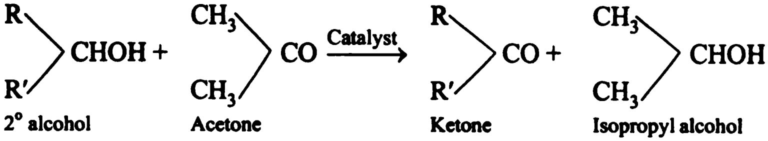


$$(CH_3)_2C=O \xrightarrow{[(CH_3)_2CHO]_3Al} (CH_3)_2CHOH$$

Acetone Isopropyl alcohol

### 39. Oppenauer oxidation

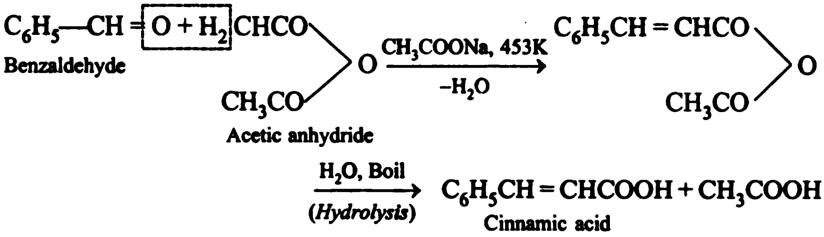
The oxidation of secondary alcohols to ketones by aluminium *t*-butoxide, $[(CH_3)_3CO]_3Al$, in acetone is known as oppenauer oxidation. The reagent aluminium *t*-butoxide is particularly useful for oxidising unsaturated alcohols because is does not affect the double bond.



Primary unsaturated alcohols may also be oxidised to aldehydes if acetone is replaced by *p*-benzoquinone.

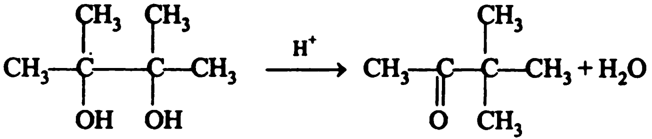
### 40. Perkin reaction

When an aromatic aldehyde is heated with acetic anhydride in presence of sodium acetate the product obtained on acid hydrolysis gives an α, β-*unsaturated acid.* This reaction is called *Perkin reaction.* For example, benzaldehyde on heating with acetic anhydride in presence of sodium acetate and subsequent hydrolysis gives cinnamic acid.



### 41. Pinacol-pinacolone rearrangement

On treating with mineral acid, pinacol undergoes dehydration in such a way that the rearrangement of the carbon skeleton occurs to form pinacolone. This is known as *pinacol-pinacolone rearrangement.*



$$CH_3-\underset{OH}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-\underset{OH}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_3 \xrightarrow{H^+} CH_3-\underset{O}{\underset{\|}{C}}-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_3 + H_2O$$

Pinacol (2, 3-Dimethyl-2, 3-butanediol) — Pinacolone (3, 3-Dimethylbutanone)

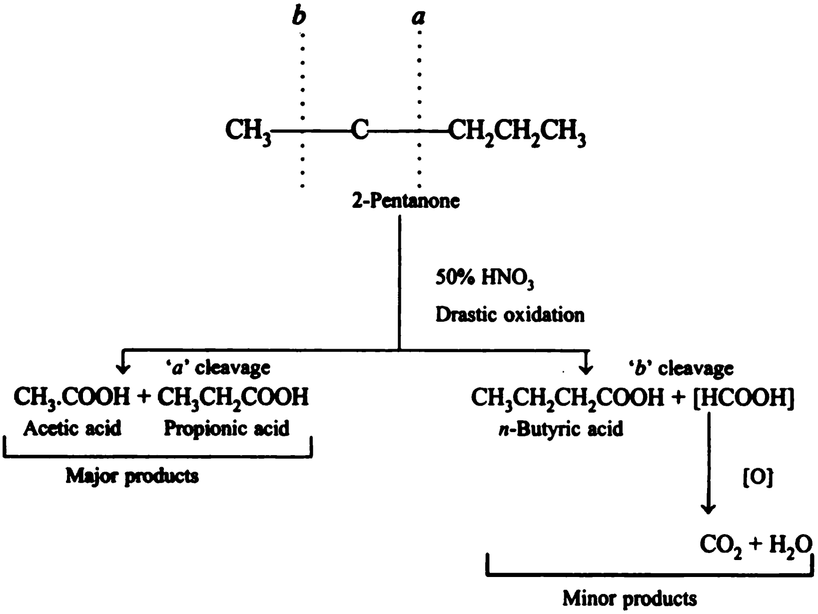
### 42. Peroxide effect or Kharasch effect (*A.I.S.B. 1998*)

The addition of HBr (no other halogen acid) to unsymmetrical alkenes in the presence of organic peroxide such as benzoyl peroxide, $(C_6H_5CO)_2O_2$ takes place contrary to Markovnikov's rule. This is known as *Peroxide effect* or *Kharasch effect.*

*e.g.*, $$\underset{\text{Propylene (Propene)}}{CH_3-CH=CH_2} + HBr \xrightarrow{(C_6H_5CO)_2O_2} \underset{\text{n-Propyl bromide (1-Bromopropane)}}{CH_3-CH_2-CH_2Br}$$

### 43. Popoff's rule

During oxidation of an unsymmetrical ketone with concentrated $HNO_3$ (50%), the smaller alkyl group goes preferentially with the carbonyl group in the resulting carboxylic acid. This is known as *Popoff's rule.* For example,

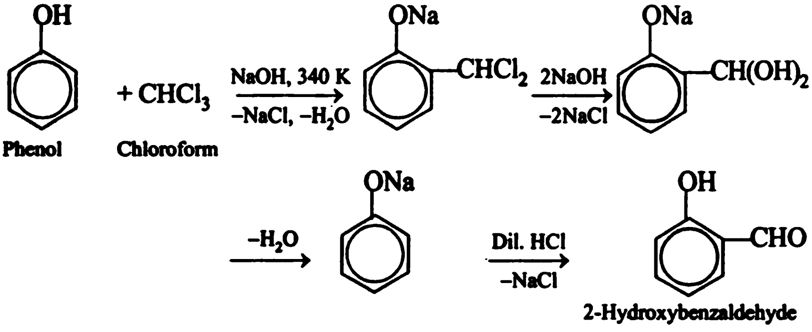


It may be noted that C—C bond undergoes cleavage on either side of carbonyl group, however, acetic acid and propionic acid are the major products according to Popoffs rule ('*a*' cleavage).

### 44. Reimer-Tiemann reaction (*A.I.S.B. 1985*)

Treatment of phenol with chloroform in presence of aqueous sodium or potassiun hydroxide at 340 K followed by hydrolysis give 2-hydroxybenzaldehyde (salicyladehyde). This reaction is called *Reimer-Tiemann reaction.*

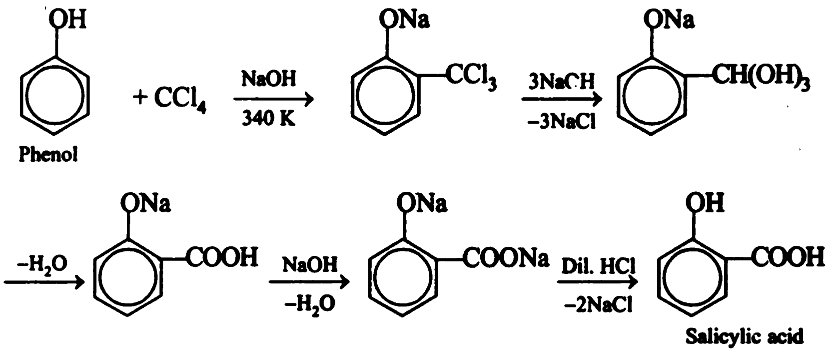
**Example :**



2-Hydroxybenzaldehyde
(*Salicylaldehyde*)

A small amout of *p*-hydroxybenzaldehyde is also formed.

If instead of chloroform, **carbon tetrachloride** is used, salicylic acid is formed.

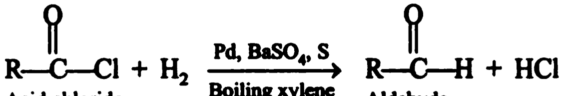


**45. Rosenmund reduction**

*(D.S.B. 1992 ; C.B.S.E. Sample Paper, 1997 ; A.I.S.B. 2000)*

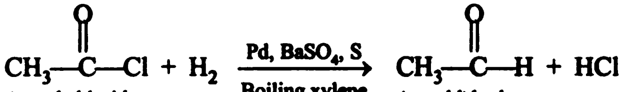
This reaction is carried out by passing $H_2$ gas through boiling xylene solution of the acid chloride in presence of Pd catalyst supported over $BaSO_4$. The acid chloride is reduced to aldehyde.

**Examples :**



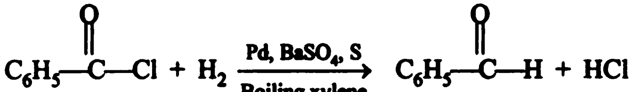
$$R-\overset{\overset{O}{\|}}{C}-Cl + H_2 \xrightarrow[\text{Boiling xylene}]{\text{Pd, }BaSO_4\text{, S}} R-\overset{\overset{O}{\|}}{C}-H + HCl$$

Acid chloride Aldehyde



$$CH_3-\overset{\overset{O}{\|}}{C}-Cl + H_2 \xrightarrow[\text{Boiling xylene}]{\text{Pd, }BaSO_4\text{, S}} CH_3-\overset{\overset{O}{\|}}{C}-H + HCl$$

Acetyl chloride Acetaldehyde



$$C_6H_5-\overset{\overset{O}{\|}}{C}-Cl + H_2 \xrightarrow[\text{Boiling xylene}]{\text{Pd, }BaSO_4\text{, S}} C_6H_5-\overset{\overset{O}{\|}}{C}-H + HCl$$

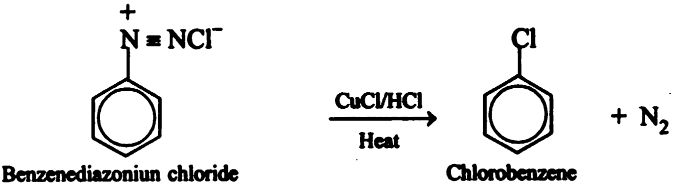
Benzoyl chloride Benzaldehyde

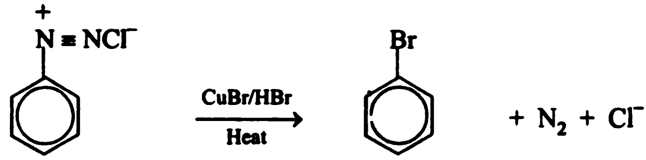
The function of $BaSO_4$ and S is to poison the catalyst as to stop further reduction of aldehydes to alcohols.

**46. Sandmeyer reaction** *(D.S.B. 1996, A.I.S.B. 1998)*

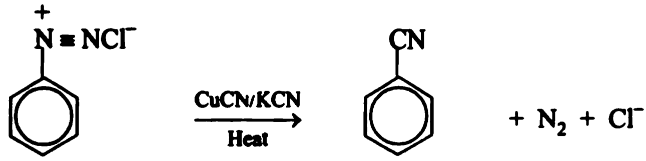
The conversion of benzenediazonium chloride to chlorobenzene, bromobenzene and benzonitirle on treatment with CuCl/HCl. CuBr/HBr or CuCN/KCN respectively is called *Sandmeyer reaction.*

**Examples :**





Benzenediazonium chloride Bromobenzene



Benzenediazonium chloride Benzonitrile

It may be noted that in this reaction, it is the halogen attached to copper which acutally enters the benzene ring.

### 47. Sabatier and Senderens reduction

The reduction of unsaturated hydrocarbons to the corresponding saturated hydrocarbons with hydrogen in presence of Raney nickel as catalyst at 473 - 573 K is called *Sabatier-Senderens reduction.*

**Examples :**

$$\underset{\text{Ethylene}}{CH_2=CH_2}+H_2 \xrightarrow[\text{473–573 K}]{\text{Raney Ni}} \underset{\text{Ethane}}{CH_3{-}CH_3}$$

$$\underset{\text{Acetylene}}{CH\equiv CH}+2H_2 \xrightarrow[\text{473–573 K}]{\text{Raney Ni}} \underset{\text{Ethane}}{CH_3{-}CH_3}$$

This catalytic hydrogenation is widely used in the manufacture of hydrogenated solid fats from edible vegetable oils.

### 48. Saytzeff's Rule (*1, 2-Elimination or β-elimination*)

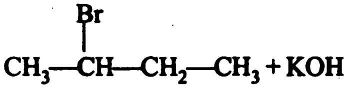
This reaction involves the treatment of an alkyl halide with concentrated alcoholic solution of a strong base like potassiun hydroxide to from alkene.

$$\underset{\text{Alkyl bromide}}{R{-}CH_2{-}CH_2{-}Br}+\underset{\substack{\text{conc.}\\\text{(alc.)}}}{KOH} \xrightarrow{\Delta} \underset{\text{Alkene}}{R{-}CH=CH_2}+KBr+H_2O$$

$$\underset{\text{Ethyl bromide}}{C_2H_5{-}Br}+KOH \xrightarrow{\Delta} \underset{\text{Ethylene}}{H_2C=CH_2}+KBr+H_2O$$

If the structure of an alkyl halide is such that it can undergo dehydrohalogenation in two different ways, the preferred product is that alkene which contains least number of hydrogen atoms on doubly bonded carbon atoms. This is due to the fact that more substituted alkene is more stable and is formed more readily. This is called *Saytzeff's Rule.*

**Example :**



$$\begin{array}{l} \qquad \mathrm{Br} \\ \qquad | \\ \mathrm{CH_3{-}CH{-}CH_2{-}CH_3} + \mathrm{KOH} \end{array}$$

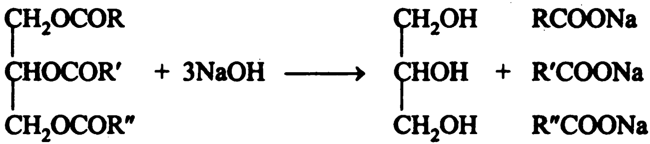
2-Bromobutane conc. (alc.)

$$\xrightarrow{\Delta} \mathrm{CH_3{-}CH=CH{-}CH_3} + \mathrm{CH_2=CH{-}CH_2{-}CH_3}$$

2-Butene (80%, more substituted) 1-Butene (20%, less substituted)

### 49. Saponification

The alkaline hydrolysis of oil or fat (glyceride) to form soap (alkali salt of higher fatty acid) and glycerol is known as saponification.

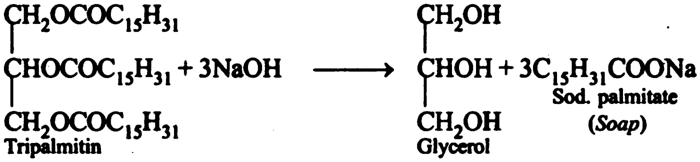


$$\begin{array}{lcccl} \mathrm{CH_2OCOR} & & & \mathrm{CH_2OH} & \quad \mathrm{RCOONa} \\ | & & & | & \\ \mathrm{CHOCOR'} & + \; 3\mathrm{NaOH} & \longrightarrow & \mathrm{CHOH} & + \; \mathrm{R'COONa} \\ | & & & | & \\ \mathrm{CH_2OCOR''} & & & \mathrm{CH_2OH} & \quad \mathrm{R''COONa} \end{array}$$

Oil or fat (*Glyceride*) Glycerol (*By-product*) Soap

R, R′, R″ (alkyl group) may be same or different. This group may be $C_{15}H_{31}$, $C_{17}H_{35}$, $C_{17}H_{33}$, etc.

**Examples :**

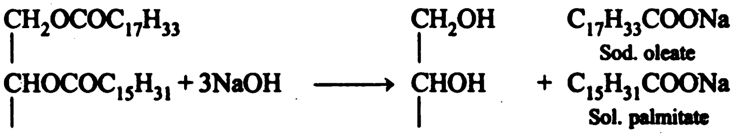


$$\begin{array}{lccl} \mathrm{CH_2OCOC_{15}H_{31}} & & & \mathrm{CH_2OH} \\ | & & & | \\ \mathrm{CHOCOC_{15}H_{31}} + 3\mathrm{NaOH} & \longrightarrow & & \mathrm{CHOH} + 3\mathrm{C_{15}H_{31}COONa} \\ | & & & | \\ \mathrm{CH_2OCOC_{15}H_{31}} & & & \mathrm{CH_2OH} \end{array}$$

Tripalmitin
or
Glyceryl tripalmitate
(*fat*)

Glycerol

Sod. palmitate (*Soap*)



$$\begin{array}{lccl} \mathrm{CH_2OCOC_{17}H_{33}} & & \mathrm{CH_2OH} & \quad \mathrm{C_{17}H_{33}COONa} \\ | & & | & \\ \mathrm{CHOCOC_{15}H_{31}} + 3\mathrm{NaOH} & \longrightarrow & \mathrm{CHOH} & + \; \mathrm{C_{15}H_{31}COONa} \\ | & & | & \\ \mathrm{CH_2OCOC_{17}H_{35}} & & \mathrm{CH_2OH} & \quad \mathrm{C_{17}H_{35}COONa} \end{array}$$

Oleopalmitostearin

Sod. oleate
Sol. palmitate
Sod. stearate
(A mixture of
three different soaps)

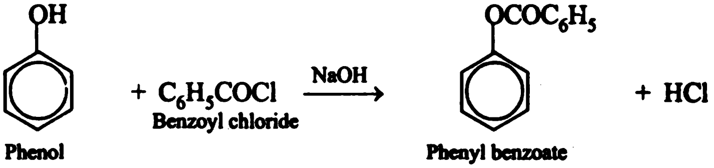
### 50. Schotten-Baumann reaction

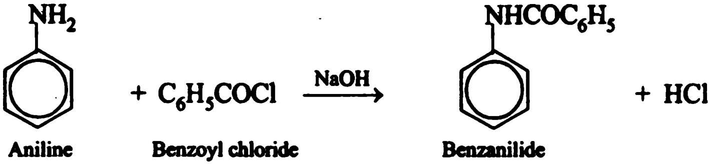
Benzoylation of compounds containing active hydrogen such as phenol, aniline, alcohol etc. with benzoyl chloride in the presence of aqueous NaOH is called *Schotten-Baumann reaction.*

**Examples :**

$$\mathrm{CH_3CH_2OH} + \mathrm{C_6H_5COCl} \xrightarrow{\mathrm{NaOH}} \mathrm{CH_3CH_2OCOC_6H_5} + \mathrm{HCl}$$

Ethyl alcohol Benzoyl chloride Ethyl benzoate





## 51. Stephen reaction or Stephen reduction

The partial reduction of alkyl or aryl cyanides to the corresponding aldehydes with stannous chloride in ether saturated with hydrogen chloride followed by hydrolysis is called *Stephen reaction* or *Stephen reduction*. During the reaction, imine hydrochloride is first formed which on hydrolysis with boiling water gives the corresponding aldehyde.

**Examples :**

$$SnCl_2 + 2HCl \longrightarrow SnCl_4 + 2[H]$$

$$\underset{\text{Acetonitrile}}{CH_3{-}C\equiv N} + 2[H] + HCl \xrightarrow[\text{290-295 K}]{\text{Ether}} \underset{\text{Acetaldimine hydrochloride}}{CH_3CH{=}NH.HCl}$$

$$\downarrow \text{Boiling } H_2O$$

$$\underset{\text{Acetaldehyde}}{CH_3CH{=}O} + NH_4Cl$$

$$\underset{\text{Benzonitrile}}{C_6H_5C\equiv N} = 2[H] + HCl \xrightarrow[\text{290-295 K}]{\text{Ether}} \underset{\text{Benzaldimine hydrochloride}}{C_6H_5CH{=}NH.HCl}$$

$$\downarrow \text{Boiling } H_2O$$

$$\underset{\text{Benzaldehyde}}{C_6H_5CH{=}O} + NH_4Cl$$

## 52. Tischenko reaction

In the presence of aluminium ethoxide, aldehydes (with or without $\alpha$-hydrogen) form esters. This is known as *Tischenko reaction*.

Like Cannizzaro reaction, one molecule of aldehyde gets oxidised to the corresponding acid whereas another molecule gets reduced to alcohol. However, these acid and alcohol appear as an ester.

*e.g.*, (*i*)

$$\underset{\text{Acetaldehyde}}{2CH_3CHO} \xrightarrow[-H_2O]{Al(OEt)_3} \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5}$$

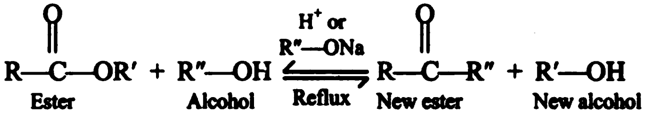
(*ii*)

$$\underset{\text{Acraldehyde}}{2CH_2{=}CH{-}CHO} \xrightarrow[-H_2O]{Al(OEt)_3} \underset{\text{Allyl acrylate}}{CH_2{=}CH{-}COOCH_2CH{=}CH_2}$$

### 53. Transesterification *(A.I.S.B. 2000)*

When an ester is treated with excess of an alcohol other than the one from which the ester has been derived, in presence of sodium or potassium alkoxide or an acid ($H_2SO_4$ or HCl) as catalyst, a new ester and a new alcohol are formed. *This displacement of one alcohol from an ester by another alcohol is called* **transesterification.**

**Example :**



$$\underset{\text{Ester}}{R-\overset{\overset{O}{\|}}{C}-OR'} + \underset{\text{Alcohol}}{R''-OH} \underset{\text{Reflux}}{\overset{H^+ \text{ or } R''-ONa}{\rightleftharpoons}} \underset{\text{New ester}}{R-\overset{\overset{O}{\|}}{C}-R''} + \underset{\text{New alcohol}}{R'-OH}$$

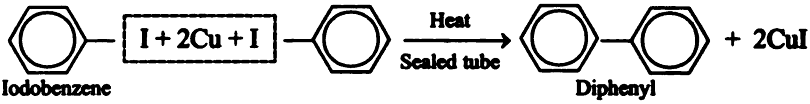
Transesterification is a reversible reaction. Therefore, to shift the equilibrium in the forward direction, generally an excess of the alcohol whose ester we wish to make is used.

Transesterification is a useful reaction particularly for the preparation of higher alcohols from the naturally occurring esters.

$$\underset{n\text{-Butyl acetate}}{CH_3COOC_4H_9} + \underset{\substack{\text{Ethyl alcohol}\\(\textit{Lower alcohol})}}{C_2H_5OH} \overset{C_2H_5ONa}{\rightleftharpoons} \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + \underset{\substack{n\text{-Butyl alcohol}\\(\textit{Higher alcohol})}}{C_4H_9OH}$$

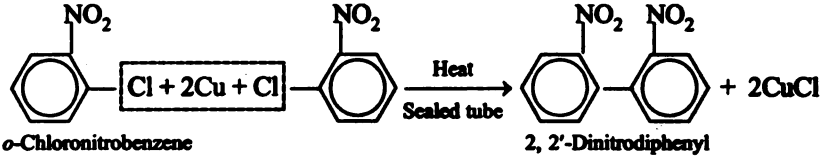
### 54. Ullmann reaction

Iodobenzene on heating with copper powder in a sealed tybe gives diphenyl. This reaction is called *Ullmann reaction.*



Aryl chlorides and aryl bromides also react if an electron-withdrawing groups is present at *o*- and/or *p*-position w.r.t. the halogen atom.

**Example :**



### 55. Wurtz reaction

Two molecules of an alkyl halide react with metallic sodium in presence of dry ether to form symmetrical alkanes containing double the number of carbon atoms present in the alkyl halide. This reaction is called *Wurtz reaction.*

**Examples :**

$$\underset{\text{Alkyl halide}}{R-X} + 2Na + X-R \xrightarrow{\text{Dry ether}} \underset{\text{Alkane}}{R-R} + 2NaX$$

$$\underset{\text{Methyl bromide}}{CH_3—Br} + 2Na + Br—CH_3 \xrightarrow{\text{Dry ether}} \underset{\text{Ethane}}{CH_3—CH_3} + 2NaBr$$

$$\underset{\text{Ethyl iodide}}{CH_3CH_2—I} + 2Na + I—CH_2CH_3 \xrightarrow{\text{Dry ether}} \underset{\text{Butane}}{CH_3CH_2—CH_2CH_3} + 2NaI$$

***This reaction provides us a method for the preparation of symmetrical alkanes (R—R), i.e., alkanes containing even number of carbon atoms.***

**However, if two different alkyl halides are used, a mixture of three alkanes is acutally formed.**

$$\underset{\text{Methyl iodide}}{CH_3—I} + 2Na + \underset{\text{Ethyl iodide}}{I—CH_2CH_3} \xrightarrow{\text{Dry ether}} \underset{\text{Propane}}{CH_3—CH_2CH_3} + 2NaI$$

$$\underset{\text{Methyl iodide}}{CH_3—I} + 2Na + I—CH_3 \xrightarrow{\text{Dry ether}} \underset{\text{Ethane}}{CH_3—CH_3} + 2NaI$$

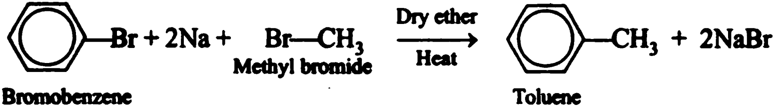
$$\underset{\text{Ethyl iodide}}{CH_3CH_2—I} + 2Na + I—CH_2CH_3 \xrightarrow{\text{Dry ether}} \underset{\text{Butane}}{CH_3CH_2—CH_2CH_3} + 2NaI$$

### 56. Wurtz-Fittig reaction (*A.I.S.B. 1990*)

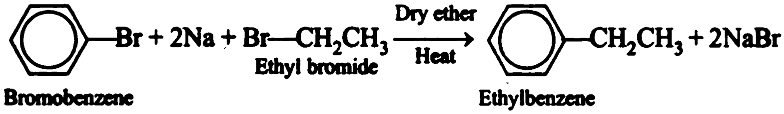
**This reaction is a form of Wurtz reaction. It is used for preparing homologues of benzene by warming a mixture of an aryl halide and an alkyl halide with metallic sodium in presence of dry ether.**

**Examples :**

(*i*)



(*ii*)



### 57. Williamson synthesis

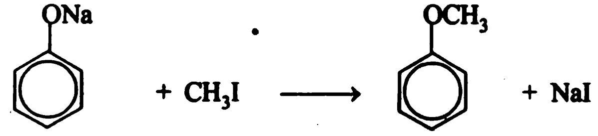
**The reaction of alkyl halides with sodium alkoxide or sodium phenoxide to form ethers is called *Williamson synthesis*.**

**Examples :**

$$\underset{\text{Alkyl halide}}{R—X} + \underset{\text{Sod. alkoxide}}{R'—ONa} \longrightarrow \underset{\text{Ether}}{R—O—R'} + NaX$$

$$\underset{\text{Methyl iodide}}{CH_3I} + \underset{\text{Sod. ethoxide}}{CH_3CH_2ONa} \longrightarrow \underset{\text{Ethyl methyl ether}}{CH_3—O—CH_2CH_3} + NaI$$

$$\underset{\text{Ethyl iodide}}{CH_3CH_2I} + \underset{\text{Sod. ethoxide}}{CH_3CH_2ONa} \longrightarrow \underset{\text{Diethyl ether}}{CH_3CH_2—O—CH_2CH_3} + NaI$$



Sod. phenoxide  Methyl iodide  Anisole

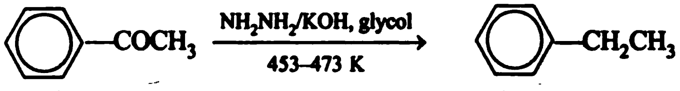
**58. Wolff-Kishner reduction** *(A.I.S.B. 1993 ; D.S.B. 1992)*

The reduction of aldehydes and ketones to the corresponding hydrocarbons by heating with hydrazine and KOH or potassium *tert*-butoxide in ethylene glycol is called ***Wolff-Kishner reduction.***

**Examples :**

$$\underset{\text{Aldehyde}}{R{-}CH=O} \xrightarrow[-H_2O]{NH_2NH_2} \underset{\text{Hydrazone}}{R{-}CH=NNH_2} \xrightarrow[453\text{–}473\text{ K}]{\text{KOH, glycol}} R{-}CH_3 + N_2$$

$$\underset{\text{Acetone}}{CH_3COCH_3} \xrightarrow[453\text{–}473\text{ K}]{NH_2NH_2/\text{KOH, glycol}} \underset{\text{Propane}}{CH_3CH_2CH_3}$$



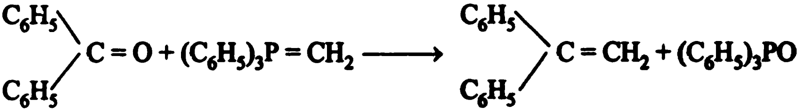
Acetophenone  Ethylbenzene

**59. Wittig reaction**

On treating carbonyl compounds (aldehydes or ketones) with an ylide, the carbonyl oxygen is replaced by the group = CRR′. This reaction is known as *Wittig reaction.*

**Example :**

$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} + \underset{\substack{\text{Methylenetriphenyl}\\ \text{phosphorane}\\ (ylide)}}{(C_6H_5)_3P=CH_2} \longrightarrow \underset{\text{Styrene}}{C_6H_5{-}CH=CH_2} + \underset{\substack{\text{Triphenyl}\\ \text{phosphine}\\ \text{oxide}}}{(C_6H_5)_3PO}$$



$$(C_6H_5)_2C=O + (C_6H_5)_3P=CH_2 \longrightarrow (C_6H_5)_2C=CH_2 + (C_6H_5)_3PO$$

Benzophenone  1, 1-Diphenylethylene

# 4

# Distinguishing between Pairs of Compounds

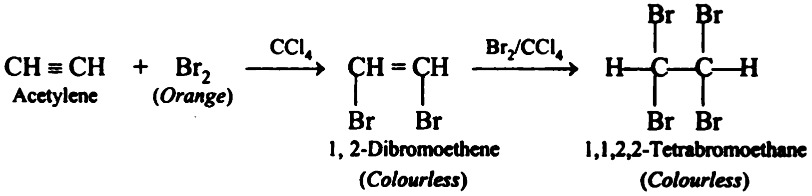
### 1. Distinguish between methane ($CH_4$) and acetylene ($C_2H_2$)

*(M.L.N.R. Allahabad 1995)*

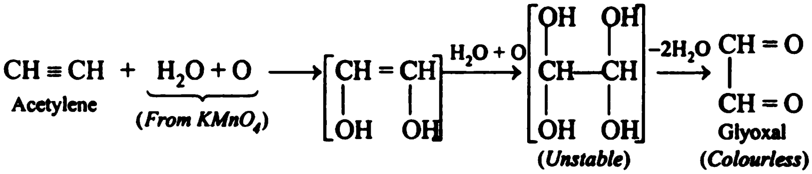
Methane is a *saturated hydrocarbon* while acetylene is an *unsaturated hydrocarbon*. These compound can be distinguished by the following tests :

Methane being a saturated hydrocarbon does not decolourize $Br_2$ in $CCl_4$. Nor does it decolourize alkaline solution of $KMnO_4$ (*Baeyer's reagent*) while acetylene being an *unsaturated hydrocarbon* decolourizes both these reagents. The following equations illustrate :

$$\underset{\text{Methane}}{CH_4} \xrightarrow{Br_2/CCl_4} \text{No action} \qquad \underset{\text{Methane}}{CH_4} \xrightarrow[\textit{(Baeyer's reagent)}]{\text{Cold dil. alk. } KMnO_4 \text{ Soln}} \text{No action}$$



$$\underset{\text{Acetylene}}{CH\equiv CH} + \underset{\textit{(Orange)}}{Br_2} \xrightarrow{CCl_4} \underset{\substack{\text{1, 2-Dibromoethene}\\ \textit{(Colourless)}}}{\underset{Br\quad\ \ Br}{CH=CH}} \xrightarrow{Br_2/CCl_4} \underset{\substack{\text{1,1,2,2-Tetrabromoethane}\\ \textit{(Colourless)}}}{H-\overset{Br}{\underset{Br}{C}}-\overset{Br}{\underset{Br}{C}}-H}$$



$$\underset{\text{Acetylene}}{CH\equiv CH} + \underbrace{H_2O+O}_{\textit{(From } KMnO_4)} \longrightarrow \left[\begin{matrix} CH=CH \\ | \quad\ \ | \\ OH \quad OH \end{matrix}\right] \xrightarrow{H_2O+O} \underset{\textit{(Unstable)}}{\left[\begin{matrix} OH \quad OH \\ | \quad\ \ | \\ CH-CH \\ | \quad\ \ | \\ OH \quad OH \end{matrix}\right]} \xrightarrow{-2H_2O} \underset{\substack{\text{Glyoxal}\\ \textit{(Colourless)}}}{\begin{matrix} CH=O \\ | \\ CH=O \end{matrix}}$$

Also acetyle being *a terminal alkyne* gives a white ppt. of silver acetylide with ammoniacal silver nitrate solution (*Tollen's reagent*) and a red ppt. of copper acetylide with an ammoniacal solution of cuprous chloride. These reactions are not given by methane.

$$\underset{\text{Acetylene}}{HC\equiv CH} + \underset{\text{Tollen's reagent}}{2[Ag(NH_3)_2]^+OH^-} \longrightarrow \underset{\substack{\text{Silver acetylide}\\ \textit{(White ppt.)}}}{Ag-C\equiv C-Ag} + 4NH_3 + 2H_2O$$

$$\underset{\text{Acetylene}}{HC\equiv CH} + 2[Cu(NH_3)_2]^+OH^- \longrightarrow \underset{\substack{\text{Copper acetylide}\\ \textit{(Red ppt.)}}}{Cu-C\equiv C-Cu} + 4NH_3 + 2H_2O$$

**2. Distinguish between ethane ($C_2H_6$) and ethylene ($C_2H_4$)**

Ethane is a saturated hydrocarbon and ethylene is an unsaturated hydrocarbon. These two compounds can be distinguished by the following tests.

(*i*) Ethane does not decolourize bromine in carbon tetrachloride whereas ethylene gives this tests.

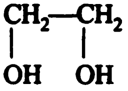
$$C_2H_6 + Br_2 \xrightarrow{CCl_4} \text{No action}$$

$$C_2H_4 + Br_2 \xrightarrow{CCl_4} \underset{\substack{\text{Dibromoethane}\\ (\textit{colourless})}}{C_2H_4\,Br_2}$$

(*ii*) Ethane does not decolourize pink colour of $KMnO_4$ wheres etheylene does.

$$C_2H_6 + \underbrace{H_2O + O}_{\text{From } KMnO_4} \longrightarrow \text{No action}$$

$$C_2H_4 + \underbrace{H_2O + O}_{\text{From } KMnO_4} \longrightarrow$$



$$\begin{array}{cc} CH_2 & \!\!-\!\! CH_2 \\ | & | \\ OH & OH \end{array}$$

Ethylene glycol
(*colourless*)

**3. Distinguish between ethylene and acetylene.**

(*M.L.N.R. Allahabad 1995*)

Both ethyle and acetylene being *unsaturated hydrocarbons* decolourize $Br_2$ in $CCl_4$ solution and a cold dilute alkaline solution of $KMnO_4$ (*Baeyer's reagent*). Following tests are performed to distinguish between them.

(*i*) **Ammoniacal silver nitrate test.** With ammoniacal silver nitrate solution (*Tollen's reagent*), acetylene gives a whie ppt. of silver acetylide whereas ethylene does not.

$$\underset{\text{Acetylene}}{HC \equiv CH} + \underset{\text{Tollen's reagent}}{2[Ag(NH_3)_2]^+ OH^-} \longrightarrow \underset{\substack{\text{Silver acetylide}\\ (\textit{White ppt.})}}{Ag{-}C \equiv C{-}Ag} + 4NH_3 + 2H_2O$$

$$\underset{\text{Ethylene}}{CH_2 = CH_2} \xrightarrow{\text{Tollen's reagent}} \text{No action}$$

(*ii*) **Ammoniacal cuprous chloride test.** With an ammoniacal solution of cuprous chloride, acetylene gives a red ppt. of copper acetylide while ethylene does not.

$$\underset{\text{Acetylene}}{HC \equiv CH} + 2[Cu(NH_3)_2]^+ OH^- \longrightarrow \underset{\substack{\text{Copper acetylide}\\ (\textit{Red ppt.})}}{Cu{-}C \equiv C{-}Cu} + 4NH_3 + 2H_2O$$

$$\underset{\text{Ethylene}}{CH_2 = CH_2} \xrightarrow{\text{Ammoniacal cuprous chloride solution}} \text{No action}$$

(*iii*) **Cold conc. $H_2SO_4$ test.** When ethylene is passed through cold conc. $H_2SO_4$, it dissolved forming ethyl hydrogen sulphate but acetylene does not dissolve.

$$\underset{\text{Ethylene}}{CH_2=CH_2} + H_2SO_4 \longrightarrow \underset{\text{Ethyl hydrogen sulphate}}{CH_3—CH_2—OSO_3H}$$

$$CH\equiv CH \xrightarrow{\text{Cold conc. } H_2SO_4} \text{No action}$$

4. **Distinguish between 1-butyne and 2-butyne.** (*I.I.T. 1985*)

Both 1-butyne and 2-butyne are alkynes. These can be distinguished by the following two tests :

(*i*) With ammoniacal cuprous chloride solution, 1-butyne gives a red ppt. of copper 1-butynide while 2-butyne does not react.

$$\underset{\text{1-Butyne}}{CH_3CH_2C\equiv CH} + [Cu(NH_3)_2]^+\,OH^- \longrightarrow \underset{\substack{\text{Copper 1-butynide}\\ (\textit{Red ppt.})}}{CH_3CH_2C\equiv C—Cu} + H_2O + 2NH_3$$

$$\underset{\text{2-Butyne}}{CH_3—C\equiv C—CH_3} + [Cu(NH_3)_2]^+\,OH^- \longrightarrow \text{No reaction.}$$

(*ii*) With ammoniacal silver nitrate solution (*Tollen's reagent*), 1-butyne gives a white ppt. of silver acetylide while 2-butyne does not react.

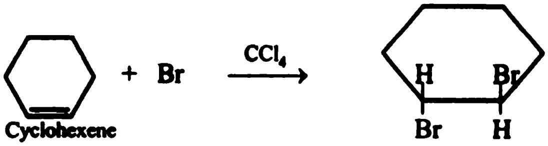
$$\underset{\substack{\text{1-Butyne}\\ (\textit{Terminal alkyne})}}{CH_3CH_2C\equiv CH} + \underset{\text{Tollen's reagent}}{[Ag(NH_3)_2]^+OH^-} \longrightarrow \underset{\substack{\text{Silver 1-butynide}\\ (\textit{White ppt.})}}{CH_3CH_2C\equiv CAg} + H_2O + 2NH_3$$

$$\underset{\substack{\text{2-Butyne}\\ (\textit{Non-terminal alkyne})}}{CH_3—C\equiv C—CH_3} + \underset{\text{Tollen's reagent}}{[Ag(NH_3)_2]^+\,OH^-} \longrightarrow \text{No reaction}$$

Thus we perform tests which are characteristic of terminal alkynes to distinguish between the two. While 1-butyne is a terminal alkyne, 2-butyne is a non-terminal alkyne.

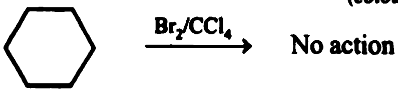
5. **Distinguish between cyclohexane and cyclohexene**

(*i*) Cyclohexene is an unsaturated compound, it contains a double bond. It decolourises the orange colur of $Br_2$ in $CCl_4$ solution by forming the addition product. In contrast, cyclohexane is a saturated compound. As such it does not decolorize bromine in carbon tetrachloride.



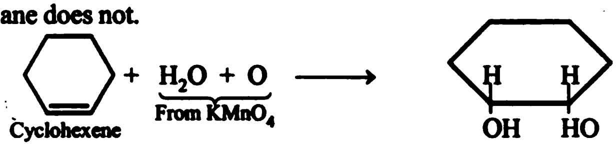
Cyclohexene

*trans*-1, 2-Dibromocyclohexane (*colourless*)



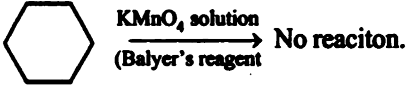
Cyclohexane

(*ii*) A cold dilute alkaline of $KMnO_4$ (*Baeyer's reagent*) is another reagent that can be used to distinguish between these two compounds. Cyclohexene decolourises the pink colur of $KMnO_4$ solution, whereas cyclohexane does not.



Cyclohexene

*cis*-1, 2-Cyclohexanediol
(*Colourless*)



Cyclohexane

**6. Distinguish between Ehyl bromide ($C_2H_5Br$) and bromobenzene ($C_6H_5Br$)** (*A.I.S.B. 1991 S*)

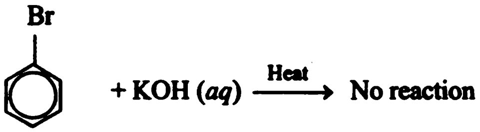
Ethyl bromide is a *haloalkane while bromobenzene* is a *haloarene.* Halokanes are more reactive than haloarenes towards *nuclephilic substitution reactions.* When ethyl bromide is heated with aqueous KOH, it undergoes hydrolysis to produce ethyl alcohol and KBr.

$$\underset{\text{Ethyl bromide}}{C_2H_5Br} + KOH\,(aq) \xrightarrow{\text{Heat}} \underset{\text{Ethyl alcohol}}{C_2H_5OH} + K^+ + Br^-$$

The reaction mixture on acidification with dil. $HNO_3$ and treatment with $AgNO_3$ solution produces a light yellow ppt. of AgBr.

$$KBr + AgNO_3 \longrightarrow \underset{(\textit{Light yellow ppt.})}{AgBr \downarrow} + KNO_3$$

In contrast, bromobenzene does not undergo hydrolysis under these conditions to produce phenol and KBr. Therefore, light yellow ppt. of AgBr is not formed.



Bromobenzene

**7. Distinguish between chlorobenzene ($C_6H_5Cl$) and n-hexyl chloride ($C_6H_{13}Cl$)** (*A.I.S.B. 1988; P.S.B. 1989*)

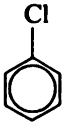
*n*-Hexyl chloride is a *haloalxane* while chlrobenzene is a *haloarene.* Haloakanes are more reactive than haloarenes towards *nucleophilic substitution reactions.* When *n*-hexyl chloride is heated with *aq*. KOH, is undergoes hydrolysis to produce *n*-hexyl alcohol and KCl.

$$\underset{n\text{-Hexyl chloride}}{CH_3(CH_2)_4CH_2{-}Cl} + KOH(aq) \xrightarrow{\text{Heat}} \underset{n\text{-Hexyl alcohol}}{CH_3(CH_2)_4CH_2{-}OH} + KCl$$

The reaction mixture on acidification with dil. $HNO_3$ and treatment with $AgNO_3$ solution produces a white ppt. of AgCl.

$$KCl + AgNO_3 \longrightarrow \underset{(\textit{White ppt.})}{AgCl\downarrow} + KNO_3$$

It contrast, chlorobenzene does not undergo hydrolysis under these conditions to produce phenol and KCl. Therefore, white ppt. of AgCl is not formed.



$$+ KOH\ (aq) \xrightarrow{\text{Heat}} \text{No reaction.}$$

Chlorobenzene

**8. Distinguish between chlorobenzene ($C_6H_5Cl$) and benzyl chloride ($C_6H_5CH_2Cl$)**

*(P.S.B. 1989; H.S.B. 1992; D.S.B. 1995; C.B.S.E. Sample Paper, 1997)*

Benzyl chloride is an *aralkyl halide* while chlorobenzene is an *aryl halide.* Aralkyl halides behave like alkyl halides and are more reactive than aryl halides towards *nucleophilic substituion reaction.* Therefore, benzyl chloride on boiling with aq. KOH produces benzyl alcohol and KCl.

$$\underset{\text{Benzyl chloride}}{C_6H_5CH_2Cl} + KOH\ (aq) \xrightarrow{\text{Boil}} \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} + KCl$$

The reaction mixture on acidification with dil. $HNO_3$ and treatment with $AgNO_3$ solution produces white ppt. of AgCl due to the formation of KCl.

$$KCl + AgNO_3 \longrightarrow \underset{(\textit{White ppt.})}{AgCl\downarrow} + KNO_3$$

However, chlorobenzene does not undergo hydrolysis under these mild conditions to give phenol and KCl.

$$\underset{\text{Cholorobenzene}}{C_6H_5Cl} + KOH(aq) \xrightarrow{\text{Boil}} \text{No reaction}$$

Therefore, acidification of the reaction mixture with dil. $HNO_3$ and addition of $AgNO_3$ solution does not produce a white ppt. of AgCl.

**9. Distinguish between bromobenzene ($C_6H_5Br$) and benzyl bromide ($C_6H_5CH_2Br$)**

Benzyl bromide is an *aralkyl halide* while bromobenzene is an *aryl halide.* Since arakyl halides are more reactive than aryl halides towards *neucleophilic substitution reactions,* therefore, benzyl bromide on boiling with an aqueous solution of KOH undergoes hydrolysis to produce benzyl alchol and KBr.

$$\underset{\text{Benzyl bromide}}{C_6H_5CH_2Br} + KOH\ (aq) \xrightarrow{\text{Boil}} \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} + KBr$$

The reaction mixture of acidification with dil. $HNO_3$ and addition of $AgNO_3$ solution produces light yellow ppt. of AgBr due to the formation of KBr.

$$KBr + AgNO_3 \longrightarrow \underset{\textit{(Light yellow ppt.)}}{AgBr\downarrow} + KNO_3$$

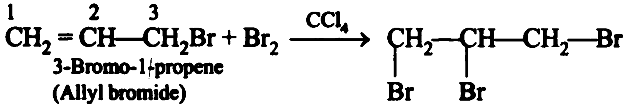
In contrast bromobenzene does not undergo hydrolysis under these mild conditions to give phenol and KBr.

$$\underset{\textbf{Bromobenzene}}{C_6H_5Br} + KOH(aq) \xrightarrow{\text{Boil}} \text{No reaction}$$

Therefore, on acidification of the reaction mixture with dil. $HNO_3$ and addition of $AgNO_3$ a light yellow ppt. of AgBr is not obtained.

**10. Distinguish between 3-bromo-1-propene ($CH_2 = CH—CH_2Br$) and 1-bromopropane ($CH_3CH_2CH_2Br$)** *(D.S.B. 1985)*

(*i*) 3-Bromo-1-propene is a halogenated alkene and thus decolourises the orange colour of $Br_2$ in $CCl_4$ solution by forming the addition product.



$$\overset{1}{C}H_2 = \overset{2}{C}H—\overset{3}{C}H_2Br + Br_2 \xrightarrow{CCl_4} \underset{Br}{\underset{|}{C}}H_2—\underset{Br}{\underset{|}{C}}H—CH_2—Br$$

3-Bromo-1-propene
(Allyl bromide)

1,2,3-Tribromopropane
*(Colourless)*

In contrast, 1-bromopropane does not give this test since it does not contain a double bond.

$$\underset{\textbf{1-Bromopropane}}{CH_3CH_2CH_2Br} + Br_2 \xrightarrow{CCl_4} \text{No reaction.}$$

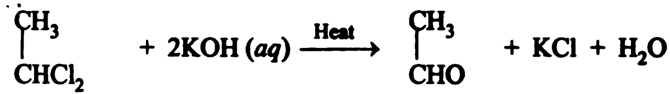
A cold dilute alkaline solution of $KMnO_4$ (*Baeyer's reagent*) is another reagent that can also be used to distinguish between these compounds. Whereas 3-bromo-1-propene decolourises the pink colour of Baeyer's reagent, 1-bromopropane does not.

$$\underset{\textbf{3-Bromo-1-propene}}{CH_2 = CH—CH_2Br} + \underbrace{H_2O + O}_{\textbf{From } KMnO_4} \longrightarrow \underset{\substack{\textbf{3-Bromo-1, 2-propanediol}\\ \textit{(Colourless)}}}{HOCH_2—CHOH—CH_2Br}$$

$$\underset{\textbf{1-Bromopropane}}{CH_3CH_2CH_2—Br} \xrightarrow{KMnO_4 \text{ solution}} \text{No reaction.}$$

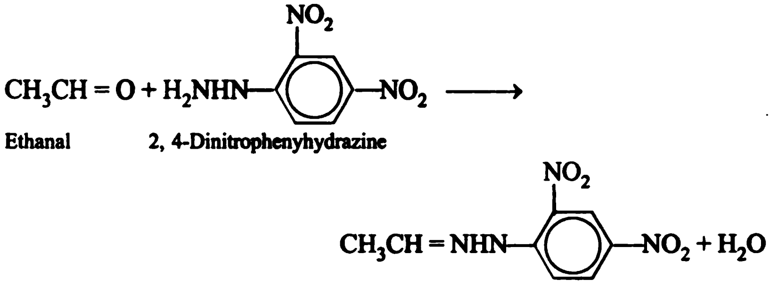
**11. 1, 1-dichloroethane and 1, 2-dichloroethane**

**1, 1-Dichloroethane** is a *gem-dihalide.* This upon hydrolysis with aq. KOH gives ethanal which upon treatment with 2, 4-dinitrophenylhydrazine forms a yellow ppt. of ethanal 2, 4-dinitrophenylhydrazone.



$$\begin{array}{l}CH_3\\ |\\ CHCl_2\end{array} + 2KOH\,(aq) \xrightarrow{\text{Heat}} \begin{array}{l}CH_3\\ |\\ CHO\end{array} + KCl + H_2O$$

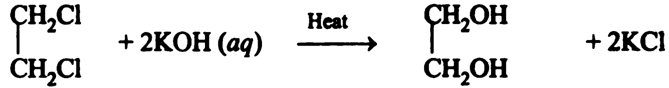
1, 1-Dichloroethane · Ethanal or acetaldehyde



Ethanal 2, 4-Dinitrophenyhydrazine

Ethanal 2, 4-dinitrophenylhydrazone (*Yellow ppt.*)

In contrast, 1, 2-dichloroethane is a *vicinal dihalide*. This upon hydrolysis with aq. KOH gvies ethane-1, 2- diol (ethylene glycol) which does not give yellow ppt. of 2, 4-dinitrohydrazone on treatment with 2, 4-dinitrophenylhdrazine. A yellow ppt. of with 2,4-dinitorpheylhydrozine is given by aldehydes and ketones and not by alcohols (like ethylene glycol)



$$\begin{array}{l}CH_2Cl\\ |\\ CH_2Cl\end{array} + 2KOH\,(aq) \xrightarrow{\text{Heat}} \begin{array}{l}CH_2OH\\ |\\ CH_2OH\end{array} + 2KCl$$

1, 2-Dichloroethane Ethane-1, 2-diol (*Ethylene glycol*)

↓ 2, 4-Dinitrophenylhydrazine

No yellow ppt. of 2,4-DNP

**12. Distinguish btween chloroform ($CHCl_3$) and carbon tetrachloride ($CCl_4$)** (*D.S.B. 1988*)

Chloroform on warming with an alcoholic solution of aniline and KOH gives carbylamine having offensive smell while carbon tetrachloride does not give this test.

$$\underset{\text{Chloroform}}{CHCl_3} + \underset{\text{Aniline}}{C_6H_5NH_2} + \underset{(alc.)}{3KOH} \xrightarrow{\text{warm}} \underset{\text{Phenyl isocyanide}}{C_6H_5N \rightleftharpoons C} + 3KCl + 3H_2O$$

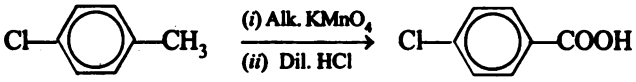
(*offensive smelling compound*)

$$CCl_4 + C_6H_5NH_2 + KOH \longrightarrow \text{No reaction}$$

**13. Distinguish between *p*-chlorotoluene (*p*-$ClC_6H_4CH_3$) and benzyl chloride ($C_6H_5CH_2Cl$)**

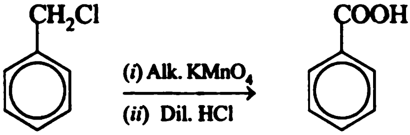
These may be distinguished by the following tests :

(*i*) **Oxidation test.** *p*-Chlorotoluene on oxidation with alkaline $KMnO_4$ solution followed by acidification gives *p*-chlorobenzoic acid.



*p*-Chlorotoluene *p*-Chlorobenzoic acid
(m.p. 512-514 K)

In contrast, benzyl chloride on oxidation with alkaline $KMnO_4$ followed by acidification gives benzoic acid.



Benzyl chloride Benzoic acid
(m.p. 394 K)

(*ii*) **$AgNO_3$ test.** Benzyl chloride on boiling with aq. KOH solution undergoes hydrolysis to give benzyl alcohol and KCl.

$$\underset{\text{Benzyl chloride}}{C_6H_5CH_2Cl} + KOH\,(aq) \xrightarrow{\text{Heat}} \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} + K^+Cl^-$$

The reaction mixture on acidification with dil. $HNO_3$ followed by treatment with $AgNO_3$ solution produces white ppt. of AgCl.

$$KCl + AgNO_3 \longrightarrow \underset{(\textit{White ppt.})}{AgCl \downarrow} + KNO_3$$

In contrast, *p*-chlorotoluene does not undergo hydrolysis under these conditions to produce *p*-cresol and KCl. Therefore, it does not give white ppt. of AgCl.

### 14. Distinguish between methanol ($CH_3OH$) and ethanol ($CH_2CH_2OH$)

(*I.I.T. 1985; A.I.S.B. 1995; D.S.B. 1989 S; C.B.S.E. Sample Paper, 1997*)

These two compounds can be distinguished by the *iodoform test.*

Ethanol contains the —$CHOHCH_3$ group and hence gives the iodoform test. When warmed with sodium hypoiodite (NaOI), or $I_2$ in NaOH, it gives yellow ppt. of iodoform.

$$\underset{\text{Ethanol}}{CH_3CH_2OH} + NaOI \longrightarrow \underset{\text{Acetaldehyde}}{CH_3CHO} + NaI + H_2O$$

$$\underset{\text{Acetaldehyde}}{CH_3CHO} + 3NaOI \longrightarrow \underset{\text{Iodoform}}{CHI_3 \downarrow} + \underset{\text{Sod. formate}}{HCOONa} + 2NaOH$$

Methanol ($CH_3OH$) does not contain the —$CHOHCH_3$ group hence it does not give the iodoform test.

$$\underset{\text{Methanol}}{CH_3OH} \xrightarrow{\text{NaOI}} \text{No yellow ppt. of } CHI_3$$

### 15. Distinguish between ethanol ($CH_3CH_2OH$) and 1-propanol ($CH_3CH_2CH_2OH$) *(D.S.B. 1995)*

These two compounds can be distinguished by the *iodoform test* :

Ethanol contains the $CH_3CHOH$— group and hence gives the iodoform test. When warmed with sodium hypoiodite (NaOI), or $I_2$ in NaOH, it gives yellow ppt. of iodoform ($CHI_3$).

$$\underset{\text{Ethanol}}{CH_3CH_2OH} + NaOI \longrightarrow \underset{\text{Ethanal}}{CH_3CHO} + NaI + H_2O$$

$$\underset{\text{Ethanal}}{CH_3CHO} + 3NaOI \longrightarrow \underset{\text{Iodoform}}{CHI_3\downarrow} + \underset{\text{Sod. formate}}{HCOONa} + 2NaOH$$

On the other hand, 1-propanol ($CH_3CH_2CH_2OH$) does not contain the $CH_3CHOH_3$— group and hence it does not give the iodoform test.

$$\underset{\text{1-Propanol}}{CH_3CH_2CH_2OH} \xrightarrow{NaOI} \text{No yellow ppt. of } CHI_3$$

### 16. 1-propanol ($CH_3CH_2CH_2OH$) and 2-propanol ($CH_3CHOHCH_3$) *(A.I.S.B. 1989; D.S.B. 1988)*

These compounds can be distinguished by the iodoform test :

2-Propanol ($CH_3CHOHCH_3$) contains the —$CHOHCH_3$ group and hence give the iodoform test. When warmed with sodium hypoiodite (NaOI), or $I_2$ in NaOH, it gives ppt. of iodoform. 1-propanol does not contain the —$CHOHCH_3$ group and hence does not respond to iodoform test.

$$\underset{\text{2-Propanol}}{CH_3\text{—}CHOHCH_3} + NaOI \longrightarrow \underset{\text{Acetone}}{CH_3\text{—}COCH_3} + NaI + H_2O$$

$$\underset{\text{Acetone}}{CH_3\text{—}COCH_3} + 3NaOI \longrightarrow \underset{\substack{\text{Iodoform}\\ \textit{(Yellow ppt.)}}}{CHI_3\downarrow} + \underset{\text{Sod. Acetate}}{CH_3COONa} + 2NaOH$$

$$\underset{\text{1-Propanol}}{CH_3CH_3CH_2OH} \xrightarrow{NaOI} \text{No yellow ppt. of } CHI_3$$

### 17. Distinguish between 1-butanol ($CH_3CH_2CH_2CH_2OH$) and 2-butanol ($CH_3CHOHCH_2CH_3$) *(A.I.S.B. 1988)*

These two compounds can be distinguished by the iodoform test :

2-Butanol ($CH_3CHOH$—$CH_2CH_3$) contains the $CH_3CHOH$— group and hence gives iodoform test. When warmed with NaOI ($I_2$/NaOH), it gives yellow ppt. of iodoform (*iodoform test*) but 1-butanol ($CH_3CH_2CH_2OH$) does not contain the $CH_3CHOH$— group and hence does not give the iodoform test.

$$\underset{\text{2-Butanol}}{CH_3CHOH\text{—}CH_2CH_3} + NaOI \longrightarrow \underset{\text{2-Butanone}}{CH_3CO\text{—}CH_2CH_3} + NaI + H_2O$$

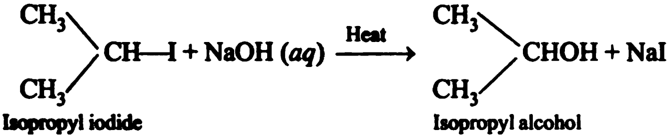
$$\underset{\text{2-Butanone}}{CH_3CO{-}CH_2CH_3} + 3NaOI \longrightarrow \underset{\substack{\text{Iodoform}\\ (\text{Yellow ppt.})}}{CHI_3\downarrow} + \underset{\text{Sod. propionate}}{CH_3CH_2COONa} + 2NaOH$$

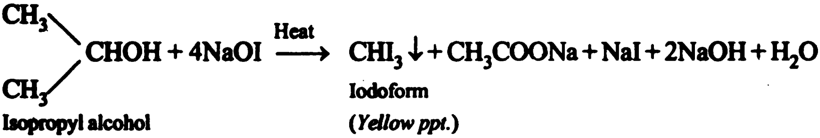
$$\underset{\text{1-Butanol}}{CH_3CH_2CH_2CH_2OH} \xrightarrow{NaOI} \text{No yellow ppt. of } CHI_3$$

**18. Distinguish between *n*-propyl iodide ($CH_3CH_2CH_2I$) and isopropyl iodide ($CH_3CHICH_3$)**

These two compounds may be distinguished as follows :

**Iodoform test.** Isopropyl iodide on hydrolysis with aqueous alkali solution gives isopropyl alcohol (*2-propanol*) which upon subsequent treatment with NaOI ($I_2$/NaOH) gives yellow ppt. of iodoform.





On the other hand, *n*-propyl iodide on alkaline hydrolysis gives *n*-propyl alcohol (*1-propanol*) which on subsequent treatment with NaOI ($I_2$/NaOH) does not give yellow ppt. of $CHI_3$ (*iodofor test*). This is because *n*-propyl alcohol obtained in the first step does not contain $CH_3CHOH$— group.

$$\underset{n\text{-Propyl iodide}}{CH_3CH_2CH_2I} + NaOH\,(aq) \longrightarrow \underset{n\text{-Propyl alcohol}}{CH_2CH_2CH_2OH} + NaI$$

$$\downarrow NaOI$$

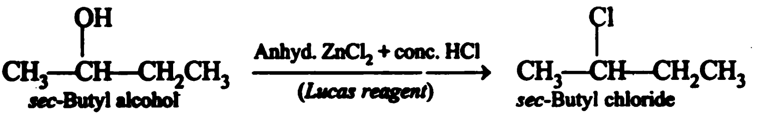
No yellow ppt. of $CHI_3$

**19. Distinguish between secondary butyl alcohol ($CH_3CHOHCH_2CH_3$) and tertiary butyl alcohol [$(CH_3)_3COH$]**

(*A.I.S.B. 1986*)

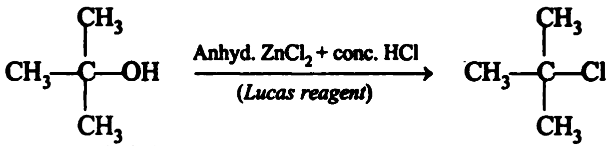
These two compounds can be easily distinguished by the folliwng tests :

(*i*) **Lucas test.** Tertiary butyl alcohol on treatment with *Lucas reagent* (anhyd. $ZnCl_2$ + conc. HCl) immediately produces turbidity but secondary butyl alcohol produces turbidity in about *five minutes*. This difference can be used to distinguish between the two compounds.



$$\underset{sec\text{-Butyl alcohol}}{CH_3{-}\overset{\overset{\large OH}{|}}{CH}{-}CH_2CH_3} \xrightarrow[\text{(Lucas reagent)}]{\text{Anhyd. }ZnCl_2\text{ + conc. HCl}} \underset{sec\text{-Butyl chloride}}{CH_3{-}\overset{\overset{\large Cl}{|}}{CH}{-}CH_2CH_3}$$

(*Turbidity appears in about five minutes*)



$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-OH \xrightarrow[\text{(Lucas reagent)}]{\text{Anhyd. }ZnCl_2+\text{conc. HCl}} CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-Cl$$

*tert*-Butyl alcohol *tert*-Butyl chloride

(*Turbidity appears immediately*)

(*ii*) **Iodoform test.** *sec.* Butyl alcohol ($CH_3CHOHCH_2CH_3$) contains the $CH_3CHOH$— group and hence responds to the iodoform test. However, tertiary butyl alcohol, $(CH_3)_3COH$ does not contain the $CH_3CHOH$— group and hence does not respond to the iodoform test.

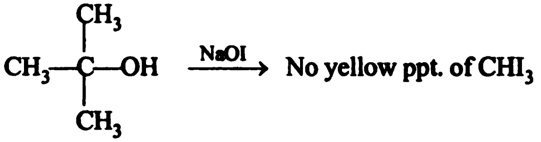
$$CH_3CHOH—CH_2CH_3 + NaOI \longrightarrow CH_3CO—CH_2CH_3 + NaI + H_2O$$

*sec*-Butyl alcohol 2-Butanone

$$CH_3CO—CH_2CH_3 + 3NaOI \longrightarrow CHI_3\downarrow + CH_3CH_2COONa + 2NaOH$$

2-Butanone Iodoform Sod. propionate

(*Yellow ppt.*)



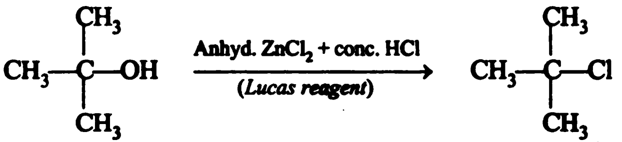
$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-OH \xrightarrow{NaOI} \text{No yellow ppt. of } CHI_3$$

*tert*-Butyl alcohol

**20. Distinguish between 1-propanol ($CH_3CH_2CH_2OH$) and 2-methyl-2-propanol or tert-butyl alcohol, $(CH_3)_3COH$** (*A.I.S.B. 1995*)

1-Propanol ($CH_3CH_2CH_2OH$) is a *primary alcohol* while 2-methyl-2-propanol $[CH_3)_3COH]$ is a *tertiary alcohol.* Therefore, these can may be easily distinguished by performing the *Lucas tests.*

2-Methyl-2-propanol (tert-butyl alcohol) being a tertiary alcohol on treatment with *Lucas reagent* (anhyd. $ZnCl_2$ + conc. HCl) immediately produces *turbidity* due to the formation of 2-chloro-2-methylpropane (*tert*-butyl chloride).



$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-OH \xrightarrow[\text{(Lucas reagent)}]{\text{Anhyd. }ZnCl_2+\text{conc. HCl}} CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-Cl$$

2-Methyl-2-propanol 2-Chloro-2-methylpropane

(*Turbidity appears immediately*)

On the other hand, 1-propanol being a 1° alcohol does not produce turbidity at room temperature on treatment with Lucas reagent, even on standing for some time.

$$CH_3CH_2CH_2OH \xrightarrow[\text{(Lucas reagent)}]{\text{Anhyd. }ZnCl_2+\text{conc. HCl}} \text{No turbidity at room temperature}$$

1-Propanol

**21. Distinguish between ethanol ($CH_3CH_2OH$) and phenol ($C_6H_5OH$)**

(*A.I.S.B. 1985; D.S.B. 1987*)

These two compounds may be distinguished by the following four tests :

(*i*) **Litmus test.** Phenol being *acidic* turns blue litmus red while ethanol being *neutral* does not give this test.

(*ii*) **$FeCl_3$ test.** Phenol gives a *violet colour* with $FeCl_3$ solution while ethanol does not.

$$\underset{\text{Phenol}}{3C_6H_5OH} + FeCl_3 \longrightarrow \underset{(\textit{Violet colour})}{(C_6H_5O)_3Fe} + 3HCl$$

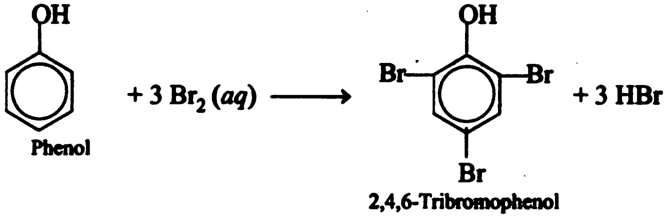
$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow{FeCl_3} \text{No violet colour}$$

(*iii*) **Iodoform test.** Ethanol on warming with NaOI ($I_2$/NaOH) gives yellow ppt. of iodoform while phenol does not give this test.

$$\underset{\text{Ethanol}}{CH_3CH_2OH} + 4NaOI \longrightarrow \underset{\substack{\text{Iodoform}\\(\textit{Yellow ppt.})}}{CHI_3\downarrow} + HCOONa + NaI + 2NaOH + H_2O$$

$$\underset{\text{Phenol}}{C_6H_5OH} \xrightarrow{NaOI} \text{No yellow ppt.}$$

(*iv*) **Bromine-water test.** Phenol readily undergoes electrophilic substituion reactions. Therefore, it decolourises bromine water giving white ppt. of 2, 4, 6-tribromophenol. Ethanol does not give this test.



$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow{Br_2\text{-water}} \text{No white ppt.}$$

(*v*) Distinction between the two compounds may also be made by performing *iodoform test.* Ethanol, which contains the $CH_3CHOH$— grouping responds to iodoform test and gives a yellow ppt. of iodoform with $I_2$ and NaOH. Phenol does not respond to this test.

### 22. Distinguish between ethanol ($CH_3CH_2OH$) and benzyl alcohol ($C_6H_5CH_2OH$)

Iodoform test may be performed to distinguish between the two :

Ethanol ($CH_3CH_2OH$) contains the —$CHOHCH_3$ group hence with $I_2$/NaOH it gives yellow ppt. of iodoform (*iodoform test*). Benzyl alcohol which does not contain the grouping —$CHOHCH_3$ doest not respond to iodoform test.

$$\underset{\text{Ehtanol}}{CH_3CH_2OH} + NaOI \longrightarrow \underset{\text{Acetalehyde}}{CH_3CHO} + H_2O + NaI$$

$$\underset{\text{Acetaldhyde}}{CH_3CHO + 3NaOI} \longrightarrow \underset{\substack{\text{Iodoform}\\(\textit{Yellow ppt.})}}{CHI_3\downarrow} + \underset{\text{Sod. formate}}{HCOONa} + 2NaOH$$

$$\underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} \xrightarrow{NaOI} \text{No yellow ppt.}$$

### 23. Distinguish between phenol ($C_6H_5OH$) and cyclohexanol ($C_6H_{11}OH$)

Following tests may be performed to distinguish between the two compounds.

(*i*) **Limtus test.** Phenol being *acidic* turns litmus red while cyclohexanol being *neutral* does not give this test.

(*ii*) **$FeCl_3$ test.** Phenol gives a *violet colour* with $FeCl_3$ solution but cyclohexanol does not.

(*iii*) **$Br_2$—water test.** Phenol decolourises bromine water giving a white ppt. of 2, 4, 6-tribromophenol while cyclohexanol does not give this test.

### 24. Distinguish between methanol ($CH_3OH$) and phenol ($C_6H_5OH$)

(*D.S.B. 1988; A.I.S.B. 1990 S*)

These two compounds may be distinguished by the following tests :

(*i*) **Litmus test.** Phenol being *acidic* turns blue litmus red while methanol being *neutral* has no effect on blue litmus.

(*ii*) **$FeCl_3$ test.** Phenol gives a violet colouration with $FeCl_3$ solution while methanol does not.

$$3C_6H_5OH + FeCl_3 \longrightarrow (C_6H_5O)_3Fe + 3HCl$$

(*iii*) **$Br_2$-water test.** Phenol readily decolourises bromine water giving a white ppt. of 2, 4, 6-tribromophenol but methanol does not.

$$C_6H_5OH + 3Br_2 \longrightarrow C_6H_2Br_3OH + 3HBr$$

### 25. Distinguish between acetaldehyde ($CH_3CHO$) and benzaldehyde ($C_6H_5CHO$)

(*D.S.B. 1998*)

These compounds can be distinguished by the following tests :

(*i*) **Fehling's solution test.** Aliphatic aldehydes reduce *Fehling's solution* but aromatic aldehydes do not. Thus, acetaldehyde gives a red ppt. of $Cu_2O$ with *Fehling's solution* but benzaldehyde does not.

$$\underset{\substack{\text{Acetaldehyde}\\(\textit{aliphatic})}}{CH_3CHO} + \underbrace{2Cu^{2+} + 5OH^-}_{(\textit{From Fehling's soln.})} \longrightarrow \underset{\text{Acetate ion}}{CH_3COO^-} + \underset{\substack{\text{Cuprous oxide}\\(\textit{Red. ppt.})}}{Cu_2O\downarrow} + 3H_2O$$

$$\underset{\substack{\text{Benzaldehyde}\\(\textit{aromatic})}}{C_6H_5CHO} \xrightarrow{\text{Fehling's solution}} \text{No red ppt. of } Cu_2O$$

(*ii*) **Iodoform test.** Acetaldehyde reacts with NaOl ($I_2$/NaOH) to form yellow ppt. of iodoform but benzaldehyde does not give this test.

$$\underset{\text{Acetaldehyde}}{CH_3CHO} + 3NaOI \longrightarrow \underset{\text{Sod. formate}}{HCOONa} + \underset{\substack{\text{Iodoform}\\ (\textit{Yellow ppt.})}}{CHI_3\downarrow} + 2NaOH$$

$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} \xrightarrow{I_2/NaOH} \text{No yellow ppt.}$$

### 26. Distinguish between acetaldehyde ($CH_3CHO$) and acetone ($CH_3COCH_3$) (*I.I.T. 1987; A.I.S.B. 1989; D.S.B. 1996*)

These compounds can be distinguished by the following two tests :

(*i*) **Fehling's solution test.** Acetadehyde reduces *Fehling's solution* to a red ppt. of $Cu_2O$ but acetone does not.

$$\underset{\text{Acetaldehyde}}{CH_3CHO} + \underbrace{2Cu^{2+} + 5OH^-}_{(\textit{From Fehling's soln.})} \longrightarrow \underset{\text{Acetate ion}}{CH_3COO^-} + \underset{\substack{\text{Cuprous oxide}\\ (\textit{Red ppt.})}}{Cu_2O\downarrow} + 3H_2O$$

$$\underset{\text{Acetone}}{CH_3COCH_3} \xrightarrow{\text{Fehling's solution}} \text{No action.}$$

(*ii*) **Tollen's reagent test.** Acetaldehyde reduces *Tollen's reagent* to silver mirror but acetone does not.

$$\underset{\text{Acetaldehye}}{CH_3CHO} + \underset{\text{Tollen's reagent}}{2[Ag(NH_3)_2]^+} + 3OH^- \longrightarrow \underset{\text{Acetate ion}}{CH_3COO^-} + 2H_2O + \underset{\text{Siliver mirror}}{2Ag\downarrow} + 4NH_3$$

$$\underset{\text{Acetone}}{CH_3COCH_3} \xrightarrow{\text{Tollen's solution}} \text{No action.}$$

### 27. Distinguish between benzaldehyde ($C_6H_5CHO$) and acetone ($CH_3COCH_3$).

These compounds can be distinguished by the following tests :

(*i*) **Tollen's reagent test.** Benzaldehyde reduces *Tollen's reagent* to produce a silver mirror but acetone being a ketone does not.

$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} + \underset{\text{Tollen's reagent}}{2[Ag(NH_3)_2]^+} + 3OH^- \longrightarrow$$

$$\underset{\text{Benzoate ion}}{C_6H_5COO^-} + 2H_2O + \underset{\text{Silver mirror}}{2Ag\downarrow} + 4NH_3$$

(*ii*) **Iodoform test.** Acetone being a *methyl ketone* on treatment with $I_2$/NaOH (NaOI) gives yellow ppt. of iodoform but benzaldehyde does not. (For reactions, refer to distinction between propanal and propanone).

### 28. Distinguish between propanal ($CH_3CH_2CHO$) and propanone ($CH_3COCH_3$) (*D.S.B. 1998*)

These compounds can be distinguished by the following tests :

(*i*) **Tollen's reagent test.** Propanal being an aldehyde reduces Tollen's reagent to silver mirror but propanone does not.

$$\underset{\text{Propanal}}{CH_3CH_2CHO} + \underset{\text{Tollen's reagent}}{2[Ag(NH_3)_2]^+ + 3OH^-} \longrightarrow$$

$$\underset{\text{Propionate ion}}{CH_3CH_2COO^-} + \underset{\text{Silver mirror}}{2Ag\downarrow} + 4NH_3 + 2H_2O$$

$$\underset{\text{Propanone}}{CH_3COCH_3} \xrightarrow{\text{Tollen's solution}} \text{No silver mirror.}$$

(*ii*) **Fehling's solution test.** Propanal also reduces *Fehling's solution* to red ppt. of $Cu_2$ but propanone does not.

$$\underset{\text{Propanal}}{CH_3CH_2CHO} + \underbrace{2Cu^{2+} + 5OH^-}_{\textit{(From Fehling's soln.)}} \longrightarrow \underset{\text{Benzoate ion}}{CH_3CH_2COO^-} + \underset{\substack{\text{Cuprous oxide}\\ \textit{(Red ppt.)}}}{Cu_2O\downarrow} + 3H_2O$$

(*iii*) **Iodoform test.** Propanone is a *methyl ketone.* On treatment with $I_2/$ NaOH (NaOI) it gives a yellow ppt. of iodoform but propanal does not.

$$\underset{\text{Propanone}}{CH_3COCH_3} + \underset{\text{Sod. hypoiodite}}{3NaOI} \longrightarrow \underset{\text{Iodoform}}{CHI_3\downarrow} + \underset{\text{Sod. acetate}}{CH_3COONa} + 2NaOH$$

$$\underset{\text{Propanal}}{CH_3CH_2CHO} \xrightarrow{\text{NaOI}} \text{No yellow ppt.}$$

**29. Distinguish between phenylacetaldehyde ($C_6H_5CH_2CHO$) and acetophenone ($C_6H_5COCH_3$)** (*D.S.B. 1981*)

These can be distinguished by the following tests :

(*i*) **Tollen's test and Fehling's test.** Phenylacetaldehyde being an *aldehyde* gives a silver mirror with *Tollen's reagent* and reduces *Fehling's solution* to red ppt. of $Cu_2O$ but acetophenone does not give these tests.

$$\underset{\text{Phenylacetaldehyde}}{C_6H_5CH_2CHO} + \underset{\text{Tollen's reagent}}{2[Ag(NH_3)_2]^+ + 3OH^-} \longrightarrow$$

$$\underset{\text{Phenyl acetate ion}}{C_6H_5CH_2COO^-} + \underset{\text{Silver mirror}}{2Ag\downarrow} + 4NH_3 + 2H_2O$$

$$C_6H_5CH_2CHO + \underbrace{2Cu^{2+} + 5OH^-}_{\textit{(Fehling's solution)}} \longrightarrow \underset{\text{Phenyl acetate ion}}{C_6H_5CH_2COO^-} + \underset{\substack{\text{Cuprous oxide}\\ \textit{(Red ppt.)}}}{Cu_2O} + 3H_2O$$

$$\underset{\text{Acetophenone}}{C_6H_5COCH_3} \xrightarrow{\text{Tollen's regant}} \text{No silver mirror}$$

$$\underset{\text{Acetophenone}}{C_6H_5COCH_3} \xrightarrow{\text{Fehling's solution}} \text{No red ppt. of } Cu_2O$$

(*ii*) **Iodoform test.** Acetophenone being a *methyl ketone* gives iodoform test, whereas phenylacetaldehyde does not.

$$\underset{\text{Acetophenone}}{C_6H_5COCH_3} + 3NaOI \longrightarrow C_6H_5COONa + \underset{\substack{\text{Iodoform}\\(\textit{Yellow ppt.})}}{CHI_3\downarrow} + 2NaOH$$

$$\underset{\text{Phenylacetaldehyde}}{C_6H_5CH_2CHO} \xrightarrow{NaOI} \text{No yellow ppt. of } CHI_3$$

**30. Distinguish between pentanal ($CH_3CH_2CH_2CH_2CHO$) and diethyl ketone ($CH_3CH_2COCH_2CH_3$)** (*Roorkee 1985*)

These compounds can be distinguished by the following two tests :

(*i*) **Fehling's solution test.** Pentanal being an aldehyde reduces *Fehling's solution* to red ppt. of $Cu_2O$ but diethyl ketone does not.

$$\underset{\text{Pentanal}}{CH_3CH_2CH_2CH_2CHO} + \underbrace{2Cu^{2+} + 5OH^-}_{(\textit{Fehling's solution})} \longrightarrow$$

$$\underset{\text{Pentanoate ion}}{CH_3CH_2CH_2CH_2COO^-} + \underset{\substack{\text{Cuprous oxide}\\(\textit{Red ppt.})}}{Cu_2O\downarrow} + 3H_2O$$

$$\underset{\text{Diethyl ketone}}{CH_3CH_2COCH_2CH_3} \xrightarrow{\text{Fehling's solution}} \text{No red ppt.}$$

(*ii*) **Tollen's test.** Pentanal being an aldehyde gives a silver mirror when treated with *Tollen's reagent* whereas diethyl ketone does not.

$$\underset{\text{Pentanal}}{CH_3CH_2CH_2CH_2CHO} + \underset{\text{Tollen's reagent}}{2[Ag(NH_3)_2]^+} + 3OH^- \longrightarrow$$

$$\underset{\text{Pentanoate ion}}{CH_3CH_2CH_2CH_2COO^-} + \underset{\text{Silver mirror}}{2Ag\downarrow} + 4NH_3 + 2H_2O$$

$$\underset{\text{Diethyl ketone}}{CH_3CH_2COCH_2CH_3} \xrightarrow{\text{Tollen's solution}} \text{No silver mirror.}$$

**31. Distinguish between pentanone-2 ($CH_3COCH_2CH_2CH_3$) and pentanone-3-($CH_3CH_2COCH_2CH_3$)**

(*D.S.B. 1987, 88; A.I.S.B. 1988*)

These compounds can be distinguished by the iodoform test :

**Iodoform test.** 2-Pentanone being a *methyl ketone* when treated with NaOI ($I_2$/NaOH) gives yellow ppt. of iodoform but 3-pentanone does not.

$$\underset{\text{2-Pentanone}}{CH_3CH_2CH_2COCH_3} + 3NaOI \longrightarrow$$

$$\underset{\text{Sod. butyrate}}{CH_3CH_2CH_2COONa} + \underset{\substack{\text{Iodoform}\\(\textit{Yellow ppt.})}}{CHI_3\downarrow} + 2NaOH$$

$$\underset{\text{3-Pentanone}}{CH_3CH_2COCH_2CH_3} \xrightarrow{NaOI} \text{No yellow ppt.}$$

### 32. Distinguish between diethyl ketone ($CH_3CH_2COCH_2CH_3$) and acetone ($CH_3COCH_3$) *(Roorkee 1986; D.S.B. 1996)*

These compounds can be distinguished by the iodoform tests :

**Iodoform test.** Acetone being a *methyl ketone* gives yellow ppt. of iodoform when treated with NaOI ($I_2$/NaOH) but diethyl ketone does not give this test.

$$\underset{\text{Acetone}}{CH_3COCH_3} + 3NaOI \longrightarrow \underset{\text{Sod. acetate}}{CH_3COONa} + 2NaOH + \underset{\substack{\text{Iodoform}\\ (\textit{Yellow ppt.})}}{CHI_3\downarrow}$$

$$\underset{\text{Diethyl ketone}}{(CH_3CH_2)_2C=O} \xrightarrow{NaO1} \text{No yellow ppt.}$$

### 33. Distinguish between acetophenone ($C_6H_5COCH_3$) and benzophenone ($C_6H_5COC_6H_5$).

These compounds can be distinguished by the iodoform test.

**Iodoform test.** Acetopehnone being a *methyl ketone* when treated with NaOI ($I_2$/NaOH) gives yellow ppt. of iodoform but benzophenone does not.

$$\underset{\text{Acetophenone}}{C_6H_5COCH_3} + 3NaO1 \longrightarrow \underset{\text{Sod. benzoate}}{C_6H_5COONa} + \underset{\substack{\text{Iodoform}\\ (\textit{Yellow ppt.})}}{CHI_3\downarrow} + 2NaOH$$

$$\underset{\text{Benzophenone}}{C_6H_5COC_6H_5} \xrightarrow{NaOI} \text{No yellow ppt.}$$

### 34. Distinguish between phenol ($C_6H_5OH$) and acetic acid ($CH_3COOH$)

These compounds may be distinguished by the following tests.

(*i*) **$FeCl_3$ test.** Phenol gives a violet colouration with neutral $FeCl_3$ solution but acetic acid gives buff coloured ppt. of ferric acetate.

$$\underset{\text{Phenol}}{3C_6H_5OH} + FeCl_3 \longrightarrow \underset{(\textit{Violet colouration})}{(C_6H_5O)_3Fe + 3HCl}$$

$$\underset{\text{Acetic acid}}{3CH_3COOH} + FeCl_3 \longrightarrow \underset{(\textit{Buff coloured ppt.})}{(CH_3COO)_3Fe + 3HCl}$$

(*ii*) **$NaHCO_3$ test.** Acetic acid being a stronger acid decomposes $NaHCO_3$ to evolve $CO_2$ but phenol does not.

$$\underset{\text{Acetic acid}}{CH_3COOH} + NaHCO_3 \longrightarrow \underset{\text{Sod. acetate}}{CH_3COONa} + CO_2\uparrow + H_2O$$

$$C_6H_5OH \xrightarrow{NaHCO_3} \text{No evolution of } CO_2$$

### 35. Distinguish between benzoic acid ($C_6H_5COOH$) and phenol ($C_6H_5OH$) *( D.S.B. 1992; A.I.S.B. 2002; A.I.S.B. 2004)*

These compounds may be distinguished by the following tests :

(*i*) **$FeCl_3$ test.** Phenol gives a violet colouration with netural $FeCl_3$ solution while benzoic acid gives buff coloured ppt. of ferric benzoate.

$$\underset{\text{Phenol}}{3C_6H_5OH} + FeCl_3 \longrightarrow \underset{(\textit{Violet colouration})}{(C_6H_5O)_3Fe} + 3HCl$$

$$\underset{\text{Benzoic acid}}{3C_6H_5COOH} + FeCl_3 \longrightarrow \underset{(\textit{Buff coloured ppt.})}{(C_6H_5COO)_3Fe} + 3HCl$$

(*ii*) **$NaHCO_3$ test.** Benzoic acid being a stronger acid decomposes $NaHCO_3$ to evolve $CO_2$ but phenol does not.

$$\underset{\text{Benzoic acid}}{C_6H_5COOH} + NaHCO_3 \longrightarrow \underset{\text{Sod. benzoate}}{C_6H_5COONa} + CO_2\uparrow + H_2O$$

$$\underset{\text{Phenol}}{C_6H_5OH} \xrightarrow{NaHCO_3} \text{No evolution of } CO_2.$$

**36. Distinguish betwen formic acid (HCOOH) and acetic acid ($CH_3COOH$).**

Formic acid contains both an aldehydic $(\overset{\overset{H}{|}}{—C}=O)$ as well as a carboxyl group $(\overset{\overset{O}{\|}}{—C}—OH)$ but acetic acid contains only a carboxyl group. Therefore, formic acid behaves as a *reducing agent* whereas acetic acid does not. These acids may be distinguished by the following tests :

(*i*) **Fehling's solution test.** Formic acid reduces *Fehling's solution* to red ppt. of $Cu_2O$ but acetic acid does not.

$$\underset{\text{Formic acid}}{HCOOH} + \underbrace{2Cu^{2+} + 4OH^-}_{(\textit{Fehling's solution})} \longrightarrow \underset{\substack{\text{Cuprous oxide}\\(\textit{Red ppt.})}}{Cu_2O\downarrow} + CO_2\uparrow + 3H_2O$$

$$\underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{\text{Fehling's solution}} \text{No red ppt. of } Cu_2O.$$

(*ii*) **Tollen's reagent test.** Formic acid reduces *Tollen's reagent* to metallic silver but acetic acid does not.

$$\underset{\text{Formic acid}}{HCOOH} + \underset{\text{Tollen's reagent}}{2[Ag(NH_3)_2]^+} + 2OH^- \longrightarrow \underset{\text{Silver mirror}}{2Ag\downarrow} + CO_2\uparrow + 2H_2O + 4NH_3$$

$$\underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{\text{Tollen's solution}} \text{No silver mirror}$$

(*iii*) **$KMnO_4$ test.** Formic acid decolourises acidified $KMnO_4$ solution while acetic acid does not give this test.

$$\underset{\text{Formic acid}}{5HCOOH} + 2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 5CO_2\uparrow + 8H_2O$$

$$\underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow[H_2SO_4]{KMnO_4} \text{Does not discharge pink colour of } KMnO_4 \text{ solution}$$

(*iv*) **$HgCl_2$ test.** Formic acid reduces $HgCl_2$ to give white ppt. of $Hg_2Cl_2$ while acetic acid does not give this test.

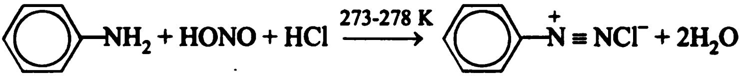
$$\underset{\text{Formic acid}}{HCOOH} + \underset{\text{Mercuric}}{2HgCl_2} \longrightarrow \underset{\substack{\text{Mercurous chloride}\\ (\textit{White ppt.})}}{Hg_2Cl_2\downarrow} + 2HCl + CO_2\uparrow$$

$$\underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{HgCl_2} \text{No white ppt. of } Hg_2Cl_2.$$

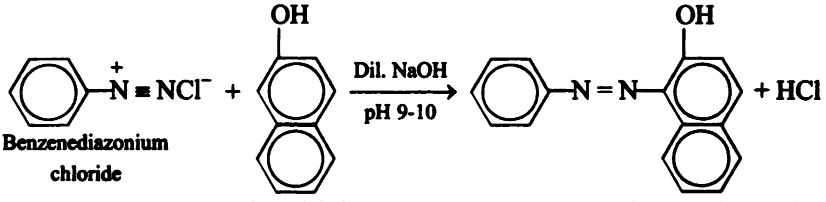
### 37. Distinguish between ethylamine ($CH_3CH_2NH_2$) and aniline ($C_6H_5NH_2$) (*A.I.S.B. 1985 S; D.S.B. 1989*)

Ethylamine is a *primary aliphatic amine* while aniline is a *primary aromatic amine.* Azo dye test may be performed to distinguish between the two.

**Azo dye test.** It involves the reaction of an aromatic priamry amine with $HNO_2(NaNO_2 + \text{dil. } HCl)$ at 273—278 K followed by treatment with an alkaline solution of 2-naphthol (β-naphthol) A brilliant yellow, orange or red colured dye is obtained.



Aniline Benzenediazonium chloride



Benzenediazonium chloride β-Naphthol 1-Phenylazo-2-naphtol (*Orange dye*)

Aliphatic priamry amines under these conditions do not give the dye test but give a brisk evolution of $N_2$ gas with the formation of primary alcohol.

$$\underset{\text{Ethylamine}}{C_2H_5NH_2} + HONO \xrightarrow{273\text{-}278\text{ K}} \underset{\text{Ethyl alcohol}}{C_2H_5OH} + N_2\uparrow + H_2O$$

### 38. Distinguish between Methylamine ($CH_3NH_2$) and dimethylamine ($CH_3NHCH_3$) (*A.I.S.B. 1990 S*)

These may be disginguished by both *carbylamine test* and *Hinsberg's test.*

(*i*) **Carbylamine test**

$$CH_3NH_2 + CHCl_3 + 3KOH\,(\text{alc}) \xrightarrow{\text{Heat}} \underset{\substack{\text{Methyl isocyanide}\\ (\textit{offensive smell})}}{CH_3NC} + 3KCl + 3H_2O$$

$$(CH_3)_2NH \xrightarrow{CHCl_3/KOH} \text{No reaction}$$

(*ii*) **Hinsberg test**

$$C_6H_5SO_2Cl + CH_3NH_2 \longrightarrow C_6H_5SO_2\text{—}NHCH_3 + HCl$$

Benzene sulphonyl Chloride (Hinsberg reagent) . Methyl amine — N-methyl benzene sulphonamide

$$\downarrow KOH$$

$$[C_6H_5SO_2\text{—}\bar{N}\text{—}CH_3]K^+ + H_2O$$

(soluble in aq. KOH)

**39. Distinguish between ethylamine ($CH_3CH_2NH_2$) and diethylamine ($CH_3CH_2NHCH_2CH_3$)** (*I.I.T. 1988*)

Ethylamine is a primary amine whereas diethylamine is a secondary amine. These may be distinguished by the following tests :

(*i*) **Hinsberg's test.** Ethylamine and diethylamine can be distinguished using *Hingsberg's reagent, i.e.,* benzenesulphonyl chloride ($C_6H_5SO_2Cl$). When treated with *Hingsberg's reagent,* ethylamine gives N-ethyl-benzene-sulphonamide which is soluble in aq. KOH solution.

$$C_6H_5SO_2Cl + CH_3CH_2NH_2 \longrightarrow C_6H_5SO_2\text{—}NHCH_2CH_3 + HCl$$

Benzenesulphonyl chloride (Hinsberg's reagent) — Ethylamine — N-Ethylbenzenesulphonamide

$$\downarrow KOH$$

$$[C_6H_5SO_2\text{—}\bar{N}CH_2CH_3]K^+ + H_2O$$

(*Soluble in aq. KOH*)

Diethylamine gives N, N-diethylbenzenesulphonamide which is insoluble in aqueous KOH solution.

$$C_6H_5SO_2Cl + (CH_3CH_2)NH \longrightarrow C_6H_5SO_2\text{—}N(CH_2CH_3)_2 + HCl$$

Hingsberg's reagent — Diethylamine — N, N-Diethylbenzenesulphonamide

(*Insoluble in aq. KOH*)

(*ii*) **Carbylamine test.** Ethylamine when heated with an alcoholic solution of KOH and $CHCl_3$ gives offensive smell of ethyl isocyanide. Diethylamine is a *secondary* amine and hence does not give this test.

$$CH_3CH_2NH_2 + CHCl_3 + 2KOH \xrightarrow{Heat} CH_3CH_2NC + 3KCl + 3H_2O$$

Ethylamine (*1° Amine*) — (*alc.*) — Ethyl isocyanide (*Offensive smell*)

$$(CH_3CH_2)_2NH \xrightarrow[Heat]{CHCl_3/KOH} \text{No reaction}$$

Diethylamine (2° *Amine*)

**40. Distinguish between ethyl cyanide ($C_2H_5CN$) and ethyl isocyanide ($C_2H_5NC$)**

These compounds may be distinguished by the hydrolysis test :

**Hydrolysis test.** Ethyl cyanide on hydrolysis with aqueous mineral acid gives propionic acid which does not reduce *Tollen's reagent.* Ethyl isocyanide on similar hydrolysis gives formic acid which reduces *Tollen's reagent.*

$$\underset{\text{Ethyl cyanide}}{CH_3CH_2CN} + 2H_2O + HCl \longrightarrow \underset{\text{Propionic acid}}{CH_3CH_2COOH} + NH_4Cl$$

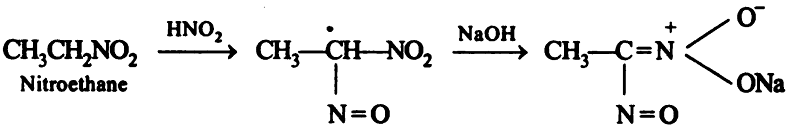
$$\underset{\text{Ethyl isocyanide}}{CH_3CH_2{-}N\overset{\rightarrow}{\equiv}C} + 2H_2O \xrightarrow{HCl} \underset{\text{Ethylamine}}{CH_3CH_2NH_2} + \underset{\text{Formic acid}}{HCOOH}$$

$$\underset{\text{Formic acid}}{HCOOH} + \underset{\text{Tollen's reagent}}{2[Ag(NH_3)_2]^+} + 2OH^- \longrightarrow \underset{\text{Silver mirror}}{2\,Ag\downarrow} + CO_2\uparrow + 4NH_3 + 2H_2O$$

**41. Distinguish between ethyl nitrite ($C_2H_5ONO$) and nitroethane ($C_2H_5NO_2$)**

These may be distinguished by the $HNO_2$ test :

Nitroethane gives a blood red colouration when treated with nitrous acid followed by aqueous NaOH solution. Ethyl nitrite does not respond the test



$$\underset{\text{Nitroethane}}{CH_3CH_2NO_2} \xrightarrow{HNO_2} \underset{\text{Nitrolic acid}}{CH_3{-}\underset{N=O}{\underset{|}{C}H}{-}NO_2} \xrightarrow{NaOH} \underset{(\textit{Blood red colouration})}{CH_3{-}\underset{N=O}{\underset{|}{C}}{=}\overset{+}{N}\langle^{O^-}_{ONa}}$$

$$\underset{\text{Ethyl nitrite}}{CH_3CH_2ONO} \xrightarrow[(ii)\ Ag.NaOH]{(i)\ HNO_2} \text{No blood red colouration.}$$

**42. Suggest a test for distinguishing between formaldehyde and acetaldehyde. (A.I.S.B. 2002)**

The two compounds may be distinguished by performing the iodoform test with NaOI ($I_2$/NaOH). Acetaldehyde gives a yellow precipitate while formaldehyde does not.

$$CH_3CHO + 3\,NaOI \longrightarrow CHCOONa + \underset{\substack{\text{Iodoform}\\\text{(yellow ppt.)}}}{CHI_3} + 2NaOH$$

**43. Describe simple chemical tests to distinguish between the following pairs of compounds :**

**(*i*) Propanal and Propanone**

**(*ii*) Phenol and Benzoic acid**

**(*iii*) Diethyl ether and Propanol (A.I.S.B. 2004)**

**Ans.** (*i*) Propanal and Propanone see Sr. No. 28 in this chapter.

(*ii*) Phenol and Benzoic acid. See Sr. No. 35 in this chapter.

(*iii*) Diethyl ether and Propanol

(*a*) **Sodium metal Test.** On treatment with a piece of sodium metal propanol evolves hydrogen gas while propanone does not.

$$\underset{\text{Propanol}}{CH_3CH_2CH_2OH} + Na \rightarrow \underset{\text{Sodium propoxide}}{CH_3CH_2CH_2ONa} + \tfrac{1}{2}H_2$$

(*b*) **$PCl_5$ Test.** On treatment with $PCl_5$ in cold, propanol reacts to form propyl chloride, while diethyl ether does not.

$$CH_3CH_2CH_2OH + PCl_5 \rightarrow CH_3CH_2CH_2Cl + POCl_3 + HCl$$

# 5

# Organic Conversions (Aliphatic and Aromatic)

## ASCENT OF SERIES

The conversion of an organic compound into its higher homologue is called *ascent of series or stepping up the series.* In ascent of series, the length of the carbon chain is increased by one more carbon atom at a time. Following reactions are carried out in order to effect ascent of series.

(*i*) **By Wurtz reaction**

(*ii*) **Through introducing cyanide (—C ≡ N group)**

(*iii*) **Through Grignard reaction**

Wurtz reaction is especially used for ascent of series of hydrocarbons.

Starting material is invariably an *alkyl halide.* Therefore, to bring about these conversions, the given compound is first converted into its corresponding alkyl halide which is then subjected to any one of the above three reactions as explained hereunder.

(*i*) *Conversion of a lower alkane, R —H to a higher alkane, R —R through Wurtz reaction.*

$$\underset{\text{Alkane}}{\text{R—H}} \xrightarrow{X_2/h\nu} \underset{\text{Alkyl halide}}{\text{R—X}} \xrightarrow[(\textit{Wurtz reaction})]{\text{Na/Dry ether}} \underset{\text{Alkane}}{\text{R—R}}$$

(*ii*) *Conversion of a lower alcohol, ROH to a higher alcohol, $RCH_2OH$ through cyanide method.*

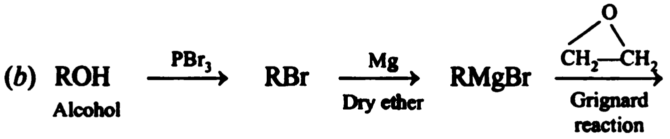
$$\underset{\text{Alcohol}}{\text{ROH}} \xrightarrow{P + I_2} \underset{\substack{\text{Alkyl}\\ \text{iodide}}}{\text{R—I}} \xrightarrow[\text{Heat}]{\text{Alc. KCN}} \underset{\substack{\text{Alkyl}\\ \text{cyanide}}}{\text{R—CN}} \xrightarrow[\substack{\text{or Na/alcohol}\\ (\textit{Reduction})}]{\text{LiAlH}_4}$$

$$\underset{1^\circ\ \text{Amine}}{RCH_2NH_2} \xrightarrow[(\text{NaNO}_2 + \text{dil. HCl})]{\text{HNO}_2} \underset{\text{Higher alcohol}}{RCH_2OH}$$

(*iii*) (*a*) *Conversion of a lower alcohol, ROH to a higher alcohol, $RCH_2OH$, through Grignard reaction.*

$$\underset{\text{Alcohol}}{\text{ROH}} \xrightarrow{\text{PBr}_3} \underset{\substack{\text{Alkyl}\\ \text{bromide}}}{\text{R—Br}} \xrightarrow[\text{in dry ether}]{\text{Mg}} \underset{\substack{\text{Gringnard}\\ \text{reagent}}}{\text{R—MgBr}} \xrightarrow{\text{HCHO}}$$

$$\underset{\text{Addition product}}{[RCH_2OMgBr]} \xrightarrow{H^+/H_2O} \underset{\text{Higher alcohol}}{RCH_2OH}$$



(*b*) $$\underset{\text{Alcohol}}{ROH} \xrightarrow{PBr_3} RBr \xrightarrow[\text{Dry ether}]{Mg} RMgBr \xrightarrow[\text{Grignard reaction}]{\overset{O}{CH_2—CH_2}}$$

$$\underset{\text{Addition product}}{[RCH_2CH_2OMgBr]} \xrightarrow{H^+/H_2O} \underset{\text{(Alcohol containing two carbons more)}}{RCH_2CH_2OH}$$

## ASCENT OF SERIES (WURTZ REACTION)

**EXAMPLES**

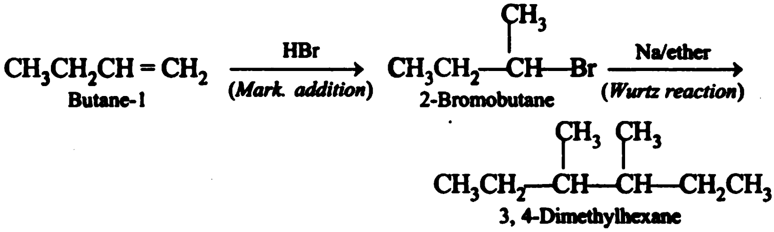
**1. Convert methane into ethane**

$$\underset{\text{Methane}}{CH_4} \xrightarrow[-HCl]{Cl_2,\ \text{light}} \underset{\text{Methyl chloride}}{CH_3Cl} \xrightarrow[\textit{(Wurtz reaction)}]{\text{Na/ether}} \underset{\text{Ethane}}{CH_3CH_3}$$

**2. Convert ethane into n-butane**

$$\underset{\text{Ethane}}{CH_3—CH_3} \xrightarrow[-HBr]{Br_2/h\nu} \underset{\text{Ethyl bromide}}{CH_3CH_2Br} \xrightarrow[\textit{(Wurtz reaction)}]{\text{Na/ether}} \underset{n\text{-Butane}}{CH_3CH_2—CH_2CH_3}$$

**3. Convert butene-1 to 3, 4-dimethylhexane**



$$\underset{\text{Butane-1}}{CH_3CH_2CH = CH_2} \xrightarrow[\textit{(Mark. addition)}]{HBr} \underset{\text{2-Bromobutane}}{CH_3CH_2—\overset{\overset{CH_3}{|}}{CH}—Br} \xrightarrow[\textit{(Wurtz reaction)}]{\text{Na/ether}}$$

$$\underset{\text{3, 4-Dimethylhexane}}{CH_3CH_2—\overset{\overset{CH_3}{|}}{CH}—\overset{\overset{CH_3}{|}}{CH}—CH_2CH_3}$$

## ASCENT OF SERIES (CYANIDE METHOD)

**EXAMPLES**

**4. Convert methyl iodide into ethyl iodide**

$$\underset{\text{Methyl iodide}}{CH_3I} \xrightarrow[-KI]{KCN} \underset{\text{Acetonitirle}}{CH_3CN} \xrightarrow[\textit{(Reduction)}]{Na/C_2H_5OH} \underset{\text{Ethylamine}}{CH_3CH_2NH_2} \xrightarrow[-N_2,\ -H_2O]{HONO}$$

$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[\text{or } PI_3]{P + I_2} \underset{\text{Ethyl iodide}}{CH_3CH_2I}$$

**5. Convert methanol into ethanol**

(*A.I.S.B. 1985 S ; D.S.B 1992 ; C.B.S.E. Sample Paper, 1997*)

$$\underset{\text{Methanol}}{CH_3OH} \xrightarrow[\text{or } PI_3]{P + I_2} \underset{\text{Methyl iodide}}{CH_3I} \xrightarrow[-KI]{KCN} \underset{\text{Acetonitrile}}{CH_3CN} \xrightarrow[\text{(Reduction)}]{Na/C_2H_5OH}$$

$$\underset{\text{Ethylamine}}{CH_3CH_2NH_2} \xrightarrow[-N_2,\ -H_2O]{HONO} \underset{\text{Ethanol}}{CH_3CH_2OH}$$

*Alternatively* $\underset{\text{Acetonitrile}}{CH_3CN} \xrightarrow[\text{(Hydrolysis)}]{H^+/H_2O} \underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow[\text{(Reduction)}]{LiAlH_4} \underset{\text{Ethanol}}{CH_3CH_2OH}$

**6. Convert acetic acid to propionic acid** (*D.S.B. 1992 S*)

$$\underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow[\text{(Reduction)}]{LiAlH_4} \underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[\text{or } PI_3]{P + I_2} \underset{\text{Ethyl iodide}}{CH_3CH_2I} \xrightarrow[-KI]{KCN}$$

$$\underset{\substack{\text{Propiononitrile} \\ \text{(Ethyl cyanide)}}}{CH_3CH_2CN} \xrightarrow[\text{(Hydrolysis)}]{H^+/H_2O} \underset{\text{Propionic acid}}{CH_3CH_2COOH}$$

**7. Convert methylamine into ethylamine**

$$\underset{\text{Methylamne}}{CH_3NH_2} \xrightarrow[-N_2,\ -H_2O]{HONO} \underset{\text{Methanol}}{CH_3OH} \xrightarrow[\text{or } PI_3]{P + I_2} \underset{\text{Methyl iodide}}{CH_3I} \xrightarrow[-KI]{KCN}$$

$$\underset{\text{Acetonitrile}}{CH_3CN} \xrightarrow[\text{(Reduction)}]{Na/C_2H_5OH} \underset{\text{Ethylamine}}{CH_3CH_2NH_2}$$

## ASCENT OF SERIES (GRIGNARD REACTION)

**EXAMPLES**

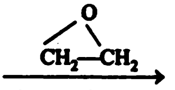
**8. Convert methanol to ethanol (Methyl alcohol to ethyl alcohol)**

(*A.I.S.B. 1985 S ; D.S.B. 1992*)

$$\underset{\text{Methanol}}{CH_3OH} \xrightarrow{P + I_2} \underset{\text{Methyl iodide}}{CH_3I} \xrightarrow{\text{Mg/Dry ether}} \underset{\text{Methylmag.iodide}}{CH_3MgI} \xrightarrow{HCHO}$$

$$\underset{\text{Addition product}}{[CH_3CH_2OMgI]} \xrightarrow{H^+/H_2O} \underset{\text{Ethanol}}{CH_3CH_2OH}$$

**9. Convert methanol to 1-propanol (Methyl alcohol to n-propyl alcohol)**



$$\underset{\text{Methanol}}{CH_3OH} \xrightarrow{PBr_3} \underset{\text{Methyl bromide}}{CH_3Br} \xrightarrow{\text{Mg/Dry ether}} \underset{\text{Methyl mag. bromide}}{CH_3MgBr} \xrightarrow[\text{(Grignard reaction)}]{\overset{O}{CH_2-CH_2}}$$

$$\underset{\text{Addition product}}{[CH_3CH_2CH_2OMgBr]} \xrightarrow[\text{Hydrolysis}]{H^+/H_2O} \underset{\text{1-Propanol}}{CH_3CH_2CH_2OH}$$

### 10. Convert ethanol to 1-propanol (Ethyl alcohol to n-propyl alcohol)

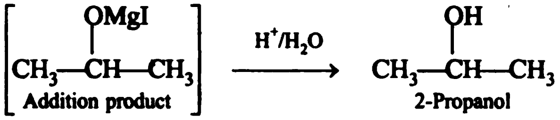
*(I.S.M. Dhanbad. 1991)*

$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow{PBr_3} \underset{\text{Ethyl bromide}}{CH_3CH_2Br} \xrightarrow{\text{Mg/Dry ether}} \underset{\text{Ethyl mag. bromide}}{CH_3CH_2MgBr} \xrightarrow[\text{(Grignard reaction)}]{HCHO}$$

$$\underset{\text{Addition product}}{[CH_3CH_2CH_2OMgBr]} \xrightarrow{H^+/H_2O} \underset{\text{1-propanol}}{CH_3CH_2CH_2OH}$$

### 11. Convert methanol to 2-propanol (Methyl alcohol to isopropyl alcohol)

$$\underset{\text{Methanol}}{CH_3OH} \xrightarrow[\text{or } PI_3]{P + I_2} \underset{\text{Methyl Iodide}}{CH_3—I} \xrightarrow{\text{Mg/Dry ether}} \underset{\text{Methyl mag. iodide}}{CH_3MgI} \xrightarrow[\text{(Grignard reaction)}]{CH_3CHO}$$

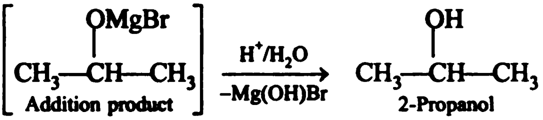


$$\left[\underset{\text{Addition product}}{CH_3—\overset{\overset{OMgI}{|}}{CH}—CH_3}\right] \xrightarrow{H^+/H_2O} \underset{\text{2-Propanol}}{CH_3—\overset{\overset{OH}{|}}{CH}—CH_3}$$

### 12. Convert ethanol into 2-propanol

*(A.I.S.B. 1994)*

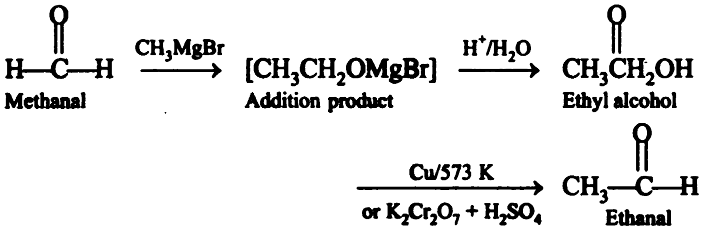
$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[\text{(Controlled oxidation)}]{K_2Cr_2O_7 + H_2SO_4} \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow[\text{(Grignard reaction)}]{CH_3MgBr}$$



$$\left[\underset{\text{Addition product}}{CH_3—\overset{\overset{OMgBr}{|}}{CH}—CH_3}\right] \xrightarrow[-Mg(OH)Br]{H^+/H_2O} \underset{\text{2-Propanol}}{CH_3—\overset{\overset{OH}{|}}{CH}—CH_3}$$

### 13. Convert methanal to ethanal (Formaldehyde to acetaldehyde)

*(I.I.T. 1981)*

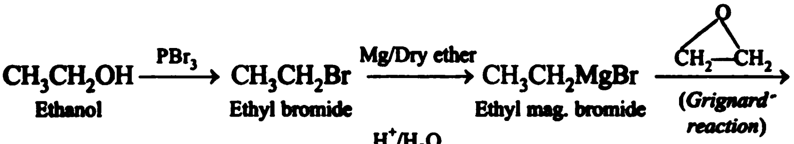


$$\underset{\text{Methanal}}{H—\overset{\overset{O}{\|}}{C}—H} \xrightarrow{CH_3MgBr} \underset{\text{Addition product}}{[CH_3CH_2OMgBr]} \xrightarrow{H^+/H_2O} \underset{\text{Ethyl alcohol}}{CH_3CH_2OH}$$

$$\xrightarrow[\text{or } K_2Cr_2O_7 + H_2SO_4]{\text{Cu/573 K}} \underset{\text{Ethanal}}{CH_3—\overset{\overset{O}{\|}}{C}—H}$$

### 14. Convert ethanol to 1-butanol (Ethyl alcohol to n-butyl alcohol)

*(I.S.M. Dhanbad, 1991)*



$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow{PBr_3} \underset{\text{Ethyl bromide}}{CH_3CH_2Br} \xrightarrow{\text{Mg/Dry ether}} \underset{\text{Ethyl mag. bromide}}{CH_3CH_2MgBr} \xrightarrow[\text{(Grignard reaction)}]{\overset{O}{CH_2—CH_2}}$$

$$\underset{\text{Addition product}}{[CH_3CH_2CH_2CH_2OMgBr]} \xrightarrow{H^+/H_2O} \underset{\text{1-Butanol}}{CH_3CH_2CH_2CH_2OH}$$

## DESCENT OF SERIES

The conversion an organic compound into lower homologue is called *descent of series or steping down the series.* In these conversions, the length of the carbon chain is decreased by one or more carbon atoms at a time. Following two methods are utilized for this purpose.

(*i*) By heating sodium salt of a fatty acid with sodalime (CaO + NaOH) (decarboxylation)

(*ii*) Hofmann bromamide reaction.

## DESCENT OF SERIES BY HEATING SODIUM SALT OF A FATTY ACID WITH SODALIME (CaO + NaOH)

### EXAMPLES

**15. Convert ethane to Methane**

$$\underset{\text{Ethane}}{CH_3CH_3} \xrightarrow[-HCl]{Cl_2/h\nu} \underset{\text{Ethyl chloride}}{CH_3CH_2Cl} \xrightarrow[\textit{(Hydrolysis)}]{\text{Aq. KOH}} \underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[\textit{(Oxidation)}]{K_2Cr_2O_7 + H_2SO_4}$$

$$\underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow[\textit{(Oxidation)}]{K_2Cr_2O_7 + H_2SO_4} \underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow[-H_2O]{NaOH} \underset{\text{Sod. acetate}}{CH_3COONa}$$

$$\xrightarrow[\textit{(Decarboxylation)}]{CaO + NaOH,\ \Delta} \underset{\text{Methane}}{CH_4}$$

**16. Convert propionic acid to ethane**

$$\underset{\text{Propionic acid}}{CH_3CH_2COOH} \xrightarrow[-H_2O]{NaOH} \underset{\text{Sod. Propionate}}{CH_3CH_2COONa} \xrightarrow[\textit{(Decarboxylation)}]{CaO + NaOH,\ \Delta} \underset{\text{Ethane}}{CH_3{-}CH_3}$$

## DESCENT OF SERIES BY HOFMANN BROMAMIDE REACTION

### EXAMPLES

**17. Convert ethyl iodide into methyl iodide**

$$\underset{\text{Ethyl iodide}}{CH_3CH_2I} \xrightarrow[\textit{(Hydrolysis)}]{\text{Aq. KOH}} \underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[\textit{(Oxidation)}]{K_2Cr_2O_7 + H_2SO_4} \underset{\text{Acetaldehyde}}{CH_3CHO}$$

$$\xrightarrow[\textit{(Oxidation)}]{K_2Cr_2O_7 + H_2SO_4} \underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{NH_3} \underset{\text{Amm. acetate}}{CH_3COONH_4} \xrightarrow[-H_2O]{\Delta}$$

$$\underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow[\textit{(Hofmann bromamide reaction)}]{Br_2/KOH} \underset{\text{Methylamine}}{CH_3NH_2} \xrightarrow[-N_2,\ -H_2O]{HONO}$$

$$\underset{\text{Methanol}}{CH_3OH} \xrightarrow[\text{or } PI_3]{P + I_2} \underset{\text{Methyl iodide}}{CH_3I}$$

### 18. Convert ethanol into methanol (*D.S.B. 1992*)

$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[\text{(Oxidation)}]{K_2Cr_2O_7 + H_2SO_4} \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow[\text{(Oxidation)}]{K_2Cr_2O_7 + H_2SO_4} \underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{NH_3}$$

$$\underset{\text{Ammonium acetate}}{CH_3COONH_4} \xrightarrow[-H_2O]{\text{Heat}} \underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow[\text{(Hofmann bromamide reaction)}]{Br_2/KOH} \underset{\text{Methanamine}}{CH_3NH_2}$$

$$\xrightarrow[-N_2,\ -H_2O]{HONO} \underset{\text{Methanol}}{CH_3OH}$$

### 19. Convert acetaldehyde into formaldehyde

$$\underset{\text{Acetaldehye}}{CH_3CHO} \xrightarrow{K_2Cr_2O_7 + H_2SO_4} \underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{NH_3} \underset{\text{Amm. acetae}}{CH_3COONH_4} \xrightarrow[-H_2O]{\text{Heat}}$$

$$\underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow[\text{(Hofmann bromamide reaction)}]{Br_2/KOH} \underset{\text{Methylamine}}{CH_3NH_2} \xrightarrow[-N_2,\ -H_2O]{HONO} \underset{\text{Methyl alcohol}}{CH_3OH} \xrightarrow[573\ K]{Cu} \underset{\text{Formaldehyde}}{HCHO}$$

### 20. Convert ethylamine into methylamine

$$\underset{\text{Ethylamine}}{CH_3CH_2NH_2} \xrightarrow[-N_2,\ -H_2O]{HONO} \underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow{K_2Cr_2O_7 + H_2SO_4} \underset{\text{Acetaldehyde}}{CH_3CHO}$$

$$\xrightarrow{K_2Cr_2O_7 + H_2SO_4} \underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{NH_3} \underset{\text{amm. acetate}}{CH_3COONH_4} \xrightarrow[-H_2O]{\text{Heat}} \underset{\text{Acetamide}}{CH_3CONH_2}$$

$$\xrightarrow[\text{(Hofmann bromamide reaction)}]{Br_2/KOH} \underset{\text{Methylamine}}{CH_3NH_2}$$

### 21. Convert propionamide into acetamide

$$\underset{\text{Propionamide}}{CH_3CH_2CONH_2} \xrightarrow[\text{(Hofmann bromamide reaction)}]{Br_2/KOH} \underset{\text{Ethylamine}}{CH_3CH_2NH_2} \xrightarrow[-N_2,\ -H_2O]{HONO} \underset{\text{Ethanol}}{CH_3CH_2OH}$$

$$\xrightarrow{K_2Cr_2O_7 + H_2SO_4} \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{K_2Cr_2O_7 + H_2SO_4} \underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{NH_3}$$

$$\underset{\text{Amm. acetate}}{CH_3COONH_4} \xrightarrow[-H_2O]{\text{Heat}} \underset{\text{Acetamide}}{CH_3CONH_4}$$

### 22. Convert propionic acid into acetic acid (*A.I.S.B. 1992; D.S.B. 1992 S*)

$$\underset{\text{Propionic acid}}{CH_3CH_2COOH} \xrightarrow{NH_3} \underset{\text{Amm. propionate}}{CH_3CH_2COONH_4} \xrightarrow[-H_2O]{\text{Heat}} \underset{\text{Propionamide}}{CH_3CH_2CONH_2}$$

$$\xrightarrow{Br_2/KOH} \underset{\text{Ethylamine}}{CH_3CH_2NH_2} \xrightarrow[-N_2,\ -H_2O]{HONO} \underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow{K_2Cr_2O_7 + H_2SO_4}$$

$$\underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{K_2Cr_2O_7 + H_2SO_4} \underset{\text{Acetic acid}}{CH_3COOH}$$

**23. Convert propionic acid to isoprophyl alcohol (propanol-2)**

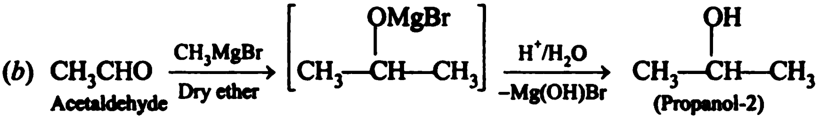
This conversion is brought about in two steps as given below

(*a*) propionic acid to acetaldehyde

(*b*) acetaldehyde to isoprophyl alcohol

$$(a)\ \underset{\text{Propionic acid}}{CH_3CH_2COOH} \xrightarrow{NH_3} \underset{\text{Amm. propionate}}{CH_3CH_2COONH_4} \xrightarrow[-H_2O]{\text{Heat}} \underset{\text{Priopionamide}}{CH_3CH_2CONH_2}$$

$$\xrightarrow{Br_2/KOH} \underset{\text{Ethylamine}}{CH_3CH_2NH_2} \xrightarrow{HNO_2} \underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \underset{\text{Acetaldehyde}}{CH_3CHO}$$



$$(b)\ \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow[\text{Dry ether}]{CH_3MgBr} \left[ CH_3-\overset{OMgBr}{\overset{|}{C}H}-CH_3 \right] \xrightarrow[-Mg(OH)Br]{H^+/H_2O} \underset{\text{(Propanol-2)}}{CH_3-\overset{OH}{\overset{|}{C}H}-CH_3}$$

## MISCELLANEOUS ALIPHATIC CONVERSIONS

### TWO-STEP CONVERSIONS

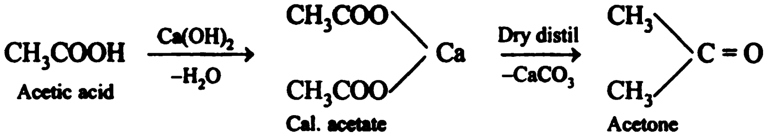
**24. Convert acetylene to ethanol**

$$\underset{\text{Acetylene}}{CH \equiv CH} \xrightarrow[HgSO_4,\ 333\ K]{H_2O,\ \text{Dil. } H_2SO_4} \underset{\text{Acetaldehyde}}{CH_3-CHO} \xrightarrow[\text{or Na/Alcohol}]{LiAlH_4} \underset{\text{Ethanol}}{CH_3CH_2OH}$$

**25. Convert acetylene into acetic acid**

$$\underset{\text{Acetylene}}{CH \equiv CH} \xrightarrow[HgSO_4,\ 333\ K]{H_2O,\ \text{Dil. } H_2SO_4} \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{K_2Cr_2O_7 + H_2SO_4} \underset{\text{Acetic acid}}{CH_3COOH}$$

**26. Convert acetic acid to acetone**

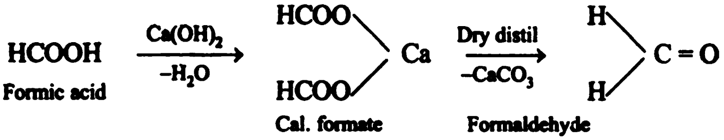


$$\underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow[-H_2O]{Ca(OH)_2} \underset{\text{Cal. acetate}}{(CH_3COO)_2Ca} \xrightarrow[-CaCO_3]{\text{Dry distil}} \underset{\text{Acetone}}{(CH_3)_2C=O}$$

**27. Convert acetic acid to acetaldehyde**

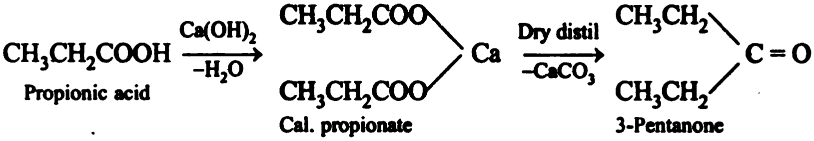
$$\underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{PCl_5} \underset{\text{Acetyl chloride}}{CH_3COCl} \xrightarrow[\textit{(Rosenmund reduction)}]{H_2 + Pd/BaSO_4 + S} \underset{\text{Acetaldehyde}}{CH_3CHO}$$

**28. Convert formic acid to formaldehyde**



$$\underset{\text{Formic acid}}{HCOOH} \xrightarrow[-H_2O]{Ca(OH)_2} \underset{\text{Cal. formate}}{(HCOO)_2Ca} \xrightarrow[-CaCO_3]{\text{Dry distil}} \underset{\text{Formaldehyde}}{H_2C=O}$$

**29. Convert propionic acid to 3-pentanone.**



**30. Convert methyl bromide to acetic acid** *(P.S.B. 1988 ; I.I.T. 1993)*.

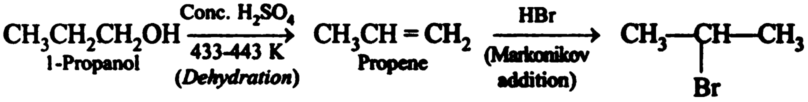
Two routes are available to effect this conversion.

$$\underset{\text{Methyl bromide}}{CH_3Br} \xrightarrow{\text{Mg/ether}} \underset{\text{Methyl mag. bromide}}{CH_3MgBr} \xrightarrow[(ii)\ H^+/H_2O]{(i)\ CO_2} \underset{\text{Acetic acid}}{CH_3COOH}$$

$$\downarrow KCN$$

$$\underset{\text{Acetonitrile}}{CH_3C \equiv N} \xrightarrow{H^+/H_2O} \underset{\text{Acetic acid}}{CH_3COOH}$$

**31. Convert 1-propanol to 2 bromopropane**



$$\underset{\text{1-Propanol}}{CH_3CH_2CH_2OH} \xrightarrow[\substack{433\text{-}443\ K \\ (\textit{Dehydration})}]{\text{Conc. } H_2SO_4} \underset{\text{Propene}}{CH_3CH=CH_2} \xrightarrow[\substack{\text{(Markonikov} \\ \text{addition)}}]{HBr} CH_3-\underset{Br}{\underset{|}{C}H}-CH_3$$

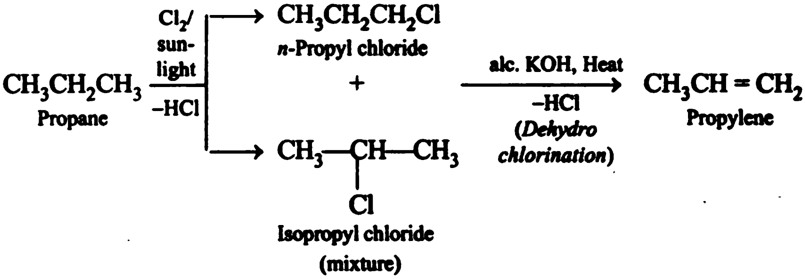
**32. Convert propyne to 2-butyne**

$$\underset{\text{Propyne}}{CH_3-C \equiv CH} \xrightarrow[196\ K]{NaNH_2/\text{liq } NH_3} \underset{\text{Sod. propynide}}{CH_3-C \equiv C^-Na^+} \xrightarrow[-NaI]{CH_3I} \underset{\text{2-Butyne}}{CH_3-C \equiv C-CH_3}$$

**33. Convert ethyl chloride into n-propyl amine**

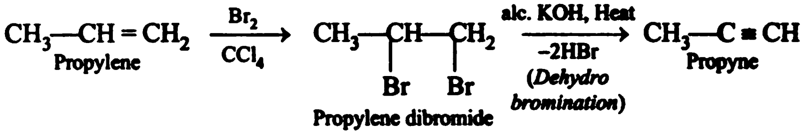
$$\underset{\text{Ethyl chloride}}{CH_3CH_2Cl} \xrightarrow[\text{Heat}]{\text{alc. KCN}} \underset{\text{Ethyl cyanide}}{CH_3CH_2CN} \xrightarrow{LiAlH_4} \underset{n\text{-Propylamine}}{CH_3CH_2CH_2NH_2}$$

**34. Convert propane into propylene**



$$\underset{\text{Propane}}{CH_3CH_2CH_3} \xrightarrow[-HCl]{Cl_2/\text{sun-light}} \left\{ \begin{array}{c} \underset{n\text{-Propyl chloride}}{CH_3CH_2CH_2Cl} \\ + \\ CH_3-\underset{Cl}{\underset{|}{C}H}-CH_3 \\ \text{Isopropyl chloride} \\ \text{(mixture)} \end{array} \right. \xrightarrow[\substack{-HCl \\ (\textit{Dehydro} \\ \textit{chlorination})}]{\text{alc. KOH, Heat}} \underset{\text{Propylene}}{CH_3CH=CH_2}$$

**35. Convert propylene to propyne**



$$\underset{\text{Propylene}}{CH_3-CH=CH_2} \xrightarrow[CCl_4]{Br_2} \underset{\text{Propylene dibromide}}{CH_3-\underset{Br}{\underset{|}{C}H}-\underset{Br}{\underset{|}{C}H_2}} \xrightarrow[\substack{-2HBr \\ (\textit{Dehydro} \\ \textit{bromination})}]{\text{alc. KOH, Heat}} \underset{\text{Propyne}}{CH_3-C \equiv CH}$$

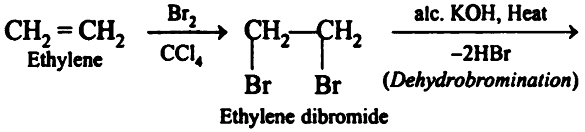
## 36. Convert ethane to diethyl ether

$$\underset{\text{Ethane}}{CH_3{-}CH_3} \xrightarrow[-HCl]{Cl_2/\text{sunlight}} \underset{\text{Ethyl chloride}}{CH_3CH_2Cl} \xrightarrow[-2AgCl]{\text{Dry } Ag_2O} \underset{\text{Diethyl ether}}{CH_3CH_2{-}O{-}CH_2CH_3}$$

## 37. Convert ethane into ethylene

$$\underset{\text{Ethane}}{CH_3{-}CH_3} \xrightarrow[-HCl]{Cl_2/\text{sunlight}} \underset{\text{Ethyl chloride}}{CH_3{-}CH_2Cl} \xrightarrow[\substack{-HCl \\ (\textit{Dehydrochlorination})}]{\text{alc. KOH, Heat}} \underset{\text{Ethylene}}{CH_2=CH_2}$$

## 38. Convert ethylene to acetylene

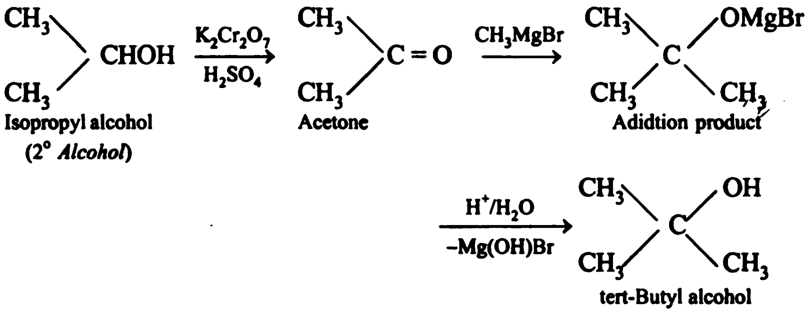


$$\underset{\text{Ethylene}}{CH_2=CH_2} \xrightarrow[CCl_4]{Br_2} \underset{\text{Ethylene dibromide}}{\underset{Br\qquad Br}{CH_2{-}CH_2}} \xrightarrow[\substack{-2HBr \\ (\textit{Dehydrobromination})}]{\text{alc. KOH, Heat}} \underset{\text{Acetylene}}{CH\equiv CH}$$

## 39. Convert acetylene into propyne

$$\underset{\text{Acetylene}}{CH\equiv CH} \xrightarrow[196\,K]{NaNH_2/\text{liq } NH_3} \underset{\text{Sod. acetylide}}{CH\equiv C^-Na^+} \xrightarrow[-NaI]{CH_3I} \underset{\text{Propyne}}{CH_3{-}C\equiv CH}$$

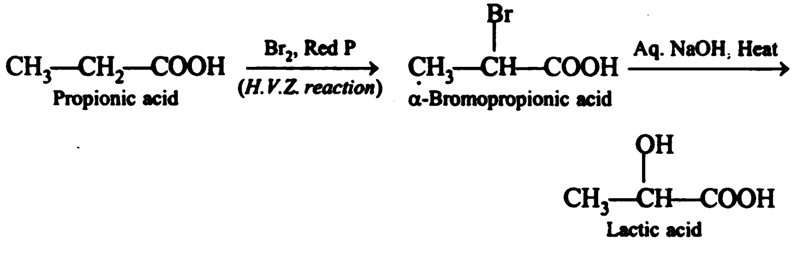
## 40. Convert isopropyl alcohol to tert-butyl alcohol (2° alcohol to 3° alcohol)



## 41. Convert ethyl alcohol to diethyl ether. (*A.I.S.B. 1993*)

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow{P/I_2} \underset{\text{Ethyl iodide}}{CH_3CH_2{-}I} \xrightarrow[\substack{-NaI \\ (\textit{Williamson's} \\ \textit{synthesis})}]{CH_3CH_2ONa} \underset{\text{Diethyl ether}}{CH_3CH_2{-}O{-}CH_2CH_3}$$

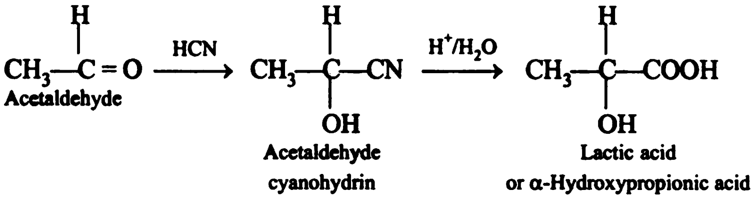
## 42. Convert propionic acid to lactic acid



$$\underset{\text{Propionic acid}}{CH_3{-}CH_2{-}COOH} \xrightarrow[(\textit{H.V.Z. reaction})]{Br_2,\ \text{Red P}} \underset{\alpha\text{-Bromopropionic acid}}{CH_3{-}\overset{\overset{Br}{|}}{CH}{-}COOH} \xrightarrow{\text{Aq. NaOH, Heat}} \underset{\text{Lactic acid}}{CH_3{-}\overset{\overset{OH}{|}}{CH}{-}COOH}$$

**43. Convert acetaldehyde to lactic acid (α-hydroxypropionic acid)**

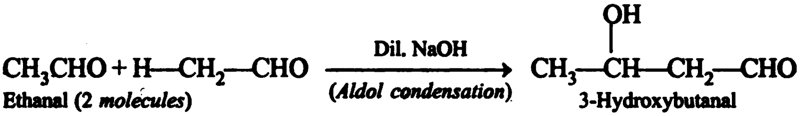
*(Roorkee 1984)*



$$\underset{\text{Acetaldehyde}}{CH_3-\overset{\overset{\large H}{|}}{C}=O} \xrightarrow{HCN} \underset{\text{Acetaldehyde cyanohydrin}}{CH_3-\overset{\overset{\large H}{|}}{\underset{\underset{\large OH}{|}}{C}}-CN} \xrightarrow{H^+/H_2O} \underset{\text{Lactic acid or α-Hydroxypropionic acid}}{CH_3-\overset{\overset{\large H}{|}}{\underset{\underset{\large OH}{|}}{C}}-COOH}$$

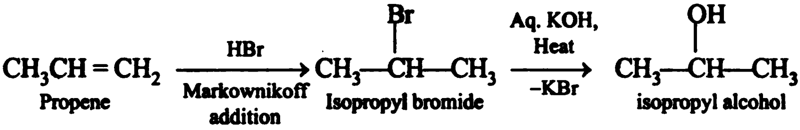
**44. Convert ethyne to 3-hydroxybutanal**

$$\underset{\text{Ethyne}}{CH\equiv CH} \xrightarrow[\text{Dil. } H_2SO_4,\ HgSO_4,\ 333\ K]{+H_2O} \underset{\text{Ethanal}}{CH_3-CHO}$$



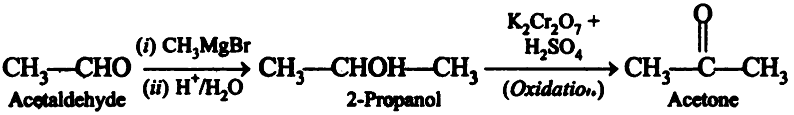
$$\underset{\text{Ethanal (2 \textit{molecules})}}{CH_3CHO + H-CH_2-CHO} \xrightarrow[\text{(\textit{Aldol condensation})}]{\text{Dil. NaOH}} \underset{\text{3-Hydroxybutanal}}{CH_3-\overset{\overset{\large OH}{|}}{CH}-CH_2-CHO}$$

**45. Convert propene to isopropyl alcohol**



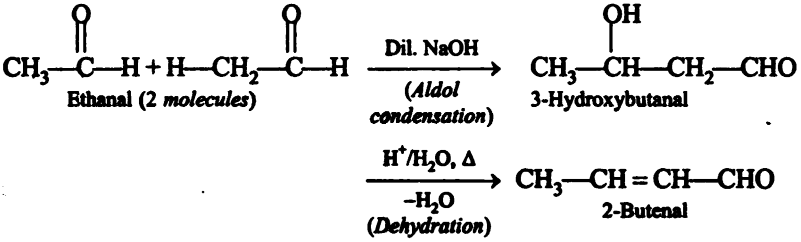
$$\underset{\text{Propene}}{CH_3CH=CH_2} \xrightarrow[\text{Markownikoff addition}]{HBr} \underset{\text{Isopropyl bromide}}{CH_3-\overset{\overset{\large Br}{|}}{CH}-CH_3} \xrightarrow[-KBr]{\text{Aq. KOH, Heat}} \underset{\text{isopropyl alcohol}}{CH_3-\overset{\overset{\large OH}{|}}{CH}-CH_3}$$

**46. Convert acetaldehyde to acetone** *(A.I.S.B. 1995)*



$$\underset{\text{Acetaldehyde}}{CH_3-CHO} \xrightarrow[(ii)\ H^+/H_2O]{(i)\ CH_3MgBr} \underset{\text{2-Propanol}}{CH_3-CHOH-CH_3} \xrightarrow[\text{(\textit{Oxidation})}]{K_2Cr_2O_7 + H_2SO_4} \underset{\text{Acetone}}{CH_3-\overset{\overset{\large O}{\|}}{C}-CH_3}$$

**47. Convert ethanal into 2-butenal**

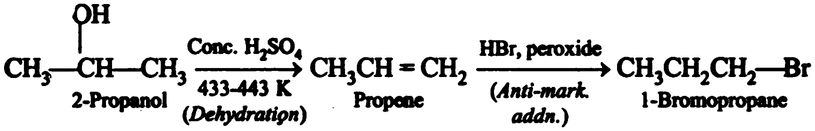


$$\underset{\text{Ethanal (2 \textit{molecules})}}{CH_3-\overset{\overset{\large O}{\|}}{C}-H + H-CH_2-\overset{\overset{\large O}{\|}}{C}-H} \xrightarrow[\text{(\textit{Aldol condensation})}]{\text{Dil. NaOH}} \underset{\text{3-Hydroxybutanal}}{CH_3-\overset{\overset{\large OH}{|}}{CH}-CH_2-CHO}$$

$$\xrightarrow[\substack{-H_2O \\ \text{(\textit{Dehydration})}}]{H^+/H_2O,\ \Delta} \underset{\text{2-Butenal}}{CH_3-CH=CH-CHO}$$

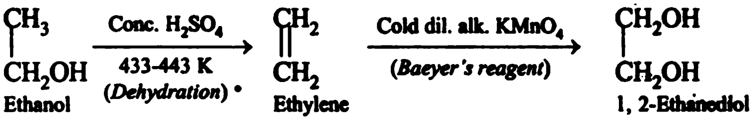
**48. Convert 2-propanol to 1-bromopropane**

*(C.B.S.E. Sample Paper, 1997)*



$$\underset{\text{2-Propanol}}{CH_3-\overset{\overset{\large OH}{|}}{CH}-CH_3} \xrightarrow[\substack{433\text{–}443\ K \\ \text{(\textit{Dehydration})}}]{\text{Conc. } H_2SO_4} \underset{\text{Propene}}{CH_3CH=CH_2} \xrightarrow[\text{(\textit{Anti-mark. addn.})}]{\text{HBr, peroxide}} \underset{\text{1-Bromopropane}}{CH_3CH_2CH_2-Br}$$

**49. Convert ethanol into 1, 2-ethanediol** (*A.I.S.B. 1994; D.S.B. 1996*)

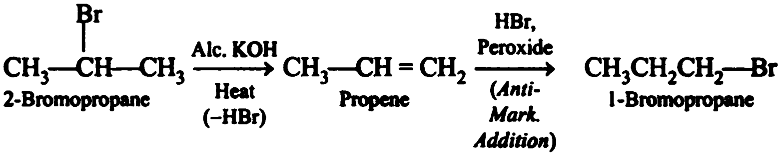


$$\underset{\text{Ethanol}}{CH_3-CH_2OH} \xrightarrow[\text{433-443 K (Dehydration)}]{\text{Conc. } H_2SO_4} \underset{\text{Ethylene}}{CH_2=CH_2} \xrightarrow[\text{(Baeyer's reagent)}]{\text{Cold dil. alk. } KMnO_4} \underset{\text{1, 2-Ethanediol}}{CH_2OH-CH_2OH}$$

**50. Convert Nitromethane to dimethylamine** (*A.I.S.B. 1990 S*)

$$\underset{\text{Nitromethane}}{CH_3NO_2} \xrightarrow[\text{(Reduction)}]{\text{Sn/HCl}} \underset{\text{Methylamine}}{CH_3NH_2} \xrightarrow[\text{(Hofmann's ammonolysis)}]{CH_3I/373\text{ K}} \underset{\text{Dimethyiamine}}{CH_3NHCH_3}$$

**51. Convert 2-bromopropane to 1-bromopropane**



$$\underset{\text{2-Bromopropane}}{CH_3-\overset{\overset{\large Br}{|}}{C}H-CH_3} \xrightarrow[\text{Heat (-HBr)}]{\text{Alc. KOH}} \underset{\text{Propene}}{CH_3-CH=CH_2} \xrightarrow[\text{(Anti-Mark. Addition)}]{\text{HBr, Peroxide}} \underset{\text{1-Bromopropane}}{CH_3CH_2CH_2-Br}$$

**52. Convert methyl iodide to 2-butyne**

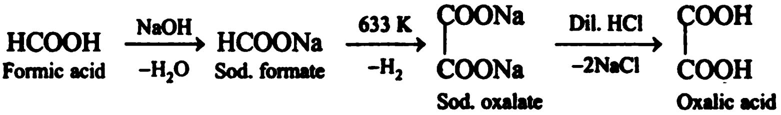
$$2CH_3I + \underset{\text{Disodium acetylide}}{NaC\equiv C-Na} \xrightarrow{-2NaI} \underset{\text{2-Butyne}}{CH_3-C\equiv C-CH_3}$$

## THREE-STEP CONVERSIONS

**53. Convert methane to acetic acid** (*A.I.S.B. 1985 S*)

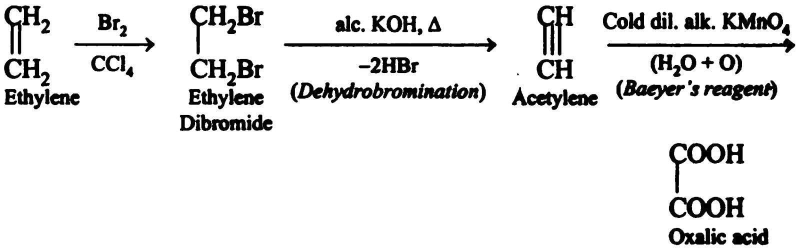
$$\underset{\text{Methane}}{CH_4} \xrightarrow[-HBr]{Br_2/h\nu} \underset{\text{Methyl bromide}}{CH_3Br} \xrightarrow[-KBr]{\text{alc. KCN, Heat}} \underset{\text{Acetonitrile}}{CH_3CN} \xrightarrow[\text{(Hydrolysis)}]{H^+/H_2O} \underset{\text{Acetic acid}}{CH_3COOH}$$

**54. Convert formic acid to oxalic acid**



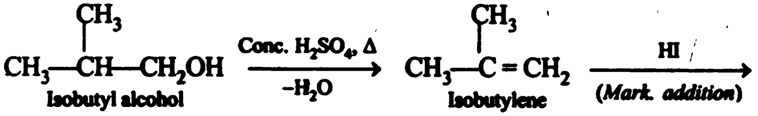
$$\underset{\text{Formic acid}}{HCOOH} \xrightarrow[-H_2O]{NaOH} \underset{\text{Sod. formate}}{HCOONa} \xrightarrow[-H_2]{633\text{ K}} \underset{\text{Sod. oxalate}}{COONa-COONa} \xrightarrow[-2NaCl]{\text{Dil. HCl}} \underset{\text{Oxalic acid}}{COOH-COOH}$$

**55. Convert ethylene to oxalic acid**

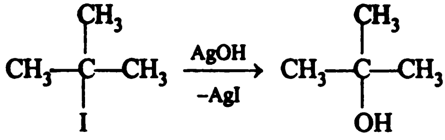


$$\underset{\text{Ethylene}}{CH_2=CH_2} \xrightarrow[CCl_4]{Br_2} \underset{\text{Ethylene Dibromide}}{CH_2Br-CH_2Br} \xrightarrow[\text{-2HBr (Dehydrobromination)}]{\text{alc. KOH, }\Delta} \underset{\text{Acetylene}}{CH\equiv CH} \xrightarrow[\text{(Baeyer's reagent)}]{\text{Cold dil. alk. } KMnO_4\ (H_2O + O)} \underset{\text{Oxalic acid}}{COOH-COOH}$$

**56. Convert isobutyl alcohol to tert-butyl alcohol (1° alcohol to 3° alcohol)**



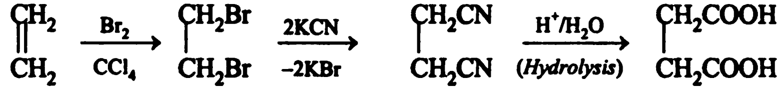
$$\underset{\text{Isobutyl alcohol}}{CH_3-\overset{\overset{\large CH_3}{|}}{C}H-CH_2OH} \xrightarrow[-H_2O]{\text{Conc. } H_2SO_4,\ \Delta} \underset{\text{Isobutylene}}{CH_3-\overset{\overset{\large CH_3}{|}}{C}=CH_2} \xrightarrow[\text{(Mark. addition)}]{HI}$$



$$\mathrm{CH_3-\underset{\underset{I}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3} \xrightarrow[-\mathrm{AgI}]{\mathrm{AgOH}} \mathrm{CH_3-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3}$$

*tert*-Butyl iodide *tert*-Butyl alcohol

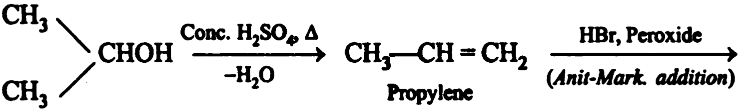
**57. Convert ethylene to succinic acid**



$$\begin{matrix}\mathrm{CH_2}\\ \|\\ \mathrm{CH_2}\end{matrix} \xrightarrow[\mathrm{CCl_4}]{\mathrm{Br_2}} \begin{matrix}\mathrm{CH_2Br}\\ |\\ \mathrm{CH_2Br}\end{matrix} \xrightarrow[-2\mathrm{KBr}]{2\mathrm{KCN}} \begin{matrix}\mathrm{CH_2CN}\\ |\\ \mathrm{CH_2CN}\end{matrix} \xrightarrow[(\textit{Hydrolysis})]{\mathrm{H^+/H_2O}} \begin{matrix}\mathrm{CH_2COOH}\\ |\\ \mathrm{CH_2COOH}\end{matrix}$$

Ethylene Ethylene Dibromide Butane-1, 4-dinitrile Succinic acid

**58. Convert isopropyl alcohol to *n*-propyl alcohol (2° alcohol to 1° alcohol)** *(I.I.T. 1982)*



$$\begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_3}\end{matrix}\!>\!\mathrm{CHOH} \xrightarrow[-\mathrm{H_2O}]{\text{Conc. }\mathrm{H_2SO_4},\ \Delta} \mathrm{CH_3-CH=CH_2} \xrightarrow[(\textit{Anit-Mark. addition})]{\text{HBr, Peroxide}}$$

Isopropyl alcohol Propylene

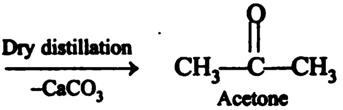
$$\mathrm{CH_3CH_2CH_2-Br} \xrightarrow[\substack{-\mathrm{KBr}\\ (\textit{Hydrolysis})}]{\text{aq. KOH}} \mathrm{CH_3CH_2CH_2-OH}$$

*n*-Propyl bromide *n*-Propyl alcohol

**59. Convert acetaldehyde to acetone**

$$\mathrm{CH_3CHO} \xrightarrow[(\textit{Oxidation})]{\mathrm{K_2Cr_2O_7/H_2SO_4}} \mathrm{CH_3COOH} \xrightarrow[-\mathrm{H_2O}]{\mathrm{Ca(OH)_2}} \mathrm{(CH_3COO)_2Ca}$$

Acetaldehyde Acetic acid Cal. acetate



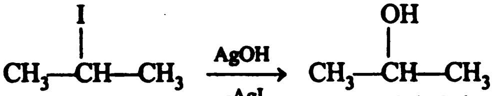
$$\xrightarrow[-\mathrm{CaCO_3}]{\text{Dry distillation}} \mathrm{CH_3-\overset{\overset{O}{\|}}{C}-CH_3}$$

Acetone

**60. Convert n-propyl alcohol to isopropyl alcohol (1°alcohol to 2°alcohol)**

$$\mathrm{CH_3CH_2CH_2OH} \xrightarrow[-\mathrm{H_2O}]{\text{Conc. }\mathrm{H_2SO_4},\ \Delta} \mathrm{CH_3CH=CH_2} \xrightarrow[(\textit{Mark. addition})]{\mathrm{HI}}$$

*n*-Propyl alcohol Propylene



$$\mathrm{CH_3-\overset{\overset{I}{|}}{CH}-CH_3} \xrightarrow[-\mathrm{AgI}]{\mathrm{AgOH}} \mathrm{CH_3-\overset{\overset{OH}{|}}{CH}-CH_3}$$

Isopropyl iodide Isopropyl alcohol

**61. Convert acetone to acetamide**

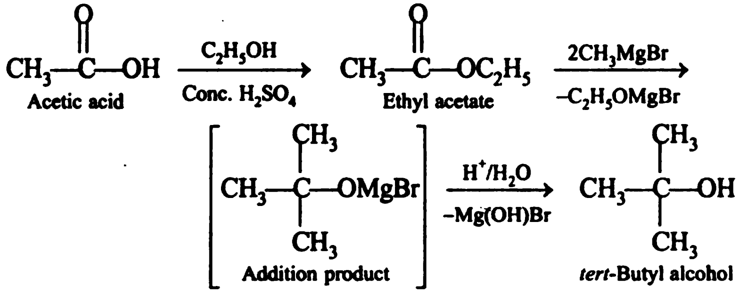
$$\mathrm{CH_3COCH_3} \xrightarrow[\mathrm{[O]}]{\text{Conc. }\mathrm{HNO_3}} \mathrm{CH_3COOH} \xrightarrow[-\mathrm{SO_2},\ -\mathrm{HCl}]{\mathrm{SOCl_2}} \mathrm{CH_3COCl}$$

Acetone Acetic acid Acetyl chloride

$$\xrightarrow[-\mathrm{NH_4Cl}]{\mathrm{NH_3}\text{ (excess)}} \mathrm{CH_3CONH_2}$$

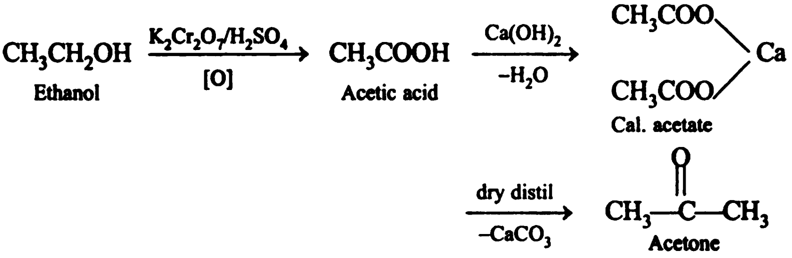
Acetamide

**62. Convert acetic acid to tert-butyl alcohol.** (*I.I.T. 1989*)



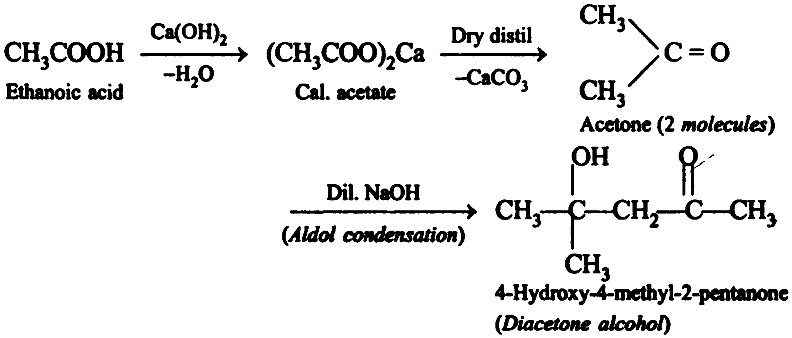
$$\underset{\text{Acetic acid}}{CH_3-\overset{\overset{O}{\|}}{C}-OH} \xrightarrow[\text{Conc. } H_2SO_4]{C_2H_5OH} \underset{\text{Ethyl acetate}}{CH_3-\overset{\overset{O}{\|}}{C}-OC_2H_5} \xrightarrow[-C_2H_5OMgBr]{2CH_3MgBr} \underset{\text{Addition product}}{\left[CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OMgBr\right]} \xrightarrow[-Mg(OH)Br]{H^+/H_2O} \underset{\textit{tert}\text{-Butyl alcohol}}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH}$$

**63. Convert ethanol to acetone** (*A.I.S.B. 1992*)



$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[{[O]}]{K_2Cr_2O_7/H_2SO_4} \underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow[-H_2O]{Ca(OH)_2} \underset{\text{Cal. acetate}}{\begin{matrix} CH_3COO \\ CH_3COO \end{matrix}\!\!>Ca} \xrightarrow[-CaCO_3]{\text{dry distil}} \underset{\text{Acetone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3}$$

**64. Convert ethanoic acid to 4-hydroxy-4-methyl-2-pentanone (diacetone alcohol)**



$$\underset{\text{Ethanoic acid}}{CH_3COOH} \xrightarrow[-H_2O]{Ca(OH)_2} \underset{\text{Cal. acetate}}{(CH_3COO)_2Ca} \xrightarrow[-CaCO_3]{\text{Dry distil}} \underset{\text{Acetone (2 \textit{molecules})}}{\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>C=O} \xrightarrow[\textit{(Aldol condensation)}]{\text{Dil. NaOH}} \underset{\text{4-Hydroxy-4-methyl-2-pentanone (\textit{Diacetone alcohol})}}{CH_3-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-\overset{\overset{O}{\|}}{C}-CH_3}$$

**65. Convert propanoic acid to ethylamine**

$$\underset{\text{Propanoic acid}}{CH_3CH_2COOH} \xrightarrow[-SO_2,\,-HCl]{SOCl_2} \underset{\text{Propanoyl chloride}}{CH_3CH_2COCl} \xrightarrow[-NH_4Cl]{NH_3\text{ (excess)}} \underset{\text{Propionamide}}{CH_3CH_2CONH_2} \xrightarrow{Br_2/KOH} \underset{\text{Ethylamine}}{CH_3CH_2NH_2}$$

**66. Convert calcium carbide into hexachloroethane** (*M.L.N.R. Allahabad 1995*)

$$\underset{\text{Cal. carbide}}{CaC_2} \xrightarrow[-Ca(OH)_2]{+2H_2O} \underset{\text{Acetylene}}{HC\equiv CH} \xrightarrow[473\text{-}523\text{ K}]{+\,2H_2/Ni} \underset{\text{Ethane}}{CH_3-CH_3} \xrightarrow[\substack{\text{sunlight} \\ -HCl}]{Cl_2\text{(excess)}} \underset{\text{Hexachloroethane}}{CCl_3-CCl_3}$$

**67. Convert acetic acid to 2-butanol**

$$\underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow[-SO_2,\ -HCl]{SOCl_2} \underset{\text{Acetyl chloride}}{CH_3COCl} \xrightarrow[\text{in dry ether}]{(CH_3CH_2)_2Cd} \underset{\text{Butanone}}{CH_3COCH_2CH_3}$$

$$\xrightarrow{LiAlH_4} \underset{\text{2-Butanol}}{CH_3CHOHCH_2CH_3}$$

**68. Convert acetaldehyde into acetoacetic ester**

(*M.L.N.R. Allahabad 1995*)

$$\underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow[{[O]}]{K_2Cr_2O_7 + H_2SO_4} \underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{C_2H_5OH/\text{Conc. } H_2SO_4} \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5}$$

$$\xrightarrow[(\textit{Claisen condensation})]{C_2H_5OH/C_2H_5OH} \underset{\substack{\text{Ethyl acetoacetate or}\\ \text{Acetoacetic ester}}}{CH_3COCH_2COOC_2H_5}$$

**69. Convert 1, 1-dichloroethane to 1, 2-dichloroethane**

$$\underset{\text{1, 1-Dichloroethane}}{CH_3CHCl_2} \xrightarrow[\text{Heat}]{\text{Alc. KOH}} \underset{\text{Ethyne}}{HC \equiv CH} \xrightarrow[\text{(Lindlar's catalyst)}]{H_2, Pd/BaSO_4} \underset{\text{Ethene}}{H_2C = CH_2} \xrightarrow{Cl_2} \underset{\text{1,2-Dichloroethane}}{ClCH_2{-}CH_2Cl}$$

## MULTI-STEP CONVERSIONS

**70. Convert acetylene into acetone**

$$\underset{\text{Acetylene}}{CH \equiv CH} \xrightarrow[HgSO_4,\ 333\ K]{H_2O,\ \text{Dil. } H_2SO_4} \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow[{[O]}]{K_2Cr_2O_7/H_2SO_4} \underset{\text{Acetic acid}}{CH_3COOH}$$

$$\xrightarrow[-H_2O]{Ca(OH)_2} \underset{\text{Cal. acetate}}{(CH_3COO)_2Ca} \xrightarrow[-CaCO_3]{\text{Dry distil}} \underset{\text{Acetone}}{CH_3COCH_3}$$

**71. Convert ethyl alcohol to vinyl acetate** (*I.I.T. 1986*)

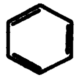
$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow[\substack{433\text{-}443\ K\\ (\textit{Dehydration})}]{\text{Conc. } H_2SO_4} \underset{\text{Ethylene}}{CH_2 = CH_2} \xrightarrow{Br_2} \underset{\text{1, 2-Dibromoethane}}{BrCH_2{-}CH_2Br} \xrightarrow[-2HBr]{\text{Alc. KOH, Heat}}$$

$$\underset{\text{Acetylene}}{HC \equiv CH} \xrightarrow[HgSO_4]{CH_3COOH} \underset{\text{Vinyl acetate}}{CH_2 = CH{-}OCOCH_3}$$

**72. Convert lime into benzene** (*I.I.T. 1987*)

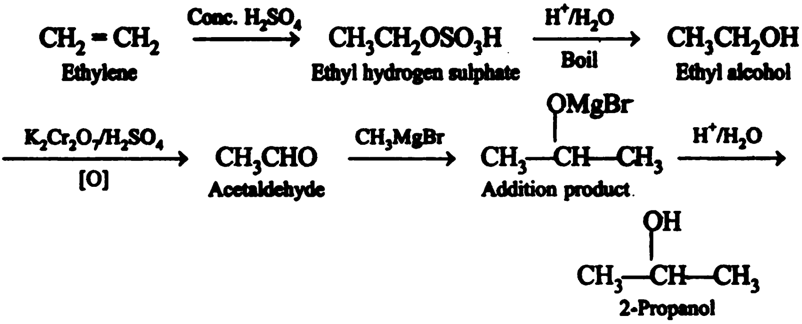
$$\underset{\text{Lime}}{CaCO_3} \xrightarrow[-CO_2]{\text{Heat}} CaO \xrightarrow[-CO]{3C,\ 2273\ K} \underset{\text{Cal. carbide}}{CaC_2} \xrightarrow[-Ca(OH)_2]{H_2O} \underset{\text{Acetylene}}{CH \equiv CH}$$

$$\xrightarrow[773\ K]{\text{Red hot copper tube}}$$



Benzene

### 73. Convert ethylene to 2-propanol (*D.S.B. 1991*)



$$\underset{\text{Ethylene}}{CH_2=CH_2} \xrightarrow{\text{Conc. } H_2SO_4} \underset{\text{Ethyl hydrogen sulphate}}{CH_3CH_2OSO_3H} \xrightarrow[\text{Boil}]{H^+/H_2O} \underset{\text{Ethyl alcohol}}{CH_3CH_2OH}$$

$$\xrightarrow[{[O]}]{K_2Cr_2O_7/H_2SO_4} \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{CH_3MgBr} \underset{\text{Addition product}}{CH_3-\overset{OMgBr}{\overset{|}{C}}H-CH_3} \xrightarrow{H^+/H_2O}$$

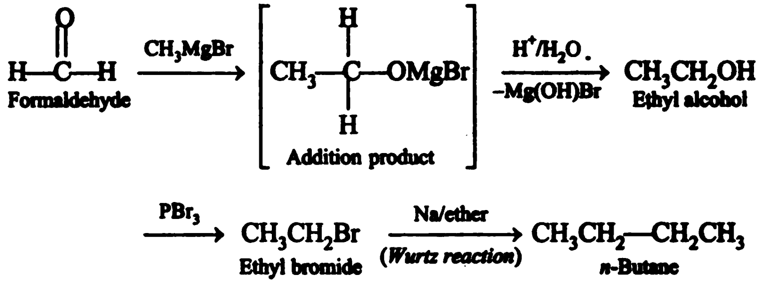
$$\underset{\text{2-Propanol}}{CH_3-\overset{OH}{\overset{|}{C}}H-CH_3}$$

### 74. Convert propanoic acid to n-butylamine (*Roorkee 1985*)

$$\underset{\text{Propanoic acid}}{CH_3CH_2-COOH} \xrightarrow{LiAlH_4} \underset{n\text{-Propyl alcohol}}{CH_3CH_2CH_2-OH} \xrightarrow{PBr_3} \underset{n\text{-Propyl bromide}}{CH_3CH_2CH_2-Br}$$

$$\xrightarrow[\text{Heat}]{\text{Alc. KCN}} \underset{n\text{-Butyronitrile}}{CH_3CH_2CH_2-CN} \xrightarrow[\text{in ether}]{LiAlH_4} \underset{n\text{-Butylamine}}{CH_3CH_2CH_2CH_2-NH_2}$$

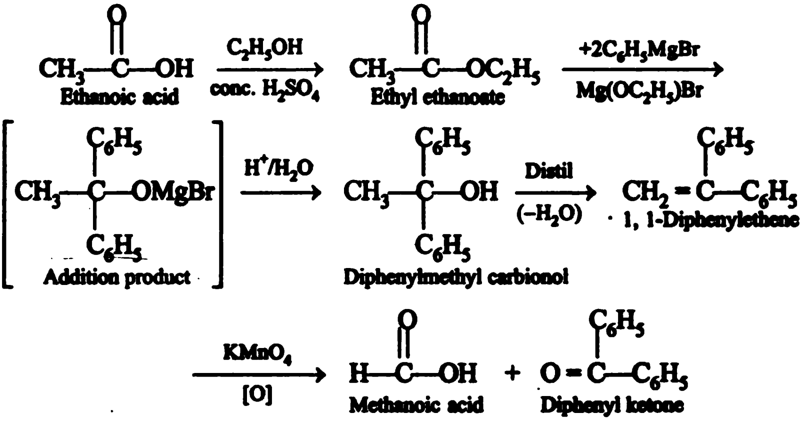
### 75. Convert formaldehyde to n-butane



$$\underset{\text{Formaldehyde}}{H-\overset{O}{\overset{\|}{C}}-H} \xrightarrow{CH_3MgBr} \left[\underset{\text{Addition product}}{CH_3-\overset{H}{\overset{|}{\underset{H}{\underset{|}{C}}}}-OMgBr}\right] \xrightarrow[-Mg(OH)Br]{H^+/H_2O.} \underset{\text{Ethyl alcohol}}{CH_3CH_2OH}$$

$$\xrightarrow{PBr_3} \underset{\text{Ethyl bromide}}{CH_3CH_2Br} \xrightarrow[(\textit{Wurtz reaction})]{Na/ether} \underset{n\text{-Butane}}{CH_3CH_2-CH_2CH_3}$$

### 76. Convert ethanoic acid to a mixture of methanoic acid and diphenyl ketone (*I.I.T. 1990*)



$$\underset{\text{Ethanoic acid}}{CH_3-\overset{O}{\overset{\|}{C}}-OH} \xrightarrow[\text{conc. } H_2SO_4]{C_2H_5OH} \underset{\text{Ethyl ethanoate}}{CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5} \xrightarrow[Mg(OC_2H_5)Br]{+2C_6H_5MgBr}$$

$$\left[\underset{\text{Addition product}}{CH_3-\overset{C_6H_5}{\overset{|}{\underset{C_6H_5}{\underset{|}{C}}}}-OMgBr}\right] \xrightarrow{H^+/H_2O} \underset{\text{Diphenylmethyl carbionol}}{CH_3-\overset{C_6H_5}{\overset{|}{\underset{C_6H_5}{\underset{|}{C}}}}-OH} \xrightarrow[(-H_2O)]{\text{Distil}} \underset{\text{1, 1-Diphenylethene}}{CH_2=\overset{C_6H_5}{\overset{|}{C}}-C_6H_5}$$

$$\xrightarrow[{[O]}]{KMnO_4} \underset{\text{Methanoic acid}}{H-\overset{O}{\overset{\|}{C}}-OH} + \underset{\text{Diphenyl ketone}}{O=\overset{C_6H_5}{\overset{|}{C}}-C_6H_5}$$

### 77. Convert ethanoic anhydride to but-2-enal.

$$\underset{\text{Ethanoic anhydride}}{CH_3CO.O.COCH_3} + 8[H] \xrightarrow{Na/C_2H_5OH} \underset{\text{Ethanol}}{2C_2H_5OH} + H_2O$$

$$\xrightarrow{Cu,\ 773\ K} \underset{\text{Ethanal}}{CH_3CHO} \xrightarrow[\text{(Aldol condensation)}]{\text{Dil. NaOH}} \underset{\text{Acetaldol}}{CH_3CH(OH)CH_2CHO}$$

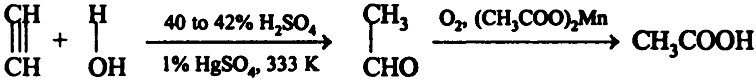
$$\xrightarrow{\Delta,\ \text{dil. HCl}} CH_3CH=CH.CHO + H_2O$$

But-2-enal

(*Crotonaldehyde*)

### 78. Convert calcium carbide to accetoacetic ester.

$$\underset{\text{Cal. carbide}}{CaC_2} \xrightarrow[-Ca(OH)_2]{2H_2O} \underset{\text{Acetylene}}{HC{\equiv}CH}$$



$$\begin{matrix} CH \\ ||| \\ CH \end{matrix} + \begin{matrix} H \\ | \\ OH \end{matrix} \xrightarrow[1\%\ HgSO_4,\ 333\ K]{40\ \text{to}\ 42\%\ H_2SO_4} \begin{matrix} CH_3 \\ | \\ CHO \end{matrix} \xrightarrow{O_2,\ (CH_3COO)_2Mn} CH_3COOH$$

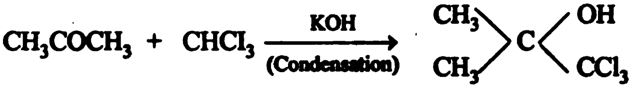
Acetaldehyde Acetic acid

$$\xrightarrow{C_2H_5OH} \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} \xrightarrow[\text{(Claisen condensation)}]{C_2H_5ONa} \underset{\text{Acetoacetic ester}}{CH_3COCH_2COOC_2H_5}$$

### 79. Convert 2-butene to 1,1, 1-trichloro-2-methyl-2-propanol.

$$\underset{\text{2-Butene}}{CH_3{-}CH{=}CH{-}CH_3} \xrightarrow{\text{Oz onolysis}} CH_3{-}CHO \xrightarrow[K_2Cr_2O_7/H^+]{[O]} CH_3COOH$$

$$\xrightarrow{Ca(OH)_2} (CH_3COO)_2Ca \xrightarrow{\text{Dry distillation}} CH_3COCH_3$$

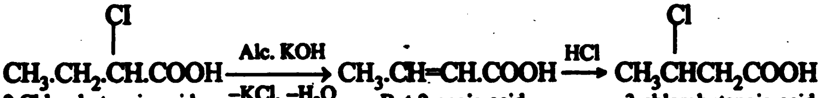


$$CH_3COCH_3 + CHCl_3 \xrightarrow[\text{(Condensation)}]{KOH} (CH_3)_2C(OH)CCl_3$$

1, 1, 1-Trichloro-2-methyl-2-propanol

(*Chloretone*)

### 80. Convert 2-chlorobutanoic acid to 3-chlorobutanoic acid. (2 steps)



$$\underset{\text{2.Chlorobutanoic acid}}{CH_3.CH_2.\overset{\overset{\Large Cl}{|}}{C}H.COOH} \xrightarrow[-KCl,\ -H_2O]{\text{Alc. KOH}} \underset{\text{But-2-enoic acid}}{CH_3.CH{=}CH.COOH} \xrightarrow{HCl} \underset{\text{3-chlorobutanoic acid}}{CH_3\overset{\overset{\Large Cl}{|}}{C}HCH_2COOH}$$

(*Crotonic acid*)

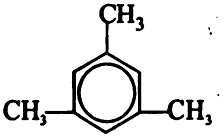
### 81. Convert butanone to mesitylene.

$$\underset{\text{Butanone}}{CH_3COCH_2CH_3} + 3NaOI \xrightarrow{NaOH/I_2} CI_3COCH_2CH_3 + 3NaOH$$

$$\xrightarrow{NaOH} \underset{\text{Iodoform}}{CHI_3} \xrightarrow{Ag,\ \Delta} \underset{\text{Acetylene}}{CH{\equiv}CH} \xrightarrow[1\%\ HgSO_4,\ 333K]{H_2O,\ 40\ \text{to}\ 42\%\ H_2SO_4} \underset{\text{Acetaldehyde}}{CH_3CHO}$$

$$\xrightarrow{O_2,\ (CH_3COO)_2Mn} \underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{Ca(OH)_2} (CH_3COO)_2Ca \xrightarrow{\text{Dry distillation}} \underset{\text{Acetone}}{CH_3COCH_3}$$

$$3CH_3COH_3 \xrightarrow[\text{(Condensation)}]{\text{Conc. } H_2SO_4}$$



$+ 3H_2O$

Mesitylene

**82. Convert acetonitrile to methyl carbylamine.**

$$\underset{\text{Acetonitrile}}{CH_3CN} \xrightarrow[\text{(conc. HCl or alk. } H_2O_2)]{\text{Partial hydrolysis}} \underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow{Br_2/KOH,\ \Delta} \underset{\text{Methylamine}}{CH_3NH_2}$$

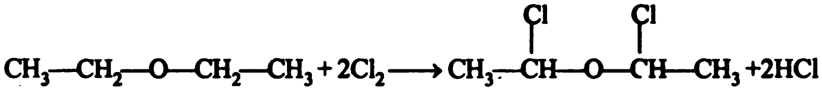
$$\xrightarrow[\text{Warm}]{CHCl_3\text{+alc. KOH}} \underset{\text{Methyl carbylamine}}{CH_3NC}$$

**83. Convert alumnium carbide to α, α' - dichlorodiethyl ether.**

$$\underset{\text{Aluminium carbide}}{Al_4C_3} + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4$$

$$CH_4 \xrightarrow[-HCl]{Cl_2,h\nu} CH_3Cl \xrightarrow{\text{Na, Dry ether}} C_2H_6 \xrightarrow[-HCl]{Cl_2,h\nu} C_2H_2Cl \xrightarrow{\text{Aq. KOH}} C_2H_5OH$$

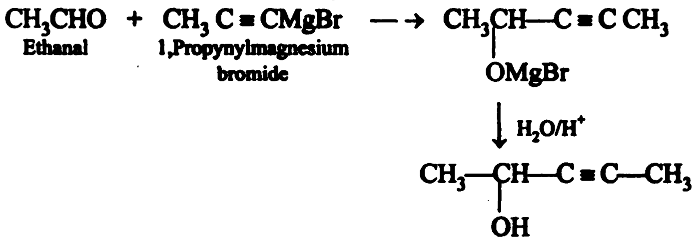
$$\underset{\text{Ethyl alcohol (in excess)}}{2C_2H_5OH} \xrightarrow{\text{conc. } H_2SO_4,\ 413\text{ K}} \underset{\text{Diethyl ether}}{C_2H_5{-}O{-}C_2H_5} + H_2O$$



$$CH_3{-}CH_2{-}O{-}CH_2{-}CH_3 + 2Cl_2 \longrightarrow CH_3{-}\overset{Cl}{\overset{|}{C}}H{-}O{-}\overset{Cl}{\overset{|}{C}}H{-}CH_3 + 2HCl$$

α, α'-Dichlorodiethyl ether

**84. Convert ethanal to 3-Pentyn-2-ol.**



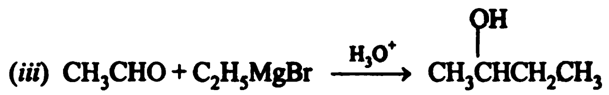
$$\underset{\text{Ethanal}}{CH_3CHO} + \underset{\text{1,Propynylmagnesium bromide}}{CH_3C{\equiv}CMgBr} \longrightarrow CH_3\underset{\underset{OMgBr}{|}}{C}H{-}C{\equiv}C\,CH_3 \xrightarrow{H_2O/H^+} CH_3{-}\underset{\underset{OH}{|}}{C}H{-}C{\equiv}C{-}CH_3$$

3.Pentyn-2-ol

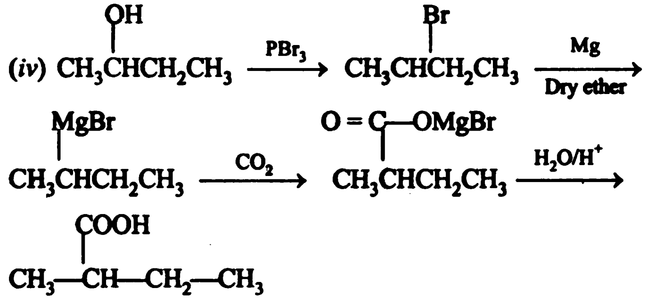
**85. Convert ethanol into α-methylbutyric acid.**

(*i*) $C_2H_5OH \xrightarrow{PBr_3} C_2H_5Br \xrightarrow[\text{Dry ether}]{Mg} \underset{\text{Ethyl mag. bromide}}{C_2H_5MgBr}$

(*ii*) $C_2H_5OH \xrightarrow{\text{Cu, 573 K}} \underset{\text{Acetaldehyde}}{CH_3CHO} + H_2$



$$(iii)\ CH_3CHO + C_2H_5MgBr \xrightarrow{H_3O^+} CH_3\overset{OH}{\overset{|}{C}}HCH_2CH_3$$



$$(iv)\ CH_3\overset{OH}{\overset{|}{C}}HCH_2CH_3 \xrightarrow{PBr_3} CH_3\overset{Br}{\overset{|}{C}}HCH_2CH_3 \xrightarrow[\text{Dry ether}]{Mg}$$

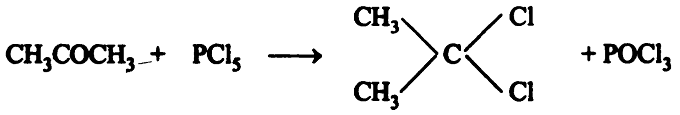
$$CH_3\overset{MgBr}{\overset{|}{C}}HCH_2CH_3 \xrightarrow{CO_2} CH_3\overset{O=C-OMgBr}{\overset{|}{C}}HCH_2CH_3 \xrightarrow{H_2O/H^+}$$

$$CH_3-\overset{COOH}{\overset{|}{C}}H-CH_2-CH_3$$

α-Methylbutyric acid

**86. Convert acetyl chloride to Isopropylidene chloride.**

$$\underset{\text{Acetyl chloride}}{CH_3COCl} + \underset{\text{Methyl cadmium chloride}}{CH_3CdCl} \longrightarrow \underset{\text{Acetone}}{CH_3COCH_3} + CdCl_2$$

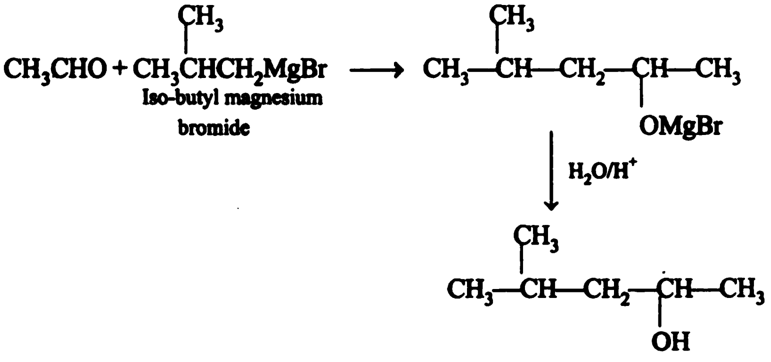


$$CH_3COCH_3 + PCl_5 \longrightarrow (CH_3)_2CCl_2 + POCl_3$$

Isopropylidene chloride

**87. Convert ethyne to 4-Methyl-2-Pentanol.**

$$\underset{\text{Ethyne}}{HC\equiv CH} + H_2O \xrightarrow[\text{1\% HgSO}_4\text{, 333 K}]{\text{40 to 42\% H}_2\text{SO}_4} \underset{\text{Ethanal}}{CH_3CHO}$$



$$CH_3CHO + CH_3\overset{CH_3}{\overset{|}{C}}HCH_2MgBr \longrightarrow CH_3-\overset{CH_3}{\overset{|}{C}}H-CH_2-\underset{OMgBr}{\underset{|}{C}}H-CH_3$$

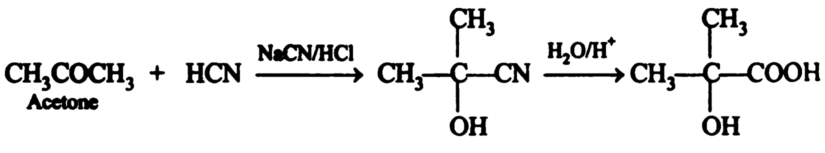
Iso-butyl magnesium bromide

$$\Big\downarrow H_2O/H^+$$

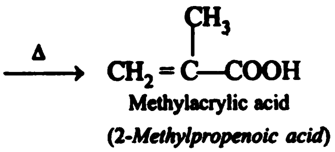
$$CH_3-\overset{CH_3}{\overset{|}{C}}H-CH_2-\underset{OH}{\underset{|}{C}}H-CH_3$$

4-Methyl-2-pentanol

**88. Convert acetone to methylacrylic acid.**

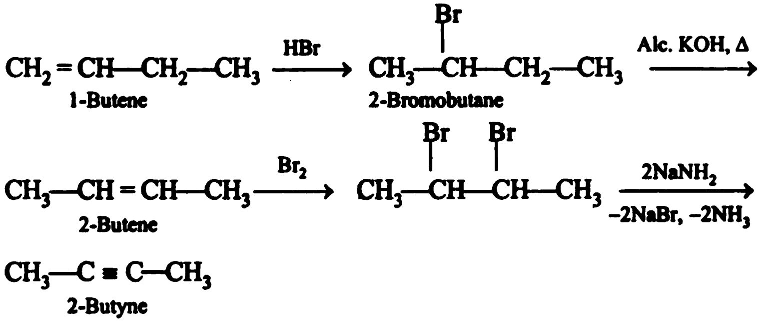


$$\underset{\text{Acetone}}{CH_3COCH_3} + HCN \xrightarrow{NaCN/HCl} CH_3-\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CN \xrightarrow{H_2O/H^+} CH_3-\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-COOH$$



$$\xrightarrow{\Delta} CH_2=\overset{\overset{\displaystyle CH_3}{|}}{C}-COOH$$

## 89. Convert 1-butene to 2-butyne.

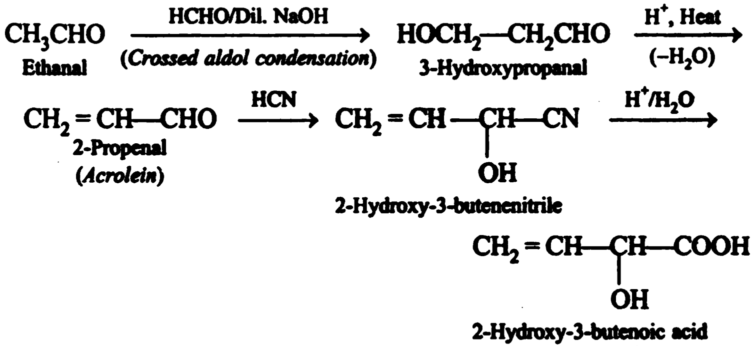


$$\underset{\text{1-Butene}}{CH_2=CH-CH_2-CH_3} \xrightarrow{HBr} \underset{\text{2-Bromobutane}}{CH_3-\overset{\overset{\displaystyle Br}{|}}{C}H-CH_2-CH_3} \xrightarrow{\text{Alc. KOH, }\Delta}$$

$$\underset{\text{2-Butene}}{CH_3-CH=CH-CH_3} \xrightarrow{Br_2} CH_3-\overset{\overset{\displaystyle Br}{|}}{C}H-\overset{\overset{\displaystyle Br}{|}}{C}H-CH_3 \xrightarrow[-2NaBr,\ -2NH_3]{2NaNH_2}$$

$$\underset{\text{2-Butyne}}{CH_3-C\equiv C-CH_3}$$

## 90. Convert ethanal to 2-hydroxy-3-butenoic acid (*I.I.T. 1990*)

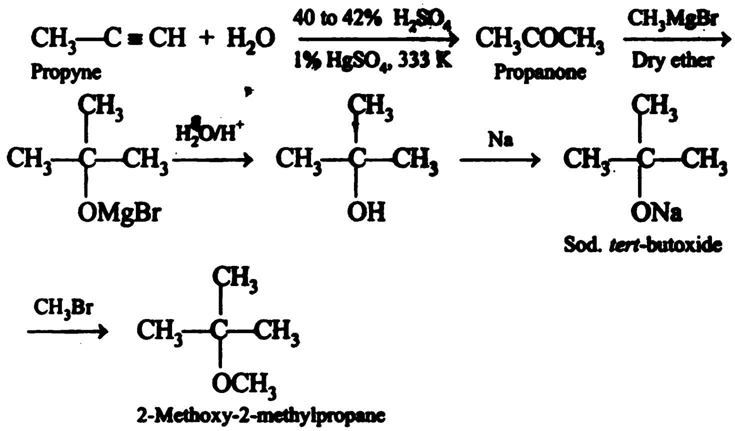


$$\underset{\text{Ethanal}}{CH_3CHO} \xrightarrow[\textit{(Crossed aldol condensation)}]{HCHO/Dil.\ NaOH} \underset{\text{3-Hydroxypropanal}}{HOCH_2-CH_2CHO} \xrightarrow[(-H_2O)]{H^+,\ Heat}$$

$$\underset{\substack{\text{2-Propenal}\\ \textit{(Acrolein)}}}{CH_2=CH-CHO} \xrightarrow{HCN} \underset{\text{2-Hydroxy-3-butenenitrile}}{CH_2=CH-\underset{\underset{\displaystyle OH}{|}}{C}H-CN} \xrightarrow{H^+/H_2O}$$

$$\underset{\text{2-Hydroxy-3-butenoic acid}}{CH_2=CH-\underset{\underset{\displaystyle OH}{|}}{C}H-COOH}$$

## 91. Convert propyne to 2-methoxy-2-methylpropane.



$$\underset{\text{Propyne}}{CH_3-C\equiv CH} + H_2O \xrightarrow[1\%\ HgSO_4,\ 333\ K]{40\ to\ 42\%\ H_2SO_4} \underset{\text{Propanone}}{CH_3COCH_3} \xrightarrow[\text{Dry ether}]{CH_3MgBr}$$

$$CH_3-\underset{\underset{\displaystyle OMgBr}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_3 \xrightarrow{H_2O/H^+} CH_3-\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_3 \xrightarrow{Na} \underset{\text{Sod. \textit{tert}-butoxide}}{CH_3-\underset{\underset{\displaystyle ONa}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_3}$$

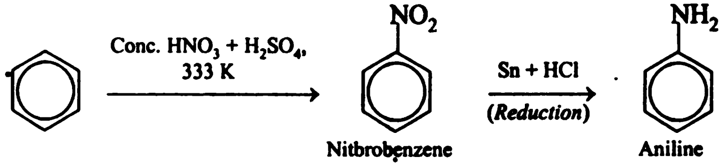
$$\xrightarrow{CH_3Br} \underset{\text{2-Methoxy-2-methylpropane}}{CH_3-\underset{\underset{\displaystyle OCH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_3}$$

## AROMATIC CONVERSTIONS

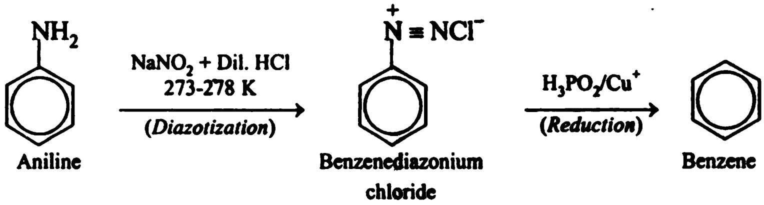
### TWO-STEP CONVERSIONS

**92. Convert benzene to aniline**

*(I.I.T. 1983 ; D.S.B. 1990 ; B.I.T. Ranchi 1990)*

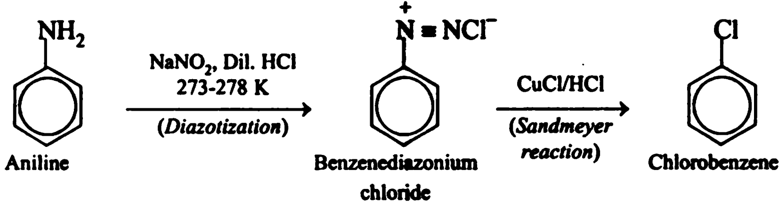


**93. Convert aniline to benzene**

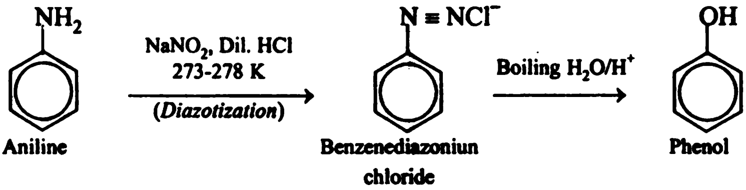


**94. Convert aniline to chlorobenzene**

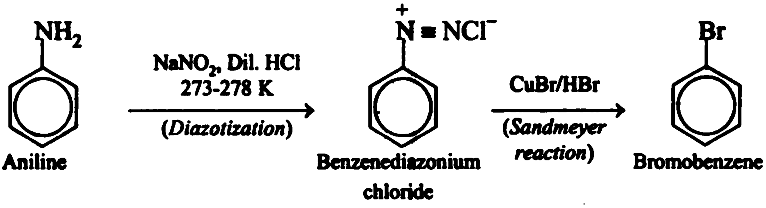
*(I.I.T. 1985 ; D. S. B. 1987 ; A. I. S. B. 1994)*



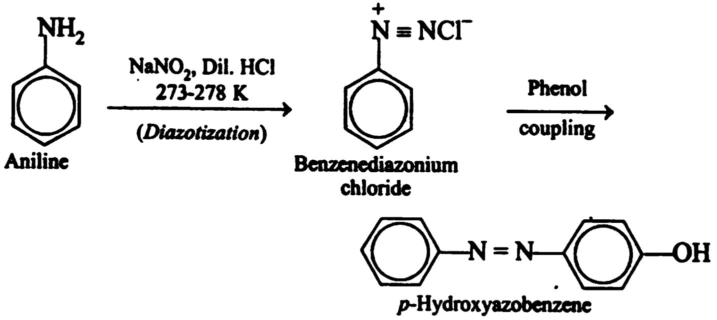
**95. Convert aniline to phenol** *(Roorkee 1980)*



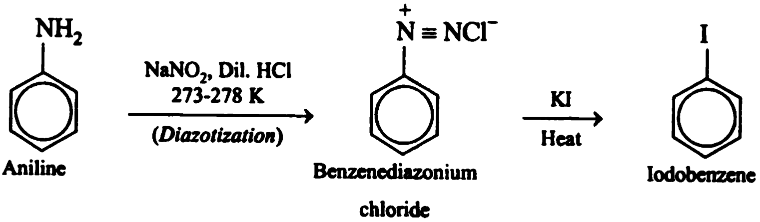
**95a. Convert aniline to bromobenzene**



### 96. Convert aniline to p-hydroxyazobenzene

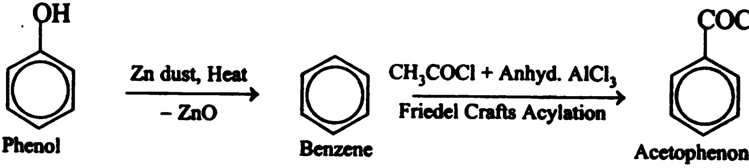


### 97. Convert aniline to iodobenzene



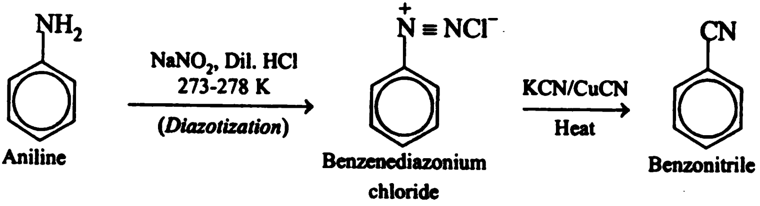
### 98. Convert phenol to acetophenone

*(I.I.T. 1989)*



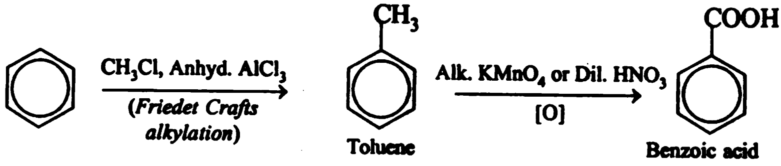
### 99. Concert aniline to benzonitrile

*(A.I.S.B. 1991)*

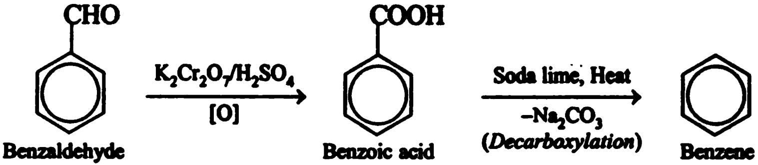


### 100. Concert benzene to benzoic acid

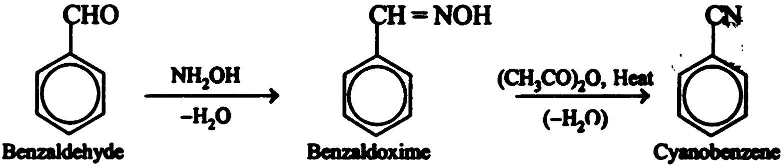
*(Roorkee 1980)*



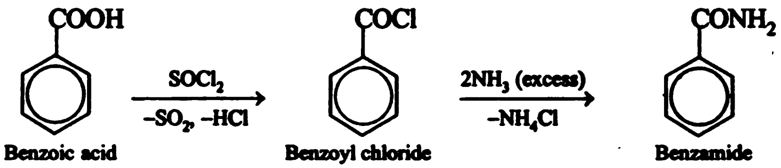
**101. Convert benzaldehyde to benzene**



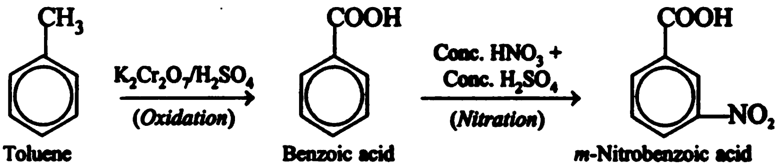
**102. Convert benzaldehyde to cyanobenzene** *(I.I.T. 1988)*



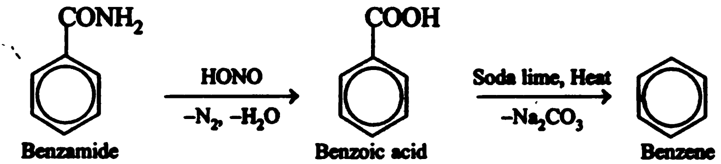
**103. Convert benzoic acid to benzamide** *(D.S.B. 1992)*



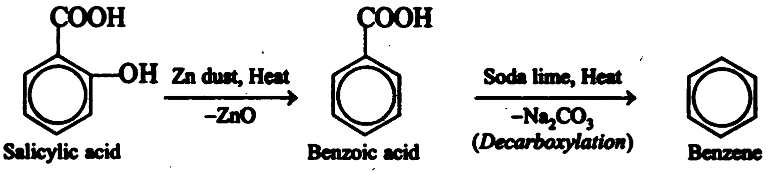
**104. Convert toluene to m-nitrobenzoic acid** *(I.I.T. 1987 ; D.S.B. 1995)*



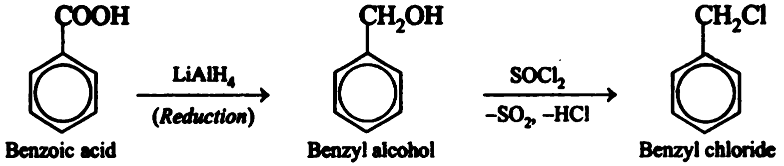
**105. Convert benzamide to benzene**



**106. Convert salicylic acid to benzene**

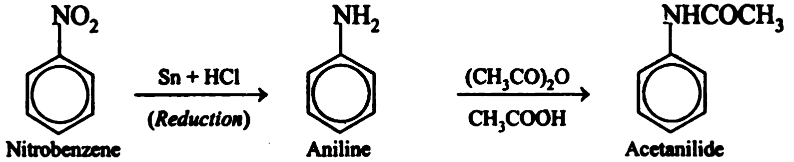


### 107. Convert benzoic acid to benzyl chloride



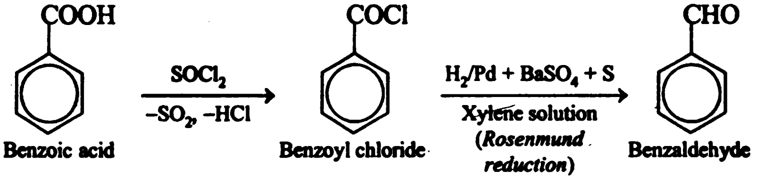
### 108. Convert nitrobenzene to acetanilide

(*H.S.B. 1996*)



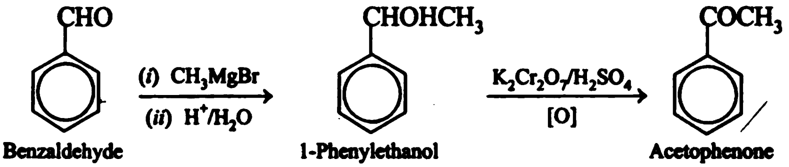
### 109. Convert benzoic acid to benzaldehyde

(*A.I.S.B. 1991 S*)



### 110. Convert benzaldehyde to acetophenone

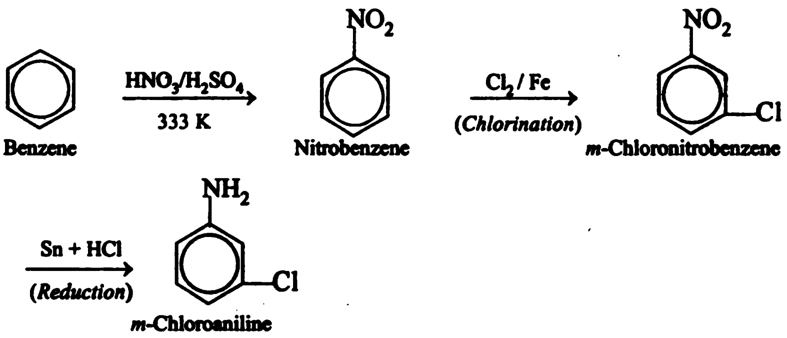
(*A.I.S.B. 1995*)



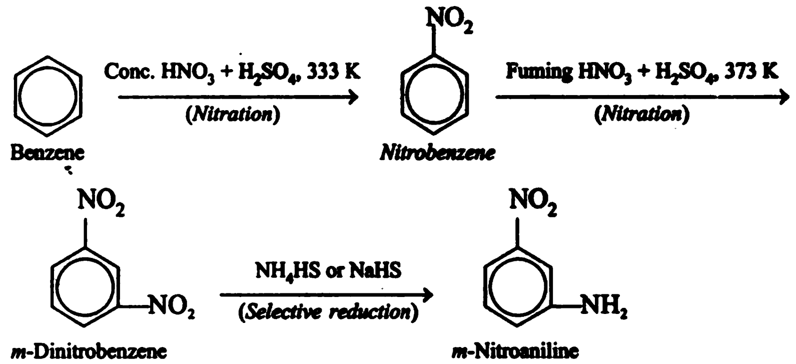
## THREE-STEP CONVERSIONS

### 111. Convert benzene to m-chloroaniline

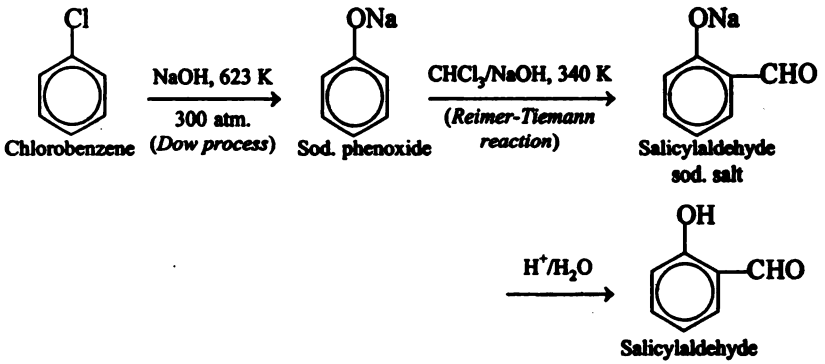
(*Roorkee 1988*)



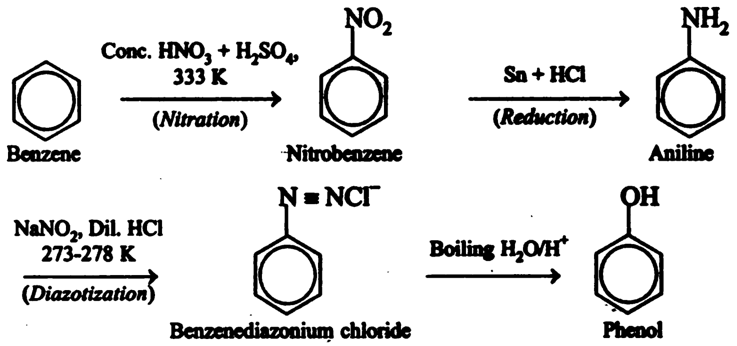
### 112. Convert benzene to m-nitroaniline



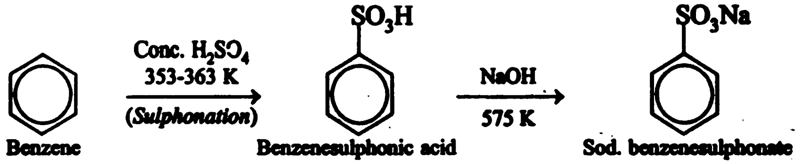
### 113. Convert chlorobenzene to salicylaldehyde *(A.I.S.B. 1990)*

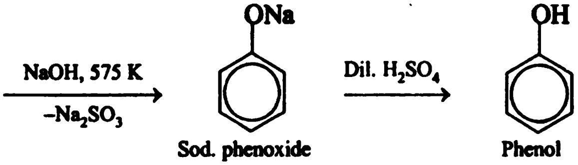


### 114. Convert benzene to phenol. *(A.I.S.B. 1985 S ; P.S.B. 1992)*



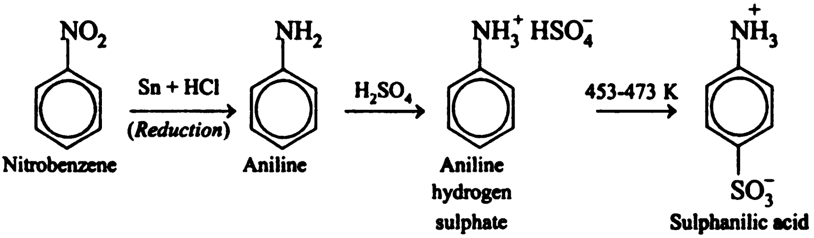
This conversion can also be achieved as follows :



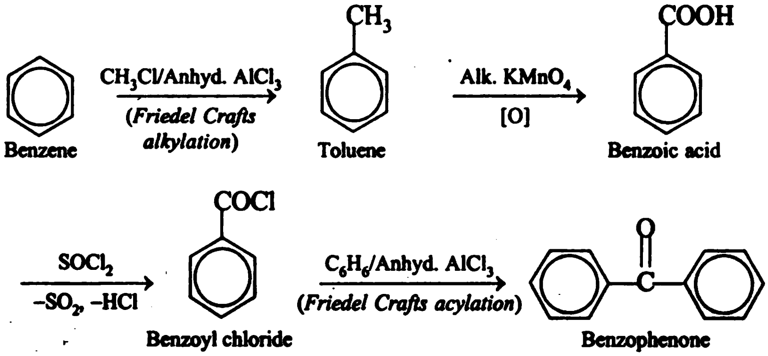


## 115. Convert nitrobenzene to sulphanilic acid

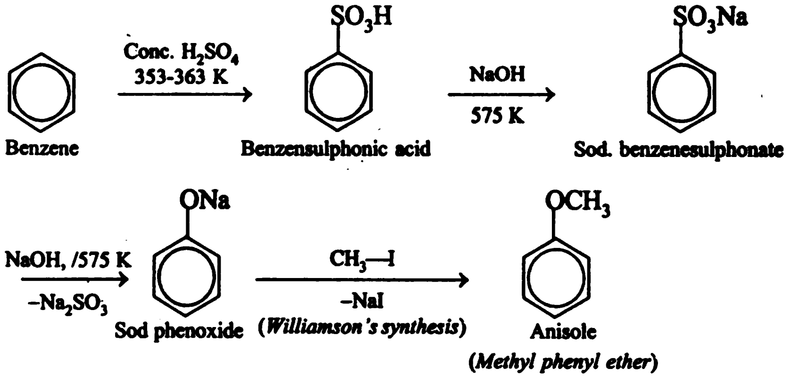
*(H.S.B. 1990 ; P.S.B. 1993)*



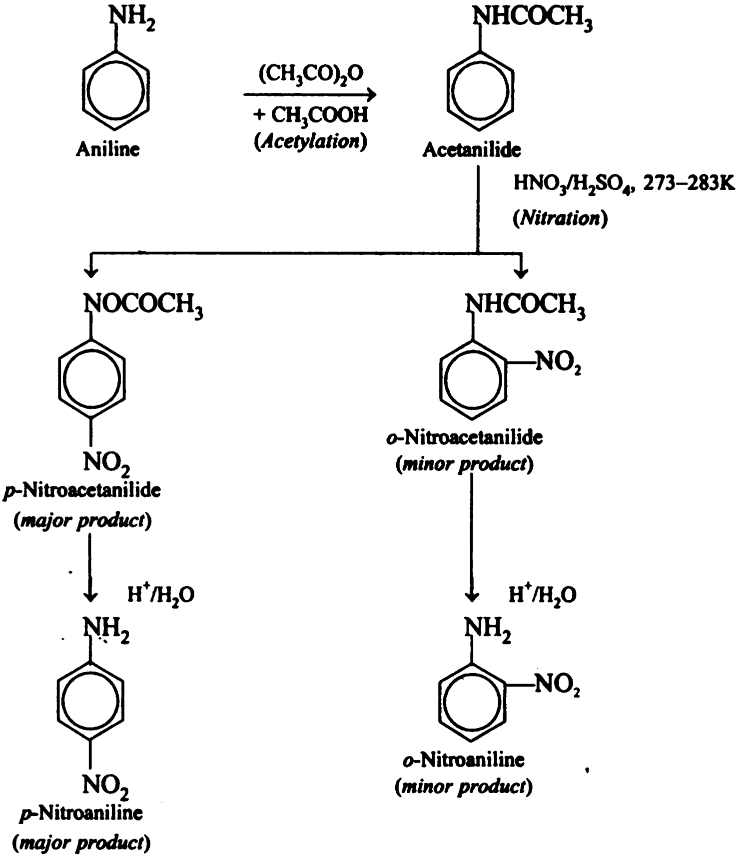
## 116. Convert benzene to benzophenone



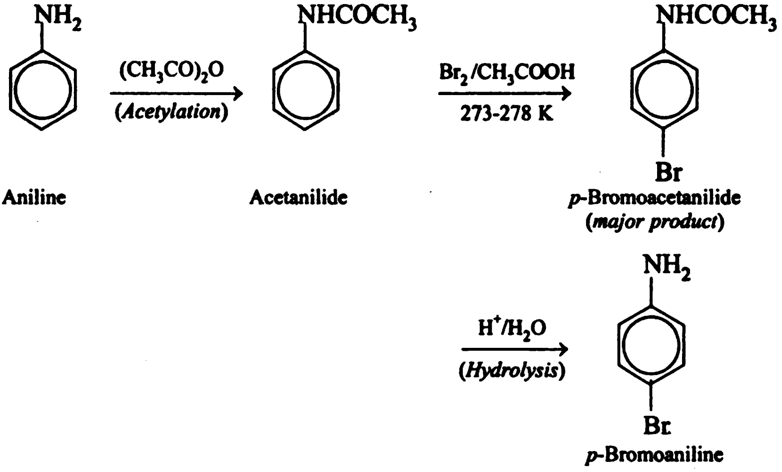
## 117. Convert benzene to anisole



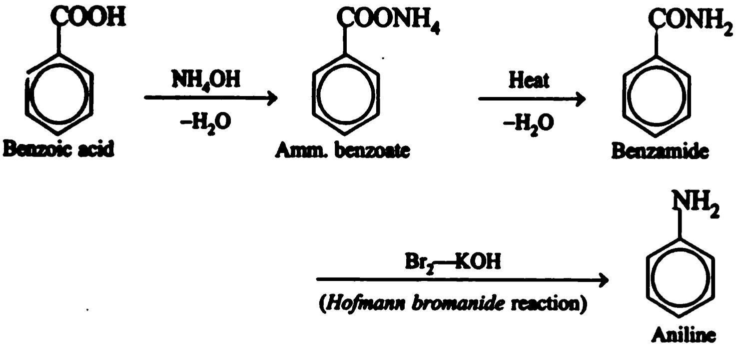
**118. Convert aniline to o- and p-nitroaniline.** (*Roorkee 1986, DSB 1992*)



**119. Convert aniline to p-bromoaniline**

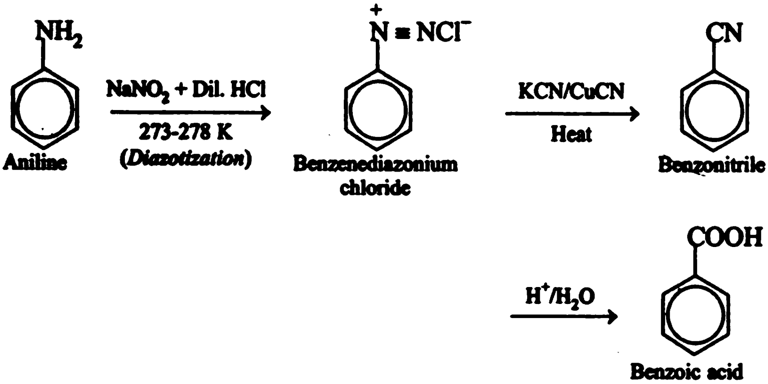


### 120. Convert benzoic acid to aniline

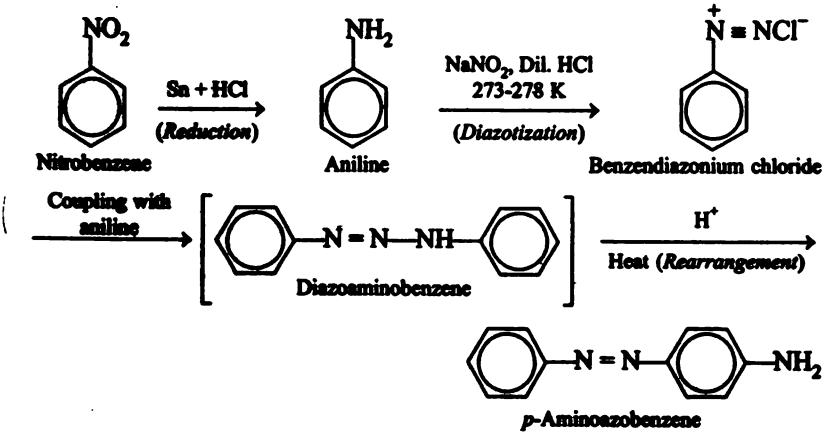


(*Roorkee 1982*)

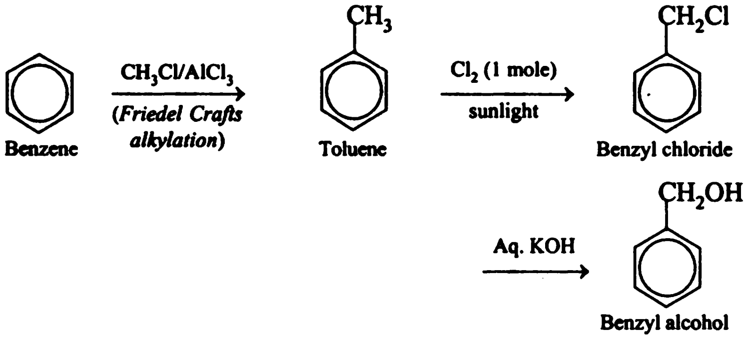
### 121. Convert aniline to benzoic acid



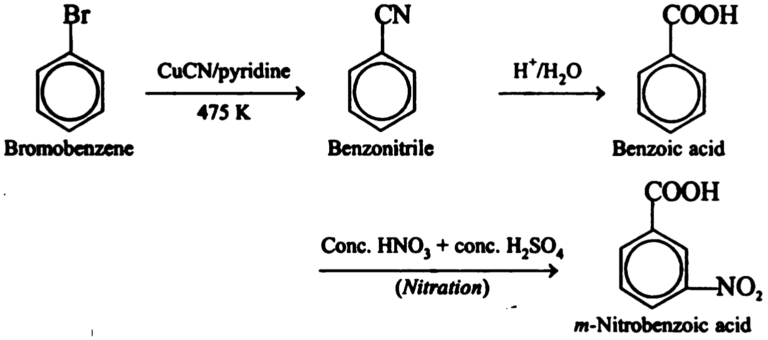
### 122. Convert nitrobenzene to p-aminoazobenzene



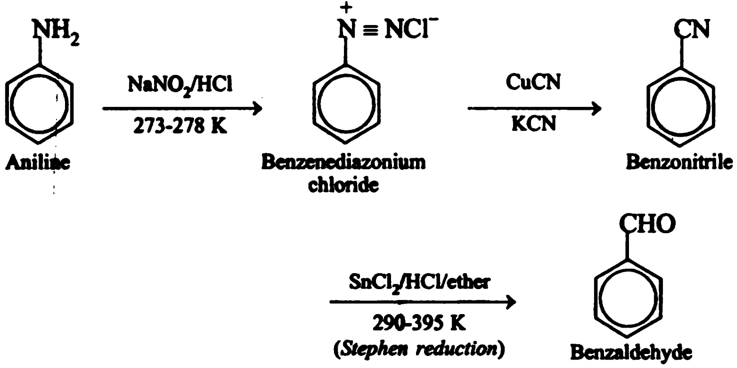
### 123. Convert benzene into benzyl alcohol *(Roorkee 1983)*



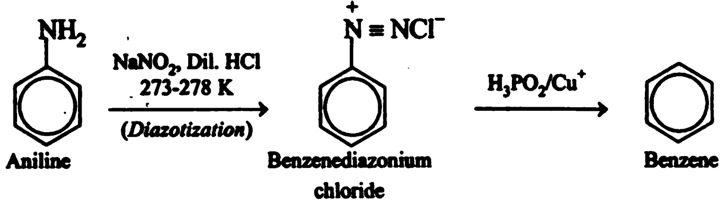
### bromobenzene to m-nitrobenzoic acid *(M.L.N.R. Allahabad, 1994)*

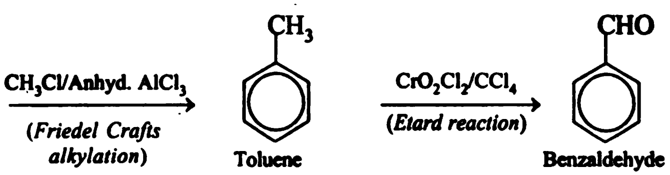


### 124. Convert aniline to benzaldehyde *(D.S.B. 1989)*



This conversion can also be brought about as under :

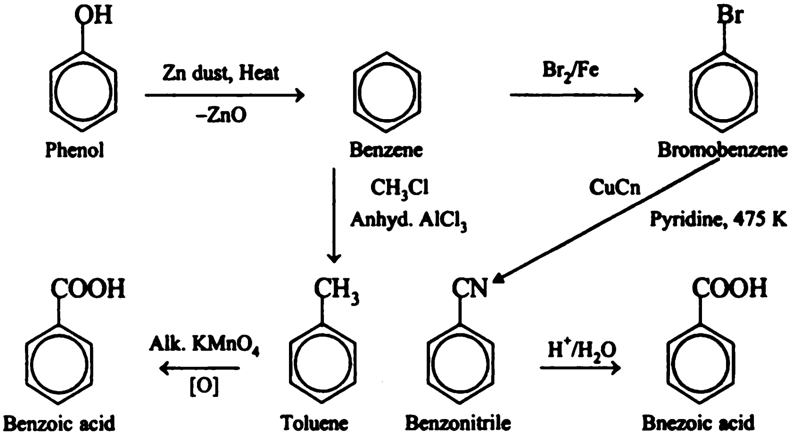




## MULTI-STEP CONVERSIONS

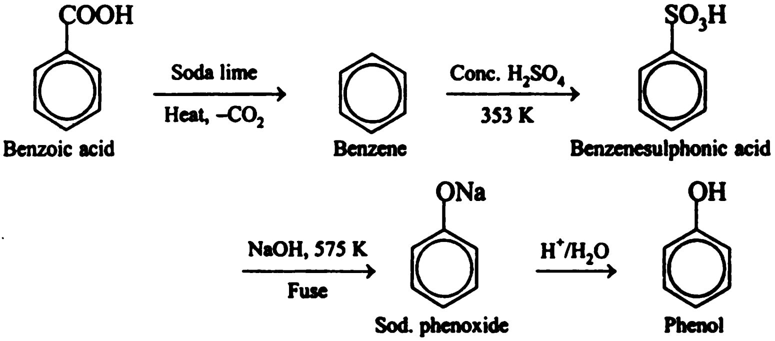
### 125. Convert phenol to benzoic acid

Two different routes are available as explained below.



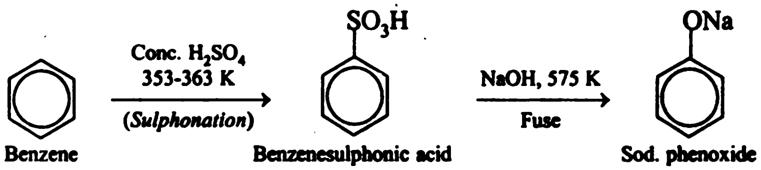
### 126. Convert benzoic acid to phenol

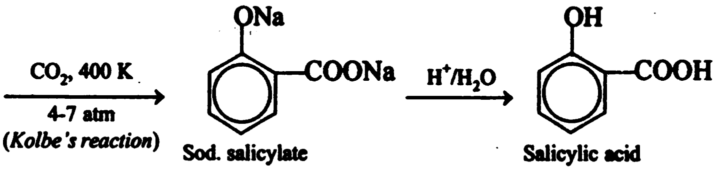
*(P.M.T. Rohtak 1988)*



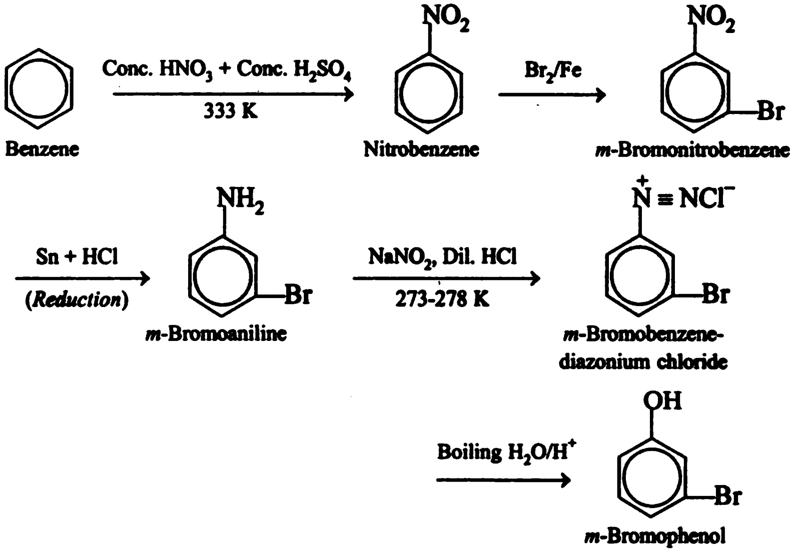
### 127. Convert benzene to salicyclic acid

*(D.S.B. 1990)*

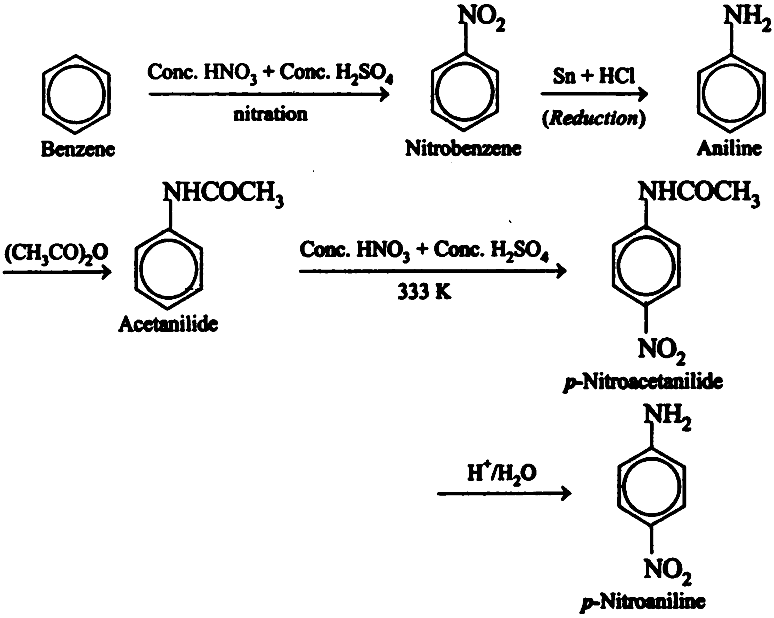




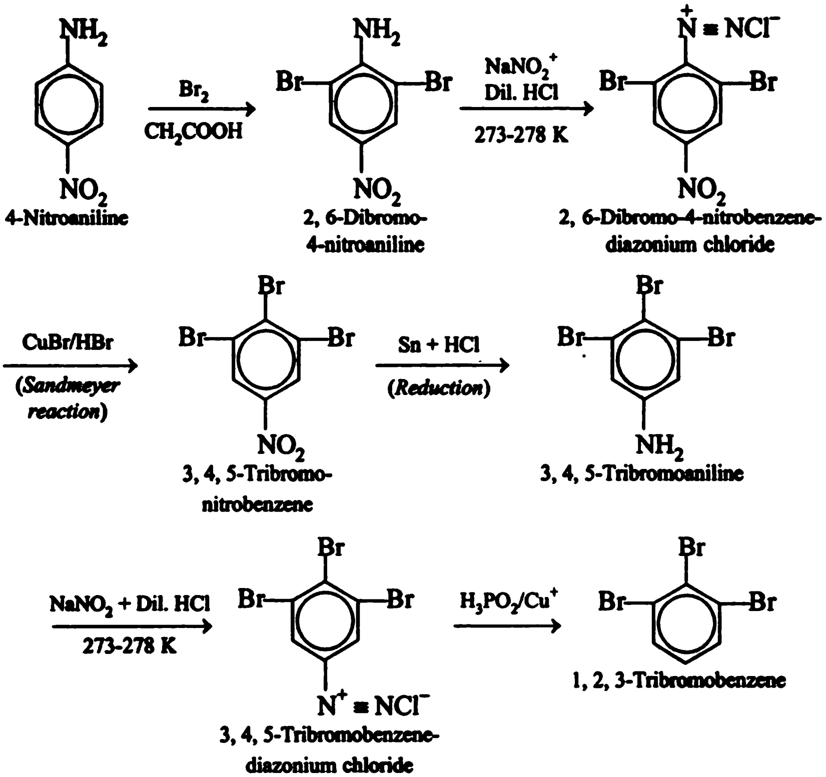
## 128. Convert benzene to m-bromophenol



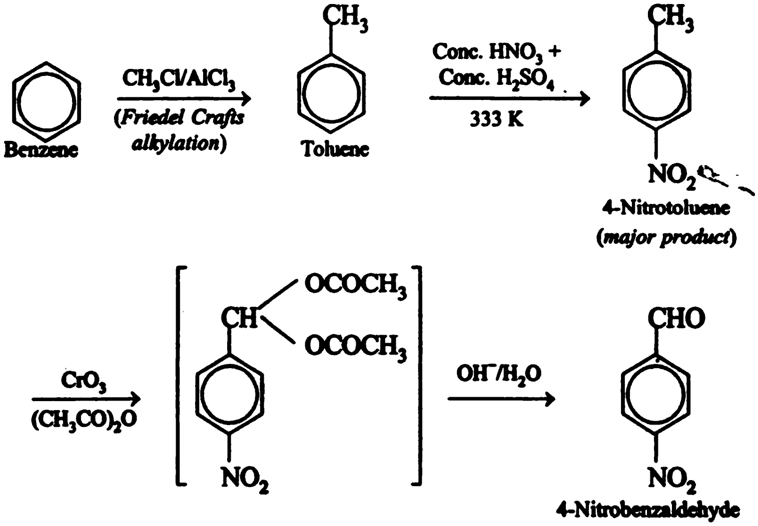
## 129. Convert benzene to p-nitroaniline



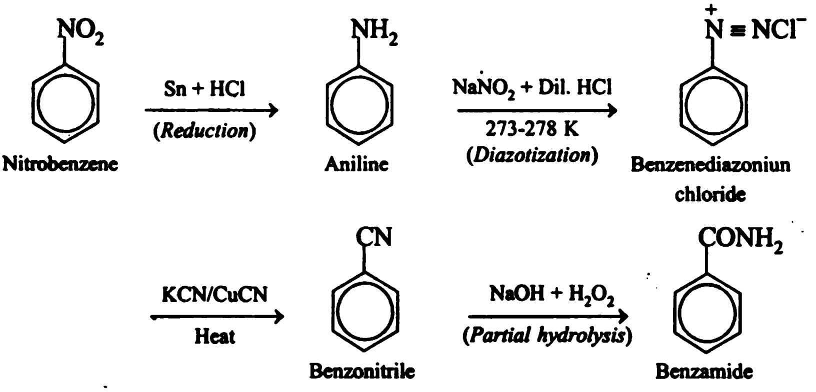
### 130. Convert 4-nitroaniline to 1, 2, 3-tribromobenzene (*I.I.T. 1990*)



### 131. Convert benzene into 4-nitrobenzaldehyde (*I.I.T. 1994*)



**132. Convert nitrobenzene to benzamide** *(I.I.T. 1994)*

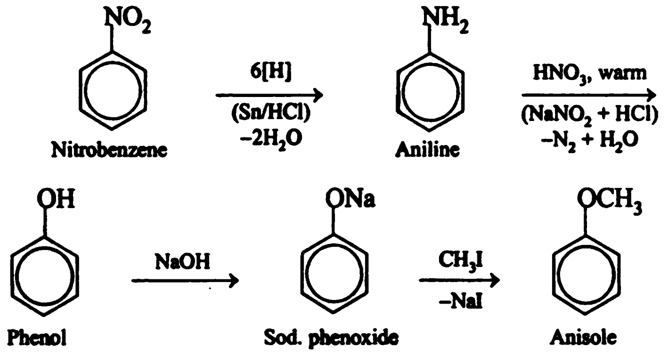


**133. Convert $CH_3CHO$ to $(CH_3)_2\overset{OH}{\overset{|}{C}}—Ph$ (Acetaldehyde into dimethylphenyl carbinol)** *(M.L.N.R. Allahabad 1994)*

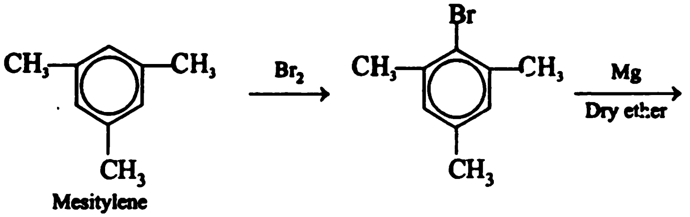
$$\underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow[\text{[O]}]{K_2Cr_2O_7 + H_2SO_4} \underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{Ca(OH)_2} \underset{\text{Cal. acetate}}{(CH_3COO)_2Ca}$$

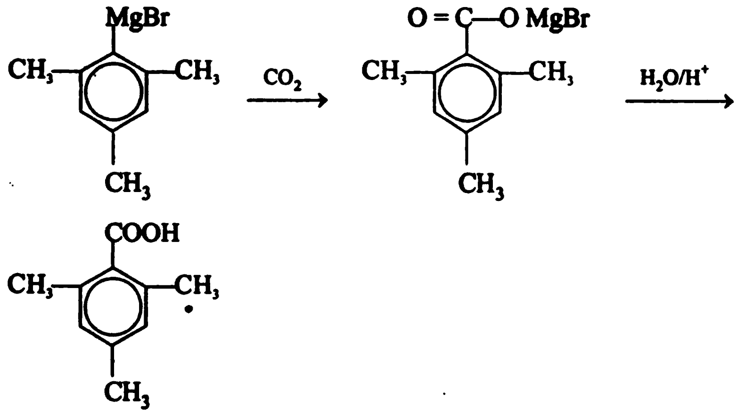
$$\xrightarrow[-CaCO_3]{\text{Dry distillation}} \underset{\text{Acetone}}{(CH_3)_2\,C=O} \xrightarrow[H^+/H_2O]{PhMgBr/ether} \underset{\text{Dimethylphenyl carbinol}}{(CH_3)_2\overset{OH}{\overset{|}{C}}—Ph}$$

**134. Convert nitrobenzene to anisole.**



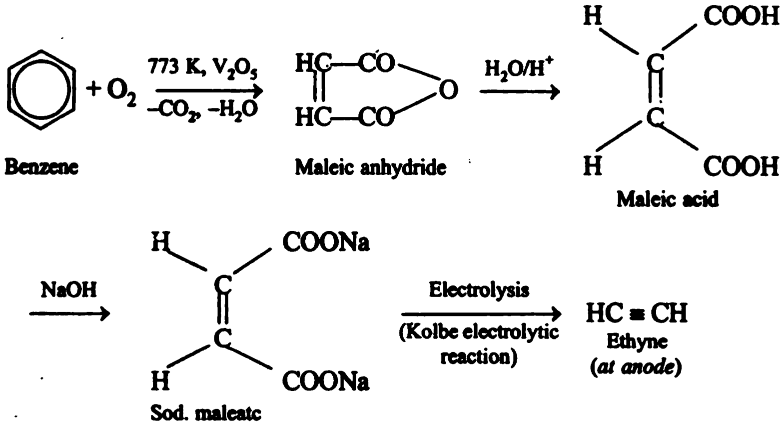
**135. Convert mesitylene to mesitoic acid.**



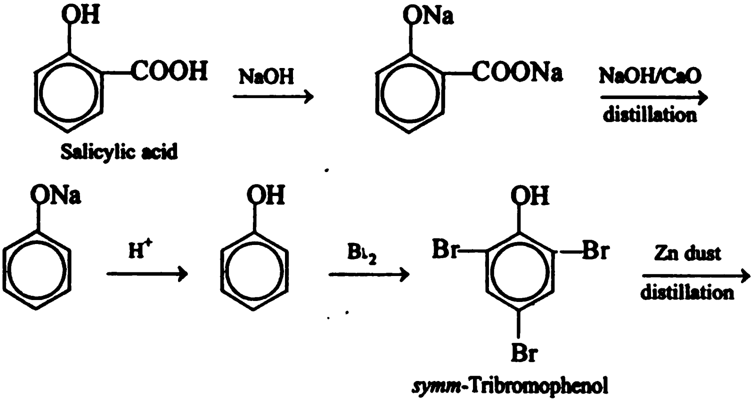


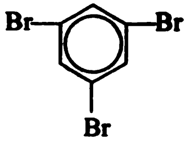
Mesitoic acid
(2, 4,-*Trimethylbenzoic acid*)

## 136. Convert benzene to ethyne.



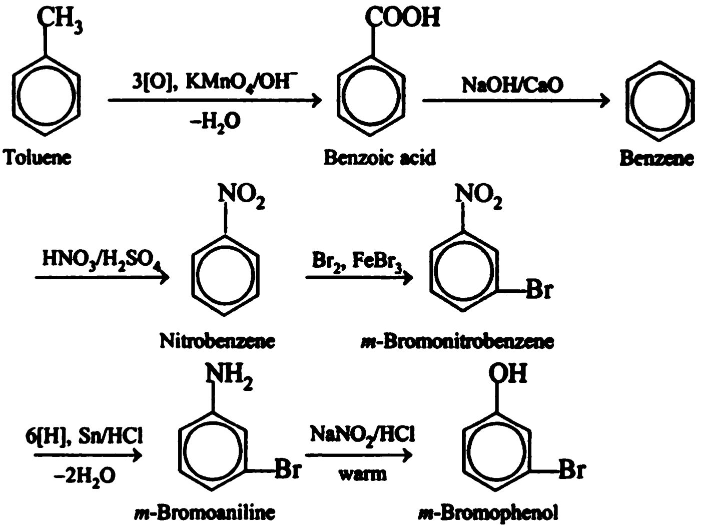
## 137. Convert salicylic acid to symm-tribromobenzene.



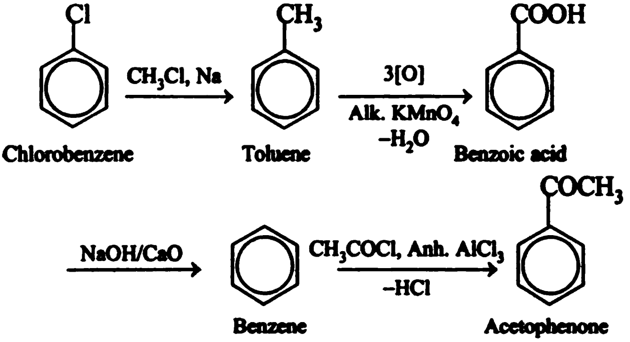


*sym*-Tribromobezene

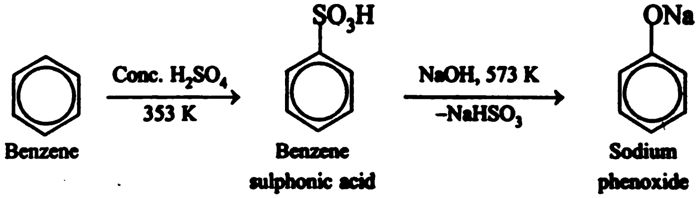
## 138. Convert toluene to m-bromophenol.

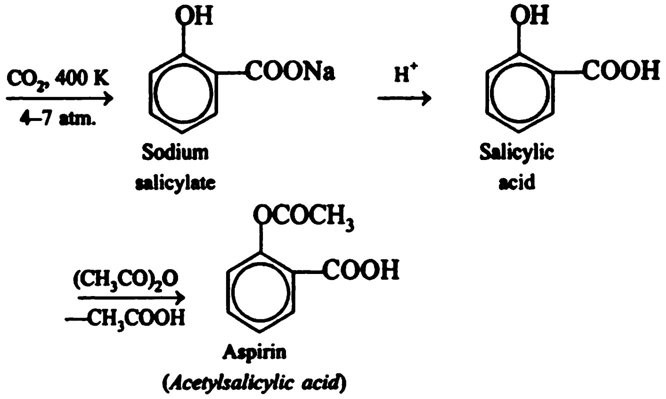


## 139. Convert chlorobenzene to acetophenone.

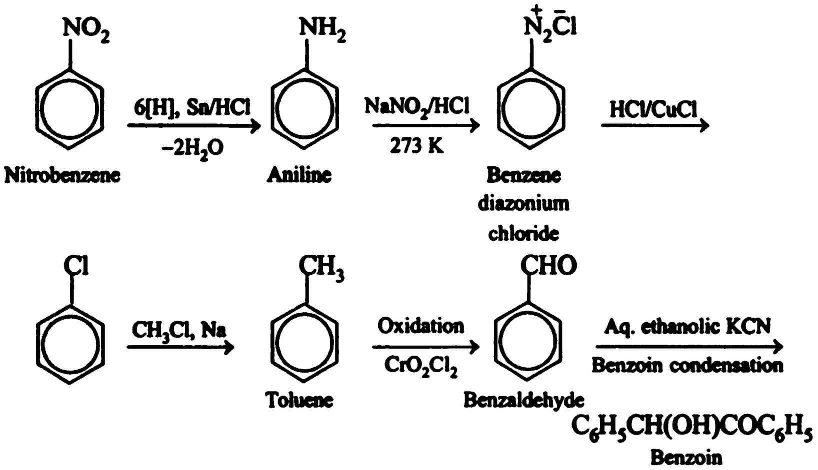


## 140. Convert benzene to aspirin.

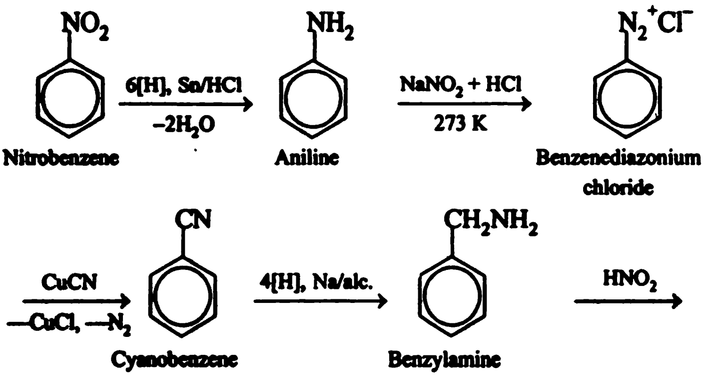


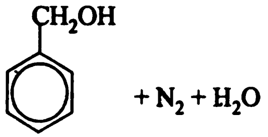


## 141. Convert nitrobenzene to benzoin.



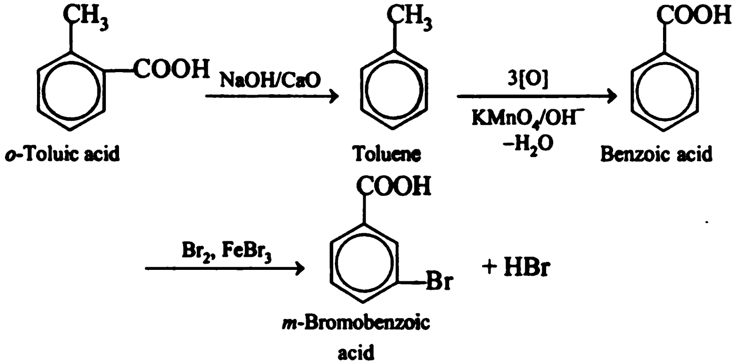
## 142. Convert nitrobenzene to benzyl alcohol.



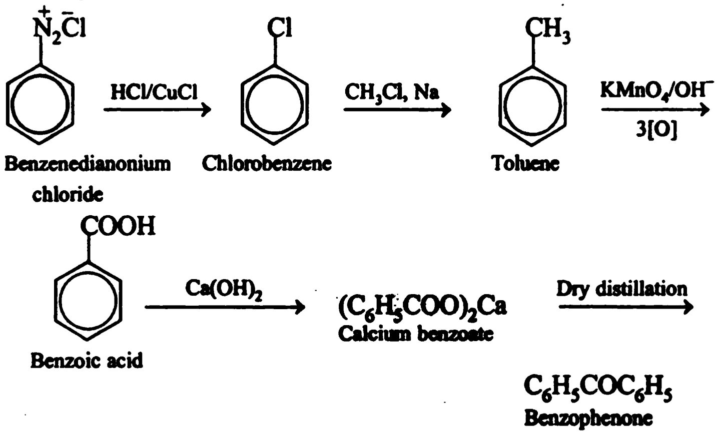


Benzyl alcohol

### 143. Convert *o*-toluic acid to *m*-bromobenzoic acid.

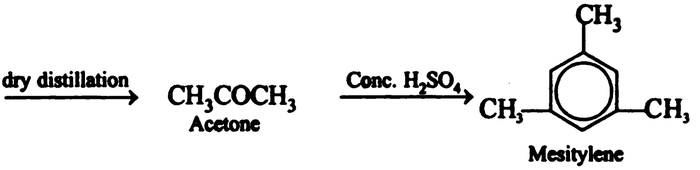


### 144. Convert benzendiazonium chloride to benzophenone.

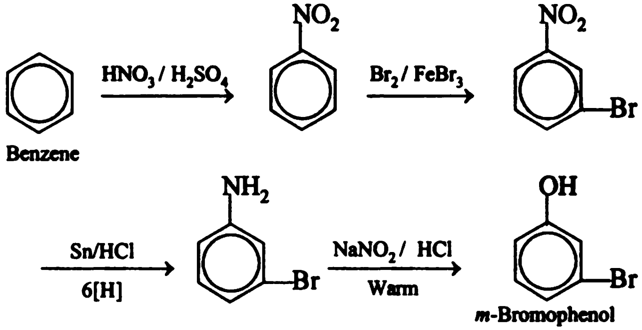


### 145. Convert acetonitrile to mesitylene.

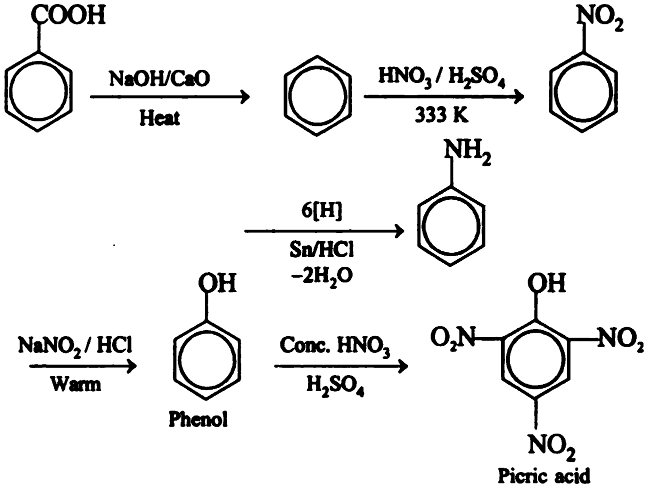
$$\underset{\text{Acetonitrile}}{CH_3CN} \xrightarrow[\text{dil. acid or alkali}]{\text{Complete hydr.}} CH_3COOH \xrightarrow{Ca(OH)_2} \underset{\text{Calcium acetate}}{(CH_3COO)_2Ca}$$



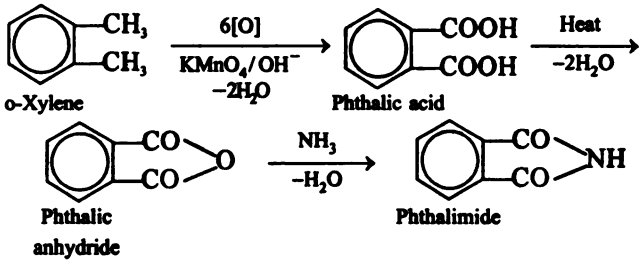
**146. Convert benzene to *m*-bromophenol.**



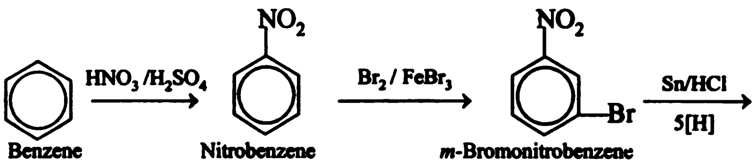
**147. Convert benzoic acid to picric acid.**

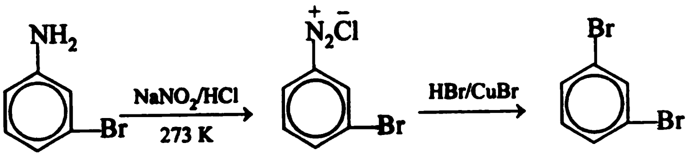


**148. Convert *o*-xylene to phthalimide.**

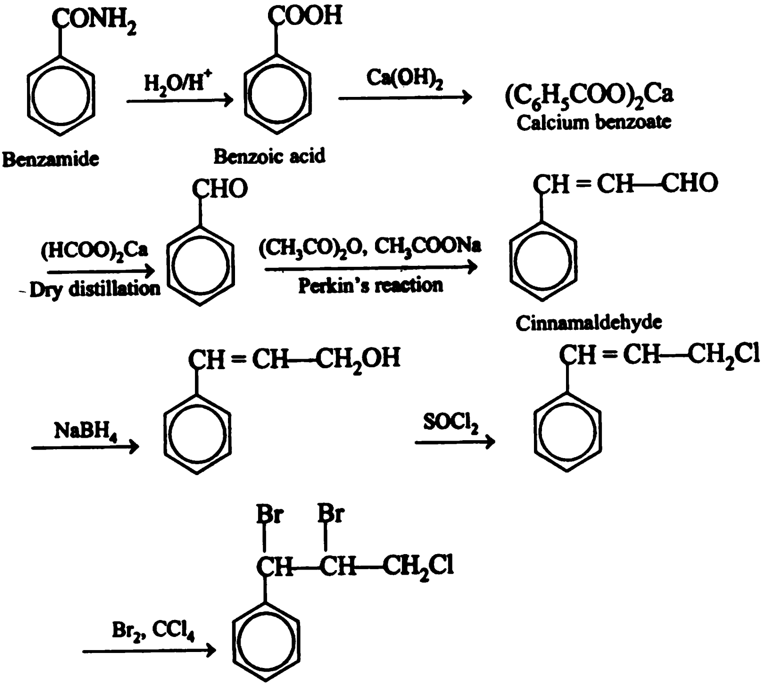


**149. Convert benzene to *m*-dibromobenzene.**

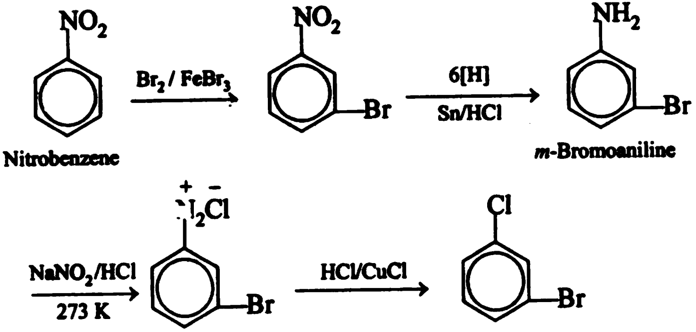




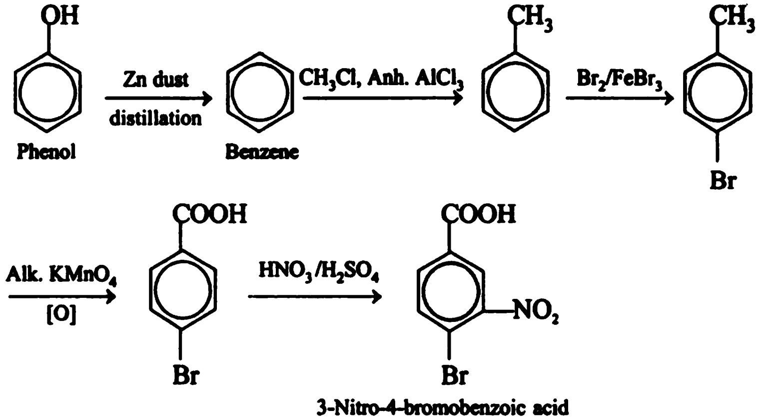
## 150. Convert benzamide to 1-Phenyl-1, 2-dibromo-3-chloropropane.



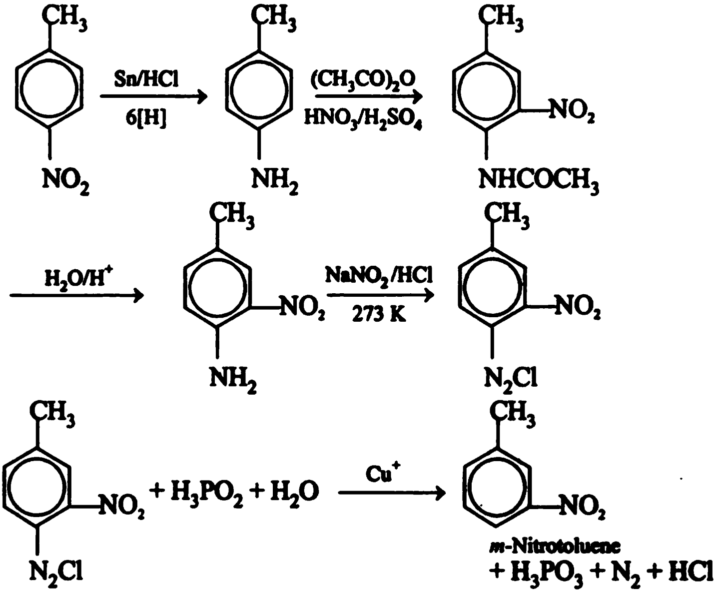
## 151. Convert nitrobenzene to *m*-bromochlorobenzene.



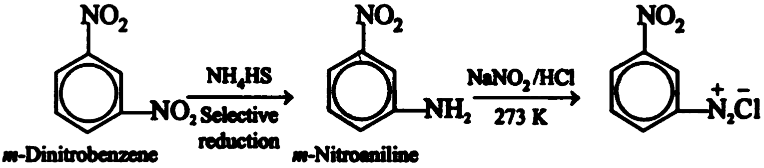
**152. Convert phenol to 3 nitro-4-bromobenzoic acid.**

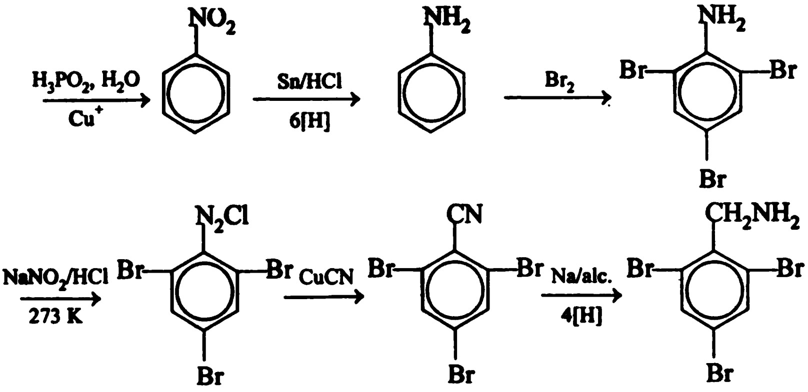


**153. Convert *p*-nitrotoluene to *m*-nitrotoluene.**



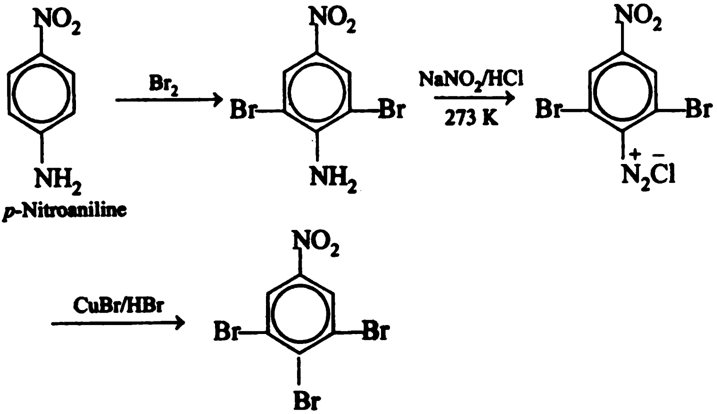
**154. Convert *m*-dinitrobenzene to 2, 4, 6-tribromobenzylamine.**





2, 4, 6-Tribromobenzylamine

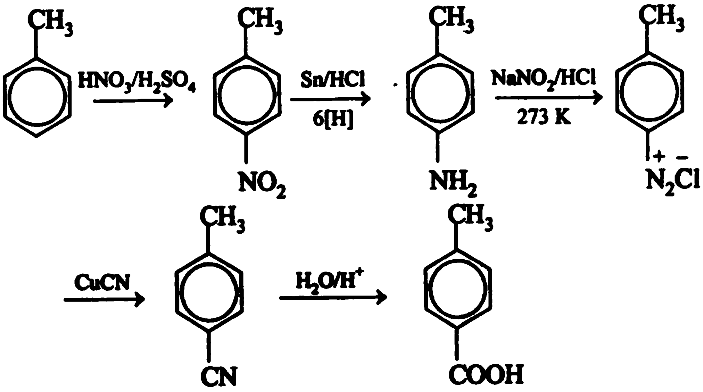
## 155. Convert *p*-nitroaniline to 3, 4, 5-tribromonitrobenzene.



*p*-Nitroaniline

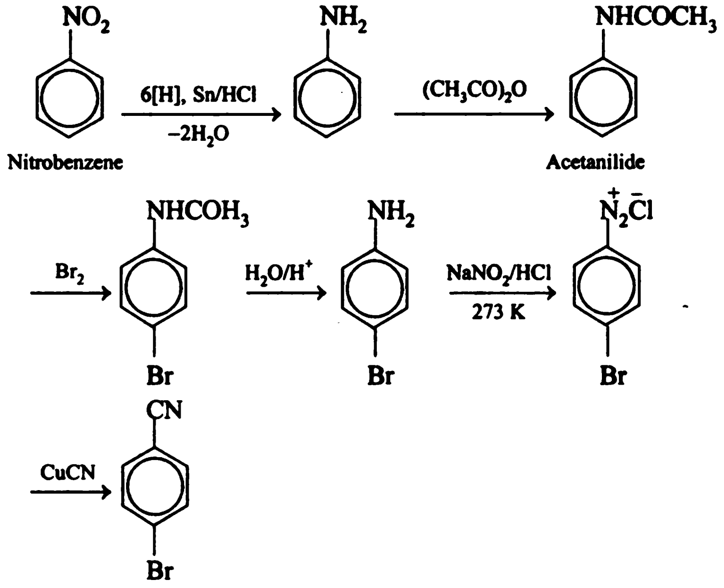
3, 4, 5-Tribromonitrobenzene

## 156. Convert toluene to *p*-Toluic acid.



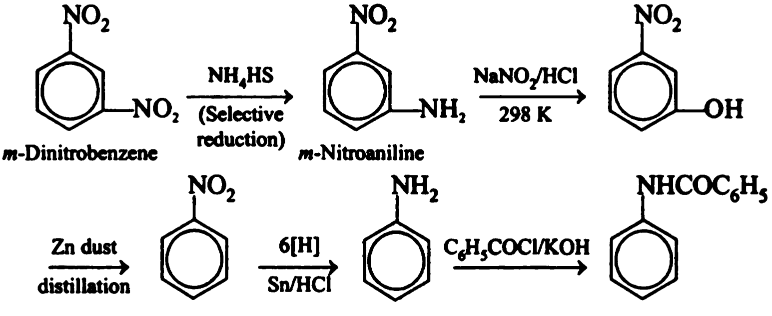
*p*-Toluic acid

### 157. Convert nitrobenzene to *p*-bromobenzonitrile.



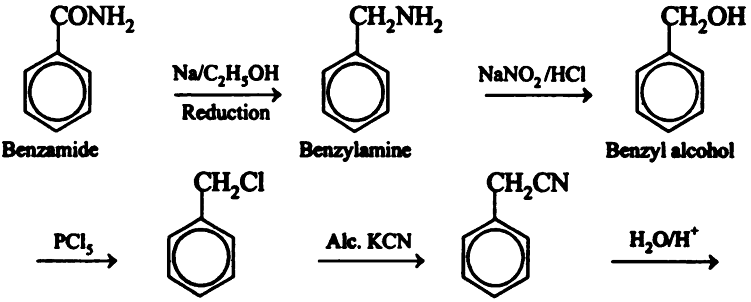
*p*-Bromobenzonitrile

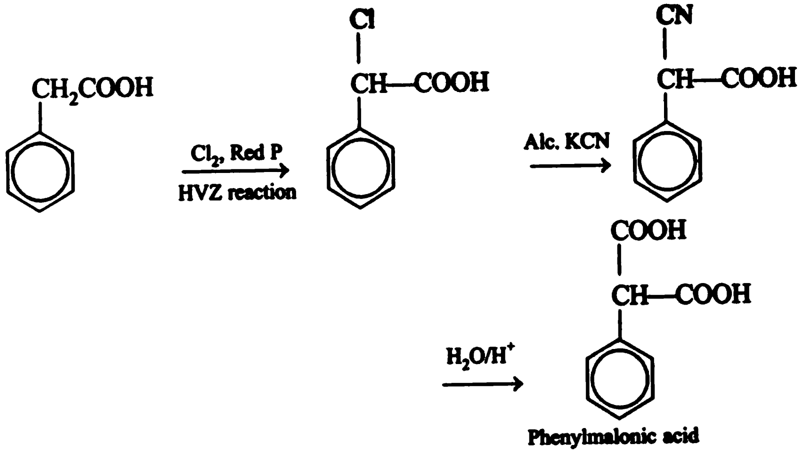
### 158. Convert *m*-dinitrobenzene to Benzanilide.



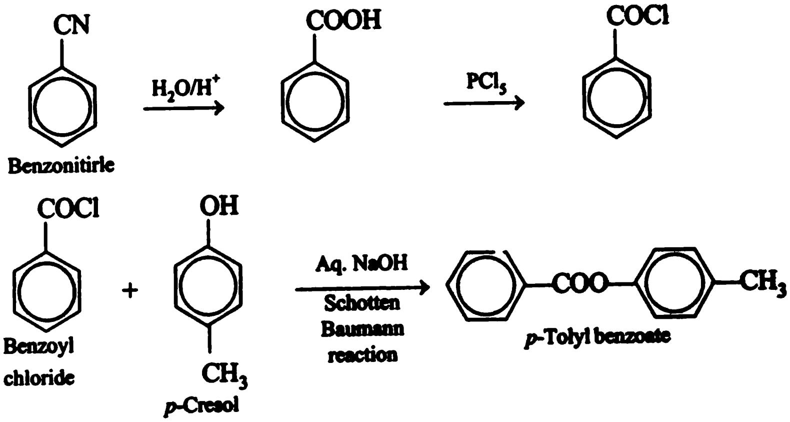
Benzanilide

### 159. Convert benzamide to phenylmalonic acid.

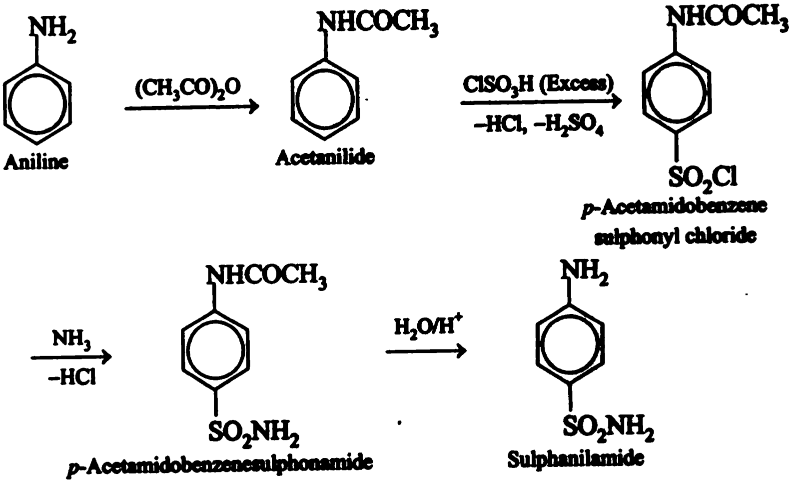




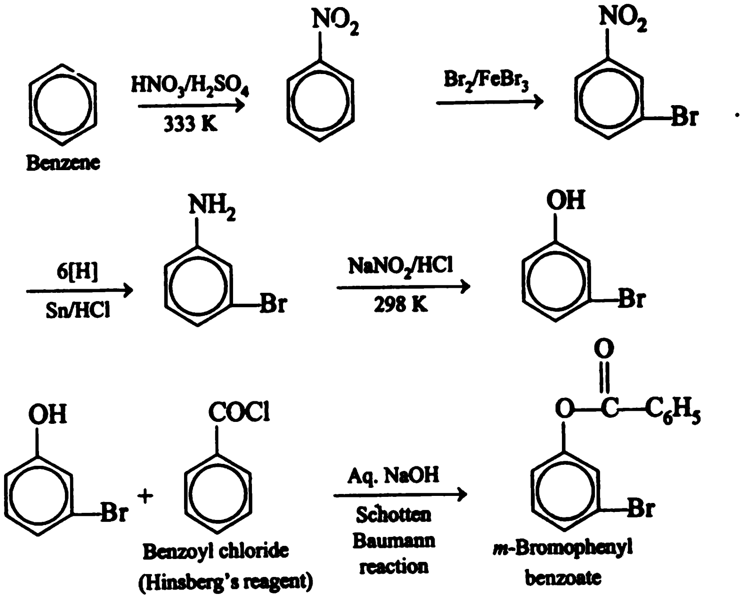
### 160. Convert benzonitrile to *p*-toyl benzoate.



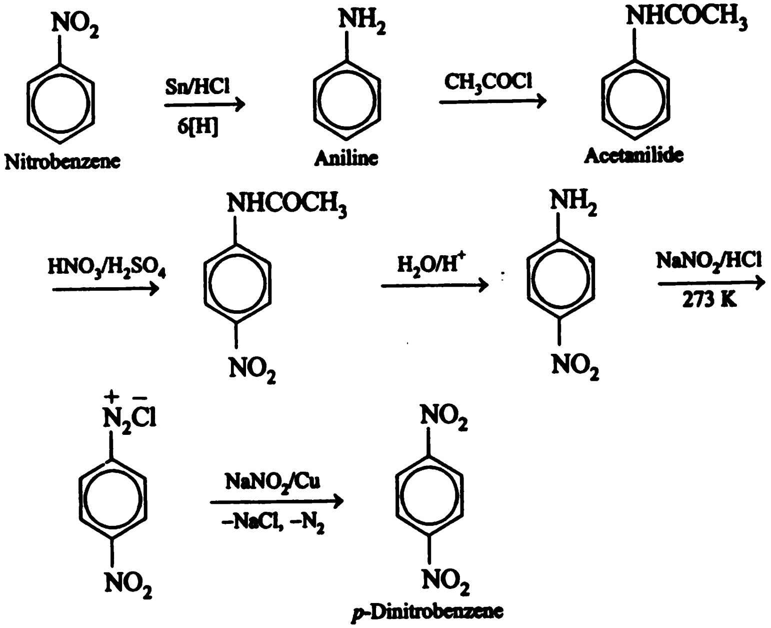
### 161. Convert aniline to sulphanilamide.



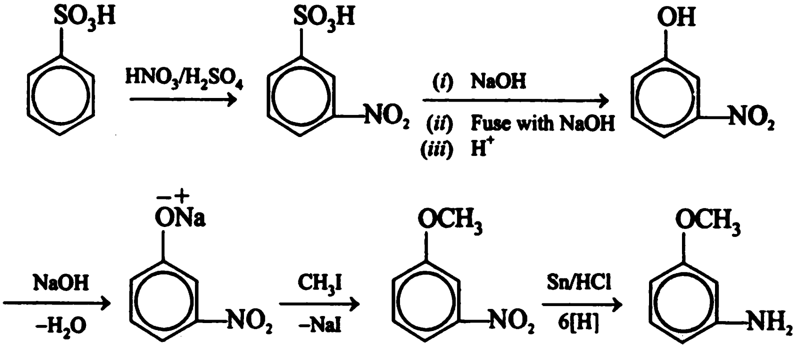
**162. Convert benzene to *m*-bromophenyl benzoate.**



**163. Convert nitrobenzene to *p*-dinitrobenzene.**



**164. Convert benzenesulphonic acid to *m*-anisidine.**



*m*-Anisidine
(*m*-Methoxyaniline)

## MISCELLANEOUS EXAMPLES

**165. How will you convert :**

**(*i*) Propanoic acid to acetic acid.**

**(*ii*) Acetaldehyde to acetone ?** *(A.I.S.B. 1992)*

(*i*)
$$\underset{\text{Propanoic acid}}{CH_3CH_2COOH} \xrightarrow{NH_3} \underset{\text{Ammonium propionate}}{CH_3CH_2COONH_4} \xrightarrow[-H_2O]{\text{Heat}}$$

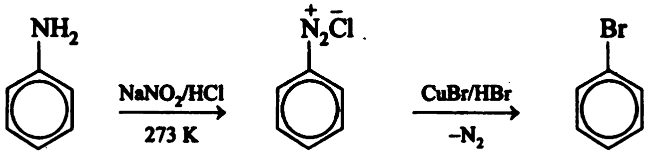
$$\underset{\text{Propionamide}}{CH_3CH_2CONH_2} \xrightarrow[\Delta]{Br_2/KOH} \underset{\text{Ethylamine}}{CH_3CH_2NH_2} \xrightarrow[(NaNO_2 + HCl)]{HNO_2} \underset{\text{Ethyl alcohol}}{CH_3CH_2OH}$$

$$\xrightarrow[[O]]{K_2Cr_2O_7/H^+} \underset{\text{Acetic acid}}{CH_3COOH}$$

(*ii*)
$$\underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow[[O]]{K_2Cr_2O_7/H^+} \underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{Ca(OH)_2} \underset{\text{Calcium acetate}}{(CH_3COO)_2Ca}$$

$$\xrightarrow{\text{Dry distillation}} \underset{\text{Acetone}}{CH_3COCH_3} + CaCO_3$$

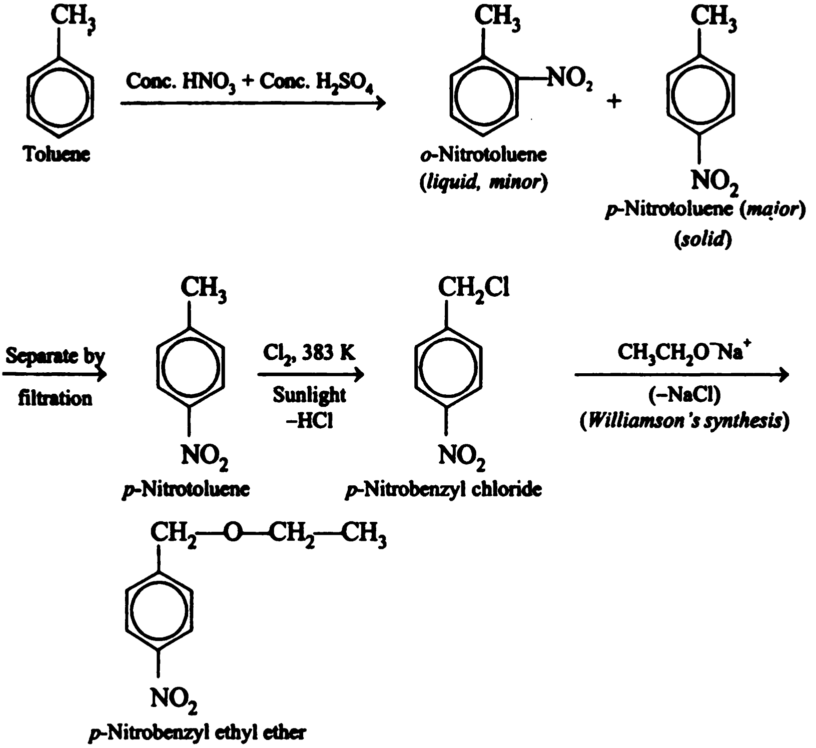
**166. How is aniline converted into bromobenzene ?** *(A.I.S.B. 1992)*



Aniline Benzenediazonium chloride Bromobenzene

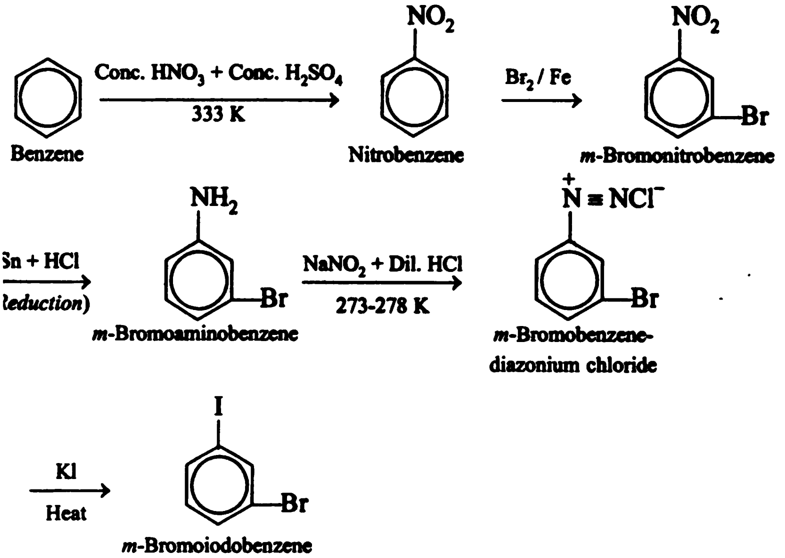
### 167. Convert toluene into p-nitrobenzyl ethyl ether

(*M.L.N.R. Allahabad, 1995*)

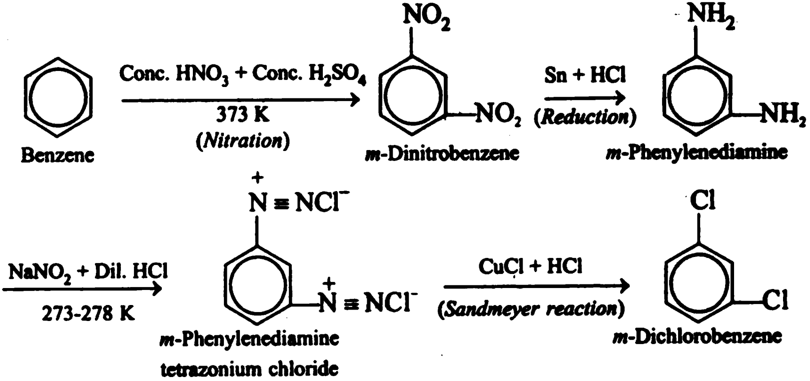


### 168. Convert benzene into m-bromoiodobenzene

(*I.I.T. 1996*)



**169. Convert benzene into m-dichlorobenzene** (*H.S.B. 1994*)



**170. Convert aluminium carbide into methyl chloride** (*I.I.T. 1983*)

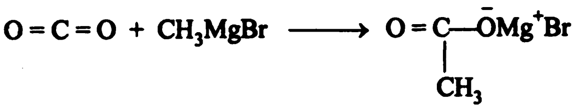
$$\underset{\text{Aluminium carbide}}{Al_4C_3} + 12H_2O \longrightarrow \underset{\text{Methane}}{3CH_4} + 4Al(OH)_3$$

$$CH_4 + \underset{\text{(Calculated) amount}}{Cl_2} \longrightarrow \underset{\text{Methyl chloride}}{CH_3Cl} + HCl$$

**171. Convert methyl cyanide to ethylamine.** (*Punjab P.M.T. 1989*)

$$\underset{\text{Methyl cyanide}}{CH_3CN} + 4[H] \xrightarrow[\text{Mendius reaction}]{\text{Na/alcohol}} \underset{\text{Ethylamine}}{CH_3CH_2NH_2}$$

**172. Convert carbon dioxide to acetic acid.** (*Punjab P.M.T. 1989*)

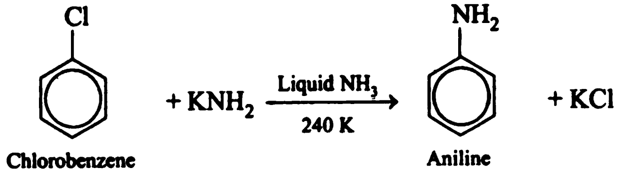


$$O=C=O + CH_3MgBr \longrightarrow O=\underset{\substack{|\\ CH_3}}{C}-\bar{O}Mg^+Br$$

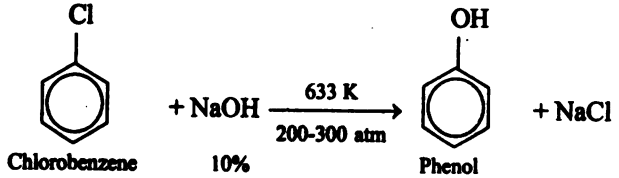
$$\xrightarrow{H_2O/H^+} \underset{\text{Acetic acid}}{CH_3COOH} + MgBr(OH)$$

**173. How will you convert chlorobenzene into (*i*) aniline (*ii*) phenol and (*iii*) benzene ?** (*Punjab P.M.T. 1990*)

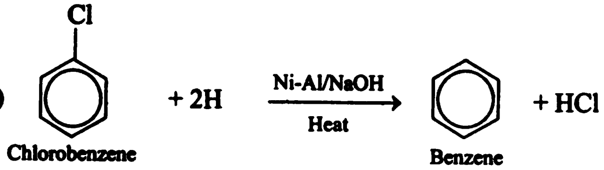
(*i*)



(*ii*)



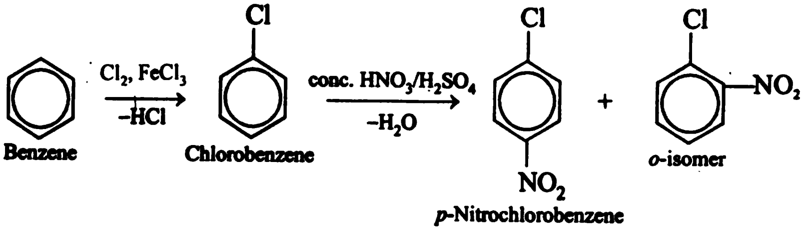
(*iii*)



**174. Convert acetaldehyde to ethyl alcohol.** (*Punjab P.M.T. 1988*)

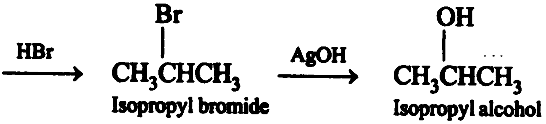
$$\underset{\text{Acetaldehyde}}{CH_3CHO} + 2[H] \xrightarrow{\text{Na/alcohol}} \underset{\text{Ethyl alcohol}}{CH_3CH_2OH}$$

**175. Convert benzene to *p*-Nitrochlorobenzene.**



**176. Convert *n*-Propyl alcohol to isopropyl alcohol** (*Punjab P.M.T. 1986*)

$$\underset{n\text{-Propyl alcohol}}{CH_3CH_2CH_2OH} \xrightarrow[-H_2O]{\text{Conc. } H_2SO_4,\ \Delta} \underset{\text{Propene}}{CH_3CH=CH_2}$$



$$\xrightarrow{\text{HBr}} \underset{\text{Isopropyl bromide}}{CH_3\overset{\overset{\displaystyle Br}{|}}{C}HCH_3} \xrightarrow{\text{AgOH}} \underset{\text{Isopropyl alcohol}}{CH_3\overset{\overset{\displaystyle OH}{|}}{C}HCH_3}$$

**177. Convert methyl iodide to acetic acid.** (*Punjab C.E.T. 1990*)

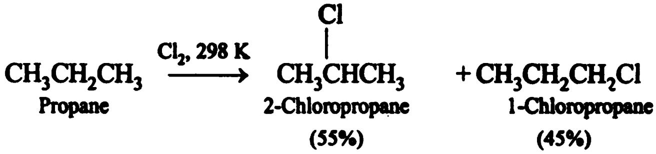
$$\underset{\text{Methyl iodide}}{CH_3I} \xrightarrow[-KI]{\text{Alc. KCN}} \underset{\text{Methyl cyanide}}{CH_3CN} \xrightarrow[\text{dil. acid or alkali, } 2H_2O]{\text{Complete hydr.}} \underset{\text{Acetic acid}}{CH_3COOH} + NH_3$$

**78. Convert ethylamine to ethane.** (*Punjab C.E.T. 1988*)

$$\underset{\text{Ethylamine}}{C_2H_5NH_2} \xrightarrow[-N_2,\ -H_2O]{HNO_2} \underset{\text{Ethyl acohol}}{C_2H_5OH} \xrightarrow[333\text{ K}]{\text{Conc. } H_2SO_4} \underset{\text{Ethylene}}{CH_2=CH_2}$$

$$\xrightarrow[\Delta]{H_2,\ Ni} \underset{\text{Ethane}}{CH_3\text{—}CH_3}$$

**179. Convert propane to ethane.** (*Punjab C.E.T. 1990*)



$$\underset{\text{Propane}}{CH_3CH_2CH_3} \xrightarrow{Cl_2,\ 298\ K} \underset{\substack{\text{2-Chloropropane}\\(55\%)}}{CH_3\overset{\overset{\displaystyle Cl}{|}}{C}HCH_3} + \underset{\substack{\text{1-Chloropropane}\\(45\%)}}{CH_3CH_2CH_2Cl}$$

$$\xrightarrow[-KCl,\ -H_2O]{\Delta,\ Alc.\ KOH} \underset{\text{Propene}}{CH_3CH=CH_2} \xrightarrow{\text{Ozonolysis}} \underset{\substack{\text{Ethanal}\\(\textit{liquid})}}{CH_3CHO} + \underset{\substack{\text{Methanal}\\(\textit{gas})}}{HCHO\uparrow}$$

$$\underset{\text{Ethanal}}{CH_3CHO} + 4HI \xrightarrow{Red\ P} \underset{\text{Ethane}}{CH_3CH_3} + H_2O + 2I_2$$

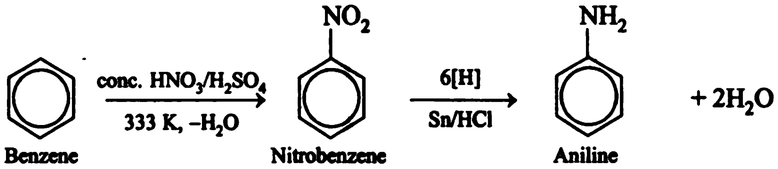
**180. Convert ethylene to acetylene** (*Indian School of Mines, Dhanbad 1986*)

$$\underset{\text{Ethylene}}{CH_2=CH_2} + Br_2 \xrightarrow{CCl_4} \underset{\text{Ethylene dibromide}}{BrCH_2—CH_2Br}$$

$$\xrightarrow[-KBr,\ -H_2O]{\text{conc. alc. KOH}} \underset{\text{Vinyl bormide}}{CH_2=CH—Br} \xrightarrow[-NaBr,\ -NH_3]{NaNH_2} \underset{\text{Acetylene}}{HC\equiv CH}$$

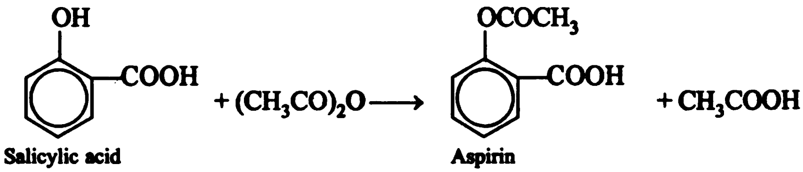
**180a. Convert benzene to Aniline.**

(*Punjab C.E.T. 1990, B.I.T. Mesra, Ranchi 1990*)



**181. Convert salicylic acid to aspirin.**

(*Indian School of Mines, Dhanbad 1990*)



**182. Convert methyl alcohol to acetic acid.**

(*Indian School of Mines, Dhanbad 1987*)

$$\underset{\substack{\text{Methyl}\\\text{alcohol}}}{CH_3OH} \xrightarrow{PCl_3} CH_3Cl \xrightarrow{Alc.\ KCN} CH_3CN \xrightarrow[\substack{\text{hydrolysis}\\(H^+\text{ or }OH^-)}]{\text{Complete}} \underset{\text{Acetic acid}}{CH_3COOH}$$

**183. Convert ethylene to ethane.** (*B.I.T. Mesra : Ranchi 1990*)

$$\underset{\text{Ethylene}}{H_2C=CH_2 + H_2} \xrightarrow{Ni,\ \Delta} \underset{\text{Ethane}}{H_3C—CH_3}$$

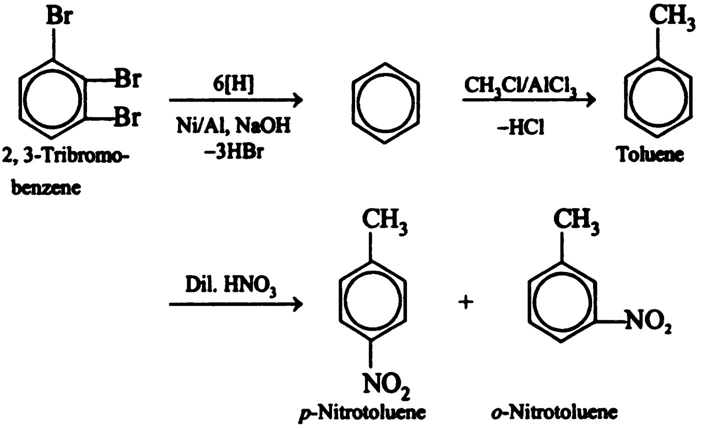
**184. How will you obtain diethyl ether starting from ethyl chloride and ethyl alcohol ?** (*Indian School of Mines. Dhanbad 1987*)

$$\underset{\text{Ethyl alcohol}}{2C_2H_5OH} + 2Na \longrightarrow \underset{\text{Sodium ethoxide}}{2C_2H_5\overset{-}{O}\overset{+}{Na}} + H_2$$

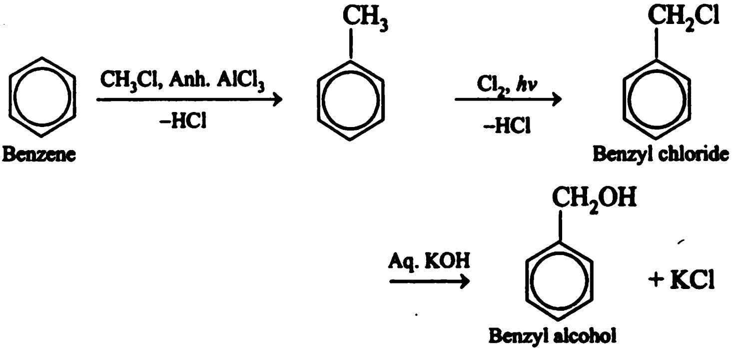
$$\underset{\text{Ethyl chloride}}{C_2H_5Cl} + \overset{+}{Na}\overset{-}{O}C_2H_5 \longrightarrow \underset{\text{Diethyl ether}}{C_2H_5OC_2H_5} + NaCl$$

**185. Convert 1, 2, 3-tribromobenzene to *p*-nitrotoluene.**

(*Indian School of Mines, Dhanbad 1990*)



**186. Convert benzene to benzyl alcohol.** (*Roorkee 1983*)



**187. Convert acetone to acetamide.** (*Roorkee 1983*)

$$\underset{\text{Acetone}}{CH_3COCH_3} \xrightarrow[50\%\ HNO_3]{(O)} \underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{NH_3} \underset{\text{Ammonium acetate}}{CH_3COONH_4}$$

$$\xrightarrow{\Delta} \underset{\text{Acetamide}}{CH_3CONH_2} + H_2O$$

**188. Starting from propanoic acid, how would you prepare ?**

**(*i*) butylamine (maximum 4 steps)**

**(*ii*) ethylamine (maximum 3 steps)** (*Roorkee 1985*)

(*i*) $$\underset{\text{Propanoic acid}}{CH_3CH_2COOH} + 6HI \xrightarrow{\text{Red P}} \underset{\text{Propane}}{CH_3CH_2CH_3} + 2H_2O + 3I_2$$

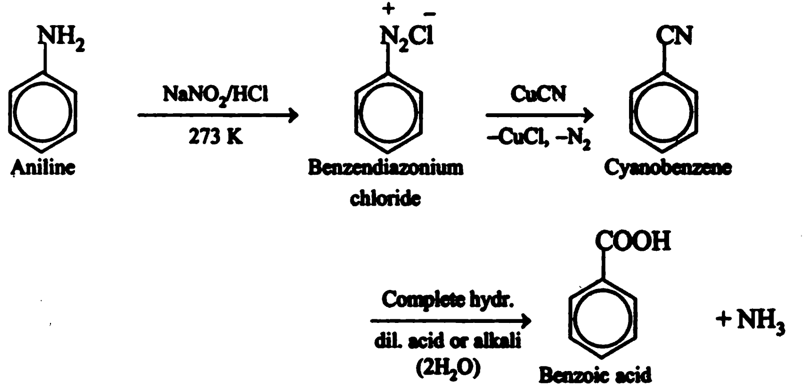
$$\xrightarrow{Cl_2,\ h\nu} C_3H_7Cl \xrightarrow[-KCl]{\text{Alc. KCN}} C_3H_7CN \xrightarrow[\text{Red, Na/alc.}]{4[H]} \underset{\text{Butylamine}}{C_3H_7CH_2NH_2}$$

(*ii*) $$\underset{\text{Propanoic acid}}{CH_3CH_2COOH} \xrightarrow{NH_3} \underset{\text{Ammonium propionate}}{CH_3CH_2COONH_4}$$

$$CH_3CH_2COONH_4 \xrightarrow{\Delta} \underset{\text{Propionamide}}{CH_3CH_2CONH_2} + H_2O$$

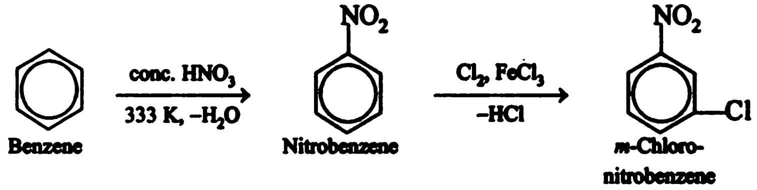
$$CH_3CH_2CONH_4 + Br_2 + \underset{\text{Aqueous}}{4KOH} \xrightarrow{\Delta} \underset{\text{Ethylamine}}{CH_3CH_2NH_2} + 2KBr + K_2CO_3 + 2H_2O$$

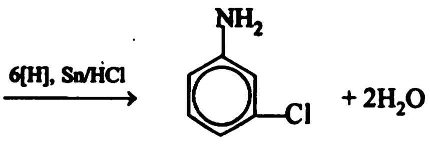
**189. Convert aniline to benzoic acid.** (*Roorkee 1983*)



**190. Starting from benzene give a method of preparation of *m*-chloroaniline (3 steps). Give experimental condition of each step.**

(*Roorkee 1988*)

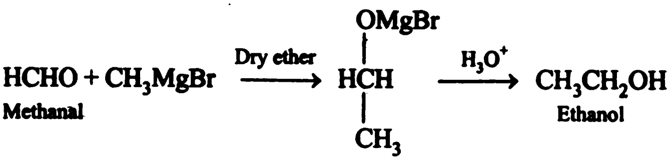




$\xrightarrow{6[H],\ Sn/HCl}$ m-Chloroaniline $+ 2H_2O$

*m*-Chloroaniline

**191. Convert methanal to ethanal.** (*I.I.T. 1981*)



$$\underset{\text{Methanal}}{HCHO + CH_3MgBr} \xrightarrow{\text{Dry ether}} HC(OMgBr)H\text{—}CH_3 \xrightarrow{H_3O^+} \underset{\text{Ethanol}}{CH_3CH_2OH}$$

$$\xrightarrow{Cu,\ 573\ K} \underset{\text{Ethanal}}{CH_3CHO} + H_2$$

**192. Convert methyl iodide to Acetic acid.** (*I.I.T. 1983*)

$$CH_3I \xrightarrow[-KI]{\text{Alc. KCN}} CH_3CN \xrightarrow[\substack{\text{dil acid or alkali}\\(2H_2O)}]{\text{Complete hydr.}} \underset{\text{Acetic acid}}{CH_3COOH} + NH_3$$

**193. Convert acetylene to ethanol.** (*I.I.T. 1983*)

$$\underset{\text{Acetylene}}{HC \equiv CH} + H_2O \xrightarrow[1\%\ HgSO_4,\ 333\ K]{40\ \text{to}\ 42\%\ H_2SO_4} \underset{\text{Acetaldehyde}}{CH_3CHO}$$

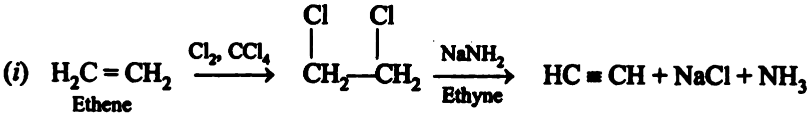
$$\xrightarrow[\text{Na/alc.}]{2[H]} \underset{\text{Ethyl alcohol}}{CH_3CH_2OH}$$

**194. How would you convert :**

**(*i*) Ethene to ethyne**

**(*ii*) Ethyne to propanone** (*M.L.N.R. 1993*)

**Solution.**

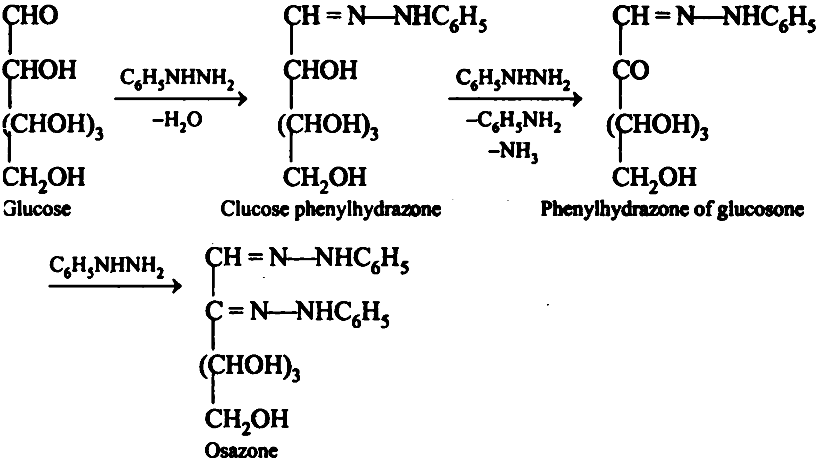


$$(i)\ \underset{\text{Ethene}}{H_2C = CH_2} \xrightarrow{Cl_2,\ CCl_4} \overset{Cl}{CH_2}\text{—}\overset{Cl}{CH_2} \xrightarrow[\text{Ethyne}]{NaNH_2} HC \equiv CH + NaCl + NH_3$$

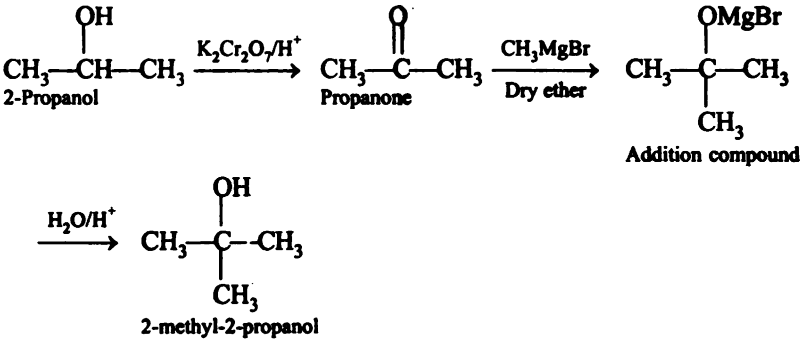
$$(ii)\ \underset{\text{Ethyne}}{HC \equiv CH} \xrightarrow{Na/NH_3} HC \equiv C.Na \xrightarrow{CH_3Br} \underset{\text{Propyne}}{HC \equiv C\text{—}CH_3}$$

$$HC \equiv C\text{—}CH_3 + H_2O \xrightarrow[1\%\ HgSO_4,\ 333\ K]{40\ \text{to}\ 42\%\ H_2SO_4} \underset{\text{Propanone}}{CH_3COCH_3}$$

**195. Convert glucose to osazone.** (*Wardha P.M.T. 1992*)



**196. Convert 2-propanol to 2-methyl-2-Propanol.** (*Wardha PMT 1992*)

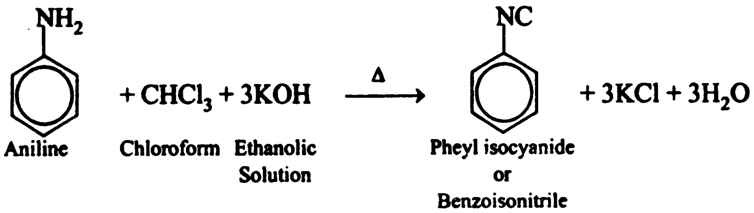


**197. Convert ethylene to diethyl ether.** (*Wardha PMT 1992*)

$$\underset{\text{Ethylene}}{CH_2=CH_2} + H_2O \xrightarrow[\text{Low temp. and high pressure}]{Al_2O_3} \underset{\text{Ethyl alcohol}}{CH_3—CH_2—OH}$$

$$C_2H_5OH + HOC_2H_5 \xrightarrow[413\text{ K}]{\text{Conc. } H_2SO_4} \underset{\substack{\text{Diethyl ether} \\ (\textit{Ethoxyethane})}}{C_2H_5—O—C_2H_5} + H_2O$$

**198. How will you convert aniline to phenyl isocyanide ?** (*Punjab P.M.T. 1992*)



**199. Carry out the following conversions** (*M.L.N.R. 1997*)

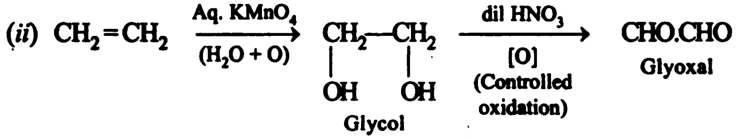
(*i*) $CaC_2 \longrightarrow CH_3CN$

(*ii*) $CH_2{=}CH_2 \longrightarrow CHO{-}CHO$

(*i*) $$\underset{}{CaC_2} \xrightarrow{H_2O} \underset{\text{Acetylene}}{CH{\equiv}CH} \xrightarrow[Pt]{2H_2} \underset{\text{Ethane}}{C_2H_6} \xrightarrow{Br_2} \underset{\text{Bromoethane}}{C_2H_5Br}$$

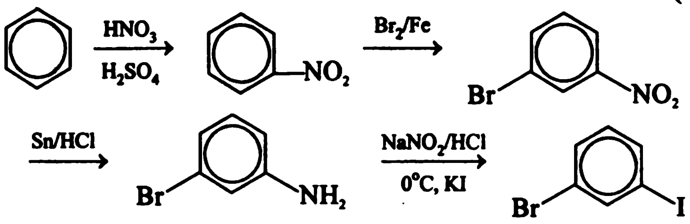
$$\xrightarrow{\text{Aq. KOH}} \underset{\text{Ethanonl}}{C_2H_5OH} \xrightarrow[{[O]}]{KMnO_4} CH_3COOH \xrightarrow[\text{CaO, Heat}]{NaOH} CH_4$$

$$\xrightarrow{Br_2} CH_3Br \xrightarrow{KCN} CH_3CN$$

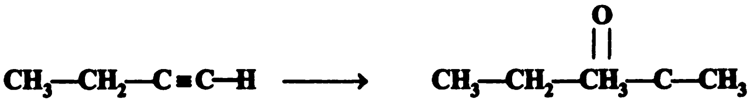


(*ii*) $$CH_2{=}CH_2 \xrightarrow[(H_2O + O)]{\text{Aq. } KMnO_4} \underset{\text{Glycol}}{\underset{OH\quad OH}{CH_2{-}CH_2}} \xrightarrow[\substack{[O]\\ \text{(Controlled}\\ \text{oxidation)}}]{\text{dil } HNO_3} \underset{\text{Glyoxal}}{CHO.CHO}$$

**200. How will you prepare *m*-bromoidobenzene from benzene** (*I.I.T. 1996*)

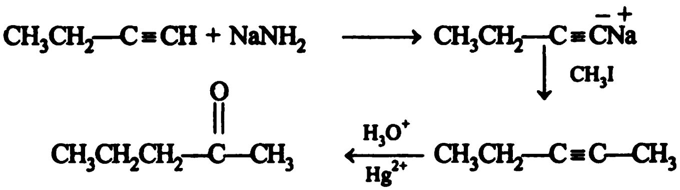


**201. Carry out the following transformation in not more than three steps**



$$CH_3{-}CH_2{-}C{\equiv}C{-}H \longrightarrow CH_3{-}CH_2{-}CH_3{-}\overset{\overset{O}{||}}{C}{-}CH_3$$

(*I.I.T. 1999*)



$$CH_3CH_2{-}C{\equiv}CH + NaNH_2 \longrightarrow CH_3CH_2{-}C{\equiv}\overset{-\,+}{CNa}$$

$$\downarrow CH_3I$$

$$CH_3CH_2CH_2{-}\overset{\overset{O}{||}}{C}{-}CH_3 \xleftarrow[Hg^{2+}]{H_3O^+} CH_3CH_2{-}C{\equiv}C{-}CH_3$$

**202. Write the chemical equation for each of the following conversion reactions :**

(*i*) **Ethyl cyanide to ethylamine**

(*ii*) **Aniline to N-phenylethanamide**

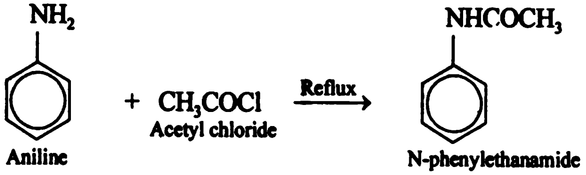
(*iii*) **Propanoic acid to 1-propanol** (*iv*) **Acetophenone to benzoic acid**

(*v*) **Acetone to *t*-butyl alcohol.** (*A.I.S.B. 2000*)

(*i*) **Ethyl cyanide to ethylamine**

**Sol.**
$$\begin{tikzcd}
\underset{\text{Ethyl cyanide}}{CH_3CH_2CH} \arrow[r, "H_2O^+"', "H^+"'] \arrow[r, phantom] & \underset{\text{Propanoic acid}}{CH_3CH_2COOH} \arrow[r, "NH_3", "\Delta"'] & \underset{\text{Propionamide}}{CH_3CH_2CONH_2} \arrow[d, "Br_2"', "KOH"] \\
 & & \underset{\text{Ethylamine}}{CH_3CH_2NH_2}
\end{tikzcd}$$

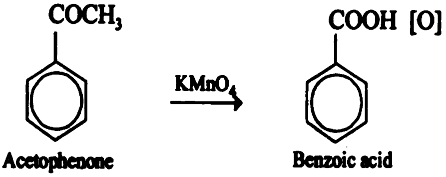
(*ii*) **Aniline to N-phenylethanamide**



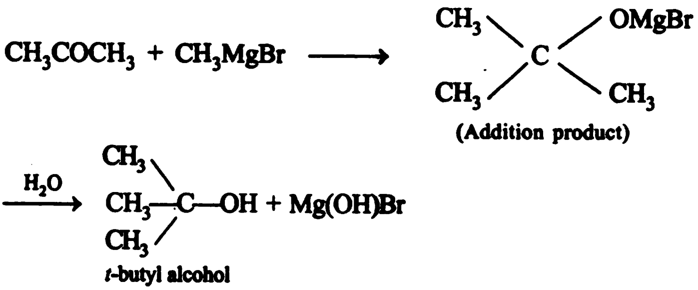
(*iii*) **Propanoic acid to 1-propanol**

$$\begin{tikzcd}
CH_3CH_2COOH \arrow[r, "NH_3", "\Delta"'] & CH_3CH_2CONH_2 \arrow[r, "Br_2", "KOH"'] & CH_3CH_2NH_2 \arrow[d, "HNO_2"] \\
CH_3CH_2MgBr \arrow[d, "HCHO"] & CH_3CH_2Br \arrow[l, "Mg"', "\text{Dry ether}"] & \underset{\text{Ethanol}}{CH_3CH_2OH} \arrow[l, "P/Br_2"'] \\
\underset{\text{Addition Product}}{[CH_3CH_2CH_2OMgBr]} \arrow[r, "H^+/H_2O"] & \underset{\text{1-Propanol}}{CH_3CH_2CH_2OH} &
\end{tikzcd}$$

(*iv*) **Acetophenone to benzoic acid**



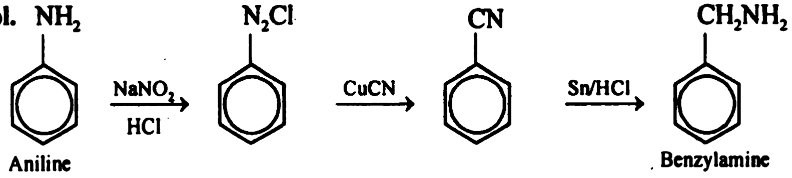
(*v*) **Acetone to t-butyl alcohol**



**203. How would you bring about the following conversion (in 3 steps)?**

**Aniline ⟶ Benzylamine** (*I.I.T. 2000*)

**Sol.**



**204. Write the reaction and state the condition for each of the following conversions :**

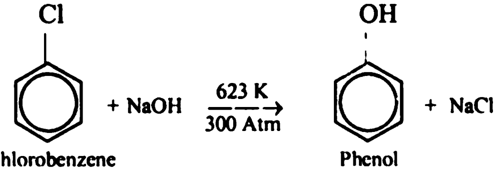
**(*i*) Ethene to ethanol (*ii*) Chlorobenzene to phenol**

**(*iii*) Ethanal to 2-propanol** (*A.I.S.B. 2002*)

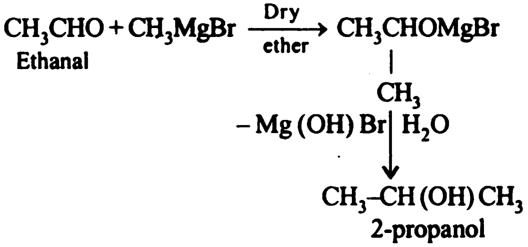
**Sol.** (*i*) Ethene to ethanol

$$\underset{\text{Ethene}}{CH_2=CH_2+H{-}OH} \xrightarrow[515\ K]{H^+} \underset{\text{Ethanol}}{CH_3CH_2OH}$$

(*ii*)



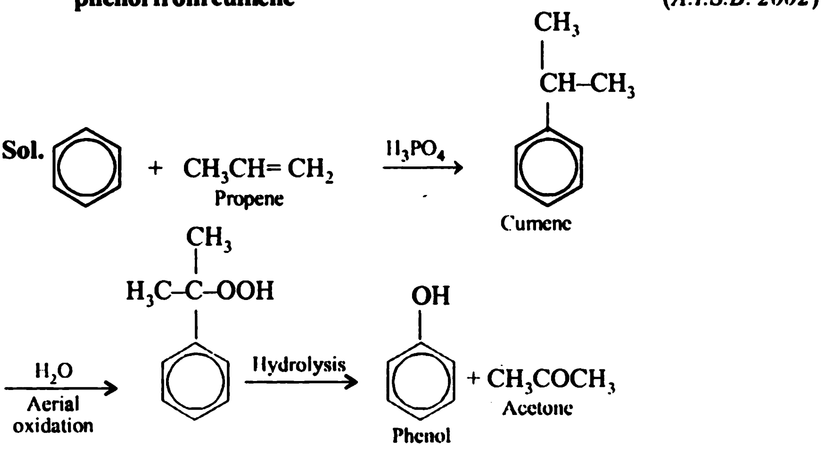
(*iii*)



$$\underset{\text{Ethanal}}{CH_3CHO+CH_3MgBr} \xrightarrow[\text{ether}]{\text{Dry}} \underset{\displaystyle CH_3}{CH_3CHOMgBr} \xrightarrow[-Mg(OH)Br]{H_2O} \underset{\text{2-propanol}}{CH_3{-}CH(OH)CH_3}$$

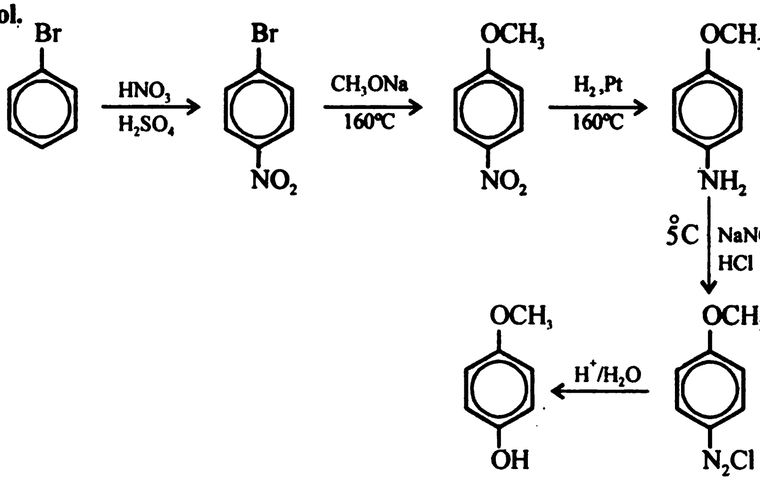
**205. Write the reaction and condition for the commercial preparation of phenol from cumene** (*A.I.S.B. 2002*)

**Sol.**



**206. How would you synthesise 4-methoxyphenol from bromobenzene in NOT more than five steps ? Study clearly the reagents used in each step and show the structure of the intermediate compounds in your synthetic scheme.** ***(I.I.T. 2001)***

**Sol.**



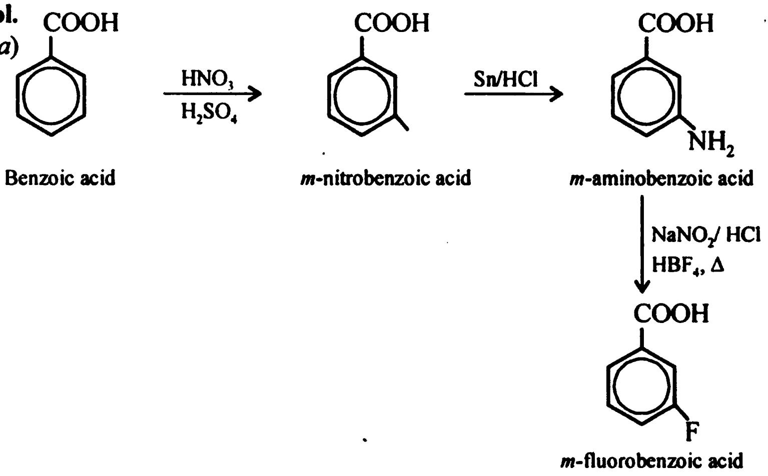
Note : Nitro group at *p*-position facilitates electrophilic substitution of methoxy group.

**207. Convert in NOT more than three steps.**

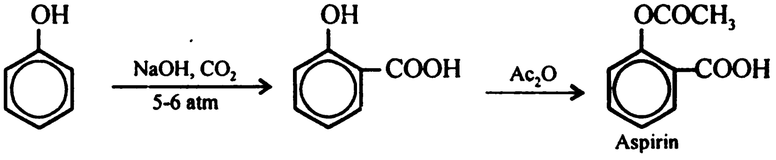
**(*a*) Benzoic acid to *m*-fluorobenzoic acid.**

**(*b*) Phenol to aspirin.** ***(I.I.T. 2003)***

**Sol.** (*a*)



(*b*)



# 6

# Identification of Compounds/ Reagents

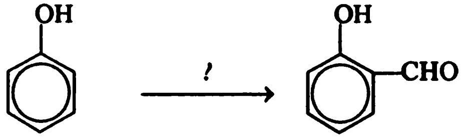
There are problems in which a sequence of reactions is given. Some of the steps of the reaction are shown as blank or the substances or reagents in some steps are represented as X, Y, Z...... or A, B, C.

You are required to identify these unknown compounds or reagents. Problems that follow in this section deal with such situations. A thorough knowledge of organic reactions is necessary to tackle such problems.

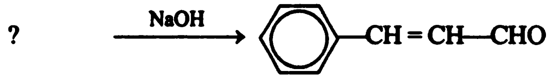
**Example 1.** *Complete the following with appropriate structures :*

(*i*) $(CH_3CO)_2O \xrightarrow{C_2H_5OH} CH_3COOH + ?$

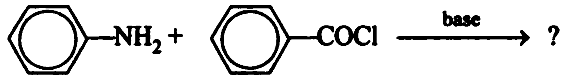
(*ii*)



(*iii*)



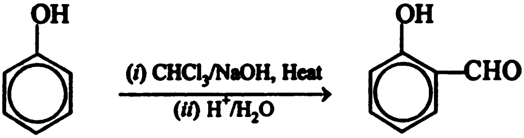
(*iv*)



(*I.I.T. 1986*)

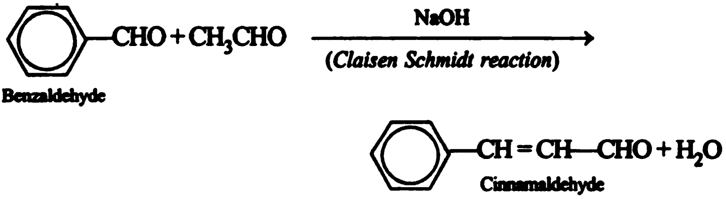
**Ans.** (*i*) $(CH_3CO)_2O \xrightarrow{C_2H_5OH} \underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5}$

(*ii*)

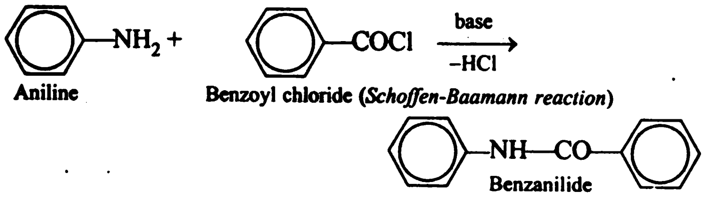


(salicyladehyde)

(*iii*)



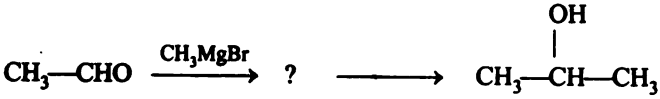
(*iv*)



Aniline  Benzoyl chloride (*Schoffen-Baamann reaction*)  Benzanilide

**Example 2.** *Complete the following reactions :*

(*i*)

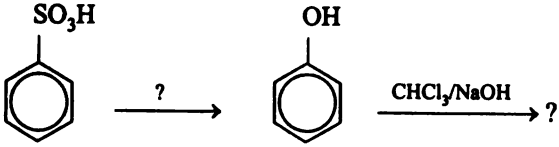


$$CH_3-CHO \xrightarrow{CH_3MgBr} ? \longrightarrow CH_3-\overset{\overset{OH}{|}}{C}H-CH_3$$

(*ii*) $CH_3COOH \xrightarrow{?} ClCH_2COOH \xrightarrow[\text{ammonia}]{\text{excess}} ?$

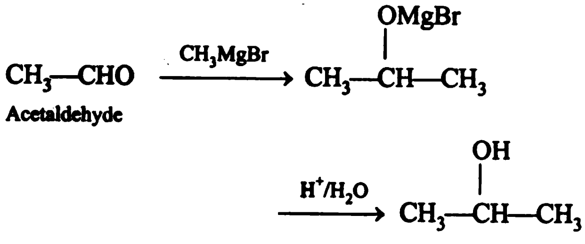
(*iii*) $2CH_3COCH_3 \xrightarrow[\text{catalyst}]{\text{base}} ? \xrightarrow[\text{catalyst}]{\text{acid}} ?$

(*iv*)



(*I.I.T. 1988*)

**Ans.** (*i*)



$$CH_3-CHO \xrightarrow{CH_3MgBr} CH_3-\overset{\overset{OMgBr}{|}}{C}H-CH_3 \xrightarrow{H^+/H_2O} CH_3-\overset{\overset{OH}{|}}{C}H-CH_3$$

Acetaldehyde  Isopropyl alcohol

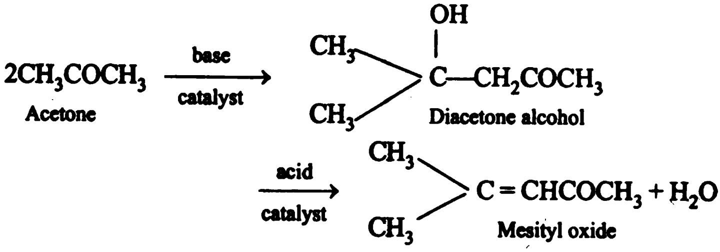
(*ii*) $CH_3COOH \xrightarrow[\text{(H.V.Z. reaction)}]{Cl_2,\ \text{Red P}} ClCH_2COOH$

Acetic acid  Chloroacetic acid

$\xrightarrow[\text{ammonia}]{\text{excess}} NH_2CH_2COONH_4$

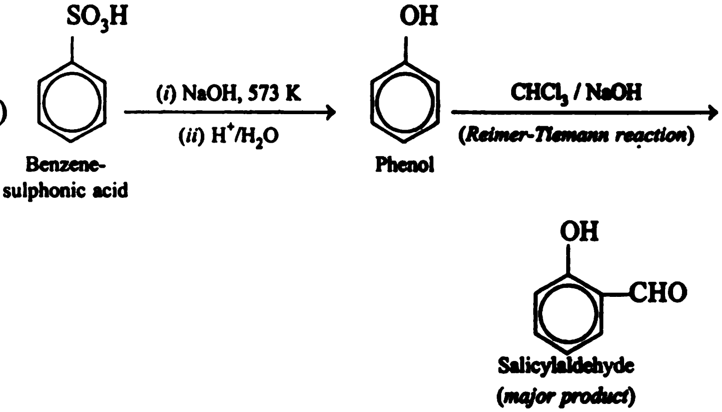
Amm. glycinate

(*iii*)



Acetone  Diacetone alcohol  Mesityl oxide

(iv)



**Example 3.** *In the following subquestions, identify the compounds/reaction conditions represented by the alphabets C, D, E, F, G and H :*

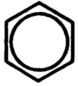
(*i*) $C_6H_5COOH \xrightarrow{PCl_5} C \xrightarrow{NH_3} D \xrightarrow{P_2O_5} C_6H_5CN \xrightarrow{H_2/Ni} E$

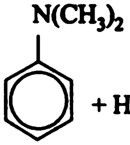
(*ii*) $CH_3—CH=CH—CHO \xrightarrow{NaBH_4} F \xrightarrow[ZnCl_2]{HCl} G \xrightarrow[H^+]{HCN} H$

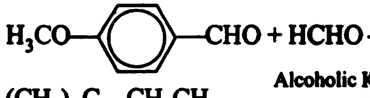
(*I.I.T. 1991*)

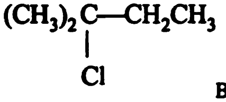
**Ans.** (*i*) C = Benzoyl chloride ($C_6H_5COCl$),
D = Benzamide ($C_6H_5CONH_2$), and
E = Benzylamine ($C_6H_5CH_2NH_2$)
(*ii*) F = Crotyl alcohol ($CH_3CH=CHCH_2OH$),
G = Crotyl chloride ($CH_3CH=CHCH_2Cl$) and
H = Crotyl cyanide ($CH_3CH=CHCH_2CN$).

**Example 4.** *Write the structure of the major organic product expected for each of the following reactions :*

(*i*)  $+ (CH_3)_2CHCH_2Cl \xrightarrow{AlCl_3}$

(*ii*)  $+ HNO_2 \longrightarrow$

(*iii*)  $+ HCHO \xrightarrow{KOH}$

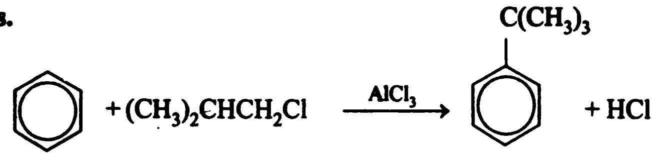
(*iv*) 

$(CH_3)_2\underset{\large Cl}{\underset{|}{C}}—CH_2CH_3 \xrightarrow{\text{Alcoholic KOH}}$

(*v*) $CH_3CH_2CHCl_2 \xrightarrow[\text{Alkali}]{\text{Boil}}$ (*I.I.T. 1992*)

**Ans.**

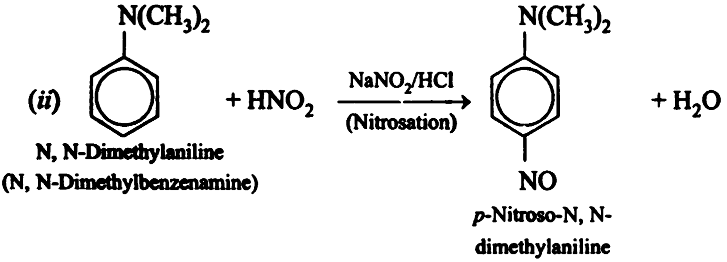
(*i*)



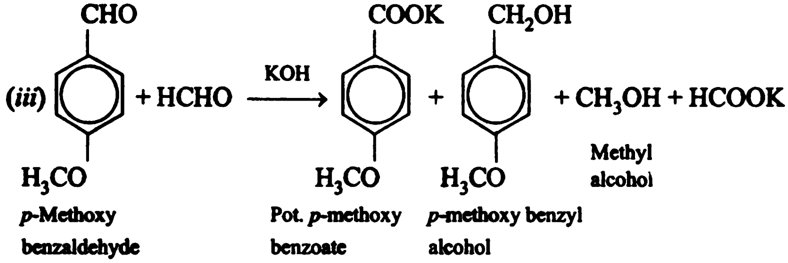
Benzene Isobutyl chloride *tert*-Butylbenzene

In this reaction (Friedel-Craft's reaction) the less stable isobutyl carbocation rearranges itself to more stable tertiary butyl carbocation. Hence, *tert*-butylbenzene is the product that is formed.

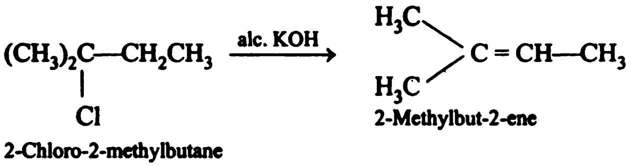
(*ii*)



(*iii*)



(*iv*)



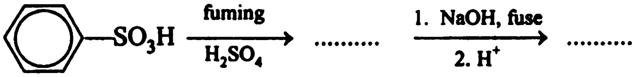
$$\underset{\text{2-Chloro-2-methylbutane}}{(CH_3)_2\underset{\displaystyle Cl}{C}—CH_2CH_3} \xrightarrow{\text{alc. KOH}} \underset{\text{2-Methylbut-2-ene}}{(H_3C)_2C=CH—CH_3}$$

(*v*)

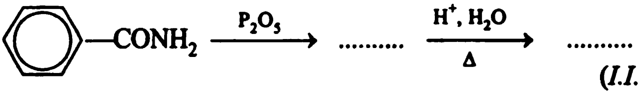
$$\underset{\substack{\text{n-Propylidene chloride}\\ \text{(1, 1-Dichloropropane)}}}{CH_3CH_2CHCl_2} \xrightarrow[\text{alkali}]{\text{Boil}} \underset{\text{(Unstable)}}{CH_3CH_2CH(OH)_2} \xrightarrow{-H_2O} \underset{\text{Propanal}}{CH_3CH_2CHO}$$

**Example 5.** *Complete the following sequence of reactions with appropriate structures :*

(*i*)

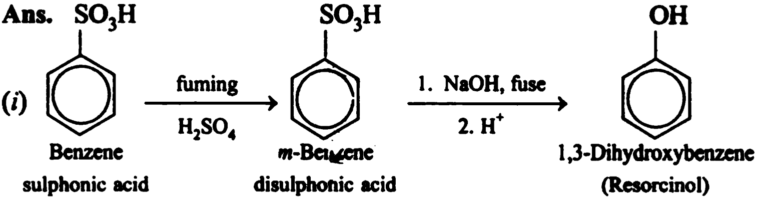


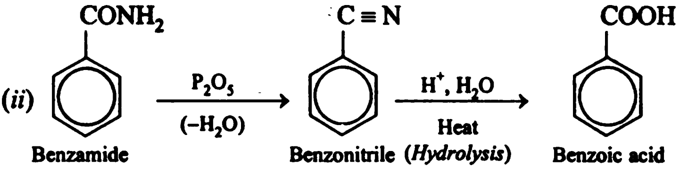
(*ii*)



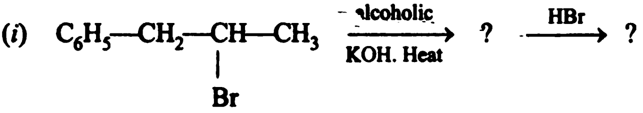
(*I.I.T. 1992*)

**Ans.**

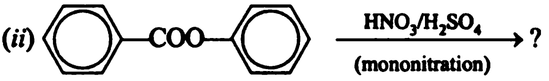




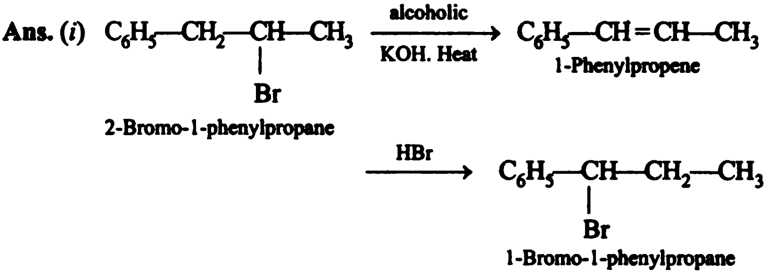
**Example 6.** *Identify the major product in the following recations :*



$$(i)\ C_6H_5\!-\!CH_2\!-\!\underset{\displaystyle Br}{\underset{|}{CH}}\!-\!CH_3 \xrightarrow[\text{KOH. Heat}]{\text{alcoholic}} ? \xrightarrow{\text{HBr}} ?$$



(*iii*) $C_6H_5COOH + CH_3MgBr \longrightarrow ? + ?$ (*I.I.T. 1993*)

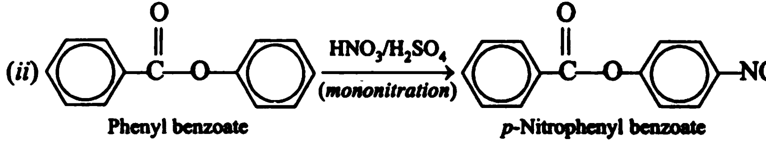


$$\textbf{Ans. } (i)\ C_6H_5\!-\!CH_2\!-\!\underset{\displaystyle Br}{\underset{|}{CH}}\!-\!CH_3 \xrightarrow[\text{KOH. Heat}]{\text{alcoholic}} C_6H_5\!-\!CH\!=\!CH\!-\!CH_3$$

2-Bromo-1-phenylpropane 1-Phenylpropene

$$\xrightarrow{\text{HBr}} C_6H_5\!-\!\underset{\displaystyle Br}{\underset{|}{CH}}\!-\!CH_2\!-\!CH_3$$

1-Bromo-1-phenylpropane



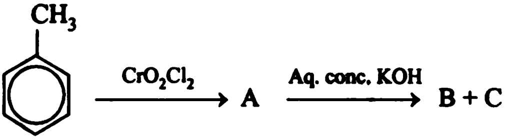
Due to electron-withdrawing effect of the C = O group, the electron density in the benzene ring directly attached to the C = O group decereases. In contrast, due to electron-donating effect of the oxygen atom, the electron-density increases in the benzene ring directly attached to the oxygen atom. Therefore, the mononitration will occur preferentially in the benzene ring directly attached to the oxygen atom. Further because of *steric hindrance*, mononitration occurs preferentially at the *p*-position to give *p*-nitrophenyl benzoate as the major product.

(*iii*) $C_6H_5COOH + CH_3MgBr \longrightarrow C_6H_5COOMgBr + CH_4$

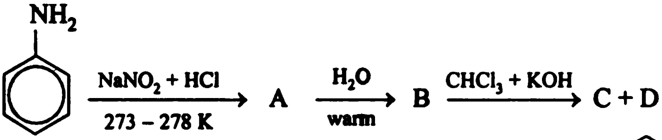
**Example 7.** *Complete the following by supplying intermediates :*

(*a*) $C_2H_5OH \xrightarrow{HCl} A \xrightarrow{KCN} B \xrightarrow{H_3O^+} C \xrightarrow{NH_3} D \xrightarrow{\Delta} E$

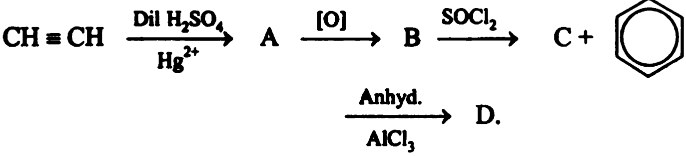
(*b*)



(*c*)



(*d*)



**Ans.** (*a*) A = Ethyl chloride ($C_2H_5Cl$)

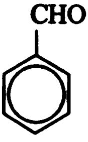
B = Ethyl cyanide ($C_2H_5CN$)

C = Propionic acid ($C_2H_5COOH$)

D = Ammonium propionate ($C_2H_5COONH_4$) and

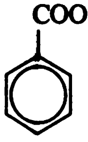
E = Propionamide ($C_2H_5CONH_2$)

(*b*) A =



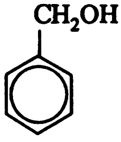
Benzaldehyde

and B + C =



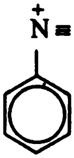
Pot. benzoate

+



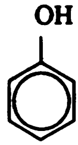
Benzyl alcohol

(*c*) A =



Benzenediazonium chloride

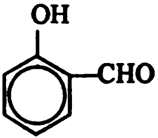
; B =



Phenol

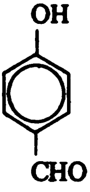
;

C + D =

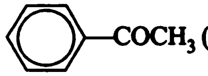


Salicylaldehyde (*major product*)

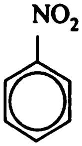
+



*p*-Hydroxybenzaldehyde (*minor product*)

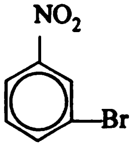
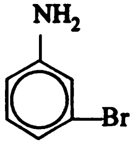
(*d*) A = Acetaldehyde ($CH_3CHO$)
B = Acetic acid ($CH_3COOH$)
C = Acetyl chloride ($CH_3COCl$),
D =  (Acetophenone)

**Example 8.** *Complete the following by supplying (A), (B), (C) and (D):*

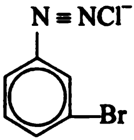
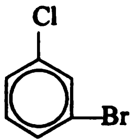
(*a*)  $\xrightarrow{Br_2/Fe} (A) \xrightarrow{Sn + HCl} (B) \xrightarrow[273\text{-}278\ K]{NaNO_2 + HCl} (C) \xrightarrow{CuCl} (D)$

(*b*) $CH_3CH_2CH_2OH \xrightarrow{PBr_3} (A) \xrightarrow[KOH]{\text{Alcoholic}} (B) \xrightarrow{HBr} (C) \xrightarrow{NH_3} (D)$ (*Roorkee 1985*)

**Ans.**

(*a*) A =  ; B =  ;

*m*-Bromonitrobenzene    *m*-Bromoaniline

C =  ; D = 

*m*-Bromobenzenediazonium chloride    *m*-Bromochlorobenzene

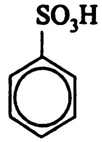
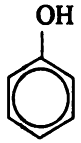
(*b*) A = *n*-Propyl bromide ($CH_3CH_2CH_2Br$)
B = Propene ($CH_3CH = CH_2$)
C = Isopropyl bromide ($CH_3CHBrCH_3$), and
D = Isopropylamine [$(CH_3)_2CHNH_2$]

**Example 9.** *Complete the following by supplying the intermediates* (*A*), (*B*), (*C*) *and* (*D*) :

(*a*)  $\xrightarrow{Br_2/Fe} (A) \xrightarrow{H_2, Pt} (B) \xrightarrow[273\text{-}278\ K]{NaNO_2 + HCl} (C) \xrightarrow{Cu_2Cl_2} (D)$

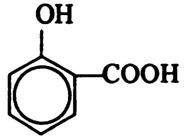
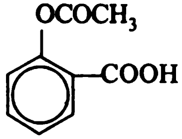
(*b*)  $\xrightarrow{H_2SO_4} (A) \xrightarrow[(ii)\ H^+]{(i)\ NaOH\ fusion} (B) \xrightarrow[(ii)\ H^+]{(i)\ CO_2,\ KOH} (C) \xrightarrow{CH_3COCl} (D)$ (*Roorkee 1987*)

**Ans.** (*a*) Same as answer 8(a)

(*b*) A =  ; B = 

Benzensulphonic acid

Phenol

C =  ; D = 

Salicylic acid

Acetylsalicylic acid or Aspirin

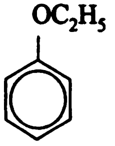
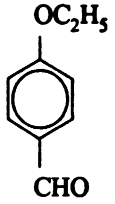
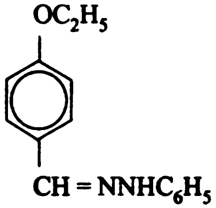
**Example 10.** *Complete the following by supplying intermediates or reactants (A), (B) and (C) :*

(*a*) Phenol $\xrightarrow{Et_2SO_4}$ (A) $\xrightarrow[AlCl_3]{HCN,\ HCl}$ (B) $\xrightarrow{PhNHNH_2}$ (C)

(*b*) $C_6H_5COOH \xrightarrow{(A)} C_6H_5COCl \xrightarrow{(NH_3)} B \xrightarrow{(C)} C_6H_5CN$

(*Roorkee 1988*)

**Ans.**

(*a*) A =  ; B =  and C = 

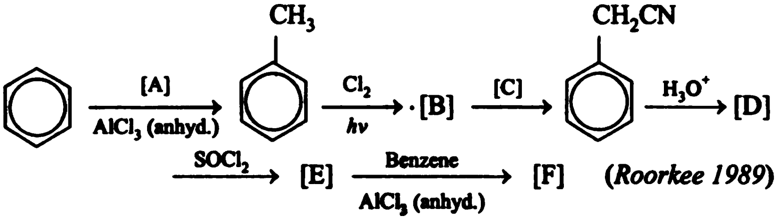
Phenetole

*p*-Ethoxybenzaldehyde

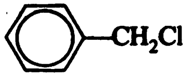
*p*-Ethoxybenzaldehyde phenylhydrazone

(*b*) A = Thionyl chloride ($SOCl_2$),
B = Benzamide ($C_6H_5CONH_2$),
C = Phosphorus pentoxide ($P_2O_5$)

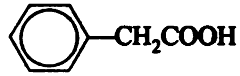
**Example 11.** *Complete the following by supplying (A) to (F) :*



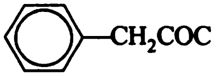
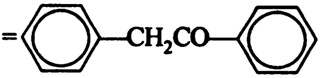
(*Roorkee 1989*)

**Ans.** [A] = Methyl chloride ($CH_3Cl$), [B] = 

Benzyl chloride

[C] = Potassium cyanide (KCN) and [D] = 

Phenylacetic acid

[E] =  and [F] = 

Phenylacetyl chloride Benzyl phenyl ketone

**Example 12.** *Complete the following by supplying [A] to [F] :*

$$[A] \xrightarrow{PBr_5} CH_3CH_2CH_2Br \xrightarrow[\text{KOH}]{\text{Alcoholic}} [B] \xrightarrow{Br_2} [C] \xrightarrow[\text{followed by } NaNH_2]{\text{Alcoholic KOH}} [D] \xrightarrow[\text{in dil. } H_2SO_4]{Hg^{2+}} [E] \xrightarrow{NH_2OH} [F]$$

(*Roorkee 1990*)

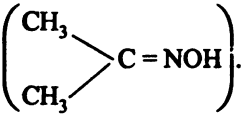
**Ans.** [A] = *n*-Propyl alcohol ($CH_3CH_2CH_2OH$),

[B] = Propene ($CH_3CH = CH_2$),

[C] = 1, 2 Dibromopropane ($CH_3CHBrCH_2Br$),

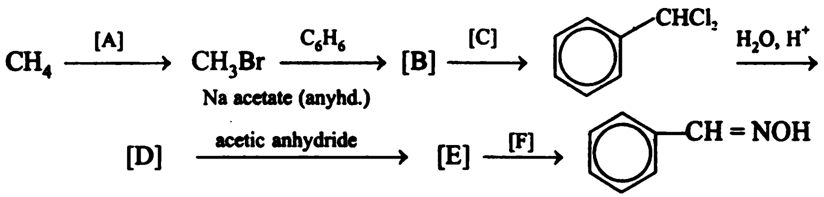
[D] = Propyne ($CH_3C \equiv CH$),

[E] = Acetone ($CH_3COCH_3$), and

[F] = Acetone oxime or Acetoxime 

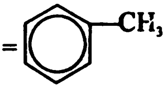
$$\left(\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>C = NOH\right).$$

**Example 13.** *Complete the following by supplying [A] to [F] :*

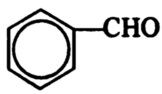
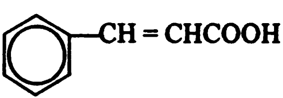


$$CH_4 \xrightarrow{[A]} CH_3Br \xrightarrow[\text{Na acetate (anyhd.)}]{C_6H_6} [B] \xrightarrow{[C]} C_6H_5CHCl_2 \xrightarrow{H_2O,\ H^+} [D] \xrightarrow{\text{acetic anhydride}} [E] \xrightarrow{[F]} C_6H_5CH = NOH$$

(*Roorkee 1991*)

**Ans.** [A] = $Br_2$, *h*ν ; [B] =  ; [C] = $Cl_2$ (2 moles), *h*ν ;

Toluene

[D] =  ; [E] = 

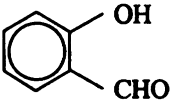
Benzaldehyde Cinnamic acid

and [F] = $NH_2OH$ (Hydroxylamine).

**Example 14.** *Complete the following equations by identifying [A] to [F]:*

(*i*) $MeCH_2C \equiv CH \xrightarrow{Na/NH_3} [A] \xrightarrow{EtBr} [B]$

(*ii*)



$\xrightarrow[CH_3COONa]{(CH_3CO)_2O}$ [C]

(*iii*) $EtNH_2 + KCN + Br_2 \xrightarrow{KOH} KBr + [D]$

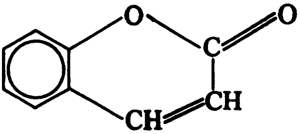
(*iv*) $[E] \xrightarrow[\text{dil. } H_2SO_4]{Hg^{2+}} CH_3CHO \xrightarrow{(CH_3CO)_2O} [F]$ (*Roorkee 1993*)

**Ans.** (*i*) A = Sodium-1-butynide ($MeCH_2C \equiv C^-Na^+$) ;

[B] = 3-Hexyne ($MeCH_2C \equiv CEt$)

(*ii*) Salicylaldehyde on treatment with $(CH_3CO)_2O$ in presence of $CH_3COONa$ undergoes Perkin reaction to give coumarin.

[C] =



(coumarin)

(*iii*) KCN reacts with $Br_2$ in presence of KOH to form cyanogen bromide (CNBr) which then reacts with ethylamine to give ethyl cyanamide (EtNHCN).

$$KCN + Br_2 \xrightarrow{KOH} BrCN + KBr$$

$$2EtNH_2 + BrCN \longrightarrow EtNHCN + EtNH_3^+Br^-$$

Thus, [D] = Ethyl cyanamide (EtNHCN)

(*iv*) E = Ethyne ($CH \equiv CH$) and

[F] = Vinyl acetate ($CH_2 = CH—OCOCH_3$).

**Example 15.** *Give the structures of A, B, C and D (explanations are not required).*

(*i*) *A ($C_3H_9N$) reacts with benzenesulphonyl chloride to give a solid insoluble in alkali.*

(*ii*) *B ($C_4H_8$) which adds on HBr in the presence and in the absence of peroxide to give the same compound, $C_4H_9Br$.*

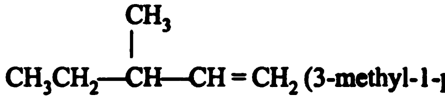
(*iii*) *C ($C_4H_8$) which when treated with $H_2O/H_2SO_4$ gives $C_4H_{10}O$ which cannot be resolved into optical isomers.*

(*iv*) *D ($C_6H_{12}$), an optically active hydrocarbon which on catalytic hydrogenation gives an optically inactive compound, $C_6H_{14}$* (*I.I.T. 1993*)

**Ans.** (*i*) A must be a secondary amine *i.e.*, $CH_3NHCH_2CH_3$ (ethylmethylamine).

(*ii*) B must be a symmetrical alkene *i.e.*, $CH_3CH = CHCH_3$ (2-butene).

(*iii*) C is $(CH_3)_2C = CH_2$ (2-methylpropene).



(*iv*) D is $CH_3CH_2{-}\overset{\overset{CH_3}{|}}{CH}{-}CH=CH_2$ (3-methyl-1-pentene)

**Example 16.** ***Predict the major product in the following reactions :***

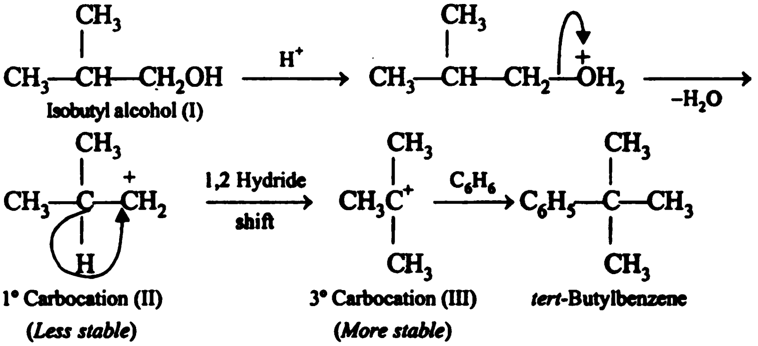
(*i*) $C_6H_6 + (CH_3)_2CHCH_2OH \xrightarrow{H_2SO_4}$

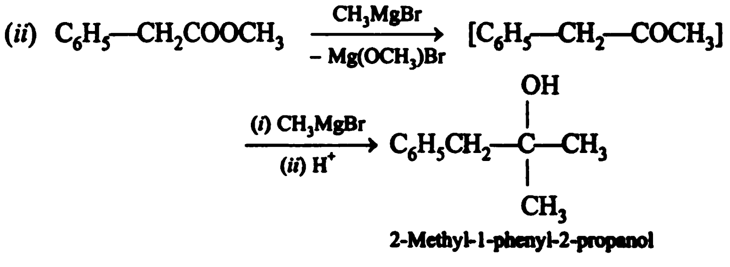
(*ii*) $C_6H_5CH_2CO_2CH_3 \xrightarrow[2.\ H^+]{1.\ CH_3MgBr(excess)}$

(*iii*) $C_6H_5C_2H_5 \xrightarrow[2.\ NaCN]{1.\ Br_2,\ Heat,\ Light}$ (*I.I.T. 1994*)

**Ans.** (*i*) $\underset{I}{C_6H_6 + (CH_3)_2CHCH_2OH} \xrightarrow{H_2SO_4} \underset{tert\text{-Butylbenzene}}{C_6H_5{-}C(CH_3)_3}$

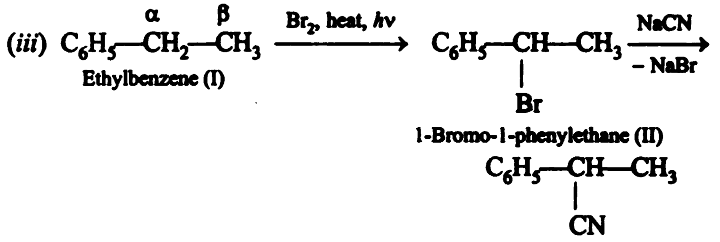
**Explanation.** In the presence of conc. $H_2SO_4$, isobutyl alcohol (I) first gives a 1° carbocation (II) which then rearranges to the more stable 3° carbocation (III) by a hydride ion shift. Carbocation (III), then reacts with benzene to form *tert*-butylbenzene.





(*ii*) $C_6H_5{-}CH_2COOCH_3 \xrightarrow[-\,Mg(OCH_3)Br]{CH_3MgBr} [C_6H_5{-}CH_2{-}COCH_3] \xrightarrow[(ii)\ H^+]{(i)\ CH_3MgBr} C_6H_5CH_2{-}\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}{-}CH_3$

2-Methyl-1-phenyl-2-propanol



(*iii*) $\underset{\text{Ethylbenzene (I)}}{C_6H_5{-}\overset{\alpha}{CH_2}{-}\overset{\beta}{CH_3}} \xrightarrow{Br_2,\ heat,\ h\nu} C_6H_5{-}\underset{\underset{Br}{|}}{CH}{-}CH_3 \xrightarrow[-\,NaBr]{NaCN} C_6H_5{-}\underset{\underset{CN}{|}}{CH}{-}CH_3$

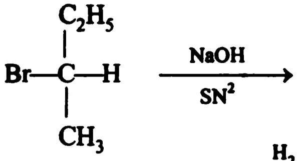
1-Bromo-1-phenylethane (II)

2-Phenylpropanenitrile (III)

**Explanation.** Ethylbenzene (I) in presence of $Br_2$ and light undergoes side chain halogenation. α-hydrogens being benzylic are more reactive than β-hydrogens. Therefore, 1-bromo-1-phenylethane (II) is formed. The alkyl halide (II) on treatment with NaCN yields 2-phenylpropanenitrile (III).

**Example 17.** *Draw the stereochemical structures of the products in the following reactions :*

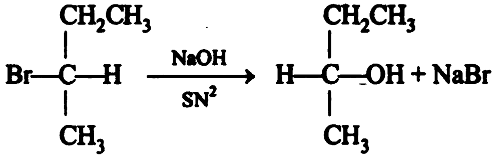
(*i*)



$$\mathrm{Br{-}\overset{\overset{\textstyle C_2H_5}{|}}{\underset{\underset{\textstyle CH_3}{|}}{C}}{-}H} \xrightarrow[SN^2]{NaOH}$$

(*ii*) $R{-}C{\equiv}C{-}R \xrightarrow[\text{Lindlar's catalyst}]{H_2}$ (*I.I.T. 1994*)

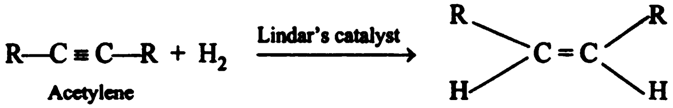
**Ans.** (*i*) $S_N2$ reactions proceed with inversion of configuration, therefore, the optically active alkyl halide (I) on treatment with NaOH gives optically active alcohol (II).



$$\mathrm{Br{-}\overset{\overset{\textstyle CH_2CH_3}{|}}{\underset{\underset{\textstyle CH_3}{|}}{C}}{-}H} \xrightarrow[SN^2]{NaOH} \mathrm{H{-}\overset{\overset{\textstyle CH_2CH_3}{|}}{\underset{\underset{\textstyle CH_3}{|}}{C}}{-}OH} + NaBr$$

I (Inverted config.) II

(*ii*) Hydrogenation of acetylenes in presence of Lindlar's catalyst gives cis-alkenes since the hydrogen adsorbed on the surface of the catalyst gets transferred to the acetylene molecule from the same side.



Acetylene cis-Alkene

**Example 18.** (*a*) *Write down the structures of the stereoisomers formed when cis-2-butene is reacted with bromine.*

(*b*) *Complete the following sequence of reactions with appropriate structures.*

(*i*) $CH_3{-}CH_2{-}COOH \xrightarrow{\text{P and bromine}} A$

$$A \xrightarrow[\text{2. } H^+]{\text{1. Alcoholic KOH (excess)}} B$$

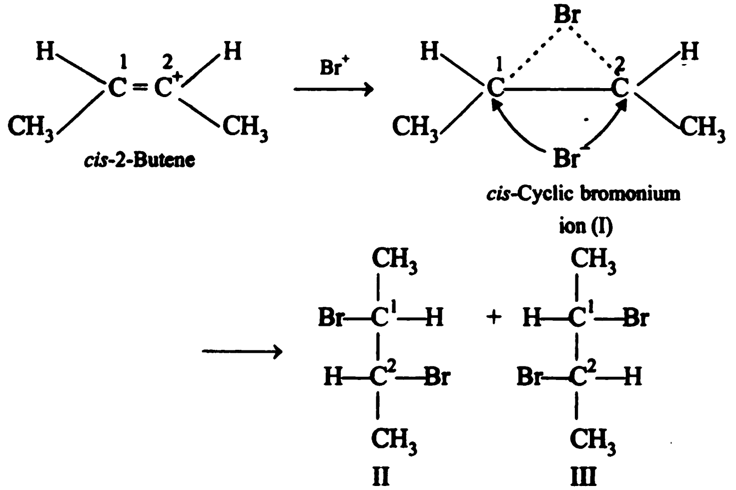
(*ii*) 2, 4-Dinitroaniline $\xrightarrow[\text{2. Anisole}]{\text{1. } NaNO_2 \text{ and HCl at } 5^\circ C} C$

(*iii*) $C_6H_5{-}CHO + CH_3{-}COOC_2H_5 \xrightarrow[C_2H_5OH \text{ and heat}]{NaOC_2H_5 \text{ in absolute}} D$ (*I.I.T. 1995*)

**Ans.** (*a*) Addition of $Br_2$ to an alkene is an example of an *electrophilic addition reaction*. Addition of the two bromine atoms occurs across the opposite faces of the alkene molecule giving *trans-addition product*. When $Br_2$ is added to *cis*-2-butene, a racemic mixture of 2, 3-dibromobutane is obtained. This may be explained as follows :

The electrophile, *i.e.*, bromonium ion first adds to *cis*-2-butene to give the *cis*-cyclic bromonium ion (I). The nucleophilic attack of the bromide ion then occurs on (I) from the *back side* (since the attack from the front side is blocked by the large size of the bromine atom).

If $Br^-$ attaches itself to $C_1$ then the first bromine (of $Br^+$) shifts to $C_2$ and *vice versa*. We get a mixture of two products represented by II and III.



*cis*-2-Butene

*cis*-Cyclic bromonium ion (I)

II

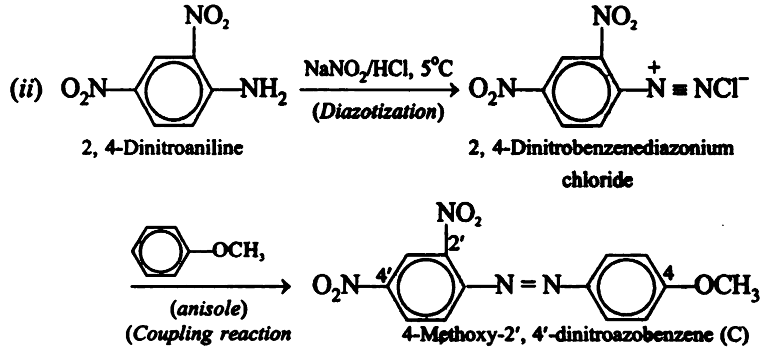
III

These two products are enantiomers of each other. Since attack by either path is equally likely, the two enantiomers are formed in equal amounts. In other words, we get a *racemic mixture of 2, 3-dibromobutane*.

(*b*) (*i*) Propionic acid on treatment with $Br_2$ in presence of red phosphorus undergoes, *Hell-Volhard Zeleunsky* (H.V.Z.) reaction to give α-bromopropionic acid (A). (A) on treatment with excess of alcoholic KOH undergoes *dehydrobromination* to yield potassium acrylate which upon acidification gives acrylic acid (B).

$$\underset{\text{Propionic acid}}{CH_3—CH_2—COOH} \xrightarrow[\textit{(H.V.Z. reaction)}]{P/Br_2} \underset{\alpha\text{-Bromopropionic acid (A)}}{CH_3—CHBr—COOH}$$

$$\xrightarrow[\substack{(-\,KBr,\,-\,H_2O)\\ \textit{(Dehydrobromination)}}]{\text{alcoholic KOH } \textit{(excess)}} \left[\underset{\text{Pot. acrylate}}{CH_2=CH—COOK}\right] \xrightarrow{H^+} \underset{\text{Acrylic acid (B)}}{CH_2=CH—COOH}$$



$$(iii)\quad \underset{\text{Benzaldehyde}}{C_6H_5—CH=}\boxed{O+H_2}\underset{\text{Ethyl acetate}}{CH—COOC_2H_5} \xrightarrow[\substack{\text{and heat}\\ \textit{(Claisen-Schmidt reaction)}}]{NaOC_2H_5 \text{ in absolute alcohol}}$$

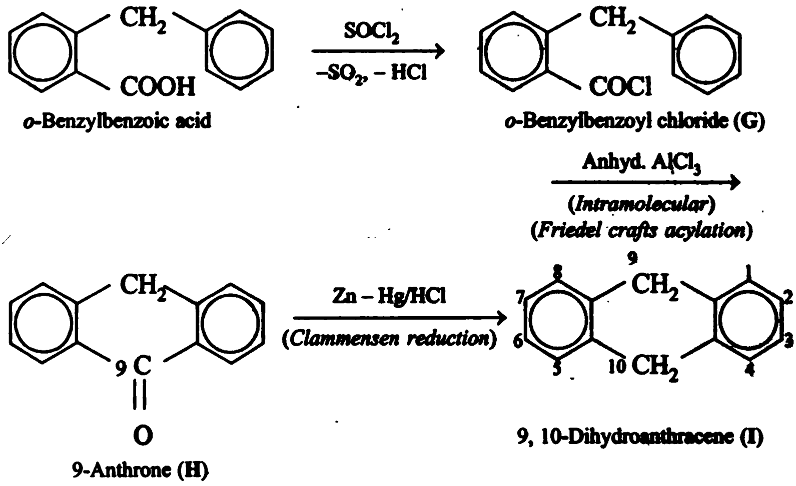
$$\underset{\text{Ethyl cinnamate (D)}}{C_6H_5—CH=CH—COOC_2H_5 + H_2O}$$

**Example 19.** *Fill in the blanks with appropriate structures of reaction products in the following transformations :*

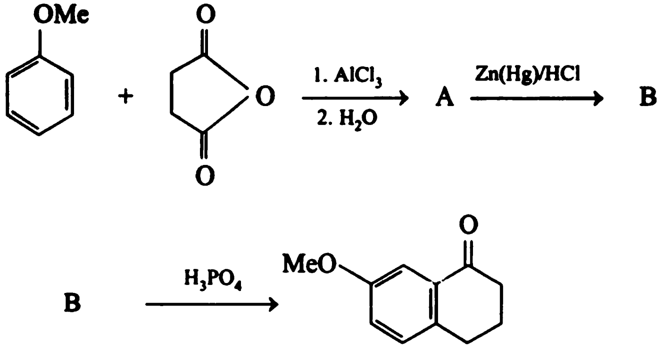
$$o\text{-}HOOC—C_6H_4—CH_2—C_6H_5 \xrightarrow{SOCl_2} G \xrightarrow[AlCl_3]{\text{anhydrous}} H \xrightarrow[HCl]{Zn-Hg} I$$

*(I.I.T. 1995)*

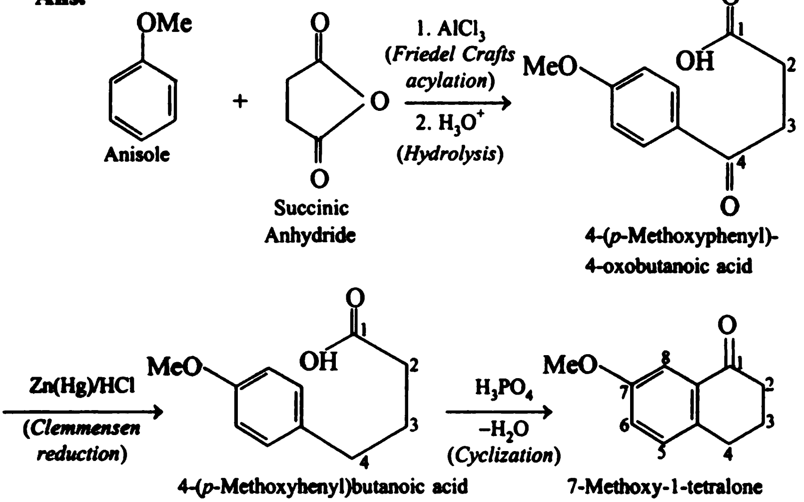
**Ans.** Treatment with $SOCl_2$ converts —COOH into COCl to give **G** which on further treatment with anhyd. $AlCl_3$ undergoes *intramolecular Friedel Crafts acylation* to yield the cyclized compound **H**. The > C = O in **H** on *Clemmensen reduction* with Zn-Hg/HCl gets converted into >$CH_2$ group thereby giving 9, 10-dihydroanthracene, **I**. The reactions are illustrated as under :



**Example 20.** *Predict the structures of the intermediates/products in the following reaction sequence :* *(I.I.T. 1996)*



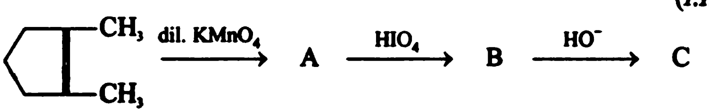
**Ans.**



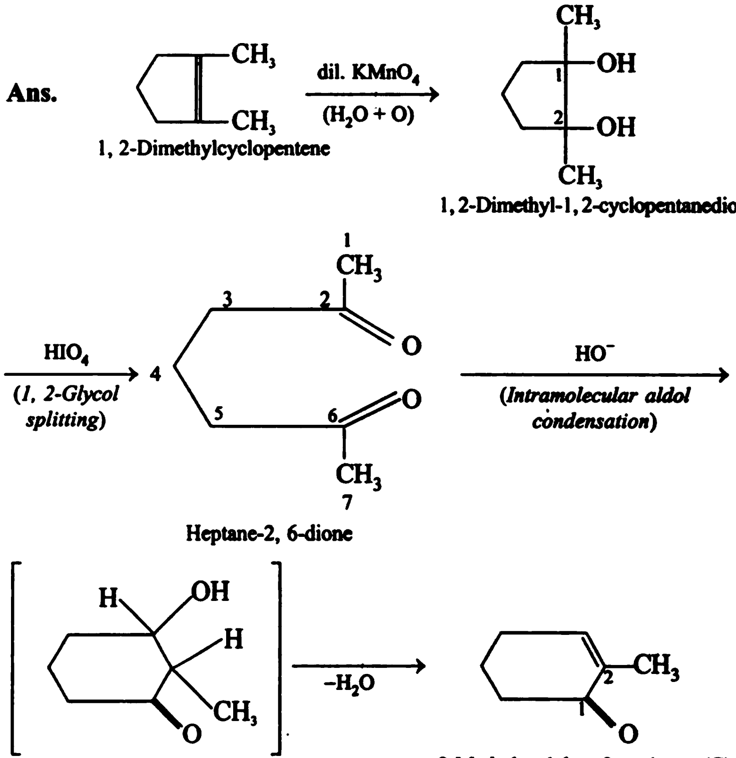
**Explanation.** Methoxy group is *o*,*p*-directing. Therefore Friedel Crafts acylation of anisole with succinic anhydride occurs predominantly at the *p*-position due to steric *hindrance* at the *o*-position to give 4-(*p*-methoxyphenyl)-4-oxobutanoic acid (A). (A) on *clemmensen reduction* gives 4-(*p*-methoxyphenyl) butanoic acid (B) which upon treatment with $H_3PO_4$ undergoes *cyclization* to give 7-methoxy-1-tetralone.

**Example 21.** *Suggest appropriate structures for the missing compounds. (The number of carbon atoms remains the same throughout the reaction).*

*(I.I.T. 1996)*



**Ans.**



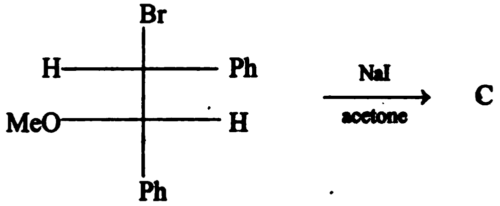
1, 2-Dimethylcyclopentene

1, 2-Dimethyl-1, 2-cyclopentanediol (A)

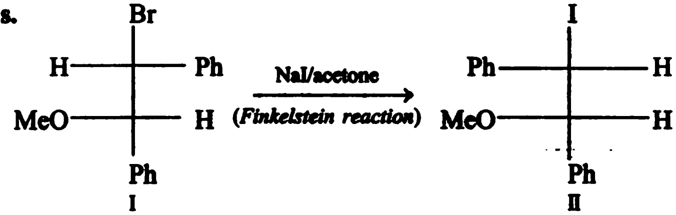
Heptane-2, 6-dione

2-Methylcyclohex-2-en-1-one (C)

**Example 22.** *Predict the structure of the product in the following reaction.* *(I.I.T. 1996)*



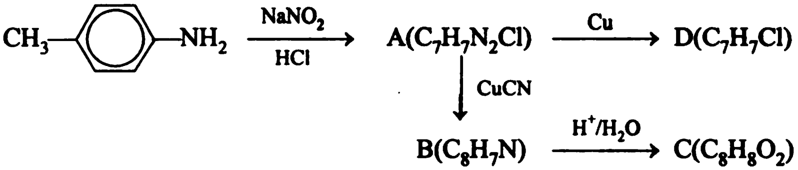
**Ans.**



***Finkelstein reaction*** **is used to convert alkyl bromides to the corresponding alkyl iodides. It is an example of a $SN^2$ reaction in which $I^-$ ion attacks from the *back side* giving the iodide (II) with *inversion of configuration* at the**

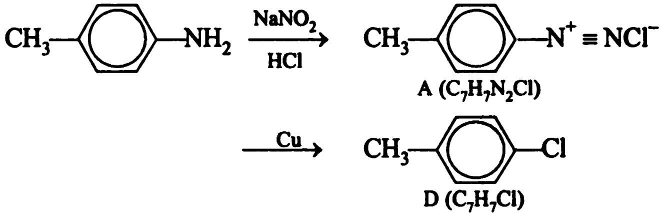
upper chiral carbon undergoing nucleophilic attack. Thus, *product (II) is an enantiomer of the original compound (I).*

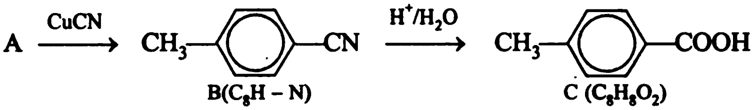
**Example 23.** *Assign structures of the compounds (A—D) :*



(*I.S.M. Dhanbad 1990*)

**Ans.**





**Example 24.** *Name the products P, Q. R, S etc.*

(*a*) $CH_2=CH_2 \xrightarrow{O_3} P \xrightarrow{H_2O} Q \xrightarrow[\text{solution}]{\text{NaOH}} R+S$

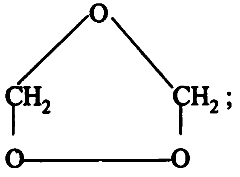
(*b*) $(HCO_2)_2Ca + (CH_3CO_2)_2\,Ca \xrightarrow{\text{heat}} P \xrightarrow{NaHSO_3} Q \xrightarrow{Na_2CO_3} R$

(*c*) $CH_3I \xrightarrow{Mg} P \xrightarrow{CO_2\text{ (solid)}} Q \xrightarrow{H_2O} R$

(*I.S.M. Dhanbad, 1991*)

**Ans.**

(*a*) P =



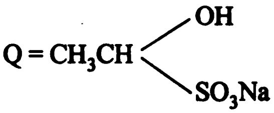
Ethylene ozonide

Q = HCHO
Formaldehyde

R = HCOONa
Sod. formate

S = $CH_3OH$
Methyl alcohol

(*b*) P = $CH_3CHO$ ;
Acetaldehyde



Acetaldehyde sod.
bisulphite addition product

(*c*) $P = CH_3MgI$ ; $Q = CH_3COOMgI$, and $R = CH_3COOH$

Methyl mag. iodide — Acetic acid

**Example 25.** *Fill in the blanks* :

$$(i)\ R{-}X + Mg \longrightarrow ? \xrightarrow[\text{followed by hydrogen}]{CO_2} ? \xrightarrow[\text{chloride}]{\text{thionyl}} ? \xrightarrow{?} R{-}CHO$$

$$(ii)\ R{-}CH_2OH \xrightarrow{?} R{-}COOH \longrightarrow ? \xrightarrow{?} R{-}H\ .$$

(*P.S.B. 1989 S*)

**Ans.** $$(i)\ R{-}X + Mg \longrightarrow \underset{\text{Grignard reagent}}{R{-}MgX} \xrightarrow[H_2O]{CO_2} R{-}COOH$$

$$\xrightarrow[-\,SO_2,\ -\,HCl]{\text{Thionyl chloride}} \underset{\text{Acid chloride}}{R{-}COCl} \xrightarrow[\text{(Rosenmund's reduction)}]{H_2/Pd + BaSO_4 + S} R{-}CHO$$

$$(ii)\ R{-}CH_2OH \xrightarrow[\text{(Oxidation)}]{K_2Cr_2O_7/H_2SO_4} \underset{\text{Carboxylic}}{R{-}COOH} \xrightarrow[-\,H_2O]{NaOH} \underset{\text{Sod. carboxylate}}{R{-}COONa}$$

$$\xrightarrow[\text{(Decarboxylation)}]{CaO + NaOH/623\ K} \underset{\text{Alkane}}{R{-}H}$$

**Example 26.** *Complete the following reactions* :

$$(i)\ CH_3CH_2OH + SOCl_2 \xrightarrow{?} \ldots\ldots\ldots\ldots$$

$$(ii)\ RCH_2OH \xrightarrow{?} RCH_2Br \xrightarrow{?} RCH_2CN \xrightarrow{?} RCH_2COOH$$

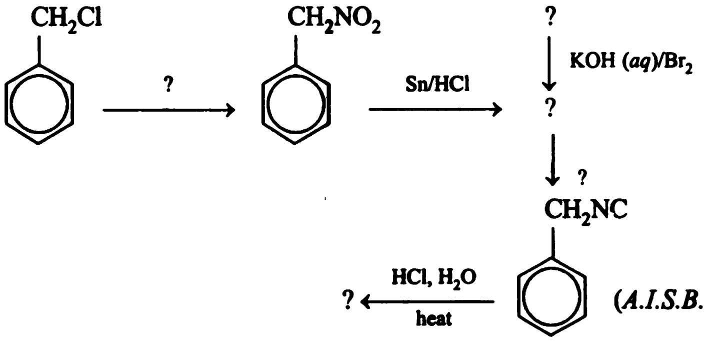
(*H.P.S.B. 1993*)

**Ans.** $$(i)\ CH_3CH_2OH \xrightarrow{SOCl_2} CH_3CH_2Cl + SO_2 + HCl$$

$$(ii)\ RCH_2OH \xrightarrow{PBr_3} RCH_2Br \xrightarrow[-\,KBr]{\text{Alc. KCN}} RCH_2CN$$

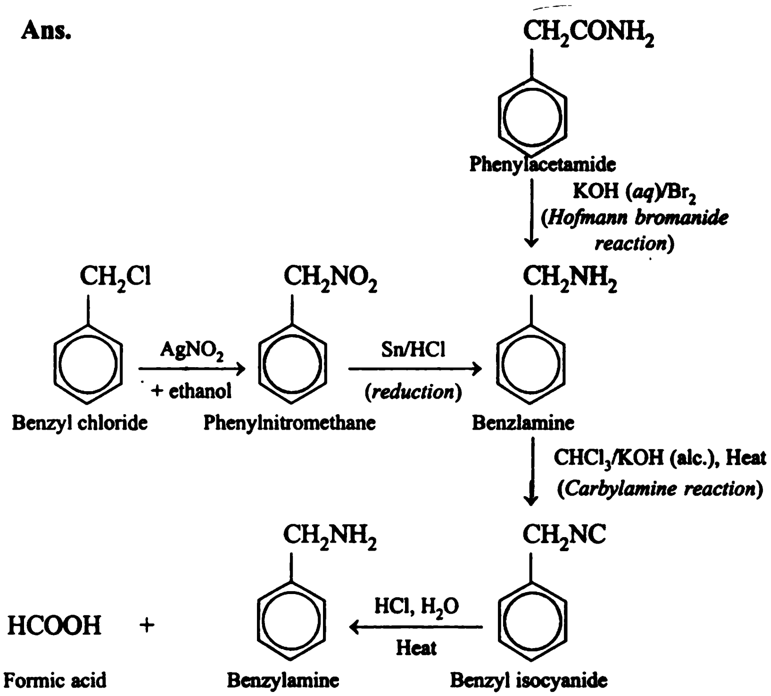
$$\xrightarrow[\text{(Hydrolysis)}]{H^+/H_2O} RCH_2COOH$$

**Example 27.** *Identify the reagents and products in the following sequence of reactions.*

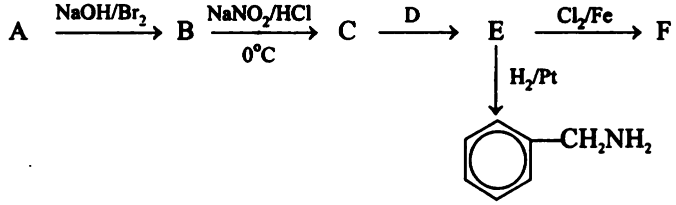


(*A.I.S.B. 1995*)

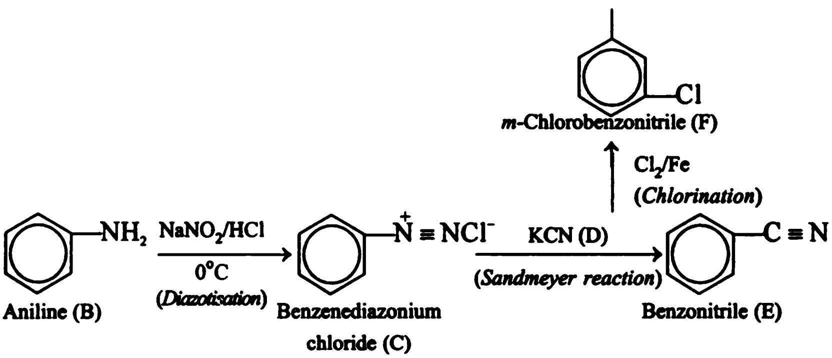
**Ans.**

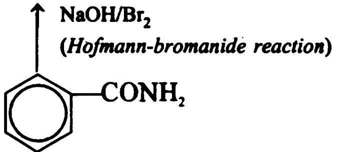


**Example 28.** *Write the structures of the reagents/organic compounds A to F in the following sequence of reactions :* *(A.I.S.B. 1996)*

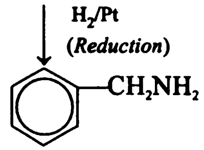


**Ans.**



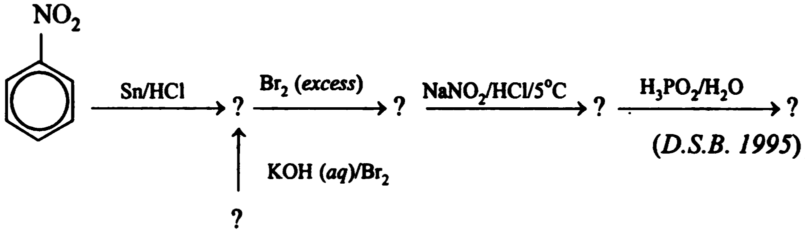


Benzamide (A)



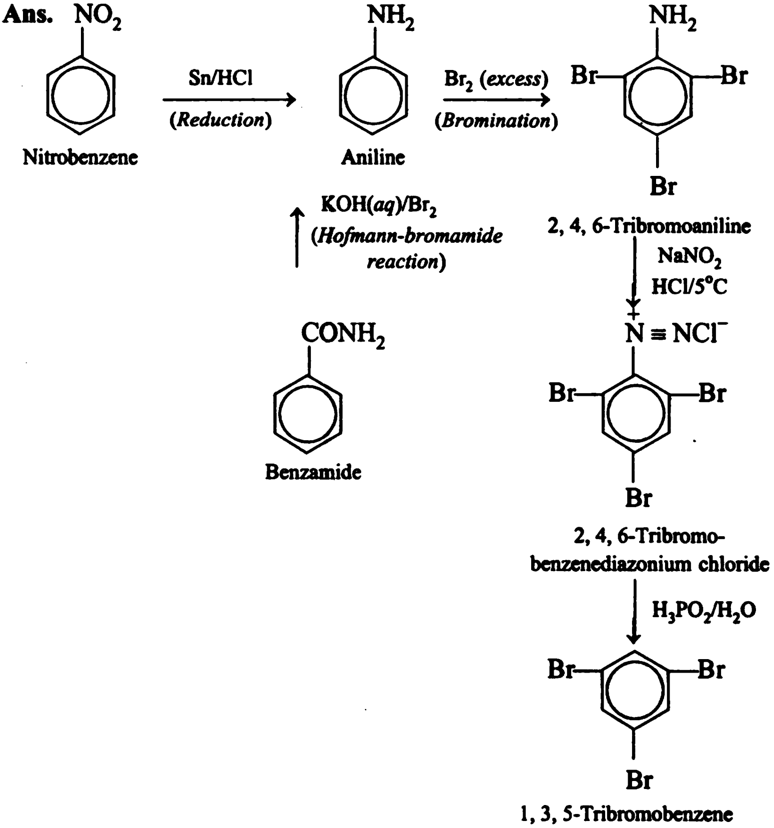
Benzylamine

**Example 29.** *Fill in the blanks with reagents/organic compounds in the following sequence of reactions :*

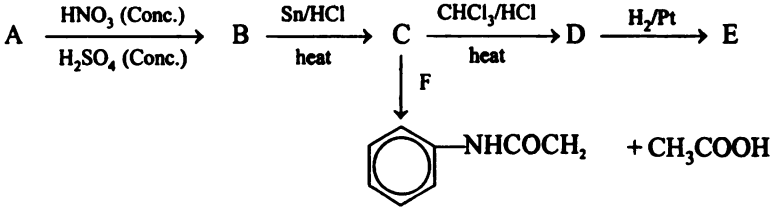


(*D.S.B. 1995*)

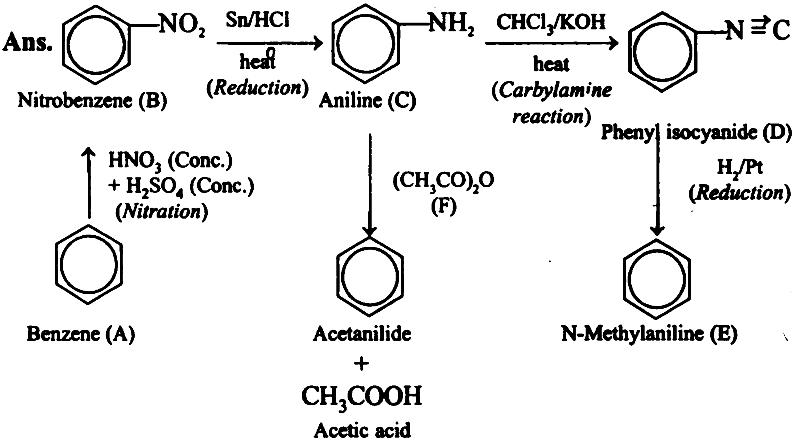
**Ans.**



**Example 30.** *Write the structures of the reagents/organic compounds A to F in the following sequence of reactions :* *(D.S.B. 1996)*



**Ans.**



**Example 31.** *Fill in the blanks in the following equation :*

$CaC_2 + \ldots\ldots \longrightarrow \ldots\ldots + C_2H_2$ *(B.I.T. Mesra : Ranchi, 1991)*

**Ans.** $\underset{\text{Calcium carbide}}{CaC_2} + 2H_2O \longrightarrow Ca(OH)_2 + \underset{\text{Acetylene}}{C_2H_2}$

**Example 32.** *Write down the structure of the main product of each of the following :*

(*i*) Benzene $\xrightarrow{CH_3CH_2COCl/AlCl_3}$

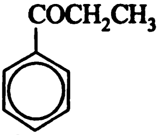
(*ii*) $CH_3COCH_3$ $\xrightarrow{\text{Bleaching powder}}$

(*iii*) $CH_3CH_2NH_2$ $\xrightarrow{\text{Aq. NaNO}_2\text{, dil. HCl}}$

(*iv*) $CH_3COOH$ $\xrightarrow[\text{Heat}]{P_2O_5}$ *(B.I.T. Mesra, Ranchi, 1992)*

**Solution :**

(*i*)



Ethyl pheyl ketone
(*Propiophenone*)

(*ii*) $CHCl_3$ Chloroform (*Trichloromethane*)

(*iii*) $CH_3CH_2OH$ Ethyl alcohol (*Ethanol*)

(*iv*) $CH_3CO—O—COCH_3$ Acetic anhydride (*Ethanoic anhydride*)

**Example 33.** *Write down the structure of the main product of each of the following :*

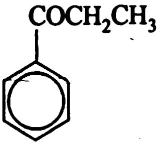
(*i*) Benzene $\xrightarrow{CH_3CH_2COCl/AlCl_3}$

(*ii*) $CH_3COCH_3 \xrightarrow{\text{Bleaching powder}}$

(*iii*) $CH_3CH_2NH_2 \xrightarrow{\text{Aq. } NaNO_2\text{, dil. } HCl}$

(*iv*) $CH_3COOH \xrightarrow{P_2O_5\text{ , Heat}}$ (*B.I.T. Mesra, Ranchi, 1992*)

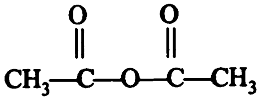
**Ans.**

(*i*) 

Propiophenone (*Ethyl phenyl ketone*)

(*ii*) $CHI_3$ Iodoform

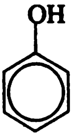
(*iii*) $CH_3CH_2OH$ Ethyl alcohol

(*iv*) 

$CH_3—\overset{O}{\overset{\|}{C}}—O—\overset{O}{\overset{\|}{C}}—CH_3$

Acetic anhydride

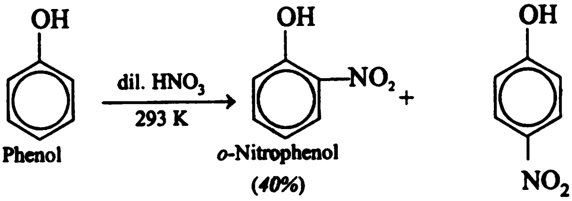
**Example 34.** *Complete the following equations :*

(*a*)  $\xrightarrow{\text{dil. } HNO_3}$ .........+.........

(*b*) $RCONH_2 \xrightarrow{P_2O_5,\ \Delta}$ .........+..........

(*c*) $CHCl_3 + O_2 \xrightarrow{\text{light}}$ ..........+......... (*Punjab P.M.T. 1991*)

**Ans.**

(*a*) 

Phenol

*o*-Nitrophenol (*40%*)

*p*-Nitrophenol (*13%*)

(*b*) $RCONH_2 \xrightarrow{P_2O_5,\ \Delta} RCN + H_2O$

Acetamide — Acid nitrile

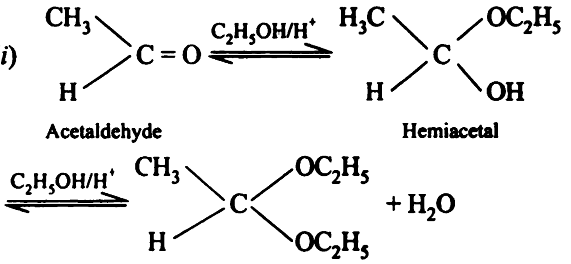
(*c*) $CHCl_3 + \frac{1}{2}O_2 \xrightarrow{\text{light}} COCl_2 + HCl$

Chloroform — Carbonyl chloride (*Phosgene*)

**Example 35.** ***Write equations for the formation of (i) an acetal (ii) oxime and cyanohydrin.*** ***(Punjab P.M.T. 1992)***

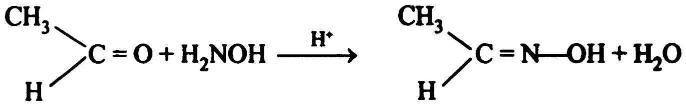
**Ans.**

(*i*)



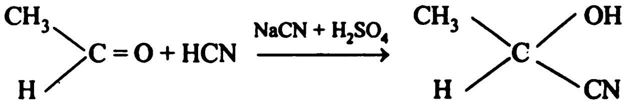
Acetal (1, 1-Diethoxyethane)

(*ii*)



Acetaldehyde — Acetaldoxime

(*iii*)



Acetaldehyde — Acetaldehyde cyanohydrine

**Example 36.** ***Depict any two methods (equations only) for conversion of anacyl halide to carbonyl compounds.*** ***(Punjab P.M.T. 1992)***

**Ans.**

(*i*) $RCOCl + H_2 \xrightarrow[410\ K]{Pd.\ BaSO_4\text{–}S} RCHO + HCl$

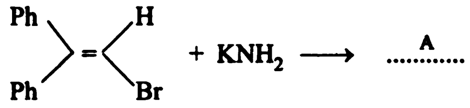
Acid chloride — (In boiling xylene) — Aldehyde

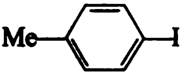
(*ii*) $RCOCl + RCdCl \longrightarrow RCOR + CdCl_2$

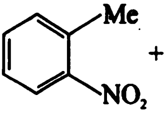
Acid chloride — Alkyl cad. chloride — Ketone

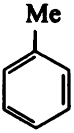
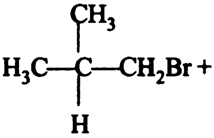
**Example 37.** ***Complete the following, giving the structures of the principal organic products :***

(*a*)

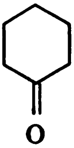


(*b*)  + Cu + Heat ⟶ $\overset{B}{\ldots\ldots\ldots\ldots}$

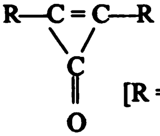
(*c*)  + $(COOEt)_2$ + EtONa ⟶ $\overset{C}{\ldots\ldots\ldots}$

(*d*)  + 

$H_3C-C(CH_3)(H)-CH_2Br$ + Anhyd. $AlCl_3$ ⟶ $\overset{D}{\ldots\ldots\ldots\ldots}$

(*e*)  + $Ph_3P=CH_2$ ⟶ $\overset{E}{\ldots\ldots\ldots\ldots}$

(*f*) $(COOH)_2 + (CH_2OH)_2$ + Conc. $H_2SO_4$ ⟶ $\overset{F}{\ldots\ldots\ldots\ldots}$

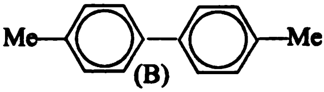
(*g*)  + $HClO_4$ ⟶ $\overset{G}{\ldots\ldots\ldots\ldots}$ [R = *n* – Pr]

(*h*)  + $CHBr_3$ + t – BuOK ⟶ $\overset{H}{\ldots\ldots\ldots\ldots}$

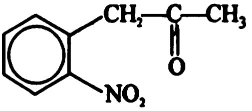
(*i*) $ClCl_2CH_2CH_2COPh$ + KOH + MeOH ⟶ $\overset{I}{\ldots\ldots\ldots\ldots}$

(*j*) $H_3CCOCOC_6H_5 + NaOH/H_3O^{\oplus}$ ⟶ $\overset{J}{\ldots\ldots\ldots\ldots}$ (*I.I.T. 1997*)

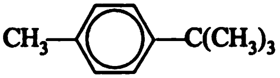
**Ans.** (*a*) Ph—C ≡ C—Ph (A)

(*b*) 

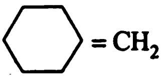
(B)

(*c*) 

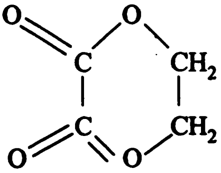
(C)

(*d*) 

(D)

(*e*) 

(E)

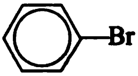
(*f*) 

(F)

(*g*) $CH_3CH_2CH_2COOH$

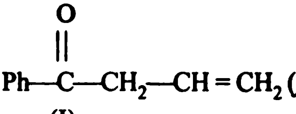
(G)

(*h*)



(H)

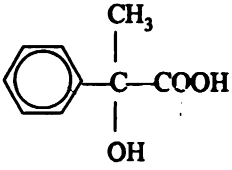
(*i*)



$Ph{-}\overset{\overset{O}{\|}}{C}{-}CH_2{-}CH{=}CH_2$

(I)

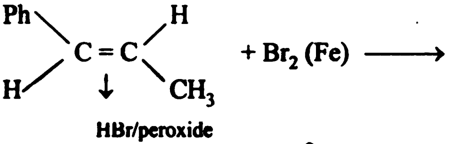
(*j*)



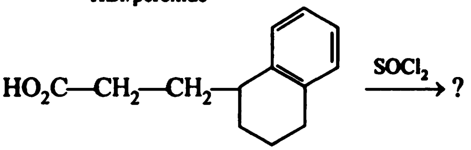
(J)

**Example 38.** *Complete the following sequence of reactions with appropriate structures :*

(*i*)

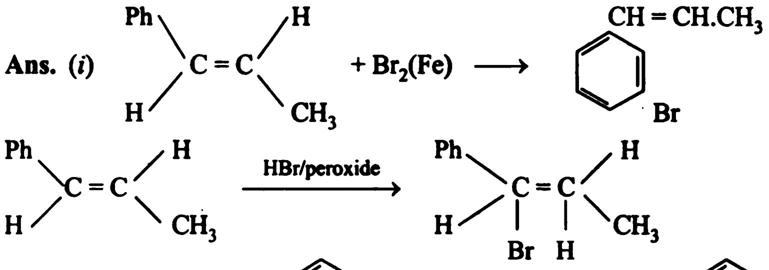


(*ii*)

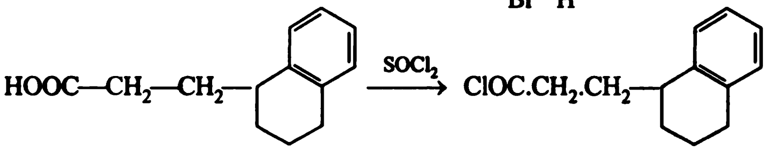


(*MLNR 1997*)

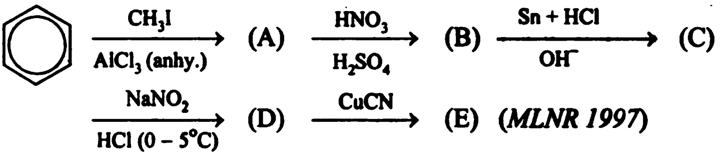
**Ans.** (*i*)



(*ii*)

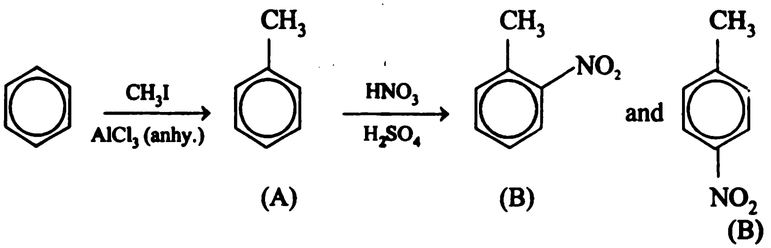


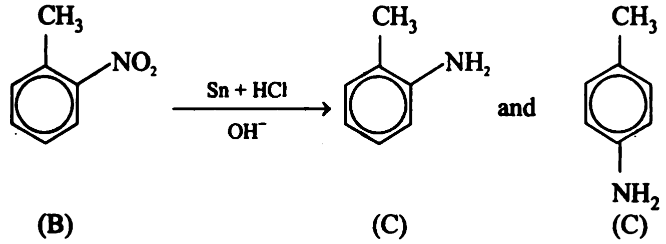
**Example 39.** *Complete the following by giving the structures of (A), (B), (C), (D) and (E).*

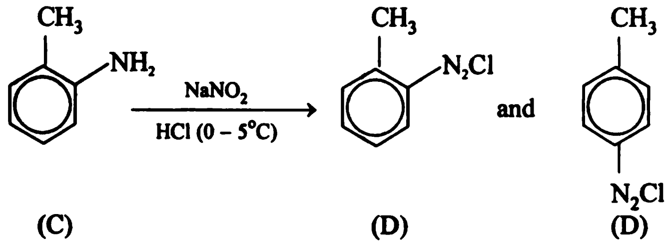


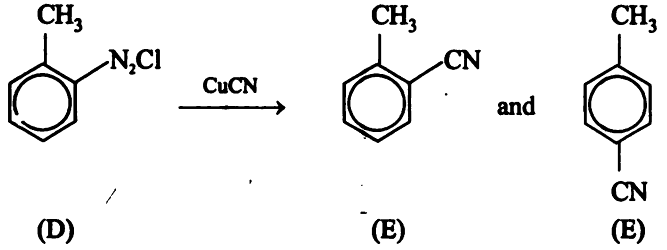
(*MLNR 1997*)

**Sol.**









**Example 40.** *Identify the products A, B, C and D in the following sequence of reactions.* *(M.L.N.R. Allahabad 1996)*

$$(A) \xrightarrow{PCl_5} (B) \xrightarrow{LiAlH_4} (C) \xrightarrow{HBr/H_2SO_4} (D) \xrightarrow[\text{ether}]{Na} CH_3CH_2CH_2CH_3$$

**Sol.** $\underset{\text{Acetic acid (A)}}{CH_3COOH} \xrightarrow[-\,POCl_3\,-\,HCl]{PCl_5} \underset{\text{Acetyl chloride (B)}}{CH_3COCl} \xrightarrow{LiAlH_4} \underset{\text{Ethyl alcohol (C)}}{CH_3CH_2OH}$

$\xrightarrow[\textit{(Nucleophilic substituion reaction)}]{HBr/H_2SO_4} \underset{\text{Ethyl bromide (D)}}{CH_3CH_2—Br} \xrightarrow[-\,2NaBr]{Na/ether} \underset{\text{Butane}}{CH_3CH_2CH_2CH_3}$

(*Wurtz reaction*)

**Example 41.** *Each of the following reactions gives two products. Wrtie the structures of the products.*

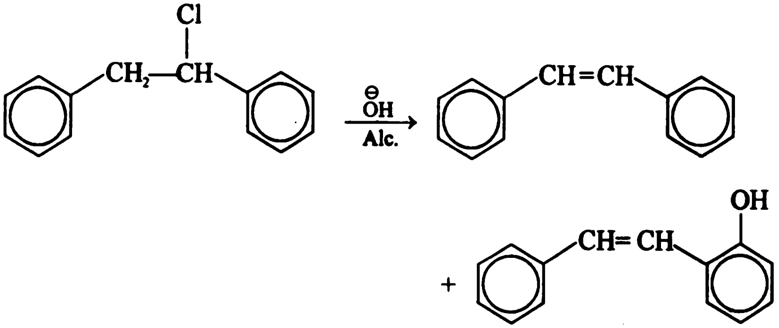
(*a*) $C_6H_5CH_2CHClC_6H_5 \xrightarrow{\text{alcoholic KOH, heat}}$

(*b*) $CH_3CH_2NH_2 \xrightarrow{(CH_3CO)_2O\text{, heat}}$

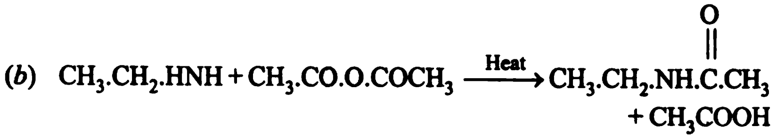
(*c*) $(CH_3)_2CHOCH_3 \xrightarrow{\text{HI (excess), heat}}$

(*d*) $CH_3CONHC_6H_5 \xrightarrow{Br_2\text{, Fe}}$ (*I.I.T. 1998*)

**Sol.** (*a*)

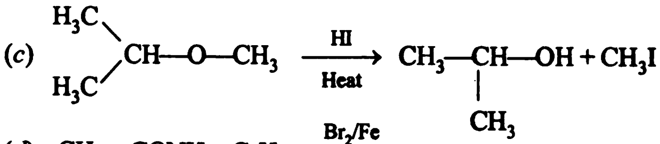


(*b*)



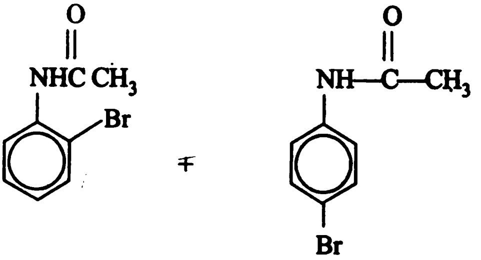
$$CH_3.CH_2.HNH + CH_3.CO.O.COCH_3 \xrightarrow{\text{Heat}} CH_3.CH_2.NH.\overset{\overset{O}{\|}}{C}.CH_3 + CH_3COOH$$

(*c*)



$$\begin{matrix} H_3C \\ H_3C \end{matrix} > CH-O-CH_3 \xrightarrow[\text{Heat}]{\text{HI}} CH_3-\underset{\underset{CH_3}{|}}{CH}-OH + CH_3I$$

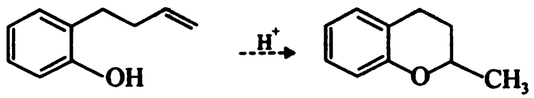
(*d*) $CH_3-CONH-C_6H_5 \xrightarrow{Br_2/Fe}$



**Example 42.** *Write the intermediate steps for each of the following reactions.*

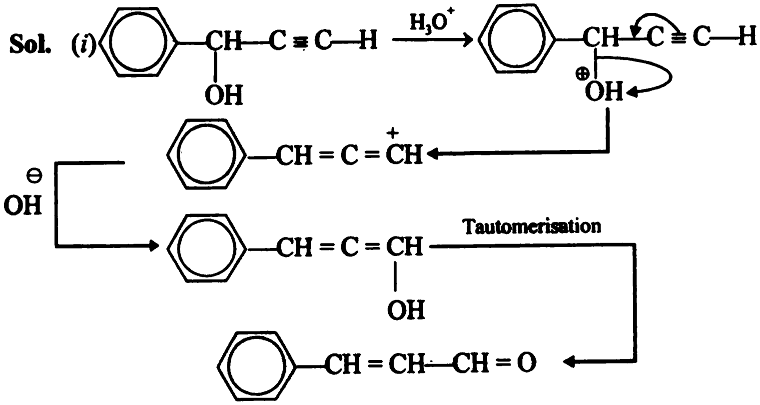
(*i*) $C_6H_5CH(OH)C \equiv CH \xrightarrow{H_3O^+} C_6H_5CH = CHCHO$

(*ii*)

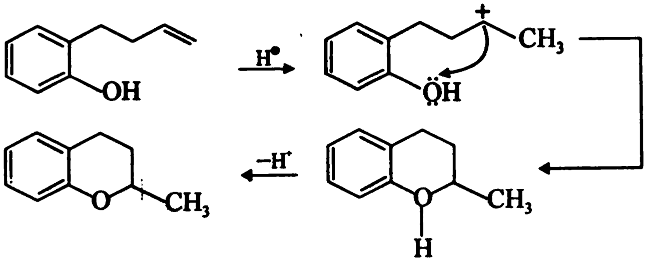


(*I.I.T. 1998*)

**Sol.** (*i*)

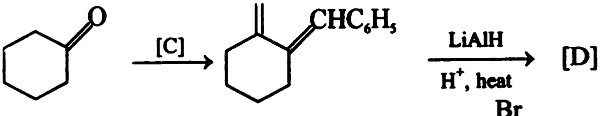


(*ii*)

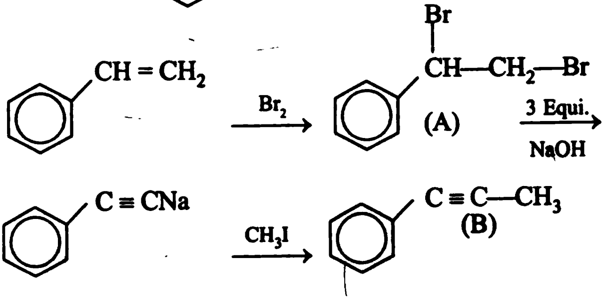


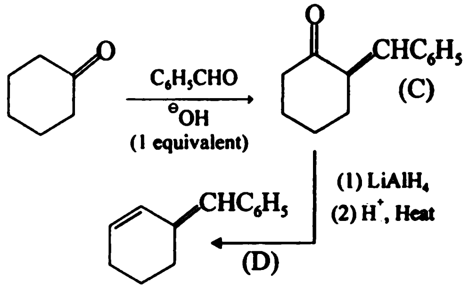
**Example 43.** *Complete tthe following reactions with appropriate structures of products/reagents.*

(*a*) $C_6H_5CH=CH_2 \xrightarrow{Br_2} [A] \xrightarrow[(ii)\ CH_3I]{(i)\ NaNH_2(3.0\ equiv.)} [B]$



**Sol.** (*a*)

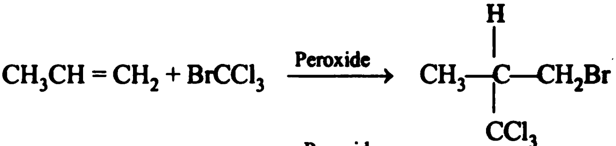


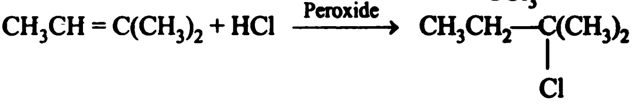
(*b*)


**Example 44.** *Write the products in the following reactions :*

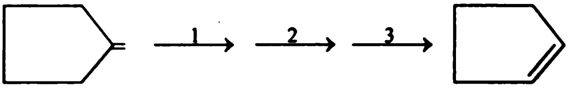
(*i*) $CH_3CH = CH_2 + BrCCl_3 \xrightarrow{\text{peroxide}}$

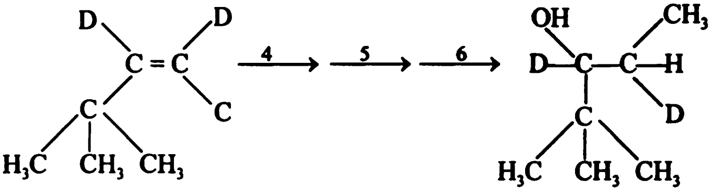
(*ii*) $CH_3CH = C(CH_3)_2 + HCl \xrightarrow{\text{peroxide}}$ (*Roorkee 1998*)

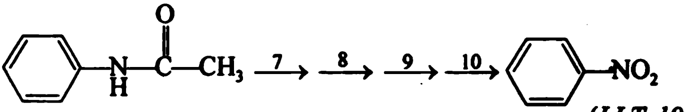
**Sol.** (*i*)

$CH_3CH = CH_2 + BrCCl_3 \xrightarrow{\text{Peroxide}} CH_3-\underset{CCl_3}{\overset{H}{C}}-CH_2Br$

(*ii*)

$CH_3CH = C(CH_3)_2 + HCl \xrightarrow{\text{Peroxide}} CH_3CH_2-\underset{Cl}{C}(CH_3)_2$

**Example 45.** *Complete the following reactions with appropriate reagents*

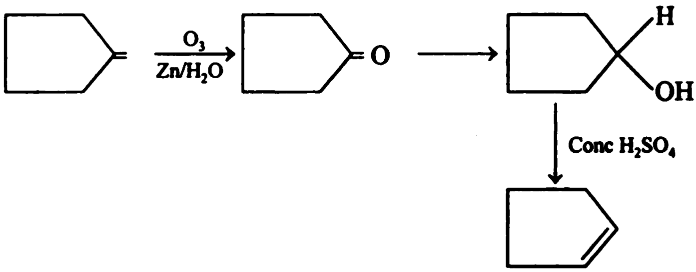
(*a*)


(*b*)


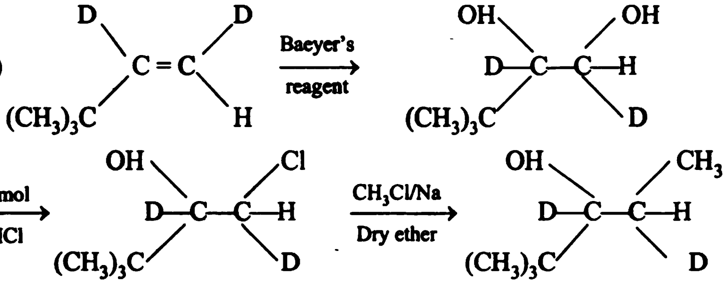
(*c*)


(*I.I.T. 1999*)

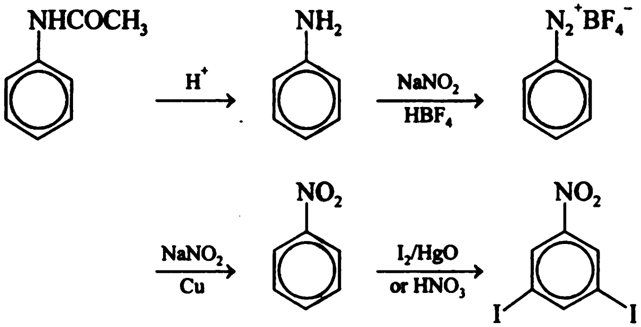
**Sol.**

(*a*)


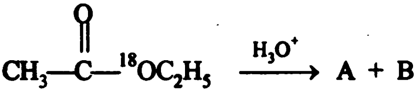
(*b*)



(*c*)



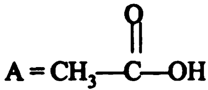
**Example 46.** *Write the structures of the products A and B :*



$$CH_3-\overset{\overset{O}{\|}}{C}-{}^{18}OC_2H_5 \xrightarrow{H_3O^+} A + B$$

(*I.I.T. 2000*)

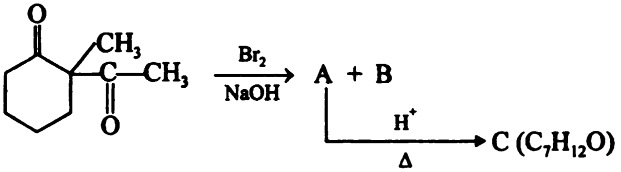
**Sol.** A =



$$CH_3-\overset{\overset{O}{\|}}{C}-OH$$

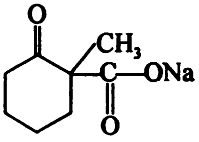
$B = C_2H_5O^{18}H$

**Example 47.** *Identify A, B and C and give their structures :*



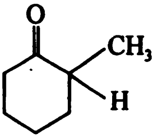
(*I.I.T. 2000*)

**Sol.** A =



$B = CHBr_3$

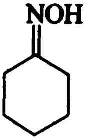
C =



**Example 48.** *Give the structures of the products in each of the following reactions :*

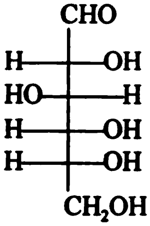
(*i*) Sucrose $\longrightarrow$ A + B

(*ii*)

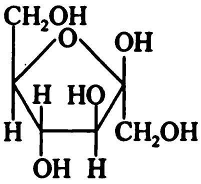


$\xrightarrow{H^+}$ C $\xrightarrow[\text{zation}]{\text{Polymari-}}$ $\{D\}_n$ (*I.I.T. 2000*)

**Sol.** (*i*)

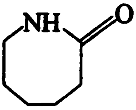


D(+) glucose
(A)



D(−) fructose
(B)

(*ii*)

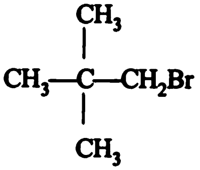


(C)

$\{ CO(CH_2)_5NH \}$
(D)

**Example 49.** *What would be the major product in each of the following reactions ?*

(*i*)

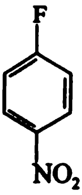


$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-CH_2Br \xrightarrow[\Delta]{C_2S_8OH}$

(*ii*)

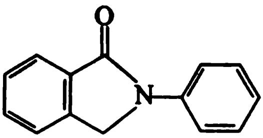
$\xrightarrow[\text{Lindlar Catalyst}]{H_2}$

(*iii*)



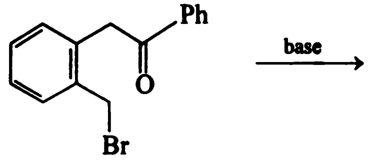
$\xrightarrow[\Delta]{NaOCH_3}$

(*iv*)



$\xrightarrow{Br_2/Fe}$

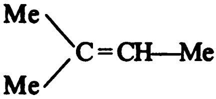
(*v*)



(*I.I.T. 2000*)

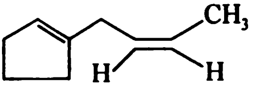
**Sol.** Major products in each of the reactions are given below :

(*i*)

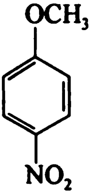


$$(Me)_2C=CH-Me$$

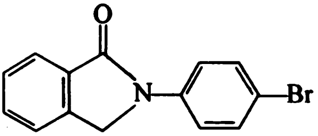
(*ii*)



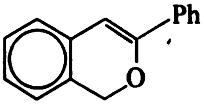
(*iii*)



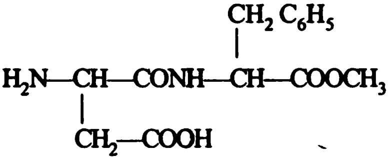
(*iv*)



(*v*)



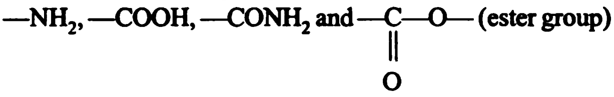
***Example 50.*** *Aspartame, an artificial sweetener, is a dipeptide and has the following structure :*



$$H_2N-\underset{\displaystyle CH_2-COOH}{CH}-CONH-\overset{\displaystyle CH_2C_6H_5}{CH}-COOCH_3$$

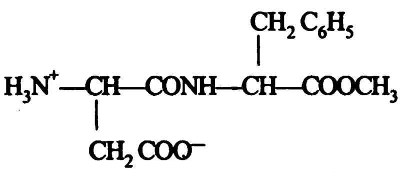
(*i*) Identify the four functional groups.
(*ii*) Write the zwitter-ionic structure.
(*iii*) Write the structures of amino acids obtained from the hydrolysis of aspartame.
(*iv*) Which of the two amino acids is more hydrophobic ? (*I.I.T. 2001*)

**Ans.** (*i*) The four functional groups are



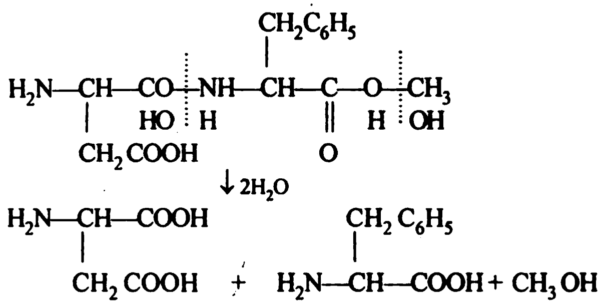
$$-NH_2, -COOH, -CONH_2 \text{ and } -\underset{\displaystyle \overset{\|}{O}}{C}-O- \text{ (ester group)}$$

(*ii*) Zwitter ionic structure is :



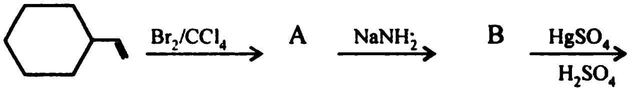
$$H_3N^+-\underset{\displaystyle CH_2COO^-}{CH}-CONH-\overset{\displaystyle CH_2C_6H_5}{CH}-COOCH_3$$

(*iii*) The hydrolysis is depicted as under :



Aspartic acid Phenylalanine

**Example 51.** *(a) Identify A, B, C, D, and E in the following schemes and write their structures :*



$C \xrightarrow{NH_2NHCONH_2} D$

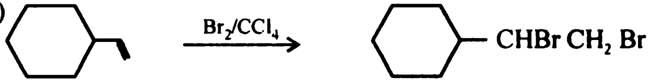
$C \xrightarrow{NaOD/D_2O(excess)} E$

(*b*) *Identify X, Y, and Z in the following synthetic scheme and write their structures. Explain the formation of labelled 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.*

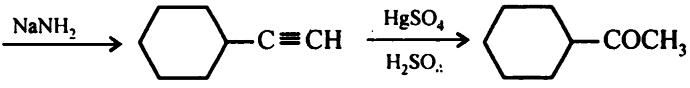
$BaC^*O_3 + H_2SO_4 \rightarrow X$ (gas) [C* denotes $C^{14}$]

$CH_2 = CH—Br \xrightarrow[\text{(ii) X, (iii) } H_3O^+]{\text{(i) Mg/Ether}} Y \xrightarrow{Li\ AlH_4} Z$ *(I.I.T. 2001)*

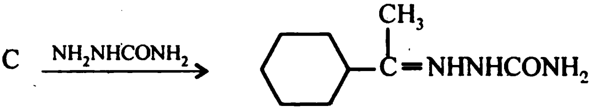
**Ans.** (*a*)



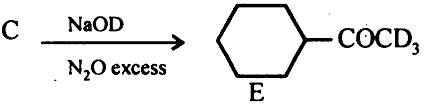
A



B C

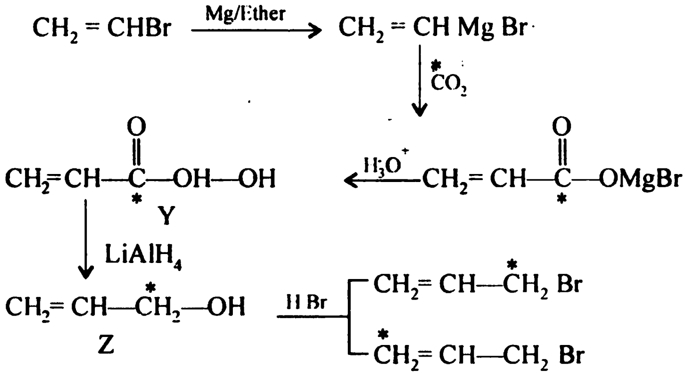


D



E

(*b*) $Ba\overset{*}{C}O_3 + H_2SO_4 \longrightarrow BaCO_4 + H_2O + \underset{X}{\overset{*}{C}O_2}$



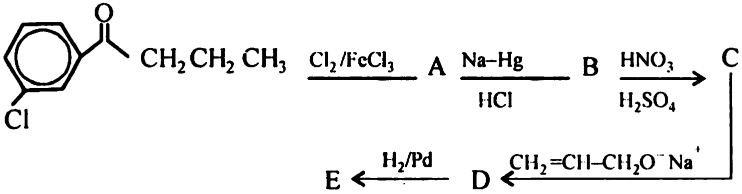
Ozonolysis of $\overset{*}{C}H_2 = CH—CH_2\,Br$ produces formaldehyde $H_2\overset{*}{C}O$

***Example 52.*** *(a) Identify X, Y, and Z in the following synthetic scheme and write their structures.*

$$CH_3 = CH_2C{\equiv}C—H \xrightarrow[\text{(ii) } CH_3CH_2Br]{\text{(i) } NaNH_2} X \xrightarrow{H_2/Pd\text{-}BaSO_4} Y \xrightarrow{AlK.KMnO_4} Z$$

*Is the compound Z optically active ? Justify your answer.*

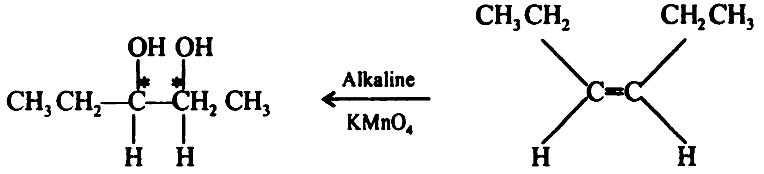
*(b) Write structures of products A, B, C, D and E in the following scheme.*



*(I.I.T. 2002)*

**Ans** (*a*) $CH_3CH_2\,C{\equiv}C—H \xrightarrow[CH_3CH_2\,Br]{NaNH_2} \underset{X}{CH_3CH_2\,C{\equiv}CCH_2\,CH_3}$

$$\Big\downarrow H_2/\,Pd/BaSO_4$$

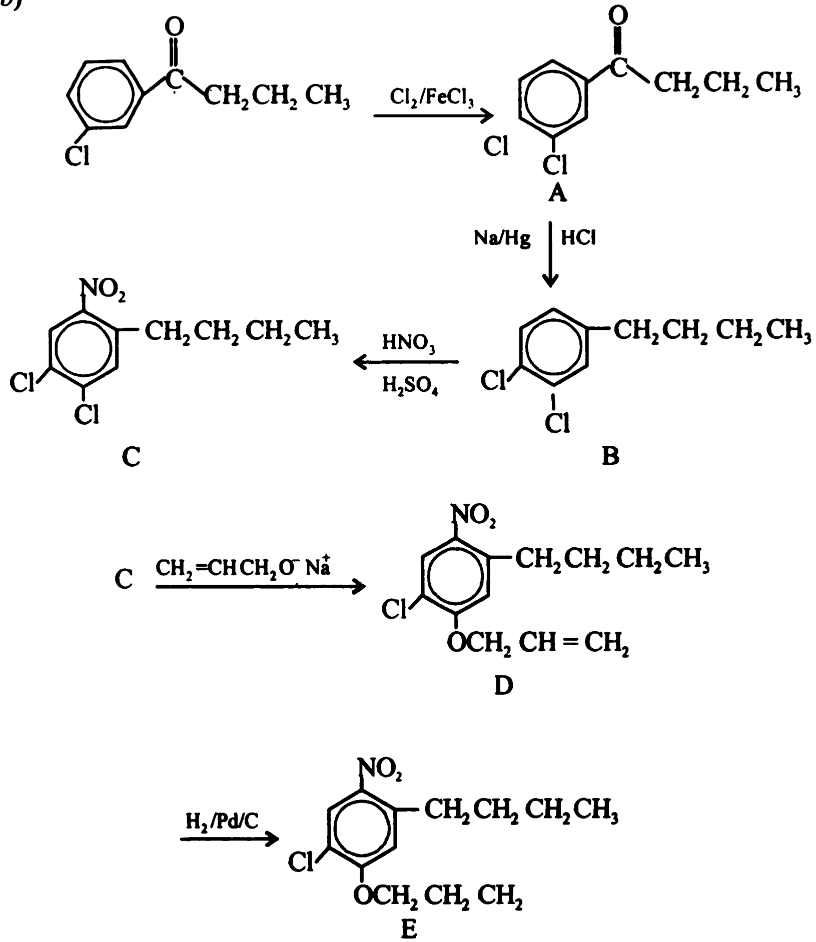


Syn-Addition

Z Y

Although Z contains two asymmetric carbon atoms but it is optically inactive. This is because it is a *meso* compound.

(*b*)



A B C D E

**Example 53.**

$$[A] \xrightarrow{\text{HCl}} \underset{C_6H_{13}Cl}{\underline{[B]}} + \underset{C_6H_{13}Cl}{\underline{[C]}}$$

$$[B] \xrightarrow{\text{Alc. KOH}} [C] \text{ (isomer of A)}$$

$$[D] \xrightarrow{\text{Ozonolysis}} [E]$$ (gives positive iodoform test but not Fehling or Tollen's solution test)

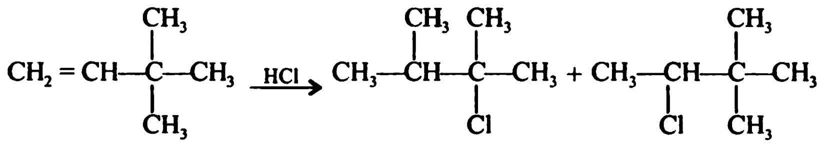
$$[A] \xrightarrow{\text{Ozonolysis}} [F] + [G]$$ (Both give positive Tollen's test but negative iodoform test)

$$[F] + [G] \xrightarrow{\text{Conc. NaOH}} \text{HCOONa} + \text{a primary alcohol}$$

**Write the structures of [A], [B], [C], [D], [E], [F] and [G]**

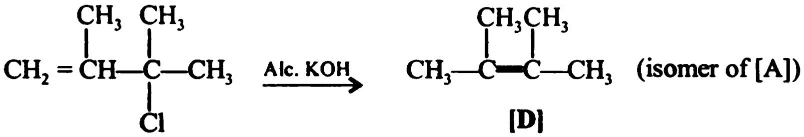
(*I.I.T. 2003*)

**Ans.**



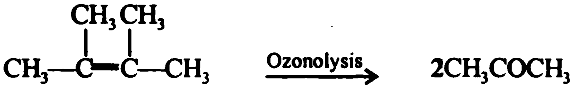
$$CH_2{=}CH{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CH_3 \xrightarrow{\text{HCl}} CH_3{-}\overset{CH_3}{CH}{-}\overset{CH_3}{\underset{Cl}{C}}{-}CH_3 + CH_3{-}\underset{Cl}{CH}{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CH_3$$

[A] [B] $C_6H_{13}Cl$ [C] $C_6H_{13}Cl$



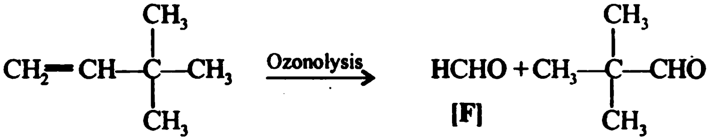
$$CH_2{=}\overset{CH_3}{CH}{-}\overset{CH_3}{\underset{Cl}{C}}{-}CH_3 \xrightarrow{\text{Alc. KOH}} CH_3{-}\overset{CH_3}{C}{=}\overset{CH_3}{C}{-}CH_3 \text{ (isomer of [A])}$$

[D]



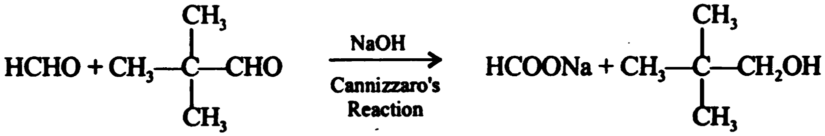
$$CH_3{-}\overset{CH_3}{C}{=}\overset{CH_3}{C}{-}CH_3 \xrightarrow{\text{Ozonolysis}} 2CH_3COCH_3$$

[D] [E]



$$CH_2{=}CH{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CH_3 \xrightarrow{\text{Ozonolysis}} HCHO + CH_3{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CHO$$

[A] [F] [G]



$$HCHO + CH_3{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CHO \xrightarrow[\text{Cannizzaro's Reaction}]{\text{NaOH}} HCOONa + CH_3{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CH_2OH$$

Primary alcohol

# 7

# What Happens When ?

**1. Ethylmagnesium bromide is treated with water.**

Ethylmagnesium bromide reacts with water to produce ethane.

$$\underset{\text{Ethylmagnesium bromide}}{CH_3\overset{\delta-}{CH_2}\overset{\delta+}{Mg}Br} + \overset{\delta+}{H}{-}\overset{\delta-}{OH} \longrightarrow \underset{\text{Ethane}}{CH_3{-}CH_3} + Mg(OH)Br$$

**2. Methyl bromide is treated with sodium in dry ether.**

When methyl bromide is treated with sodium in dry ether, ethane is formed

$$\underset{\text{Methyl bromide}}{CH_3{-}Br} + 2Na + Br{-}CH_3 \xrightarrow[\textit{(Wurtz reaction)}]{\text{Dry ether, }\Delta} \underset{\text{Ethane}}{CH_3{-}CH_3} + 2NaBr$$

**3. Ethyl alcohol is heated with conc. $H_2SO_4$ at 440 K.**

Ethylene is produced. Dehydration takes place producing ethylene

$$\underset{\text{Ethyl alcohol}}{CH_3{-}CH_2{-}OH} \xrightarrow{\text{Conc. } H_2SO_4\text{, 440 K}} \underset{\text{Ethylene}}{CH_2{=}CH_2} + H_2O$$

**4. Ethyl iodide is reduced.**

Ethyl iodide on reduction with $Na/C_2H_5OH$ or Zn/HCl or with red P and HI gives ethane

$$\underset{\text{Ethyl iodide}}{CH_3{-}CH_2{-}I} + 2[H] \xrightarrow[\text{or Zn/ HCl}]{Na/C_2H_5OH} \underset{\text{Ethane}}{CH_3{-}CH_3} + HI$$

or $$CH_3{-}CH_2{-}I + HI \xrightarrow[\Delta]{\text{Red P}} CH_3{-}CH_3 + I_2$$

**5. Ethyl iodide is treated with sodium in dry ether.**

Butane is formed. This reaction is known as Wurtz reaction

$$\underset{\text{Ethyl iodide}}{CH_3CH_2{-}I} + 2Na + I - CH_2CH_3 \xrightarrow{\text{Dry ether, }\Delta} \underset{n\text{-Butane}}{CH_3CH_2{-}CH_2CH_3} + 2NaI$$

**6. Sodium acetate is subjected to electrolysis.**

When sodium acetate is electrolysed, ethane is obtained.

$$2CH_3COONa \xrightarrow{\text{Ionization}} 2CH_3COO^- + 2Na^+$$

$$2H_2O \xrightleftharpoons{\text{Ionization}} 2OH^- + 2H^+$$

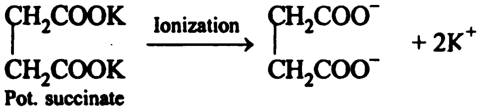
**At anode :** $2CH_3COO^- - 2e^- \longrightarrow \underset{(unstable)}{[2CH_3COO]} \longrightarrow \underset{\text{Ethane}}{CH_3{-}CH_3} + 2CO_2$

**At cathode :** $2H^+ + 2e^- \longrightarrow [2H] \longrightarrow H_2$

**7. Potassium succinate is subjected to Kolbe's electrolysis.**

(*I.I.T. 1993*)

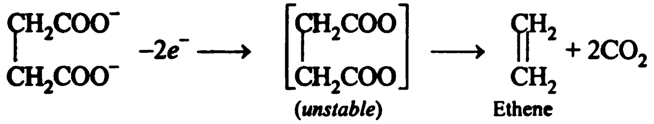
Ethene is obtained on electrolysis of potassium succinate, as explained below :



$$\underset{\text{Pot. succinate}}{\begin{array}{l} CH_2COOK \\ | \\ CH_2COOK \end{array}} \xrightarrow{\text{Ionization}} \begin{array}{l} CH_2COO^- \\ | \\ CH_2COO^- \end{array} + 2K^+$$

$$2H_2O \xrightleftharpoons{\text{Ionization}} 2OH^- + 2H^+$$

**At anode :**

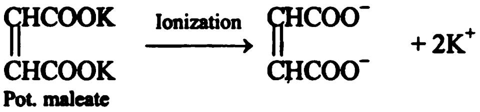


$$\begin{array}{l} CH_2COO^- \\ | \\ CH_2COO^- \end{array} -2e^- \longrightarrow \underset{(unstable)}{\left[\begin{array}{l} CH_2COO \\ | \\ CH_2COO \end{array}\right]} \longrightarrow \underset{\text{Ethene}}{\begin{array}{l} CH_2 \\ \| \\ CH_2 \end{array}} + 2CO_2$$

**At cathode :** $2H^+ + 2e^- \longrightarrow [2H] \longrightarrow H_2$

**8. Potassium meleate (or fumarate) is subjected to electrolysis.**

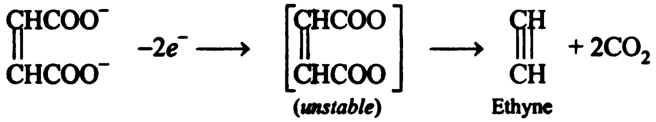
Ethyne (acetylene) is formed as a result of electrolysis



$$\underset{\text{Pot. maleate}}{\begin{array}{l} CHCOOK \\ \| \\ CHCOOK \end{array}} \xrightarrow{\text{Ionization}} \begin{array}{l} CHCOO^- \\ \| \\ CHCOO^- \end{array} + 2K^+$$

$$2H_2O \xrightleftharpoons{\text{Ionization}} 2OH^- + 2H^+$$

**At anode :**



$$\begin{array}{l} CHCOO^- \\ \| \\ CHCOO^- \end{array} -2e^- \longrightarrow \underset{(unstable)}{\left[\begin{array}{l} CHCOO \\ \| \\ CHCOO \end{array}\right]} \longrightarrow \underset{\text{Ethyne}}{\begin{array}{l} CH \\ ||| \\ CH \end{array}} + 2CO_2$$

**At cathode :** $2H^+ + 2e^- \longrightarrow [2H] \longrightarrow H_2$

**9. Sodium acetate is heated with soda lime.**

When sodium acetate is heated with soda lime, methane is formed.

$$\underset{\text{Sod. acetate}}{CH_3COONa} + NaOH \xrightarrow{\text{CaO, 630 K}} \underset{\text{Methane}}{CH_4} + Na_2CO_3$$

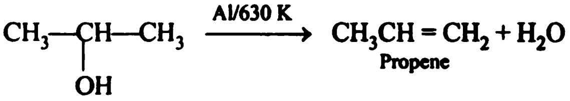
**10. Sodium propanoate is heated with soda lime.**

Decarboxylation takes place and ethane is formed

$$\underset{\text{Sod propanoate}}{CH_3CH_2COONa} + NaOH \xrightarrow{\text{CaO, 630 K}} \underset{\text{Ethane}}{CH_3{-}CH_3} + Na_2CO_3$$

**11. Propan-2-ol is heated with alumina at 630 K.**

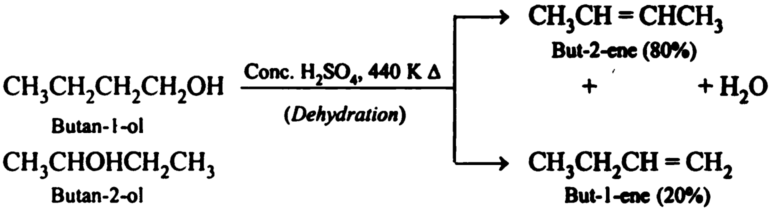
Propene is formed, as a result of dehydration



$$\underset{\text{Propan-2-ol}}{CH_3-\underset{\displaystyle OH}{\underset{|}{C}}H-CH_3} \xrightarrow{Al/630\ K} \underset{\text{Propene}}{CH_3CH=CH_2} + H_2O$$

**12. Butan-1-ol (or butan-2-ol) is heated with conc. $H_2SO_4$.**

With both substances, 80% of but-2-ene and 20% of but-1-ene (*Saytzeff rule*) are formed as a result of dehydration of alcohols.



$$\left.\begin{array}{l}\underset{\text{Butan-1-ol}}{CH_3CH_2CH_2CH_2OH} \\ \text{or } \underset{\text{Butan-2-ol}}{CH_3CHOHCH_2CH_3}\end{array}\right. \xrightarrow[\text{(Dehydration)}]{\text{Conc. } H_2SO_4,\ 440\ K\ \Delta} \begin{array}{l}\underset{\text{But-2-ene (80\%)}}{CH_3CH=CHCH_3} \\ \quad + \qquad\qquad + H_2O \\ \underset{\text{But-1-ene (20\%)}}{CH_3CH_2CH=CH_2}\end{array}$$

**13. Ethyl chloride is heated with alcoholic caustic potash.**

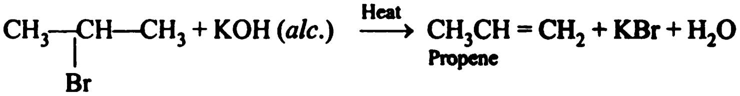
Dehydrohalogenation takes place producing ethylene

$$\underset{\text{Ethyl chloride}}{CH_3-CH_2-Cl} + KOH\,(alc.) \xrightarrow{Heat} \underset{\text{Ethylene}}{CH_2=CH_2} + KCl + H_2O$$

**14. 1-Bromopropane (or 2-bromopropane) is heated with alcoholic caustic potash.**

The same product propene (propylene) is obtained, as a result of dehydrobromination

$$\underset{\text{1-Bromopropane}}{CH_3CH_2CH_2-Br} + KOH\,(alc.) \xrightarrow{Heat} \underset{\text{Propene}}{CH_3CH=CH_2} + KBr + H_2O$$



$$\underset{\text{2-Bromopropane}}{CH_3-\underset{\displaystyle Br}{\underset{|}{C}}H-CH_3} + KOH\,(alc.) \xrightarrow{Heat} \underset{\text{Propene}}{CH_3CH=CH_2} + KBr + H_2O$$

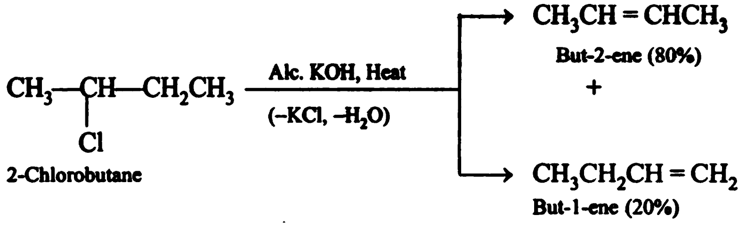
**15. 1-Chlorobutane is heated with alcoholic potash.**

With 1-chlorobutane, but-1-ene is obtained as result of dehydrochlorination

$$CH_3CH_2CH_2CH_2Cl + KOH\ alc. \xrightarrow{Heat} CH_3CH_2CH=CH_2 + KCl + H_2O$$

**16. 2-Chlorobutane is heated with alcoholic potash.**

With 2-chlorobutane, but-2-ene is the major product in accordance with *Saytzeff's rule* according to which during dehydrohalogenation of alkyl halides if two alkenes theoretically possible, more highly substituted alkene predominates, as it more stable.



$$\underset{\text{2-Chlorobutane}}{CH_3-\underset{\underset{Cl}{|}}{CH}-CH_2CH_3} \xrightarrow[(-KCl,\ -H_2O)]{\text{Alc. KOH, Heat}} \underset{\text{But-2-ene (80\%)}}{CH_3CH=CHCH_3} + \underset{\text{But-1-ene (20\%)}}{CH_3CH_2CH=CH_2}$$

**17. Calcium carbide is treated with water.**

(*A.I.S.B. 1980 ; D.S.B. 1980*)

$$\underset{\text{Calcium carbide}}{CaC_2} + 2HOH \longrightarrow HC\equiv CH + Ca(OH)_2$$

**18. Aluminium carbide is treated with water.**

Methane is produced.

$$\underset{\text{Aluminium carbide}}{Al_4C_3} + 12\,HOH \longrightarrow \underset{\text{Methane}}{3CH_4} + 4Al(OH)_3$$

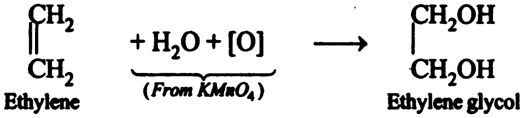
**19. Ethylene is heated with hydrogen in presence of nickel catalyst.**

Ethane is produced.

$$\underset{\text{Ethylene}}{CH_2=CH_2} + H_2 \xrightarrow{\text{Ni, 473 - 523 K}} \underset{\text{Ethane}}{CH_3-CH_3}$$

**20. Ethylene is passed through cold dilute alkaline $KMnO_4$ solution.**

Ethylene glycol is formed. This reaction is called glycollisation.

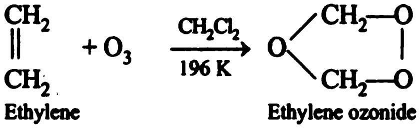


$$\underset{\text{Ethylene}}{\begin{matrix}CH_2\\ \|\\ CH_2\end{matrix}} \quad \underbrace{+H_2O+[O]}_{(\text{From } KMnO_4)} \longrightarrow \underset{\text{Ethylene glycol}}{\begin{matrix}CH_2OH\\ |\\ CH_2OH\end{matrix}}$$

**21. Ozone is passed through ethylene in an organic solvent.**

(*P.S.B. 1988*)

Ethylene ozonide is produced. This reaction is used to locate the double bond.



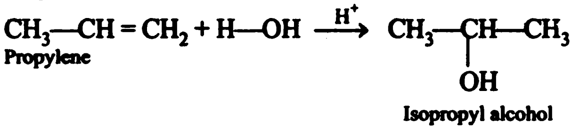
Ethylene

Ethylene ozonide

**22. Propylene reacts with water in presence of a mineral acid.**

(*A.I.S.B. 1982*)

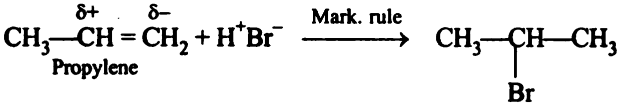
Isopropyl alcohol is produced, in accordance with Markownikov rule.



$$\underset{\text{Propylene}}{CH_3-CH=CH_2} + H-OH \xrightarrow{H^+} \underset{\text{Isopropyl alcohol}}{CH_3-\underset{\underset{OH}{|}}{CH}-CH_3}$$

**23. Propylene is treated with HBr.**

Isopropyl bromide is formed in accordance with *Markownikov's rule.* Hydrogen goes to that carbon which is linked to greater number of hydrogen atoms.



$$\underset{\text{Propylene}}{CH_3\overset{\delta+}{-}CH = \overset{\delta-}{C}H_2} + H^+Br^- \xrightarrow{\text{Mark. rule}} CH_3-\underset{\underset{Br}{|}}{C}H-CH_3$$

Isopropyl bromide

**24. Propylene is treated with HBr in presence of peroxide.**

Anti-Markownikov's addition occurs to give 1-bromopropane.

$$\underset{\text{Propylene}}{CH_3CH = CH_2} + HBr \xrightarrow[\text{addition}]{\text{Anti.-Markownikov}} \underset{\text{1-Bromopropane}}{CH_3-CH_2-CH_2Br}$$

**25. Ethyne is passed through ammoniacal silver nitrate solution.**

White ppt. of silver acetylide is formed.

$$\underset{\text{Ethyne}}{HC \equiv CH} + 2AgNO_3 + 2\,NH_4OH \longrightarrow \underset{\substack{\text{Silver acetylide} \\ (\textit{White ppt.})}}{AgC \equiv CAg} + 2NH_4NO_3 + 2H_2O$$

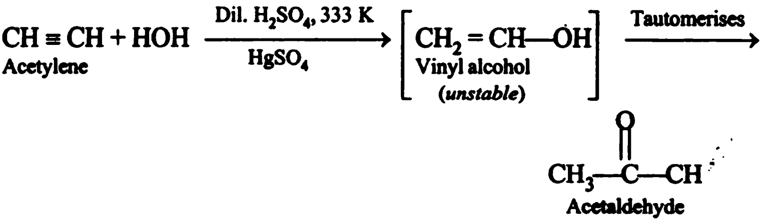
**26. Ethyne is passed through ammoniacal solution of cuprous chloride.**

Red ppt. of copper acetylide is formed.

$$\underset{\substack{\text{Ethyne} \\ (\textit{Acetylene})}}{CH \equiv CH} + 2CuCl + 2NH_4OH \longrightarrow \underset{\substack{\text{Copper acetylide} \\ (\textit{Red ppt.})}}{CuC \equiv CCu} + 2NH_4Cl + 2H_2O$$

**27. Acetylene is hydrated in the presence of dilute $H_2SO_4$ and $HgSO_4$.**

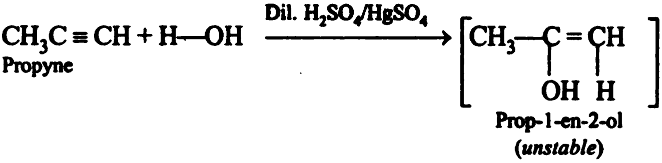
Addition of water takes place. Vinyl alcohol first formed tautomerises to more stable acetaldehyde.



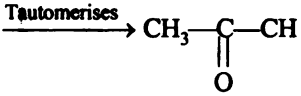
$$\underset{\text{Acetylene}}{CH \equiv CH} + HOH \xrightarrow[HgSO_4]{\text{Dil. } H_2SO_4\text{, 333 K}} \left[\underset{\substack{\text{Vinyl alcohol} \\ (\textit{unstable})}}{CH_2 = CH-OH}\right] \xrightarrow{\text{Tautomerises}} \underset{\text{Acetaldehyde}}{CH_3-\overset{\overset{O}{\|}}{C}-CH}$$

**28. Propyne is treated with dilute acid in presence of $Hg^{2+}$ ions.**

Propanone (or acetone) is formed.



$$\underset{\text{Propyne}}{CH_3C \equiv CH} + H-OH \xrightarrow{\text{Dil. } H_2SO_4/HgSO_4} \left[\underset{\substack{\text{Prop-1-en-2-ol} \\ (\textit{unstable})}}{CH_3-\underset{\underset{OH}{|}}{C} = \underset{\underset{H}{|}}{C}H}\right]$$



$$\xrightarrow{\text{Tautomerises}} CH_3-\underset{\underset{O}{||}}{C}-CH_3$$

Propanone

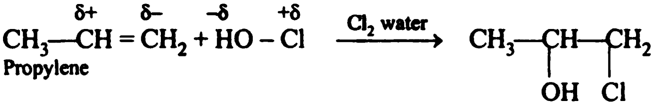
**29. Vapours of ethyl alcohol are passed over heated $Al_2O_3$ at 623 K.**

Dehydration takes place and ethylene is produced.

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow{Al_2O_3,\ 623\ K} \underset{\text{Ethylene}}{CH_2=CH_2} + H_2O$$

**30. Propylene is bubbled through chlorine water.**

Chlorine reacts with water to give HOCl in which OH is slightly negative. Addition takes place according to Markownikov rule and propylene chlorohydrin is formed.

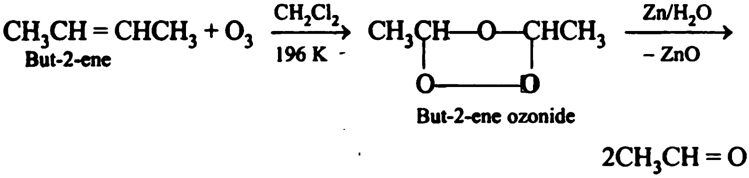


$$\underset{\text{Propylene}}{\overset{\delta+}{CH_3}-\overset{\delta-}{CH}=CH_2} + \overset{-\delta}{HO}-\overset{+\delta}{Cl} \xrightarrow{Cl_2\text{ water}} CH_3-\underset{OH}{\underset{|}{CH}}-\underset{Cl}{\underset{|}{CH_2}}$$

Propylene Chlorohydrin

**31. But-2-ene is treated with ozone and the resulting solution is treated with water in presence of zinc dust.**

Acetaldehyde is produced as shown below.



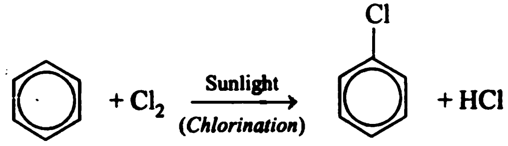
$$\underset{\text{But-2-ene}}{CH_3CH=CHCH_3} + O_3 \xrightarrow[196\ K]{CH_2Cl_2} CH_3\underset{O}{\underset{|}{CH}}-O-\underset{O}{\underset{|}{CH}}CH_3 \xrightarrow[-\,ZnO]{Zn/H_2O} 2CH_3CH=O$$

But-2-ene ozonide

Acetaldehyde

**32. Benzene is treated with chlorine in presence of anhydrous $FeCl_3$.**

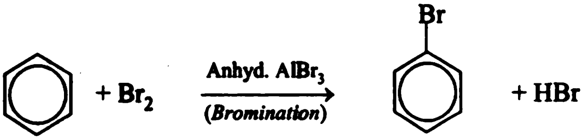
Chlorobenzene is formed by electrophilic substitution



Benzene Chlorobenzene

**33. Benzene is treated with bromine in presence of anhydrous aluminium bromide as catalyst.**

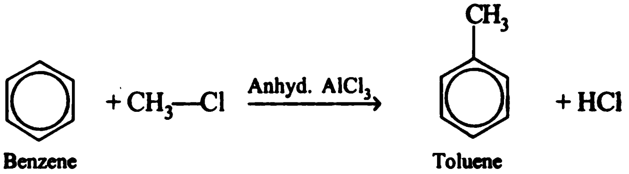
Bromobenzene is formed by electrophilic substitution.



Benzene Bromobenzene

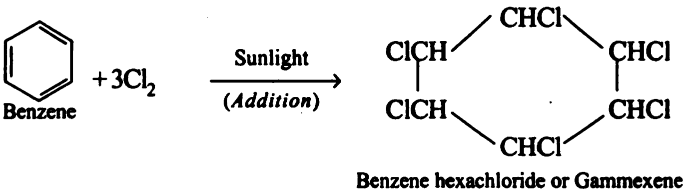
**34. Benzene is treated with methyl chloride in presence of anhydrous $AlCl_3$.**

Toluene is formed. This reaction is known as Friedel Craft reaction.



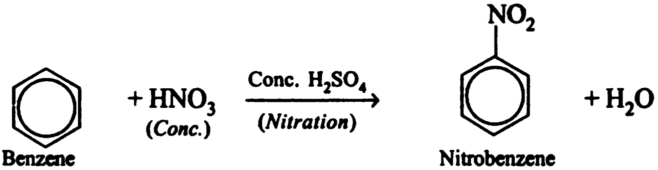
**35. Benzene is treated with chlorine in presence of sunlight and absence of halogen carrier.**

Benzene hexachloride is formed by complete addition of $Cl_2$ on the benzene ring.



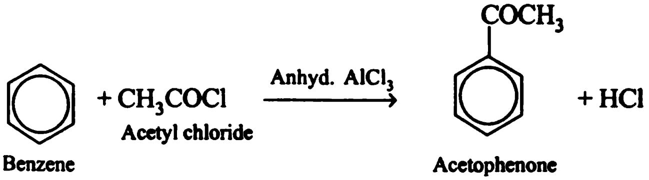
**36. Benzene is treated with a mixture of concentrated sulphuric acid and nitric acid.**

Nitrobenzene is formed. Sulphuric acid helps in the production of electrophile $\overset{+}{N}O_2$ and also removes water produced in the reaction.



**37. Benzene is treated with acetyl chloride in the presence of anhydrous $AlCl_3$.**

Acetophenone is formed. This reaction is known as Friedel Craft acylation.



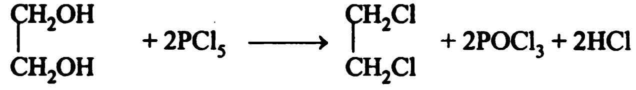
**38. When methyl bromide is treated with mono sodium methyl acetylide.**

2-Butyne is obtained.

$$CH_3—Br + NaC \equiv C—CH_3 \longrightarrow \underset{\text{2-Butyne}}{CH_3—C \equiv C—CH_3} + NaBr$$

**39. When ethylene glycol is treated with $PCl_5$.**

1,2-Dichloroethane is formed.

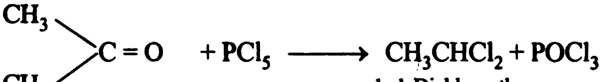


$$\begin{array}{c} CH_2OH \\ | \\ CH_2OH \end{array} + 2PCl_5 \longrightarrow \begin{array}{c} CH_2Cl \\ | \\ CH_2Cl \end{array} + 2POCl_3 + 2HCl$$

Ethylene glycol    1, 2-Dichloroethane

**40. When acetaldehyde reacts with $PCl_5$.**

1, 1-dichloroethane is formed.

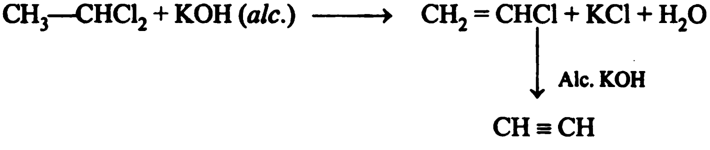


$$\begin{array}{l} CH_3 \\ \quad \rangle C = O \\ CH_3 \end{array} + PCl_5 \longrightarrow CH_3CHCl_2 + POCl_3$$

1, 1-Dichloroethane

**41. When 1, 1-Dichloroethane is treated with alcoholic KOH.**

Acetylene is obtained as the final product.



$$CH_3{-}CHCl_2 + KOH\ (alc.) \longrightarrow CH_2 = CHCl + KCl + H_2O$$

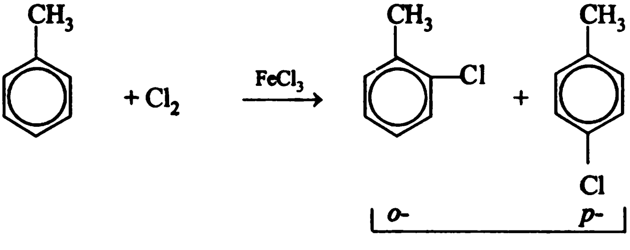
$$\downarrow \text{Alc. KOH}$$

$$CH \equiv CH$$

Acetylene

**42. Toluene is treated with chlorine in the presence of a halogen carrier.**

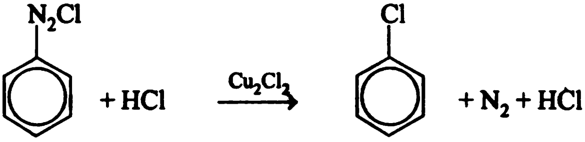
A mixture of *o*- and *p*-chlorotoluenes is obtained.



Chlorotoluenes

**43. Benzene diazonium chloride is treated with cuprous chloride in the presence of HCl.**

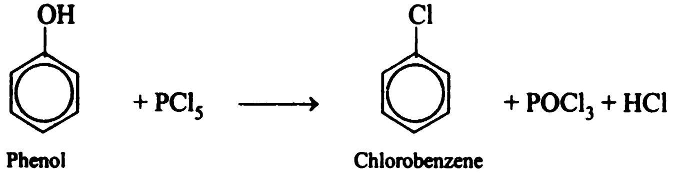
Chlorobenzene is formed.



Chlorobenzene

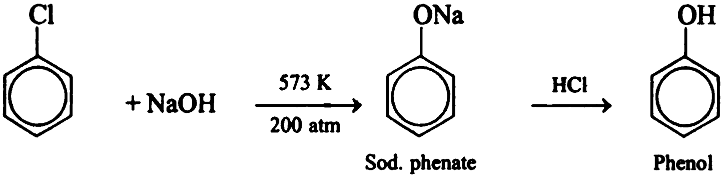
**44. Phenol is treated with phosphorus pentachloride.**

Chlorobenzene is obtained.



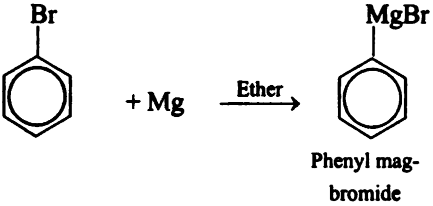
**45. When chlorobenzene is heated with aq. solution of NaOH at 573 K under a pressure of 200 atm.**

Phenol is formed.



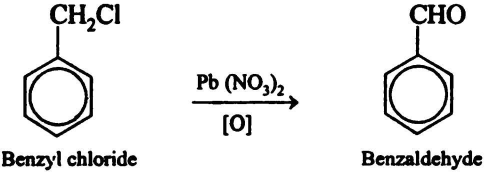
**46. When bromobenzene is treated with magnesium in dry ether.**

Grignard reagent, phenyl magnesium bromide, is formed.



**47. When benzyl chloride is heated in presence of lead nitrate.**

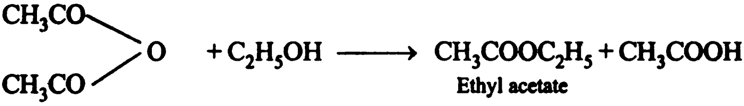
Benzaldehyde is obtained. Lead intrate is a mild oxidising agent.



**48. Ethyl alcohol is treated with acetyl chloride or acetic anhydride.**

Ethyl acetate is obtained.

$$CH_3COCl + C_2H_5OH \longrightarrow \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + HCl$$



$$\begin{matrix} CH_3CO \\ CH_3CO \end{matrix}\!\!>O + C_2H_5OH \longrightarrow \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + CH_3COOH$$

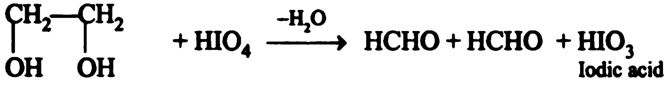
**49. Ethyl alcohol is treated with $PI_3$.**

Ethyl iodide is obtained.

$$3\,C_2H_5OH + PI_3 \longrightarrow \underset{\text{Ethyl iodide}}{3C_2H_5I} + \underset{\text{Phosphorus acid}}{H_3PO_3}$$

**50. Ethylene glycol is treated with $HIO_4$ (periodic acid).**

Formaldehyde is formed. Periodic acid is an oxidising agent.

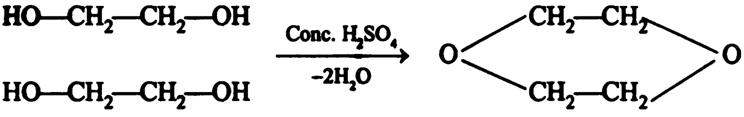


$$\underset{\text{Glycol}}{\underset{OH\quad OH}{CH_2{-}CH_2}} + HIO_4 \xrightarrow{-H_2O} HCHO + HCHO + \underset{\text{Iodic acid}}{HIO_3}$$

Glycol

**51. Ethylene glycol is distilled with conc. $H_2SO_4$.**

Dioxane is obtained.

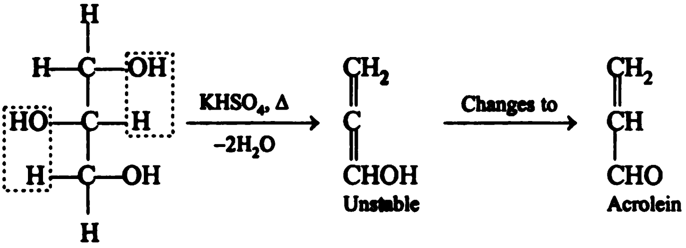


(2 molecules)

Dioxane

**52. When glycol is heated with potassium hydrogen sulphate.**

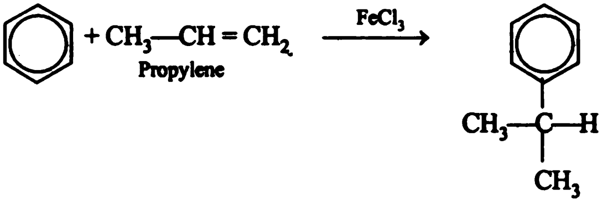
Acrolein is obtained as given below.



Glycerol

**53. Benzene reacts with propylene in the presence of ferric chloride**

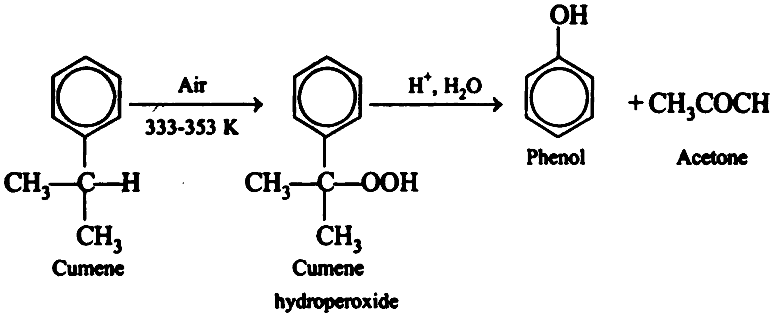
Cumene is obtained



Cumene

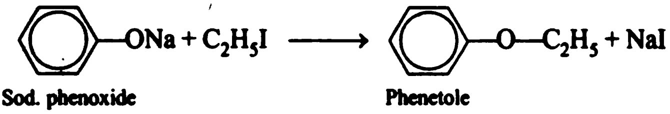
**54. Cumene is oxidised at 333-353 K and subsequently treated with an aqueous acid.**

Phenol and acetone are obtained.



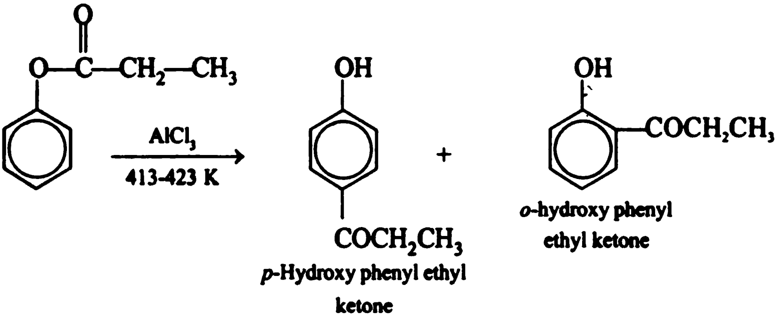
**55. Sodium phenoxide is treated with ethyl iodide.**

Phenetole (ethyl phenyl ether) is formed.



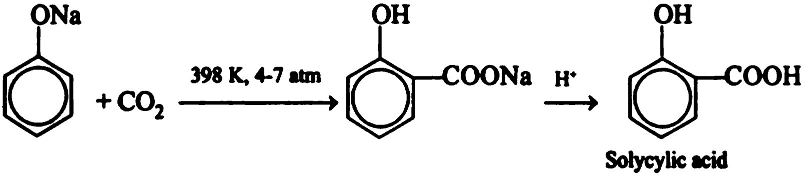
**56. Phenyl propionate is heated with aluminium chloride.**

A mixture of *p*-hydroxy phenyl ethyl ketone and *o*-hydroxy phenyl ethyl ketone is obtained. This is an example of *Fries rearrangement.*



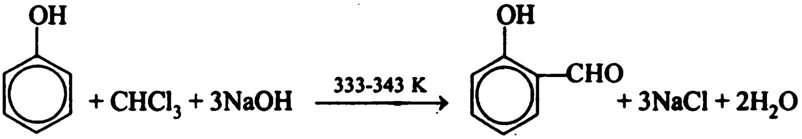
**57. Carbon dioxide is passed through sodium phenoxide at 398 K and 4-7 atm pressure.**

Salicylic acid is obtained (Kolbe's reaction).



**58. Phenol is heated with chloroform and alkali.**

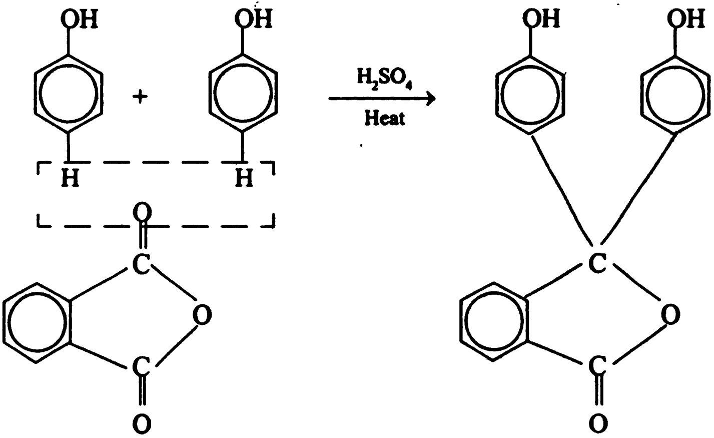
Salicylaldehyde is formed (Reimer Tiemann reaction).



Salicylaldehyde

**59. Phenol is heated with phthalic anhydride in the presence of conc. $H_2SO_4$.**

Phenolphthalein is formed.



Phenolphthalein

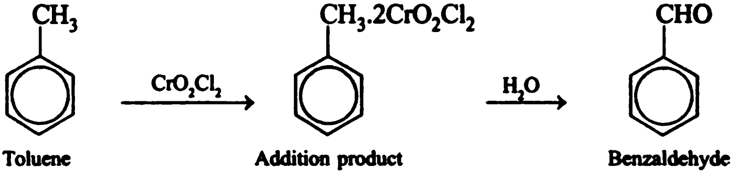
**60. Ethyl methyl ether (methoxy ethane) is treated with HI.**

Iodomethane and ethanol are obtained.

$$\underset{\text{Methoxyethane}}{CH_3OC_2H_5} + HI \longrightarrow CH_3I + C_2H_5OH$$

**61. Toluene is treated with chromyl chloride.**

Benzaldehyde is obtained (Etard's reaction).



**62. Methyl cyanide is treated with stannous chloride and HCl.**

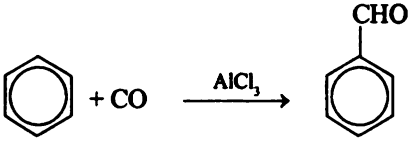
Acetaldehyde is produced (Stephen's reduction).

$$CH_3CN + 2[H] + HCl \xrightarrow{SnCl_2/HCl} \underset{\text{Acetaldimine hydrochloride}}{CH_3CH = NH.HCl}$$

$$\xrightarrow{H_2O} \underset{\text{Acetaldehyde}}{CH_3CHO} + NH_4Cl$$

**63. Carbon monoxide is passed through benzene in the presence of $AlCl_3$.**

Benzaldehyde is obtained (Gattermann's reaction).



Benzene Benzaldehyde

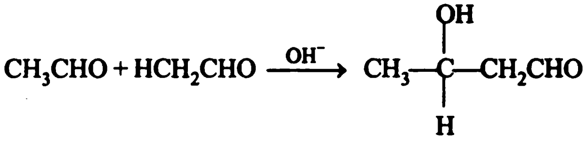
**64. Acetyl chloride is treated with diethyl cadmium.**

Ethyl methyl ketone is formed.

$$\underset{\text{Acetyl chloride}}{2\,CH_3COCl} + \underset{\text{Diethyl cadmium}}{(C_2H_5)_2\,Cd} \longrightarrow \underset{\text{Ethyl methyl ketone}}{2\,CH_3COC_2H_5} + CdCl_2$$

**65. Acetaldehyde is treated with a dilute solution of an alkali.**

Aldol (3-hydroxybutanal is formed (Aldol condensation).

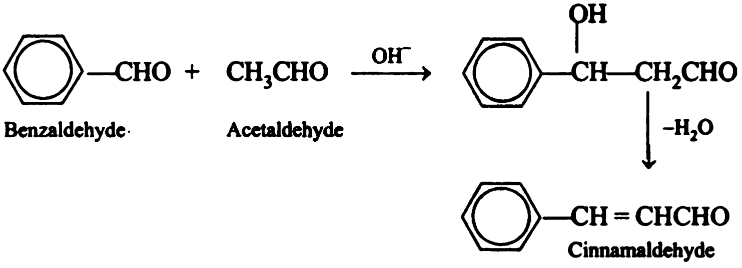


$$CH_3CHO + HCH_2CHO \xrightarrow{OH^-} CH_3-\overset{OH}{\underset{H}{C}}-CH_2CHO$$

3-Hydroxybutanol (Aldol)

**66. A mixture of benzaldehyde and acetaldehyde is treated with a dilute alkali solution.**

Cinnamaldehyde is formed (Claisen-Schmidt reaction.)

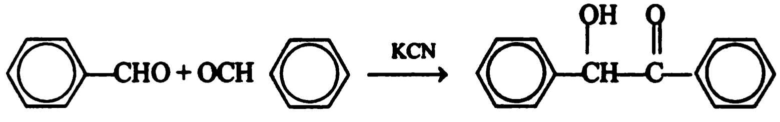


Benzaldehyde Acetaldehyde

Cinnamaldehyde

**67. Benzaldehyde is treated with KCN.**

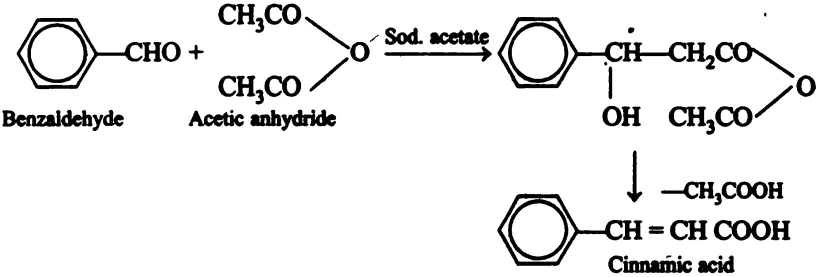
Benzoin is obtained. This is an example of **benzoin condensation.**



Benzaldehyde Benzoin

**68. Benzaldehyde is treated with acetic anhydride in the presence of sodium acetate.**

Cinnamic acid is formed (Perkin's reaction).

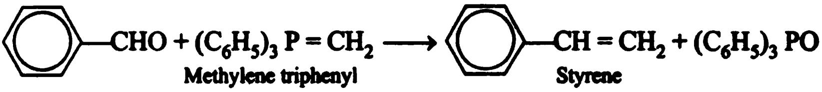


Benzaldehyde Acetic anhydride

Cinnamic acid

**69. Benzaldehyde is treated with methylene triphenyl phosphorane.**

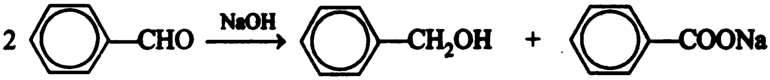
Styrene is obtained (Wittig's reaction).



Methylene triphenyl phosphorane Styrene

**70. Benzaldehyde is treated with a conc. solution of KOH.**

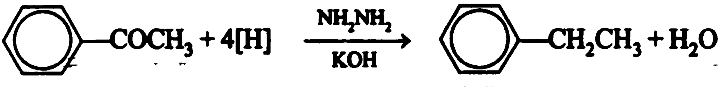
A mixture of benzyl alcohol and sod. benzoate is obtained.



Benzyl alcohol Sod. benzoate

**71. Methyl phenyl ketone is heated with hydrazine and KOH at 450-470 K.**

Ethyl benzene is formed (Wolff Kishner reduction).



Methylphenyl ketone Ethylbenzene

**72. Acetone is treated with zinc amalgam and HCl.**

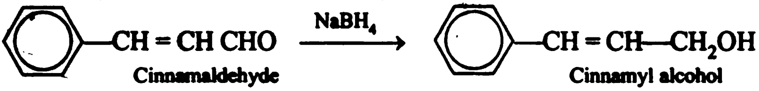
Propane is formed (Clemmenson reduction).

$$CH_3COCH_3 + 4[H] \xrightarrow[HCl]{Zn\text{-}Hg} CH_3CH_2CH_3 + H_2O$$

Propane

**73. Cinnamaldehyde is reduced with sodium borohydride.**

Cinnamyl alcohol is obtained. Ethylemic double bond is not affected.



**74. Acetamide is treated with lithium aluminium hydride ($LiAlH_4$).**

Ethylamine is obtained.

$$\underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow[\text{[H]}]{LiAlH_4} \underset{\text{Ethylamine}}{CH_3CH_2NH_2}$$

**75. Acetamide is treated with bromine in the presence of alcoholic potash.**

Methylamine is obtained (Hoffmann Bromamide Reaction)

$$\underset{\text{Acetamide}}{CH_3CONH_2} + Br_2 + KOH \longrightarrow \underset{\text{Methylamine}}{CH_3NH_2} + 2KBr + K_2CO_3 + 2H_2O$$

**76. Hydrogen gas is passed through acetyl chloride in the presence of Pd based on $BaSO_4$ in xylene solution.**

Acetaldehyde is obtained (Rosenmund's reduction).

$$\underset{\text{Acetyl chloride}}{CH_3COCl} + H_2 \xrightarrow[\text{Xylene soln.}]{Pd/BaSO_4} \underset{\text{Acetaldehyde}}{CH_3CHO} + HCl$$

**77. Propanoic acid is treated with bromine in the presence of red phosphorus.**

2-Bromopropanoic acid is obtained (Hell-Vohlard-Zelinsky reaction).

$$\underset{\text{Propanoic acid}}{CH_3CH_2COOH} + Br_2 \xrightarrow{\text{Red P}} \underset{\text{2-Bromopropanoc acid}}{CH_3CHBrCOOH} + HBr$$

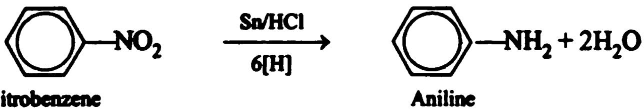
**78. Acetaldehyde is treated with ammonia at 373 K and 150 atm pressure in the presence of Ni as catalyst.**

Ethylamine is obtained

$$\underset{\text{Acetaldehyde}}{CH_3CHO + NH_3} \xrightarrow{-H_2O} CH_3—CH = NH \xrightarrow{H_2,\ Ni} \underset{\text{Ethylamine}}{CH_3CH_2NH_2}$$

**79. Nitrobenzene is treated with tin and HCl.**

Aniline is obtained.



**80. Ethylnitrile is treated with hydrogen gas in the presence of Ni at 433 K.**

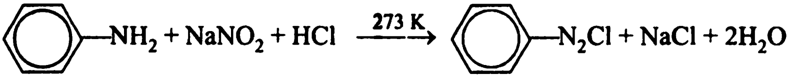
Ethylamine is obtained (Mendius reduction).

$$CH_3CH_2CN + 2H_2 \xrightarrow[433\ K]{Ni} CH_3CH_2NH_2$$

Ethyl nitrile Ethylamine

**81. Aniline is treated with a mixture of $NaNO_2$ and HCl at 273 K.**

Benzene diazonium chloride is obtained.



Aniline

Benzene diazonium chloride

**82. Methylamine is heated with chloroform and alcoholic KOH.**

Methyl isocyanide is obtained (Carbylamine reaction).

$$CH_3NH_2 + CHCl_3 + KOH\ (alc.) \longrightarrow CH_3NC + 3KCl + 3H_2O$$

Methyl isocyanide

**83. Methyl amine is warmed with carbon disulphide in the presence of mercuric chloride.**

Methyl isothiocyanate is formed.

$$CH_3NH_2 + S = C = S \xrightarrow{HgCl_2} CH_3—N = C = S + H_2S$$

Methylamine Methyl isothiocyanate

# 8

# Mechanisms of Reactions

**Q. 1. Explain the mechanism of halogenation of alkanes.**

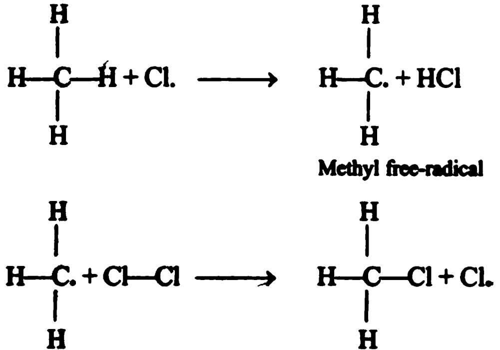
**Ans.** The halogenation of alkanes occurs by a free radical mechanism. It involves three steps : (*a*) chain initiation, (*b*) chain propagation (*c*) chain termination. Mechanism of halogenation is explained by considering the chlorination of methane.

(*a*) **Chain Initiation.** When a mixture of $CH_4$ and $Cl_2$ is heated or subjected to diffused sunlight, $Cl_2$ absorbs energy and undergoes homolytic fission producing chlorine free radicals. One molecule gives rise to two radicals.

**Step (1)** $$:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}\cdot\cdot\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}: \xrightarrow[\text{or } \Delta]{h\nu} :\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}. + .\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:$$

Chlorine free radical

(*b*) **Chain Propagation.** The chlorine free radical produced above collides with a molecule of methane forming hydrogen chloride and a methyl free-radical. The methyl free-radical in turn reacts with a molecule of chlorine forming methyl chloride and chlorine free-radical. The newly formed chlorine radical can react with another molecule of methane as in step (2) generating methyl free-radical and hydrogen chloride. The methyl free-radical can again repeate step (3) and so on. Thus, the sequence of reactions in steps (2) and (3) is repeated over and over again and thus the chain is propagated. In other words, a single photon of light initially absorbed by chlorine can bring about the conversion of a large number of molecules of methane into methyl chloride.

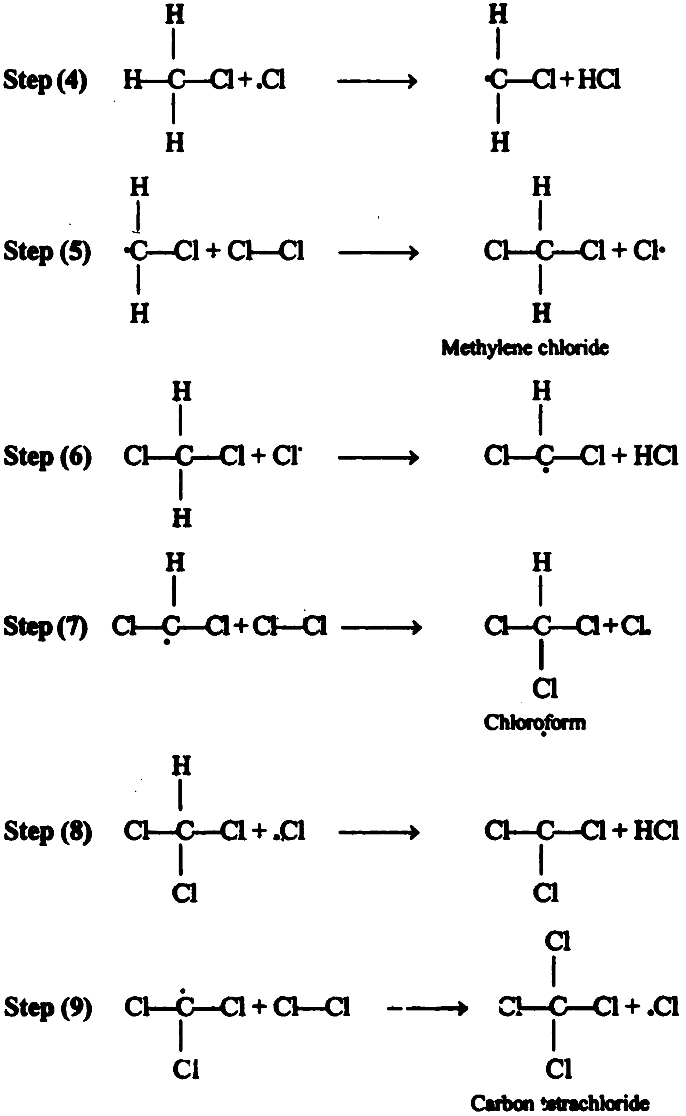


**Step (2)** $$H-\underset{H}{\overset{H}{\underset{|}{\overset{|}{C}}}}-H + Cl. \longrightarrow H-\underset{H}{\overset{H}{\underset{|}{\overset{|}{C}}}}. + HCl$$

Methyl free-radical

**Step (3)** $$H-\underset{H}{\overset{H}{\underset{|}{\overset{|}{C}}}}. + Cl-Cl \longrightarrow H-\underset{H}{\overset{H}{\underset{|}{\overset{|}{C}}}}-Cl + Cl.$$

However, the above reaction doesnot stop at methyl chloride stage but proceeds further till all the H-atoms of methane are replaced by chlorine atoms giving a mixture of mono-, di-, tri- and tetra-chloro methane



Step (4) $H{-}\overset{H}{\underset{H}{C}}{-}Cl + .Cl \longrightarrow \cdot\overset{H}{\underset{H}{C}}{-}Cl + HCl$

Step (5) $\cdot\overset{H}{\underset{H}{C}}{-}Cl + Cl{-}Cl \longrightarrow Cl{-}\overset{H}{\underset{H}{C}}{-}Cl + Cl\cdot$

Methylene chloride

Step (6) $Cl{-}\overset{H}{\underset{H}{C}}{-}Cl + Cl^{\cdot} \longrightarrow Cl{-}\overset{H}{\underset{\bullet}{C}}{-}Cl + HCl$

Step (7) $Cl{-}\overset{H}{\underset{\bullet}{C}}{-}Cl + Cl{-}Cl \longrightarrow Cl{-}\overset{H}{\underset{Cl}{C}}{-}Cl + Cl.$

Chloroform

Step (8) $Cl{-}\overset{H}{\underset{Cl}{C}}{-}Cl + .Cl \longrightarrow Cl{-}\underset{Cl}{C}{-}Cl + HCl$

Step (9) $Cl{-}\overset{\bullet}{\underset{Cl}{C}}{-}Cl + Cl{-}Cl \longrightarrow Cl{-}\overset{Cl}{\underset{Cl}{C}}{-}Cl + .Cl$

Carbon tetrachloride

**Chain Termination**

The chain reactions mentioned above, however, come to an end if the free radicals combine amongst themselves to from neutral molecules. Some of the chain terminating steps are :

$$.Cl + .Cl \longrightarrow Cl\text{—}Cl$$
$$.CH_3 + .Cl \longrightarrow CH_3\text{—}Cl$$
$$.CH_3 + .CH_3 \longrightarrow \cdot CH_3\text{—}CH_3$$

**Q. 2. Give evidence in support of free radical mechanism of halogenation of alkanes.**

**Ans.** The following points support the free radical mechanism :

(*i*) Reaction does not take place in dark at room temperature but requires energy in the form of heat or light. This is due to the fact that the chain initiation step (1) (Q. 1) is endothermic and hence needs a large amout of energy to break the Cl—Cl bond into radicals.

(*ii*) The reaction has a high quantum yield *i.e.*, many thousand molecules of methyl chloride (or alkyl halide in general) are formed for each photon of light absorbed. This fact can be explained on the basis of chain propagation steps.

(*iii*) Oxygen acts as an inhibitor. This is due to the fact oxygen combines with the alkyl free radical to form peroxyalkyl radical, (R—O—O·). This radical is much less reactive than alkyl free radical (R·) to continue the chain. As a result, the halogenation of alkyl in the presence of oxygen is slowed down or stopped. Thus the role of inhibitors like oxygen in this reaction gives support to the above mechanism.

(*iv*) If the above mechanism actually involves free radicals as reactive intermediate, then the addition of substances which are source of free radicals should initiate the reaction even in the dark at room temperature much below 523K. This has actually been found to be so. Thus chlorination of methane can be carried out in the dark at room temperature in the presence of small amount of benzoyl peroxide.

$$\underset{\text{Benzoyl peroxide}}{C_6H_5CO\text{—}O\text{—}O\text{—}COC_6H_5} \xrightarrow[298\text{ K}]{\text{dark}} \underset{\text{Benzoyl free radical}}{C_6H_5\text{—}CO\text{—}\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}\cdot}$$

$$C_6H_5\text{—}CO\text{—}\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}\cdot \longrightarrow \underset{\text{Phenyl free radical}}{C_6H_5\cdot} + CO_2$$

$$C_6H_5\cdot + Cl\text{—}Cl \longrightarrow C_6H_5\text{—}Cl + Cl.$$

Once, the chloride free radicals are produced, the reaction can take place in the manner explained above.

(*v*) Chlroination of methane takes place at 423K in dark in the presence of a little $(C_2H_5)_4$ Pb (Tetraethyl lead). Tetraethyl lead yields free radicals, when heated to 423K.

$$(C_2H_5)_4\,Pb \xrightarrow[\text{dark}]{423\text{ K}} 4C_2H_5. + Pb$$

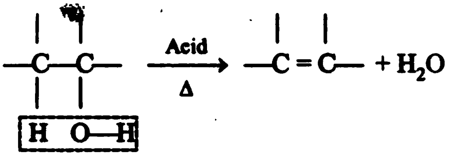
The ethyl free radical then reacts with chlorine molecule forming ethyl chloride and chlorine free radical.

$$\cdot C_2H_5 + Cl—Cl \longrightarrow C_2H_5—Cl + Cl$$

The chlorine free radical thus formed brings about chlorination of methane as explained above.

**Q. 3. Discuss the mechanism of dehydration of alcohol.** (*A.I.S.B. 2004*)

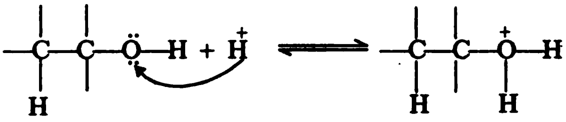
**Ans.** An alcohol is converted into an alkene by dehydration. Dehydration is brought about by the use of an acid say conc. $H_2SO_4$ and application of heat. It involves (1) heating the alcohol with $H_2SO_4$ at 433-443 K or (2) by passing the vapours of alcohol over alumina $Al_2O_3$ at 623-673 K.



$$CH_3CH_2OH \xrightarrow[433—443\ K]{H_2SO_4} \underset{\text{Ethylene}}{CH_2 = CH_2} + H_2O$$

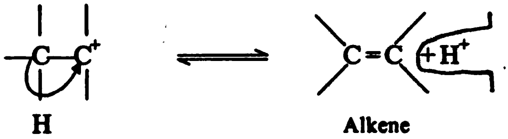
**Mechanism of dehydration of alcohols.** The mechanism of dehydration of alcohols is given schematically below :

1. *Attachment of the proton to alcoholic oxygen*



2. *Removal of water molecule*

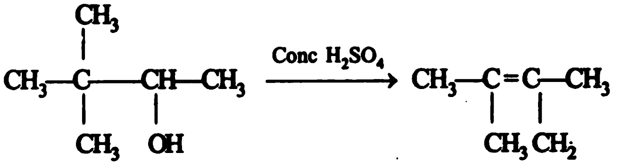
3. *Removal of proton*



**Q. 4. With suitable example, explain alkyl shift.**

**Ans.** Sometimes it is found that the alkene obtained by dehydration of alcohols does not fit in the mechanism.

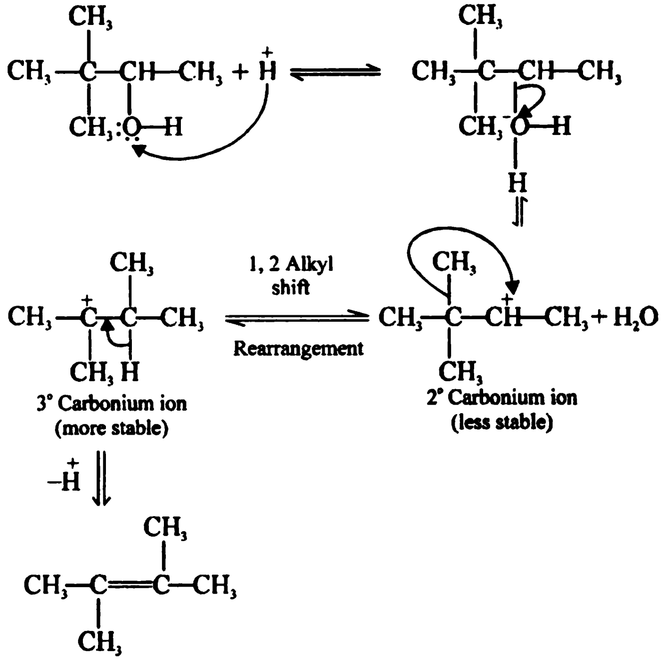
For example,



3, 3-Dimethyl butan-2-ol.

2,3-Dimethyl but -2-ene
(Major product)

This can be explained by considering a rearrangement of carbonium ions. A carbonium ion can arrange to form a more stable carbonium ion. The mechanism of rearrangement is given below :



2,3- Dimenthyl but-2-ene(major product)

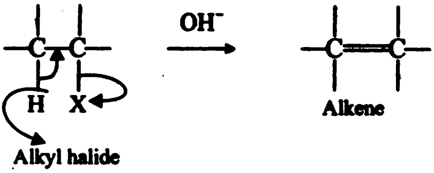
Thus, we see that the carbonium ion which is the intermediate product in the dehydration of alcohol changes to a more stable carbonium ion by the shifting of alkyl group from one position to another. If the alkyl group shifts to the neighbouring carbon atom, it is called **1,2 alkyl shift.**

**Q. 5. Discuss the mechanism of dehydrohalogenation of alkyl halides ($E_2$ and $E_1$).**

**Ans.** Alkyl halides can form alkenes by the loss of a molecule of hydrogen halide under the influence of base catalyst (alcoholic potash). The reaction is known as *dehydrohalogenation of alkyl halides.* It involves the removal of halogen atom together with the hydrogen atom from the adjacent carbon atom.

$$CH_3{-}CH_2X \xrightarrow{OH^-} CH_2 = CH_2 + H_2O + X^-$$

**Mechanism of reaction ($E_2$ mechanism)**



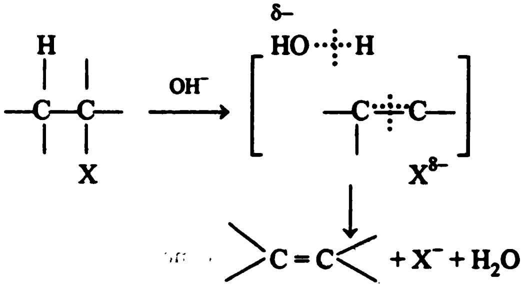
**Orientation in dehydrohalogenation.** In some cases, this reaction yields a single product (alkene) and in other cases yields a mixture of alkenes. For example, out of 1-chlorobutane and 2-chlorobutane, the former yields only but-1-ene while the latter gives but-1-ene and but-2-ene. Thus, the preferred product is the alkene that has the greater number of alkyl groups attached to the doubly bonded carbon atoms. In other words, the case of formation of alkene has the following order :

$$R_2C = CR_2 > R_2C = CHR > R_2C = CH_2 > RCH = CHR > RCH = CH_2 > CH_2 = CH_2$$

This order is based on heat of hydrogenation values.

**Hence in dehydrohalogenation, the more stable the alkene, more easily it is formed.**

This is also clear from the transition state formed in the dehydrohalogenation of alkyl halides as discussed below. The double bond is partly formed and the transition state acquires alkene character. Factors that stabilize an alkene also stabilize an *incipient* alkene in the transition state.



**Reactivity of alkyl halides in dehydrohalogenation.** The decreasing order of reactivity of alkyl halides in this reaction is :

Tert-Alkyl halides > Sec-Alkyl halides > Primary Alkyl halides

(3°) (2°) (1°)

As we move from primary to secondary and from secondary to tertiary halides, the structure becomes more branched at carbon atom bearing the halogen. This increased branching has two results (*i*) the number of hydrogen atoms available for attack by a base is more and thus there is greater probability towards elimination, (*ii*) it leads to the formation of more highly branched (hence more stable) alkene, hence more stable transition state and low $E_{act}$.

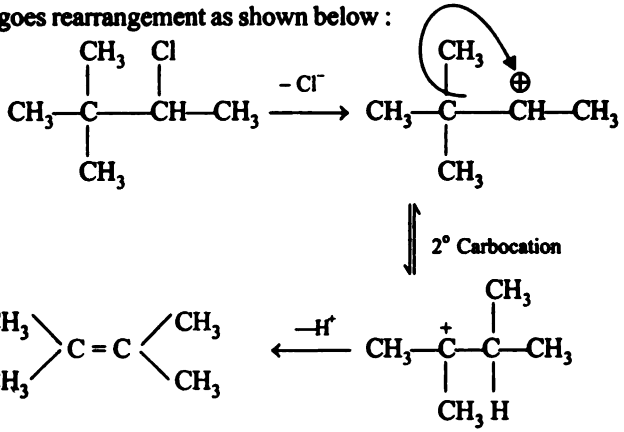
As a result of these two factors, the decreasing order of reacivity of alkyl halides for dehydrohalogenation is :

$$3^\circ > 2^\circ > 1^\circ$$

Tha above mechanism discussed is called $E_2$ type of mechanism of dehydrohalogenation.

In certain alkyl halides (say 3°), there can be slight variation in the mechanistic approach as the carbon cation initially formed undergoes rearrangement to form more stable carbocation and thus yields highly branched alkene as the chief product of the reaction.

For example, action of alcoholic potash on -2-chloro-3, 3-dimethyl butane yields chiefly 2, 3-dimethyl but-2-ene as the carbocation initially formed undergoes rearrangement as shown below :



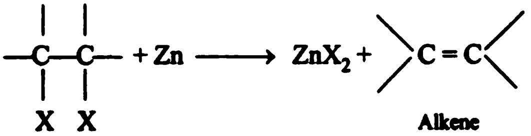
2, 3-Dimethyl but-2-ene (Chief product)

3° Carbocation (More stable)

This is an example of $E_1$ type of mechanism of dehydrohalogenation.

**Q. 6. Explain mechanism of dehalogenation of dihalides.**

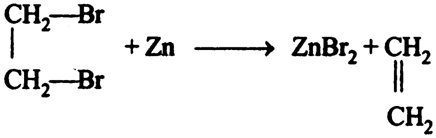
**Ans.** Dehalogenation of 1, 2-dihaloalkanes (vic-dihalides) involves the treatment of the *vic* dihalide with reactive metals like Zn in acetic acid and it yields the corresponding alkenes.



Alkene

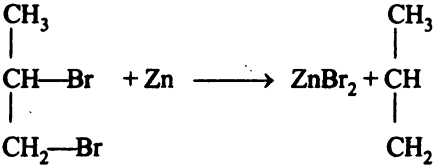
1, 2 dihaloalkane

**For example :**



$$\begin{array}{l} CH_2-Br \\ | \\ CH_2-Br \end{array} + Zn \longrightarrow ZnBr_2 + \begin{array}{c} CH_2 \\ \| \\ CH_2 \end{array}$$

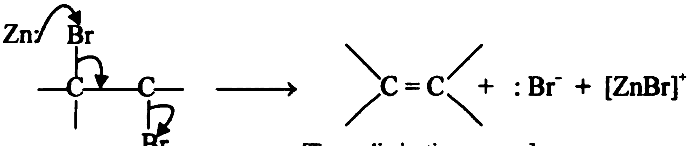
1, 2-Dibromo ethane Ethylene



$$\begin{array}{l} CH_3 \\ | \\ CH-Br \\ | \\ CH_2-Br \end{array} + Zn \longrightarrow ZnBr_2 + \begin{array}{l} CH_3 \\ | \\ CH \\ \| \\ CH_2 \end{array}$$

1, 2-Dibromo propane Propylene

**Mechanism.** The divalent Zn metal possesses a pair of electrons in its outermost shell and, therefore, it acts as a nucleophile. $Br^-$ are formed in the reaction solution andthe reaction can be represented by a concerted process.



[Trans elimination process]

$$[ZnBr]^+ \longrightarrow Zn^{2+} + Br^-$$

**Q. 7. Describe the mechanism of halogenation of a alkenes.**

**Ans.** Alkenes add a molecule of halogen to form alkyl halides.

$$CH_2=CH_2 + Cl_2 \longrightarrow CH_2Cl-CH_2Cl$$

Ethene 1, 2-Dichloroethane

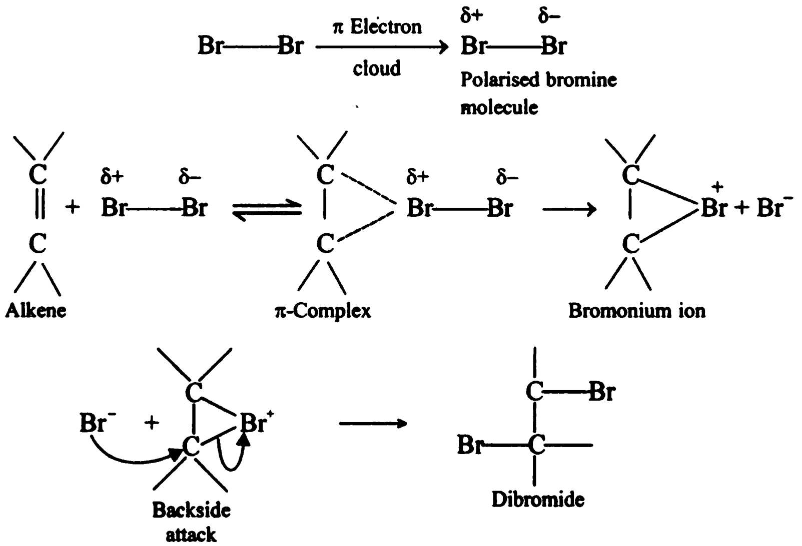
$$CH_2=CH_2 + Br_2 \longrightarrow CH_2Br-CH_2Br$$

Brown colour 1, 2-Dibromoethane (colourless)

On adding bromine water to a compound containing a double bond, brown colour due to bromine disappears.

**Mechanism of halogenation**

Halogenation of an alkene takes place by electrophilic addition mechanism. A halogen molecule ($Cl_2$, $Br_2$ or $I_2$) is non-polar in nature. But when this molecule approahces the alkene molecule, the $\pi$ bonds have the effect of polarising the halogen molecule. The positive end of the polarised halogen molecule is attached to one ethylenic carbon atom with the simultaneous attachment of the negative end to the second ethylenic carbon atom forming a halonium ion, with the release of halide ion. The halide ion then attacks the halonium ion from the back side to avoid steric hidrance, thus giving rise to dihalide. Various steps of the mechanism are shown as under, taking the example of bromination.



**Q. 8. Give evidence to prove that addition of halogen to an alkene proceeds through a halonium ion and not through carbonium ion (carbocation).**

**Ans.** Addition of halogen to an alkene proceeds through the formation of a halonium ion and not through a carbonium ion. This can be proved like this:

(1) It is observed that halogenation of alkenes gives rise to products that are optically active. The phenomenon can be explained by halonium ion mechanism and not by carbonium ion mechanism.

In halonium ion mechanism, the halide (in the second step) attacks from the back of halonium ion, giving rise to *trans* dihalide product.

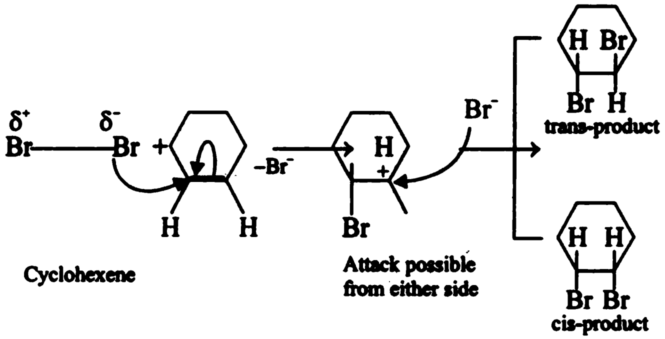
In carbonium ion mechanism, the halide can attack from both sides of the carbonium ion (as it is flat in shape), giving rise to both *cis* and *trans* isomers.

*Trans* product obtained from halonium ion mechanism explains optical activity of the actual product obtained.

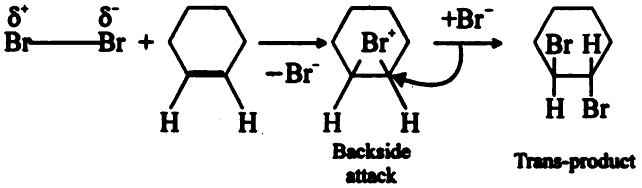
If we assume the carbonium ion mechanism, the mixture of *cis* and *trans* products will give us a racemic modification which will have no net optical activity. This a against the observations. Practically, we get an optically active compound.

This is schematically shown as under taking the example of bromination of cyclohexene.

**Carbonium ion mechanism**



**Halonium ion mechanism**

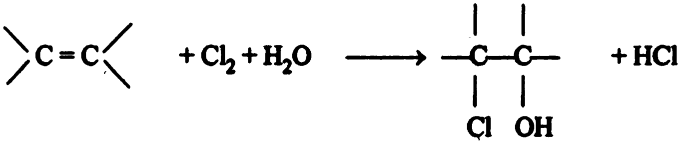


Hence halonium ion mechanism is confirmed.

**Q. 9. Give the mechanism of the reaction of alkenes with halogens in the presence of water ?**

**Ans. Reaction of alkenes with halogens in the presence of water**

Alkenes react with halogens in the presence of water to form halo-hydrins. For example :

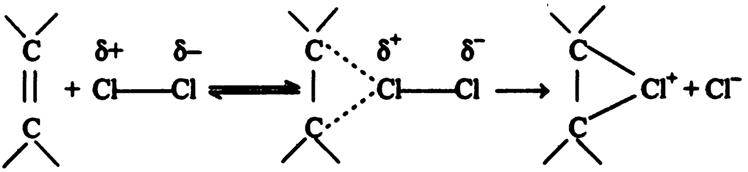


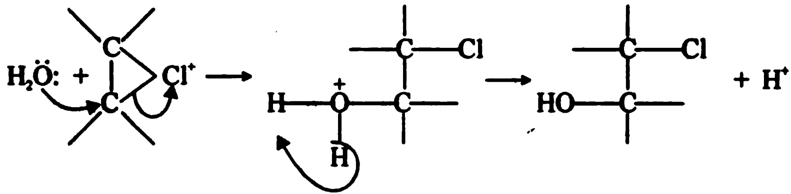
$$>C=C< + Cl_2 + H_2O \longrightarrow -\underset{Cl}{\overset{|}{C}}-\underset{OH}{\overset{|}{C}}- + HCl$$

Chlorohydrins

**Mechanism of the reaction**

The reaction takes place through the intermediate formation of a halonium ion as shown below :





**Q. 10. Explain the mechanism of addition of an unsymmetrical molecule over an unsaturated double bond.**

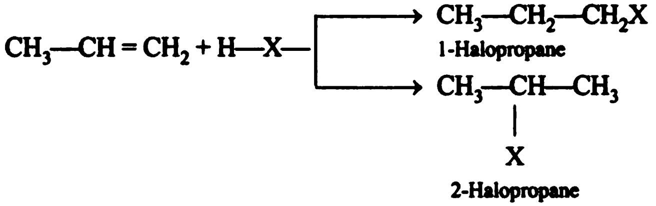
***OR***

**Describe the mechanism of Markowinkoff rule.**

**Ans.** When olefins are treated with hydrogen halides either in the gas phase or in an inert non-ionizing solvent (pentane), addition occurs to form alkylhalides.

$$\underset{\text{Ethylene}}{H_2C=CH_2} + HX \longrightarrow \underset{\text{Ethylhalide}}{H_3C—CH_2X}$$

With propylene ($CH_3—CH=CH_2$), the next higher homologue, the addition of HX can yield two products (1-halopropane and 2-halopropane.)

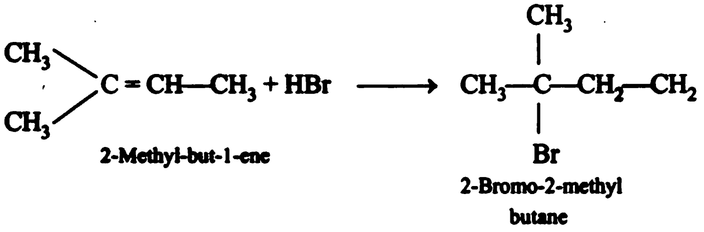


$$CH_3—CH=CH_2 + H—X— \begin{cases} \longrightarrow \underset{\text{1-Halopropane}}{CH_3—CH_2—CH_2X} \\ \longrightarrow \underset{\text{2-Halopropane}}{CH_3—\underset{X}{\underset{|}{CH}}—CH_3} \end{cases}$$

However, in actual practice 2-halopropane is exclusively obtained.

The exclusive formation of the above product is in accordance with Markownikoff Rule which is concerned with the addition of unsymmetrical regents to unsymmetrical alkenes. This states that *the ionic addition of unsymmetrical reagents to unsymmetrical olefins proceeds in such a way that the more psotive part of the reagent, becomes attached to the carbon atom with larger number of hydrogen atoms.*

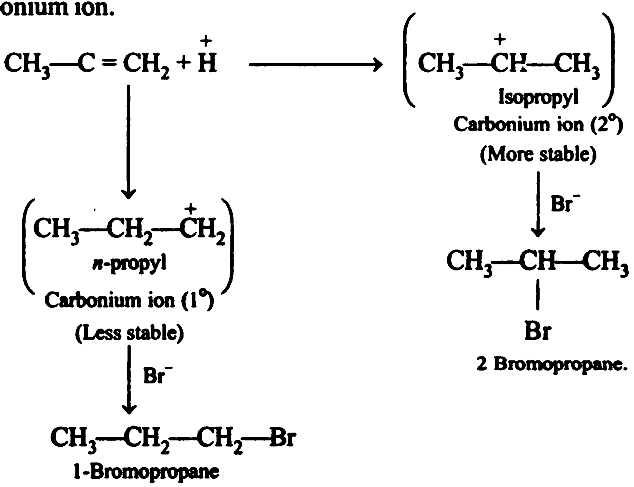
When the hydrogen halides or water is added, hydrogen atom constitutes the more positive part or in other words, the hydrogen atom becomes attached to the olefinic carbon atom which carries the larger number of hydrogen atoms, for example :



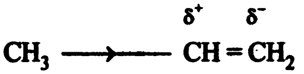
$$\underset{\text{2-Methyl-but-1-ene}}{(CH_3)_2C=CH—CH_3} + HBr \longrightarrow \underset{\text{2-Bromo-2-methyl butane}}{CH_3—\overset{CH_3}{\overset{|}{\underset{Br}{\underset{|}{C}}}}—CH_2—CH_2}$$

Theoretical explanation of the orientation of addition to olefins is related to the relative stability of carbonium ions. We know that relative stability of carbonium ions is : tertiary > secondary > primary > $CH_3^+$. If there is the probability of more than one carbonium ions being formed, the addition of electrophile yields the more stable one.

That is why **2 bromopropane** is exclusively formed by the addition of HBr to propylene (an unsymmetrical alkene) and not *1-bromo-propane* because secondary isopropyl carbonium ion is more stable than primary *n*-propyl carbonium ion.



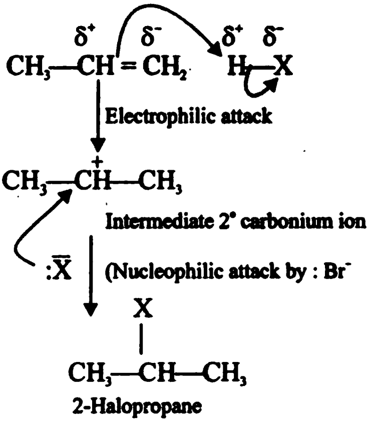
Considering the electronic effect of methyl group in propylene the polarization of the double bond due to the (+ I) electron-repelling inductive effect of the methyl group, is depicted below.



$$CH_3 \longrightarrow \overset{\delta^+}{CH} = \overset{\delta^-}{CH_2}$$

Thus, the +ve and –ve ends of the dipole (H—X) will add to the -ve and +ve ends of the double bonds, respectively yielding **2-halopropane.**

**Mechanism**



Thus the modern statment of Markownikoff's rule is :

*In the ionic addition of an unsymmetrical reagent to a double bond, the positive portion of the adding reagent becomes attached to the carbon atom of the double bond so as to yield the more stable carbonium ion.*

**Q. 11. What is meant by anti-Markownikoff's addition ? Give its mechanism.**

***OR***

**What is peroxide effect ? Explain giving mechanism.**

**Ans.** It has been observed that the addition of H—Br to propylene in the presence of peroxides, yields predominantly 1-bromo-propane, (that is the reagent adds on to the olefins under these conditions in a manner contrary to Markownikoff's rule) thus suggesting a change in the mechanistic approach.

This change in the orientation of addition due to the presence of peroxides is known as the **peroxide effect.**

Here the change in the mode of addition of the reagent is due to a change from an ionic *mechanism to a free-radical mechanism.* Markownikoff's addition requires the initiation by $H^+$. Anti Markownikoff's addition requires initiation by $\dot{Br}$ . Each species attacks the olefin molecule at the centre of highest electron density to yield the most stable intermediate carbonium ion or free radical.

**Mechanism of addition of HBr to propylene in the presence of peroxides**

It involves the following steps :

**(*i*) Chain initiation step**

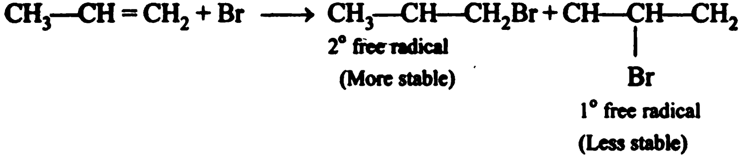
The reaction is initiated by the alkoxy radical produced by the homolytic fission of peroxides, which abstracts and atom of hydrogen from HBr generating bromine free radicals ($\dot{Br}$).

$$\underset{\text{Peroxides}}{R—O—O—R} \longrightarrow \underset{\text{Alkoxy radical}}{2R\dot{O}}$$

$$R—\dot{O} + H—Br \longrightarrow \underset{\text{(Chain initiation)}}{R—OH + \dot{Br}}$$

**(*ii*) Chain propagation step**

The $\dot{Br}$ then attacks the propylene molecule to give a more stable secondary radical addition species :



$$CH_3—CH = CH_2 + \dot{Br} \longrightarrow \underset{\substack{2^\circ \text{ free radical} \\ \text{(More stable)}}}{CH_3—\dot{C}H—CH_2Br} + \underset{\substack{\text{1° free radical} \\ \text{(Less stable)}}}{CH—\underset{\underset{Br}{|}}{C}H—\dot{C}H_2}$$

The secondary radical then reacts with another H—Br molecule to yield the product, and another Br which can further propagate the reaction :

$$CH_3—\dot{C}H—CH_2Br + H—Br \longrightarrow CH_3—CH_2—CH_2Br + \dot{B}r$$

(Chain propagation) 1-Bromopropane

This mechanism is supported by the fact that small amount of peroxide can influence addition to a large number of molecules of an alkene and small amout of an inhibitor such as hydroquinone or diphenyl amine can prevent this change.

**Q. 12. Explain why peroxide oxide effect or anti-Markownikoff rule is observed in the addition of H—Br and not H—Cl or H—I ?**

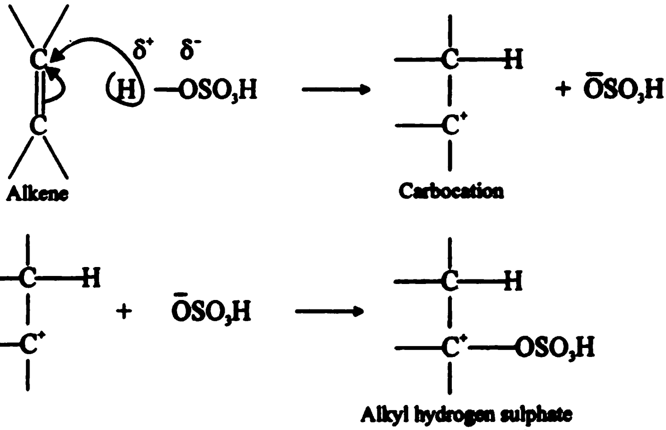
**Ans.** In case of HCl, it is probably due to the fact that H—Cl bond (430 kJ/mole) is stronger than H—Br bond (368 kJ/mole) and is not broken homolytically by the free radicals generated by peroxides. As such free radical addition of HCl to alkenes is not possible. In case of HI, H—I bond (297 kJ/mole) is no doubt weaker than H—Br bond and can be broken more easily. But the iodine atoms (I•) thus formed readily combine amonst themselves to from iodine molecules rather than add to the olefins.

**Q. 13. Give the mechanism of addition of**

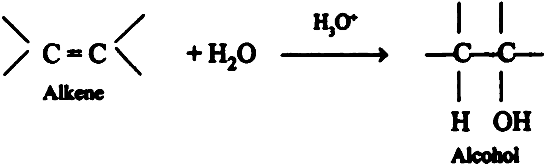
**(*i*) sulphuric acid**

**(*ii*) water to an alkene.**

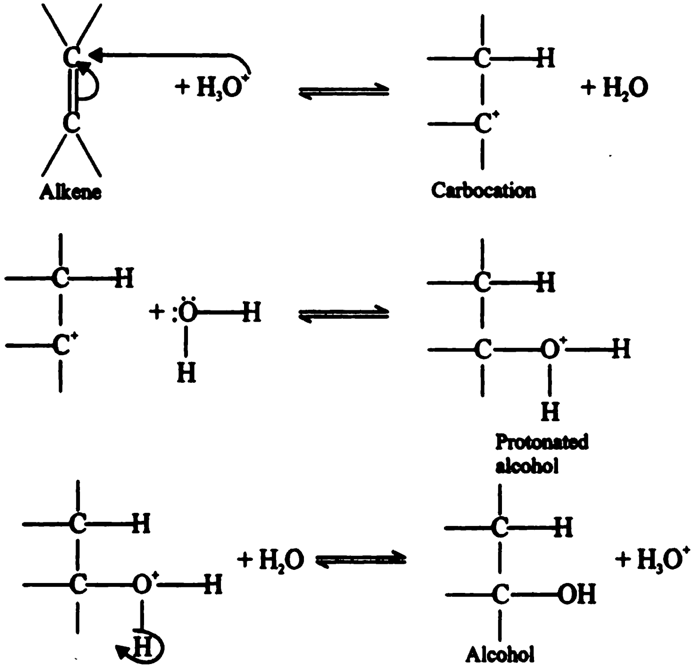
**Ans. Mechanism of addition of sulphuric acid to alkene.** It is a two step electrophilic addition reaction which takes place as follow :



**Mechanism of addition of water to an alkene.** Alkenes react on water in the presence of an acid to form alcohols.

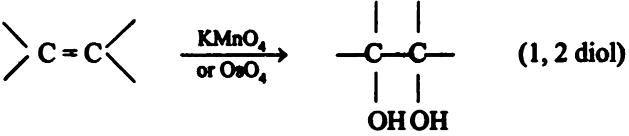


The reaction takes place by an electrophilic mechanism as depicted below

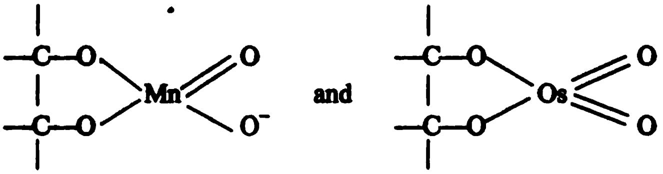


**Q. 14. Give the mechanism of glycollisation or hydroxylation alkenes.**

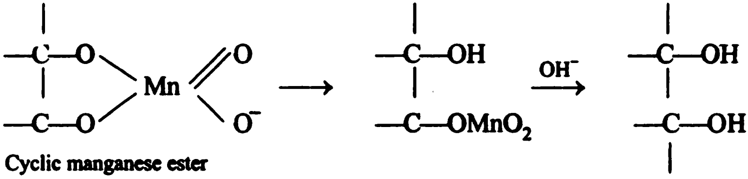
**Ans.** Conversion of alkene into 1, 2-diols is known as 1, 2-glycollisation reaction ; an —OH group is added on to each carbon atom of the double bond. The most commonly used reagents are potassium permanganate and osmium tetroxide ($OsO_4$).

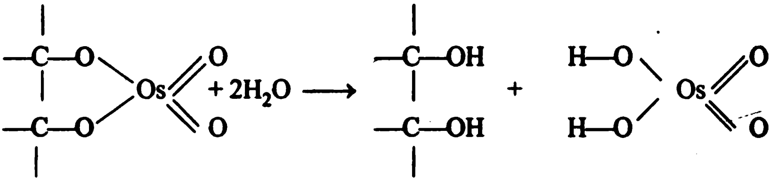


The two reagents ($KMnO_4$ and $OsO_4$) are known to react by similar mechanism which involves cyclic intermediate of the following type which are

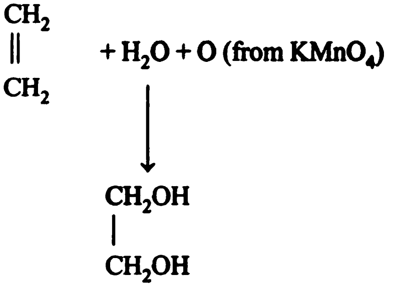


subsequently hydrolyzed in aqueous solutions to glycol and the reduced form of the reagent.



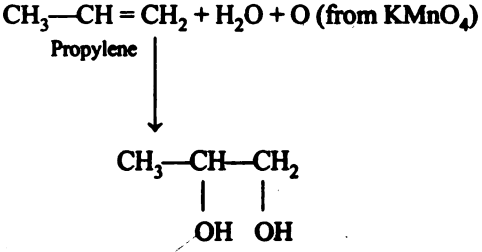


The permanganate reaction (Baeyer's test) is usually carried out in cold, aqueous alkaline solution.



$$\begin{array}{l} CH_2 \\ \| \\ CH_2 \end{array} + H_2O + O \text{ (from } KMnO_4) \longrightarrow \begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array}$$

Glycol



$$CH_3\text{—}CH = CH_2 + H_2O + O \text{ (from } KMnO_4) \longrightarrow \begin{array}{c} CH_3\text{—}CH\text{—}CH_2 \\ \quad\; | \qquad | \\ \quad\; OH \quad OH \end{array}$$

Propylene

(Propylene glycol)

**Q. 15. Explain the mechanism of hydroboration of alkenes.**

**Ans.** On treatment with diborane $(BH_3)_2$, alkenes form alkyl boranes which are further converted into di and tri alkylboranes. For example :

$$\underset{\text{Propylene}}{2CH_3\text{—}CH = CH_2} + (BH_3)_2 \longrightarrow \underset{n\text{-Propylbroane}}{2CH_3\text{—}CH_2\text{—}CH_2\,BH_2}$$

$$CH_3\text{—}CH_2\text{—}CH_2\,BH_2 + CH_3\text{—}CH = CH_2 \longrightarrow \underset{\text{Di-}n\text{-propylborane}}{(CH_3\text{—}CH_2\text{—}CH_2)_2\,BH}$$

$$(CH_3—CH_2—CH_2)_2BH + CH_3—CH = CH_2 \longrightarrow (CH_3—CH_2—CH_2)_3B$$

Tri-*n*-propylborane

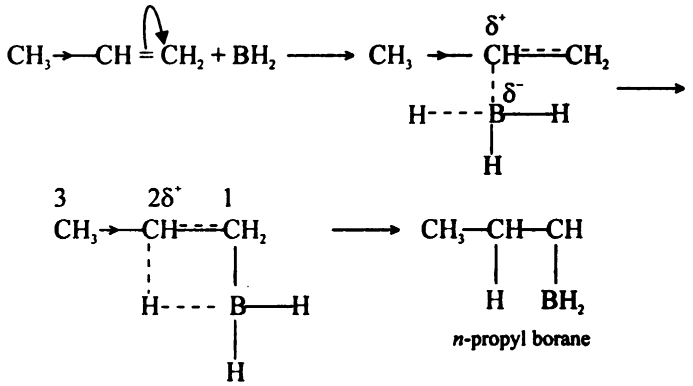
Alkylboranes in turn are readily oxidised by alkaline solution of $H_2O_2$ to form alcohols. For example :

$$CH_3—CH_2—CH_2BH_2 \xrightarrow{H_2O_2/OH-} 3CH_3—CH_2—CH_2OH$$

This reaction of preparation of alcohol from alkene is called hydroboration.

**Mechanism.** Diborane participates in the reaction in its monomeric form *i.e.*, $BH_3$. It behaves as an electrophile since the boron atom in the molecule is electron deficient as it has only six valence electrons.

Since $BH_3$ is an electrophile, hydroboration of alkanes also involves an electrophilic addition mechanism. But unlike other addition reactions of alkenes, hydroboration takes place in a single step through a transition sate as shown below by considering the hydroboration of propylene.



**Q. 16. What is meant by allylic substituion. Discuss the mechanism of the reaction.**

**Ans. Allylic substituion.** It is a substituion reaction which takes place at the carbon atom next to the double bond. Higher homologues of ethylene undergo allylic substitutution under specific conditions. For example, when propene is treated with chlorine at 773 K, it undergoes allylic substituion to yield 3-chloropropene.

$$CH_3—CH = CH_2 + Cl_2 \xrightarrow{773\ K} CH_2Cl—CH = CH_2 + HCl$$

3-Chloropropene

**Mechanism of the reaction.** Allylic substitution takes place by free radical chain mechanism as given below.

1. **Chain initiating step**

$$Cl—Cl \xrightarrow{773\ K} 2Cl^{\bullet}$$

(2) **Chain propagating steps**

$$Cl\cdot + CH_3—CH = CH_2 \longrightarrow HCl + [\cdot CH_2—CH = CH_2 \longleftrightarrow CH_2 = CH—CH_2\cdot]$$

Allyl radical

$$Cl—Cl + \cdot CH_2—CH=CH_2 \longrightarrow CH_2Cl—CH=CH_2 + Cl\cdot$$

(3) **Possible chain terminating steps**

$$Cl\cdot + Cl\cdot \longrightarrow Cl_2$$

$$Cl\cdot + \cdot CH_2—CH=CH_2 \longrightarrow CH_2Cl—CH=CH_2$$

**Q. 17. Describe the free radical chain mechanism of addition polymerisation with the help of a suitable example.** *(A.I.S.B. 2004)*

**Ans. Free radical polymerisation.** Many alkenes and substituted alkenes undergo polymerisation by free radical chain mechanism. Such reactions usually occur at high temperature under pressure or in the presence of catalysts such as peroxides and salts of peracids. The catalyst provides the free radical to initiate the chain process which is carried on by chain propagating steps. The mechanism is illustrated below with the help of polymerisation of ethylene in the presence of a peroxide.

(1) *Chain initiating stage :*

$$\underset{\text{Peroxide}}{R—O—O—R} \longrightarrow \underset{\text{Free radical}}{2R\dot{O}}$$

(2) *Chain propagating stage :*

$$R\dot{O} + CH_2=CH_2 \longrightarrow RO—CH_2—\dot{C}H_2$$

$$RO—CH_2—\dot{C}H_2 + CH_2=CH_2 \longrightarrow RO—CH_2—CH_2—CH—\dot{C}H_2$$

The free radical formed in each step adds to a fresh molecule of alkene and so the chain progresses till a large molecule of the polymer is obtained and the chain is terminated.

(3) *Possible chain terminating stage :*

(*i*) Coupling of free radicals to form a deactivated molecule. For example :

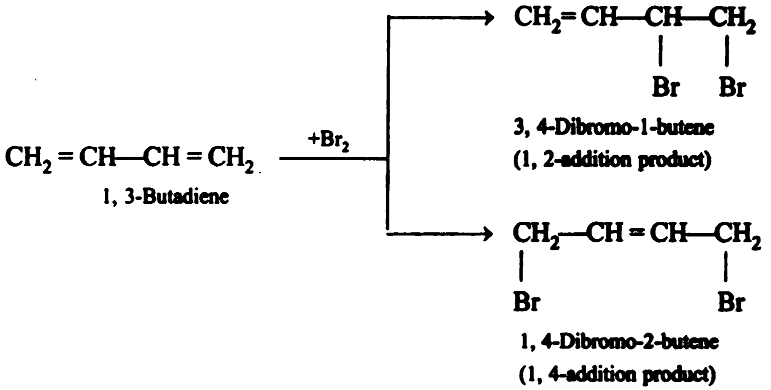
$$RO—(CH_2—CH_2)_n—CH_2—\dot{C}H_2 + \dot{C}H_2—(CH_2—CH_2)_n—OR$$
$$\longrightarrow RO—(CH_2—CH_2)_n—CH_2—CH_2—CH_2—(CH_2—CH_2)_n—OR$$

(*ii*) **Disproportionation** of free radicals in which one free radical acquires a hydrogen from another and both get deactivated.

$$RO—(CH_2—CH_2)_n—CH_2—\dot{C}H_2 + \dot{C}H_2—(CH_2CH_2)_n—OR$$
$$\longrightarrow RO—(CH_2—CH_2)_n—CH=CH_2 + CH_3—CH_2—(CH_2—CH_2)_n—OR$$

**Q. 18. Give the mechanism of addition of $Br_2$ to 1, 3 butadiene.**

**Ans.** When one mole of the addendum such as $Br_2$ is added to a conjugated diene, the resulting product obtained is a mixture of 1, 2- and 1, 4-addition products. Such an addition is known as 1, 2-and 1, 4-addition to conjugated dienes. Thus consider the addition of 1 mole of $Br_2$ to 1, 3-butadiene.

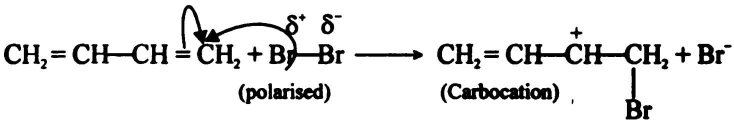


$$CH_2{=}CH{-}CH{=}CH_2 \xrightarrow{+Br_2} CH_2{=}CH{-}CH(Br){-}CH_2Br \;+\; BrCH_2{-}CH{=}CH{-}CH_2Br$$

In order to understand the occurrence of 1, 2-and 1, 4-addition reactions, the mechanism of the above reaction is discussed.

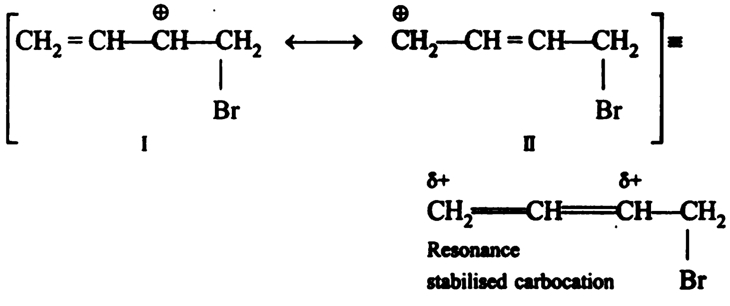
**Mechanism.** It involves two steps.

(*i*) **Formation of carbocation**



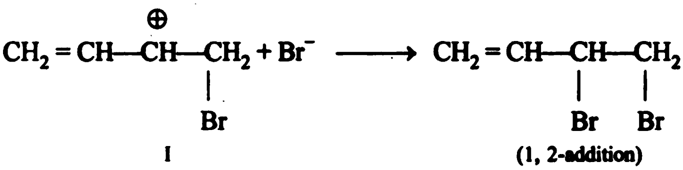
$$CH_2{=}CH{-}CH{=}CH_2 + \overset{\delta^+}{Br}{-}\overset{\delta^-}{Br} \longrightarrow CH_2{=}CH{-}\overset{+}{C}H{-}CH_2Br + Br^-$$

The above intermediate carbocation is allylic in nature and hence can be considered to be a resonance hybrid of two equivalent resonating structures I and II



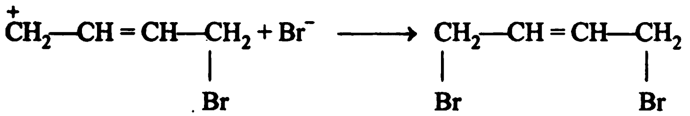
$$\left[CH_2{=}CH{-}\overset{\oplus}{C}H{-}CH_2Br \longleftrightarrow \overset{\oplus}{C}H_2{-}CH{=}CH{-}CH_2Br\right] \equiv \overset{\delta+}{C}H_2 \text{---} CH \text{---} \overset{\delta+}{C}H{-}CH_2Br$$

(*ii*) **Combination of bromide with carbocation**



$$CH_2{=}CH{-}\overset{\oplus}{C}H{-}CH_2Br + Br^- \longrightarrow CH_2{=}CH{-}CH(Br){-}CH_2Br$$

Bromide ion combines with carbocation I and II to form 1, 2 and 1, 4 addition products respectively.

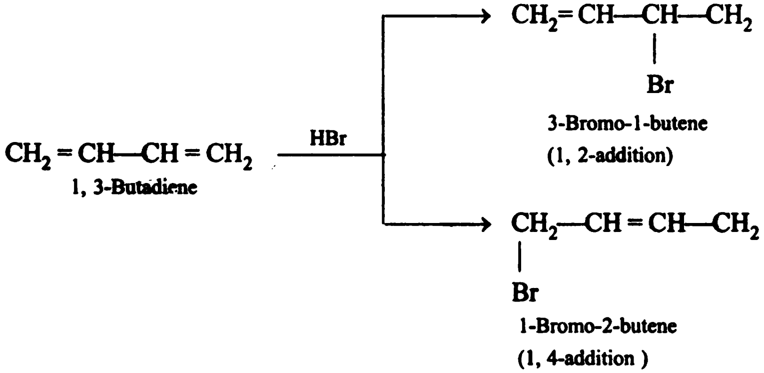


$$\overset{+}{C}H_2—CH=CH—\underset{Br}{CH_2} + Br^- \longrightarrow \underset{Br}{CH_2}—CH=CH—\underset{Br}{CH_2}$$

II (1, 4-addition)

**Q. 19. Discuss the mecahnism of the addition of HBr to 1, 3-butadiene.**

**Ans.** Addition of HBr to 1, 3-butadiene gives a mixture of 1, 2 and 1, 4 addition products as given below.



$$CH_2=CH—CH=CH_2 \xrightarrow{HBr} CH_2=CH—\underset{Br}{CH}—CH_2 \text{ (1, 2-addition)} + \underset{Br}{CH_2}—CH=CH—CH_2 \text{ (1, 4-addition)}$$

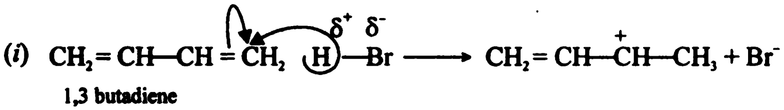
1, 3-Butadiene

3-Bromo-1-butene
(1, 2-addition)

1-Bromo-2-butene
(1, 4-addition )

This can be explained in terms of the mechanism which assumes the formation of carbocation I and II.

**Mechanism**



$$(i)\ CH_2=CH—CH=CH_2\ \overset{\delta^+}{H}—\overset{\delta^-}{Br} \longrightarrow CH_2=CH—\overset{+}{C}H—CH_3 + Br^-$$

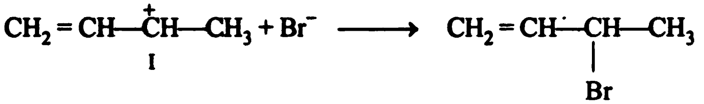
1,3 butadiene

The above carbocation is a resonance hybrid of the following two equivalent structures I and II.

$$\underset{I}{CH_2=CH—\overset{\oplus}{C}H—CH_3} \longleftrightarrow \underset{II}{\overset{\oplus}{C}H_2—CH=CH—CH_3} \equiv \overset{\delta^+}{C}H_2{\cdots}CH{\cdots}\overset{\delta^-}{C}H—CH_3$$

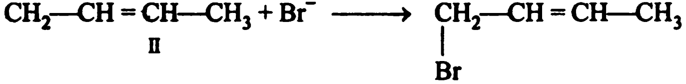
Resonance stabilised carbocation

(*ii*) Carbocations I and II react with bromide ion to give 1, 2 and 1, 4 products respectively.



$$\underset{I}{CH_2=CH—\overset{+}{C}H—CH_3} + Br^- \longrightarrow CH_2=CH—\underset{Br}{CH}—CH_3$$

(1, 2-addition)



$$\underset{II}{\overset{+}{C}H_2—CH=CH—CH_3} + Br^- \longrightarrow \underset{Br}{CH_2}—CH=CH—CH_3$$

(1, 4-addition)

**Q. 20. Discuss the mecahnism for free radical polymerisation of 1, 3-butadiene.**

**Ans.** 1, 3-Butadiene polymerises to form polybutadiene.

$$\underset{\text{1, 3-Butadiene}}{n\,CH_2=CH—CH=CH_2} \longrightarrow \underset{\text{Polybutadiene}}{(—CH_2—CH=CH—CH_2—)_n}$$

The formation of polybutadiene invovles mainly 1, 4-addition of butadiene units to each other so that the polymer obtained still contains a double bond for each butadiene unit.

**Mechanism**

In the presence of some organic peroxides, the polymerisation of 1, 3-butadiene proceeds through the formation of free radicals as illustrated below:

(*i*) Organic peroxide $\longrightarrow$ Rad•

(*ii*) $CH_2=CH—CH=CH_2 + \text{Rad}\bullet \longrightarrow \left[\begin{array}{c} CH_2=CH—\dot{C}H—CH_2\,\text{Rad} \\ \updownarrow \\ \dot{C}H_2—CH=CH—CH_2\,\text{Rad} \end{array}\right]$

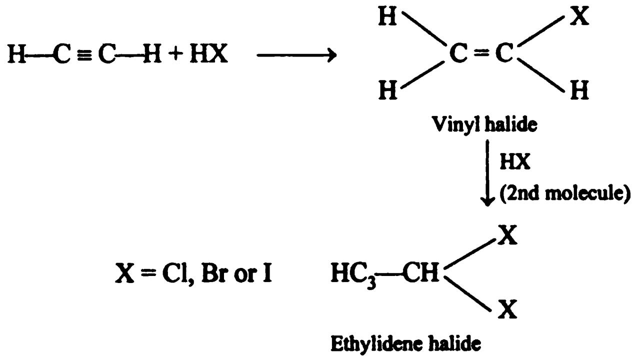
(*iii*) $CH_2=CH—CH=CH_2 + \dot{C}H_2—CH=CH—CH_2\,\text{Rad}$

$\longrightarrow \dot{C}H_2—CH=CH—CH_2—CH_2—CH=CH—CH_2\,\text{Rad}$

and so on.

**Q. 21. Describe with mechanism addition of halogen acids on alkynes.**

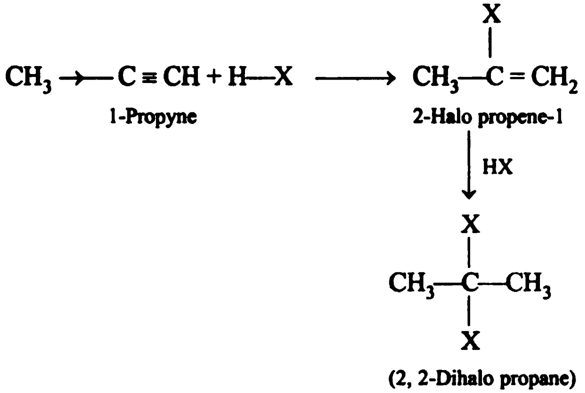
**Ans.** Treatment of alkynes with halogen acid initially yields vinyl halides and finally *alkylidene halides.* Combination with second molecule takes place in accordance with Markownikoff's rule.



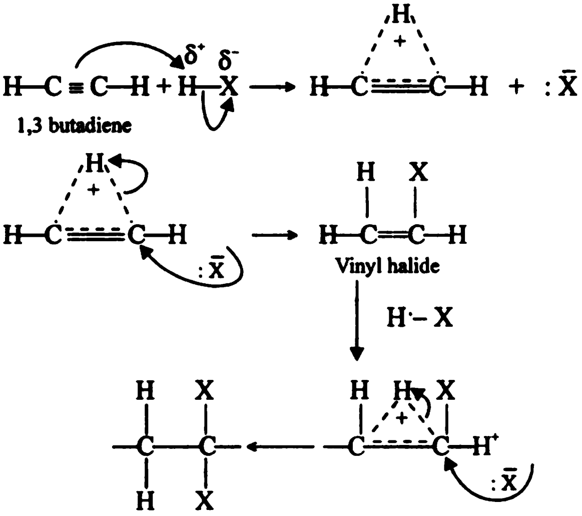
Vinyl halide

Ethylidene halide
(1, 1-Dihalo ethane)

In case of propyne (unsymmetrical alkyne), the first molecule of HX adds according to Markownikoff's rule.

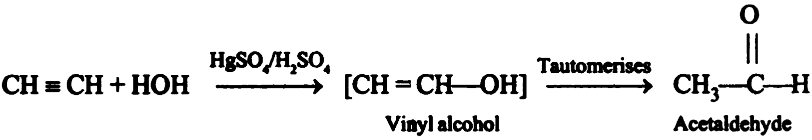


Mechanism of the reaction is depicted below :



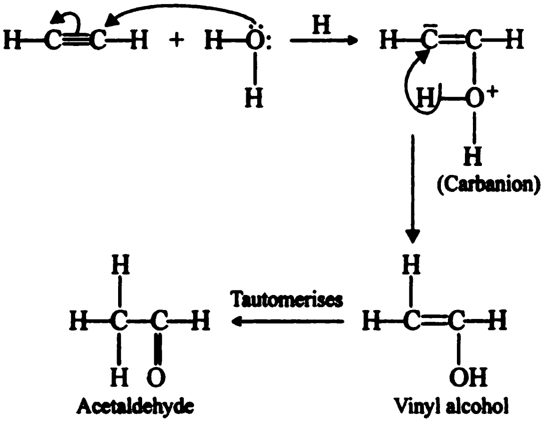
**Q. 22. What happenes when acetylene is passed through dil. sulphuric acid containing mercuric sulphate at 343 K ? Discuss the mechanism of this reaction.**

**Ans.** When treated with dil. $H_2SO_4$ in the presence of mercuric sulphate, acetylene gets hydrated to form first an enol which readily tautomerises to form acetaldehyde.



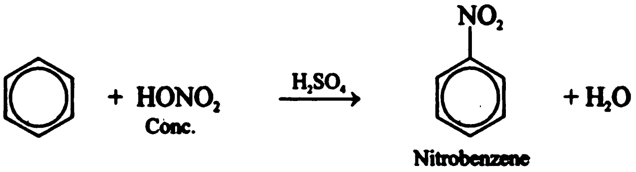
$$CH\equiv CH + HOH \xrightarrow{HgSO_4/H_2SO_4} \underset{\text{Vinyl alcohol}}{[CH=CH{-}OH]} \xrightarrow{\text{Tautomerises}} \underset{\text{Acetaldehyde}}{CH_3{-}\overset{\overset{O}{\|}}{C}{-}H}$$

**Mechanism.** The mechanism involves the nucleophilic attack of water molecule on acetylene to form a carbocation which changes into vinyl alcohol. Since vinyl alcohol is unstable, it tautomerises to form stable aldehyde.



**Q. 23. Explain the mechanism of nitration of benzene.**

**Ans. Nitration.** This reaction involves the treatment of an aromatic compound with a mixture of nitric acid and sulphuric acid. For example :

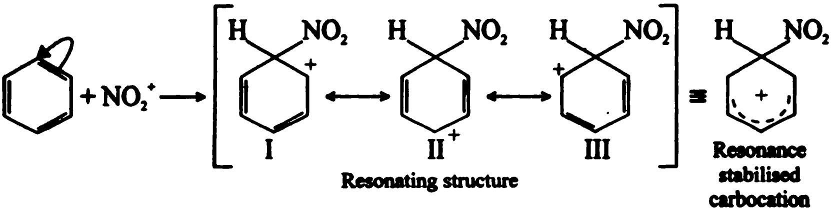


**Mechanism.** The various steps in the nitration of benzene can be outlined as below :

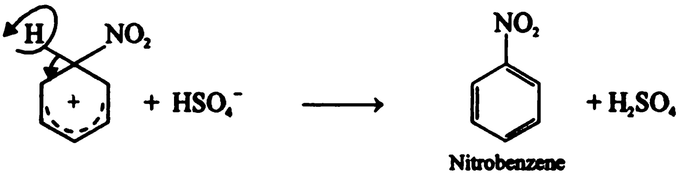
**(I) Generation of electrophile**

$$HONO_2 + 2H_2SO_4 \rightleftharpoons \underset{\text{Nitronium ion}}{NO^{2+}} + H_3O^+ + 2HSO_4^-$$

**(II) Formation of carbocation**

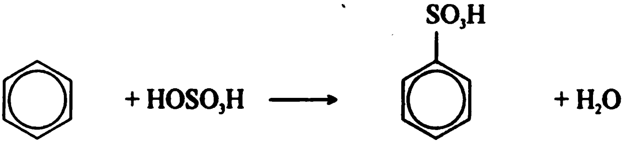


**(III) Abstraction of proton from the carbocation**



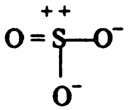
**Q. 24. Give the mechanism of sulphonation of benzene.**

**Ans. Sulphonation.** The sulphonation of an aromatic compound can be bought about by the action of conc. $H_2SO_4$ or oleum. For example :



Benzene sulphonic acid

**Mechanism.** The attacking electrophilic reagent in this reaction is believed to be sulphur trioxide which is present as such in oleum or may be formed by the dissociation of sulphuric acid. The electrophilic nature of $SO_3$ molecule is due to the presence of electron deficient sulphur atom.



$$O=\overset{++}{\underset{\underset{O^-}{|}}{S}}-O^-$$

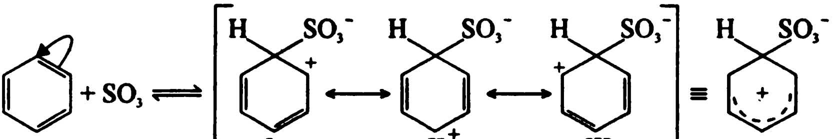
As the positive charge is concentrated on sulphur and negative charges are scattered on two oxygens, $SO_3$ molecule acts as electrophile.

The complete mechanism for this reaction may be outlined as follows :

**(I) Generation of electrophile**

$$2H_2SO_4 \rightleftharpoons \underset{\text{Electrophile}}{SO_3} + HSO_4^- + H_3O^+$$

**(II) Formation of carbocation**



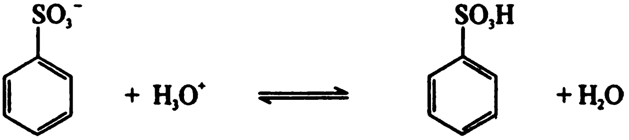
I II III

(Resonating structure)

Resonance stabilised carbocation

**(III) Abstraction of proton from the carbocation**

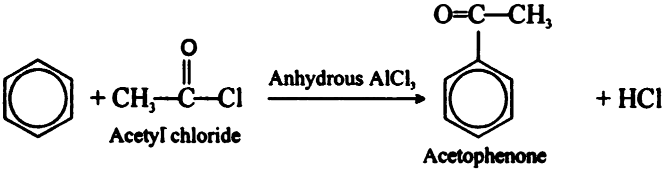
**(IV) Formation of the final product**



**Q. 25. Give the mechanism of the following reaction :**

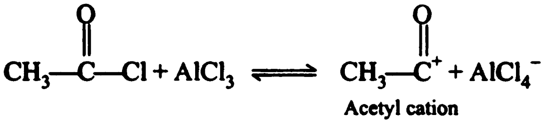
$$C_6H_6 + CH_3COCl \xrightarrow[AlCl_3]{Anhyd.} C_6H_6COCH_3 + HCl$$

**Ans.** When benzene is treated with acetyl chloride in the presence of anhydrous aluminium chloride, the formation of acetophenone takes place. This reaction is known as **Friedel-Craft's acylation.**



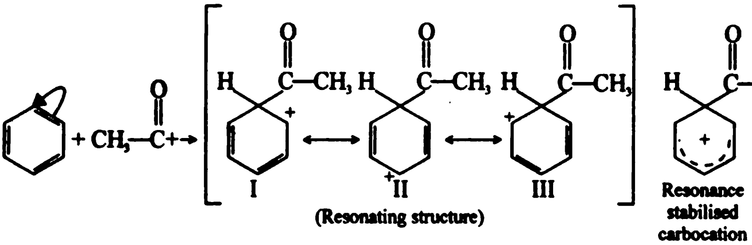
**Mechanism.** The most probable mechanism of the above reaction is discussed as under :

**(I) Generation of electrophile**

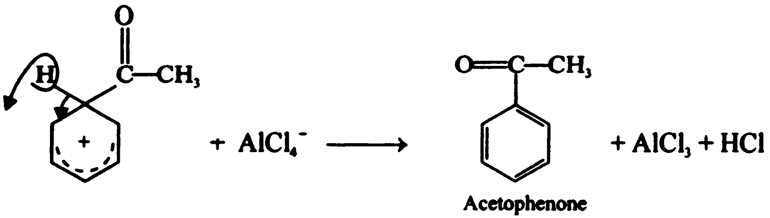


$$CH_3-\overset{\overset{O}{\|}}{C}-Cl + AlCl_3 \rightleftharpoons \underset{\text{Acetyl cation}}{CH_3-\overset{\overset{O}{\|}}{C^+}} + AlCl_4^-$$

**(II) Formation of carbocation**

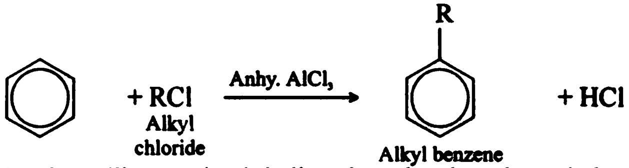


**(III) Abstraction of proton from the carbocation**



**Q. 26. Discuss the mechanism of Friedel Craft's alkylation of benzene.**

**Ans. Friedel Craft's alkylation.** This reaction consists in treating benzene or substituted benzenes with an alkyl halide in the presence of small amounts of Lewis acids ($AlCl_3$, $BF_3$, $FeCl_3$, etc.). It leads to the direct introduction of an alkyl group into the benzene ring.

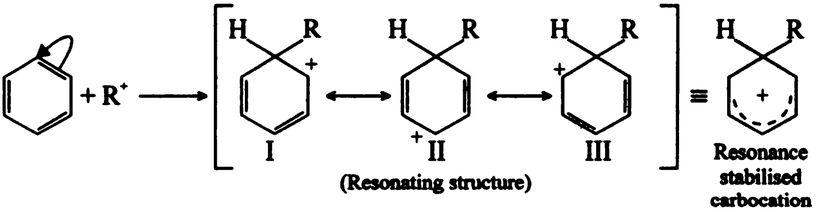


**Mechanism.** The reaction is believed to take place through the following steps :

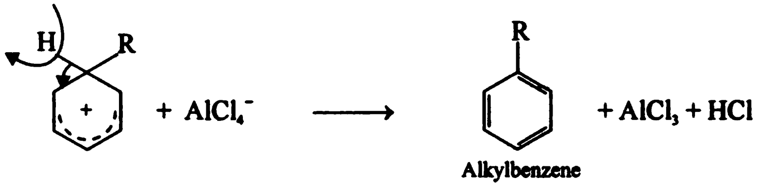
**(I) Generation of electrtophile**

$$R—Cl + AlCl_3 \rightleftharpoons \underset{\text{Electrophile}}{\overset{+}{R}} + AlCl_4^-$$

**(II) Formation of carbocation**

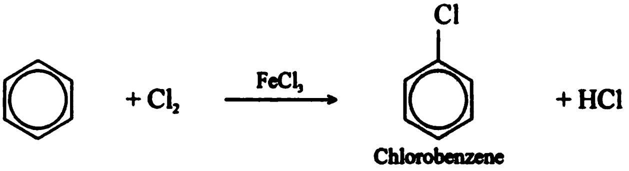


**(III) Abstraction of proton from the carbocation**



**Q. 27. Describe the mechanism of halogenation of benzene.**

**Ans. Halogenation of Benzene.** Halogenation of benzene and other aromatic hydrocarbons can be brought about by treating with halogens in the presence of Lewis acids such as ferric halides, anhydrous aluminium chloride. Chlorination of benzene is considered below :

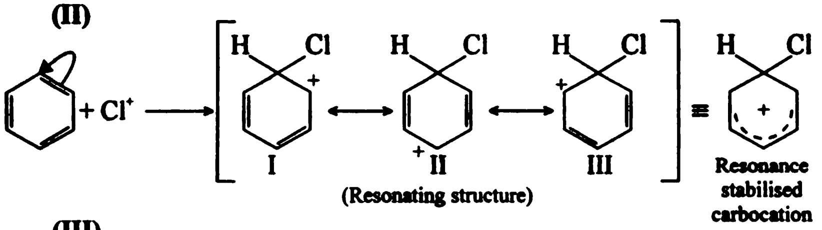


**Mechanism.** Various steps involved in the reaction are as follows :

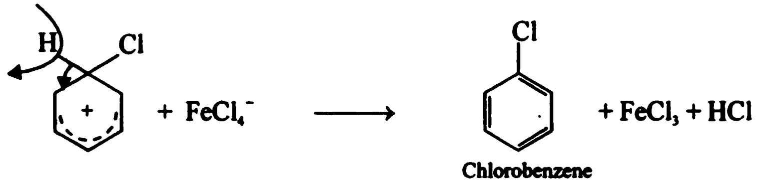
**(I) Generation of electrophile**

$$Cl—Cl + FeCl_3 \rightleftharpoons \underset{\text{Electrophile}}{\overset{+}{Cl}} + FeCl_4^-$$

(II)



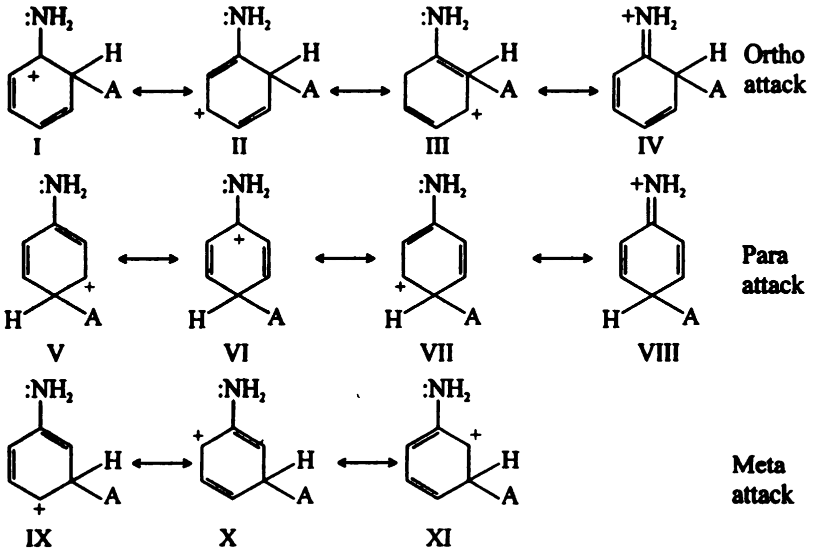
(III)



**Q. 28. Give electronic interpretion of the ortho-para directing influence of amino group.**

**Ans.** Amino group exerts electron withdrawing (–I) and electron releasing (+M) effects. Of the two opposing effects, the resonance effect dominates and thus overall behaviour of $-NH_2$ group is electron releasing, *i.e.*, it acts as an activator.

The ortho and para directing influence of $-NH_2$ group can be explained by assuming that nitrogen can share more than a pair of electrons with the benzene ring and can accommodate a positive charge. Thus, consider the case of further electrophilic substituion in aniline. The various resonating structures of the carbocations formed by ortho, para and meta attack are given below. A represents the electrophile.

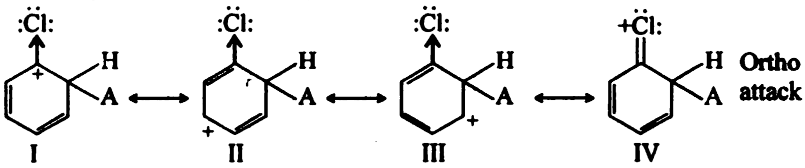


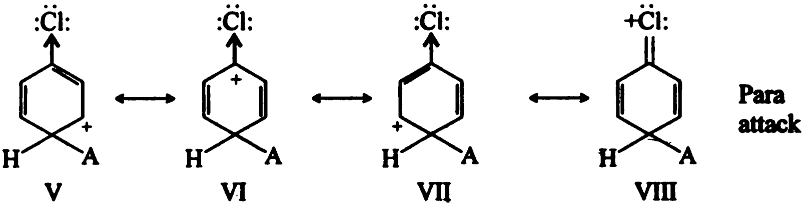
The intermediate carbocation resulting from ortho as well as para attack is a resonance hybrid of four structures while the one formed by meta attack is a resonance hybrid of three structures. Further, in structures IV and VIII, the positive charge is carries by nitrogen. These structures are more stable since every atom (except hydrogen) has a complete octet of electrons. No such structure is, however, possible in case of meta attack. It is, therefore, clear that the resonnace hybrid carbocations resulting form ortho and para attack are more stable than the carbocation formed by attack at the meta position. Consequently further electrophilic substitution in aniline occurs faster at the ortho and para positions than at the meta position. In other words —$NH_2$ group is an ortho and para directing group.

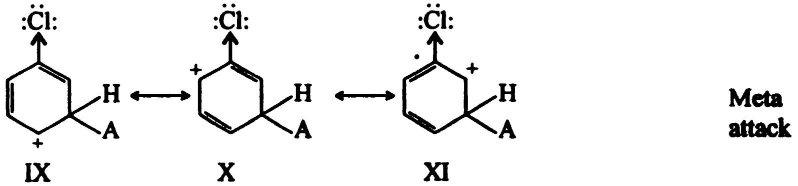
**Q. 29. Halogens are electron withdrawing and yet they direct the incoming group to ortho and para positions. Explain.**

**Ans.** Halogens exert electron withdrawing (–I) and electron releasing (+M) effects. Due to high electronegativities of halogens, the inductive effect predominates over the mesomeric effect and thus the overall behaviour of halogens is electron withdrawing. In other words, halogens act as deactivators for further substitution.

In order to account for their ortho and para directing nature, it has been assumed that halogens can share more than one pair of electrons with the benzene ring and can accommodate positive charge. Thus, consider the case of further electrophilic substituion in chlorobenzene. The various resonating structures of the carbocation formed by ortho, para and meta attack are given below: A represents new-coming group



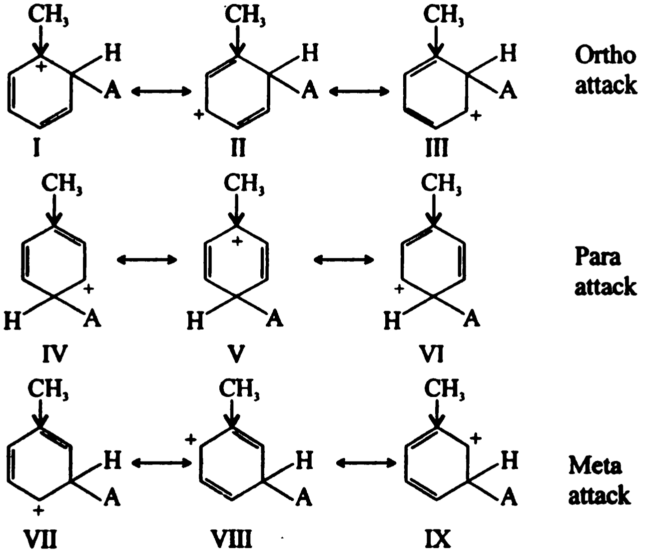




It is clear that the intermediate carbocation resulting from ortho as well as para attack is a resonance hybrid of four structures while the one formed by meta attack is a resonance hybrid of three structures. Structures (I) and (VI) are highly unstable since in these structures the positive charge is carried by that carbon which is linked to electron withdrawing chlorine atom. However, in structures (IV) and (VIII), the positive charge is carried by chlorine. These structures are extra stable since in these structures every atom (except hydrogen) has a complete octet of electrons. No such structure is, however, possible in case of meta attack. Thus, the resonance hybrid carbocations resulting from ortho and para attack are more stable than that formed by attack at the meta position. As a result, chlorine is ortho and para directing. The same is true for other halogens. It may thus be concluded that in case of halogens, the reactivity is controlled by the stronger inductive effect and the orientation is determined by mesomeric effect.

**Q. 30. Give electronic interpretation of ortho and para directing influence of alkyl groups.**

**Ans.** Alkyl groups exert electron releasing inductive effect (+ I effect). Consider the case of further electrophilic substitution in toluene which contains an electron releasing methyl group. The various resonating structures of the carbocations formed by ortho, para and meta attack are given below :

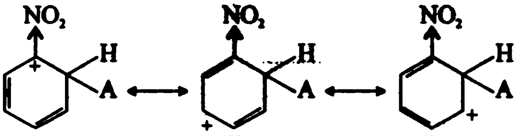


We find that in each case, the intermediate carbocation is a resonance hybrid of three structures. In structures (I) and (V), the positive charge is located on the carbon atom to which electron releasing methyl group is attached. Therefore, the positive charge on such a carbon is highly dispersed and thus the corresponding structures (I) and (V) are more stable than all other structures. No such structure is, however, possible in case of meta attack. Hence the resonance hybrid carbocations resulting from ortho and para attack are more stable than the one formed by attack at the meta position. Therefore, further electrophilic substitution in toluene occurs faster at the ortho and para position than at the meta position. In other words, methyl group is an ortho and para directing group. Other alkyl groups behave similarly.

**Q. 31. Explain deactivating and meta directing nature of nitro group towards electrophilic aromatic substituion.**

**Ans.** Nitro group is electron withdrawing in nature. In this case, the electron withdrawal occurs through electron withdrawing effect (–I-effect) as well as electron withdrawing resonance effect (–M-effect). Due to its electron withdrawing character, nitro group deactivates the benzene ring towards further electrophilic substitution.

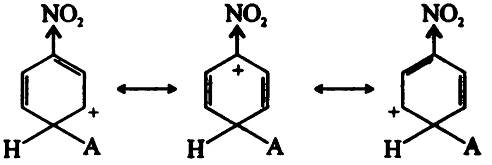
Let us examine the directing influence of —$NO_2$ group by considering electrophilic substituion in nitrobenzene. The various resonating structures of the carbocations formed by ortho, para and meta attack are give below :



I specially unstable

II

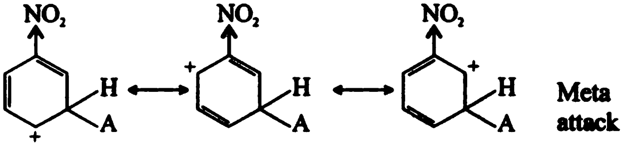
III



IV

V specially unstable

VI



VII

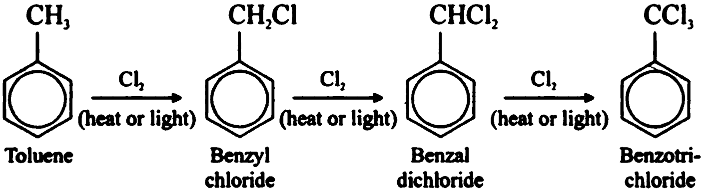
VIII

IX

In the contributing structures (I) and (V), the positive charge is located on that carbon atom which is directly linked to electron withdrawing nitro group. Although —$NO_2$ group withdraws electrons from all positions, it does so most from the carbon directly attached to it. Hence this carbon atom, already made positive by nitro group has little tendency to accommodate the positive charge of the carbocation. Consequently structures (I) and (V) are unstable and their contribution towards stabilization of the carbocation is almost negligible. Thus carbocations formed by ortho and para attack are virtually resonance hybrids of only two structures while the one formed by meta attack is a resonance hybrid of three structures. Therefore, the resonance hybrid carbocation resulting from meta attack is more stable than the carbocations resulting from ortho and para attack. Consequently, further electrophilic substituion takes place at the meta position. Thus, nitro group is meta directing.

**Q. 32. Discuss the mechanism of side chain halogenation of toluene.**

**Ans. Side chain halogenation.** The reaction in which one or more hydrogen atoms of the side chain are replaced by the halogen atoms, is called side chain halogenation. It can be brought about by treating an arene with a suitable halogen in the presence of light or heat and in the absence of halogen carriers. For example,



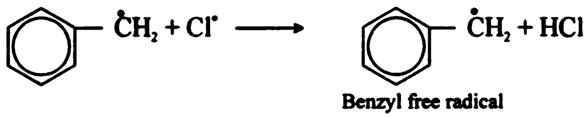
**Mechanism of halogenation.** Side chain halogenation of toluene occurs by a free radical mechanism as given below :

**(*a*) Chain initiation step**

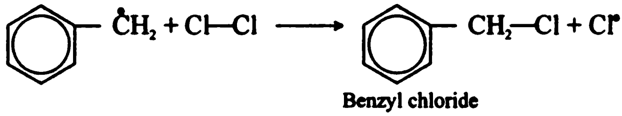
$$Cl—Cl \xrightarrow[\text{(homolytic fission)}]{\text{heat or light}} 2\,Cl\cdot$$

**(*b*) Chain propagating steps**

(I)



(II)



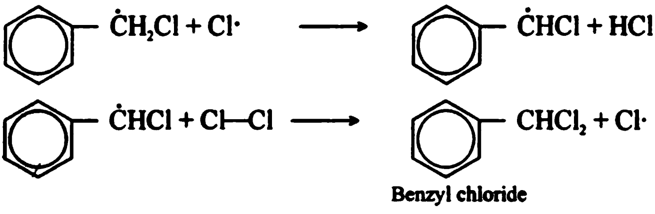
The above steps (I) and (II) are repeated again and again.

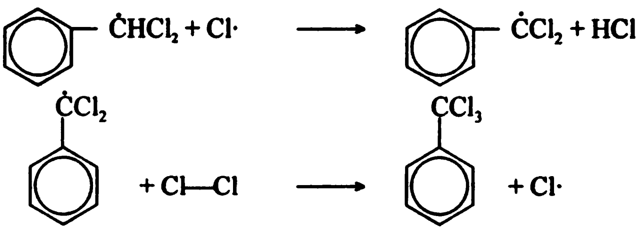
**(c) Chain terminating steps**

When the free radicals combine with each other, the reaction comes to a stop and thus the chain of reaction gets terminated.

$$Cl. + Cl. \longrightarrow Cl—Cl$$

When excess of chlorine is used, other hydrogen atoms are also replaced in the same manner. Thus,





Benzotrichloride

**Q. 33. Give the mechanism of the following reaction :**

$$\mathbf{CH_3Br + KOH\ (aq) \longrightarrow CH_3OH + KBr}$$

**OR**

**Discuss the $SN^2$ reaction mechanism of substitution in alkyl halides. Whey does $SN^2$ reaction take place with stereochemical inversion ?**

**Ans.** Hydrolysis of methyl bromide proceeds by $SN^2$, (meaning substituion nucleophilic reaction of the second order), mechanism. $SN^2$ reaction may also be termed as bimolecular sustitution reaction. The term bimolecular implies that there are two reacting species in the rate determining step of the reaction.

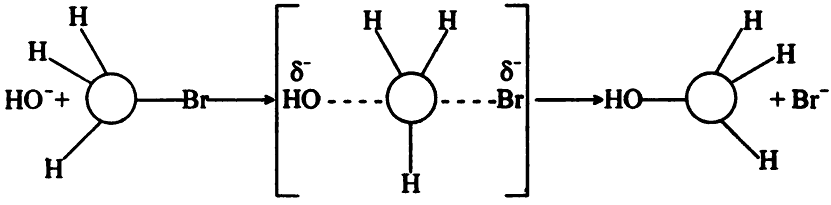
A simple and typical example of $SN^2$ substituion is the hydrolysis of methyl bromide with aqueous sodium hydroxide.

$$CH_3Br + OH^- \longrightarrow CH_3OH + Br^-$$

The kinetic data reveal that the rate of the reaction is dependent upon the concentration of both these reactants

$$\text{Rate} = k\,[CH_3Br]\,[OH^-]$$

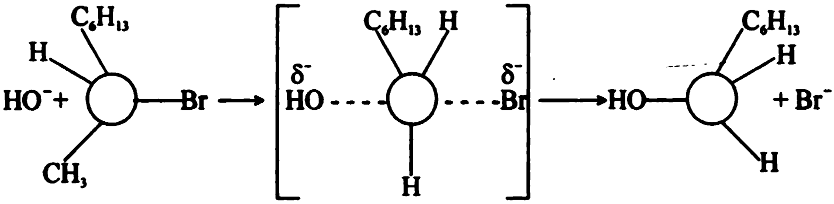
The reaction is of second order and thus it proceeds by a direct displacement mechanism in which both the reactants are present in the rate determining step. It is assumed that the nucleophile attacks the side of the carbon atom opposite to that of bromine. This is referred to as **backside attack.** As a result of this attack, a transition state is formed in which carbon atom is partially bonded to both —OH and —Br groups. In the transition state, the central carbon is $sp^2$ hybridised and the three hydrogens attached to it lie in the same plane with mutual bond angles of 120°. The reaction may be depicted as :



Transition State

It may be noted that in the transition state, the hydroxide ion has diminished negative charge since it has started sharing its electrons with carbon. Similarly bromine develops a partial negative charge as it is tending to depart with the bonding electrons. When carbon-oxygen bond is completely formed, the carbon-bromine bond is altogether broken. The energy required for breaking a bond is compensated by the formation of a new bond. The overall reaction is thus a concerted process occuring in one step through the intervention of a single transition state. In a single step, C—Br bond is broken and C—OH bond is formed resulting in the formation of alcohol molecule.

**Stereochemistry of $SN^2$ reactions.** In $SN^2$ reactions, it is assumed that the nucleophile ($OH^-$ in the present case) attacks the side of the carbon opposite to that of the leaving group. As a result, the configuration of the resulting product is inverted. In other words $SN^2$ reaction proceedes with **stereochemical inversion.** This has been found to be so in actual practice. Thus when (–)-2-bromooctane is hydrolysed under $SN^2$ conditions, it gives exclusively (+)-2-octanol. The reaction may thus be represented as :



(–)-2- Bromooctane Transition State (+)-2-Octanol
(Inversion in $SN^2$ reaction)

We have cited the example of (–)-2-bromooctane because it contains a chiral carbon atom ( a carbon linked to four different groups). The configurations of the reactants and the products are different in such $SN^2$ reaction. We normally check the configuration by measuring the direction of rotation of plane polarised light although it is not necessary always that inversion of configuration should be accompanied by change in direction of rotation of plane-polarised light.

**Q. 34. Discuss relative reactivities of alkyl halides in $SN^2$ substituion.**

**Ans.** In $SN^2$ reactions, the nucleophile attacks the side of the carbon opposite to that of the leaving group because both groups are to be accommodated in the transition state. Thus consider the alkaline hydrolysis of methyl bromide which follows $SN^2$ mechanism. It involves the backside attack of the nucleophile ($OH^-$) on the carbon bearing the bromine atom. Evidently, when the hydrogen atoms of methyl group are successively replaced by bulkier alkyl groups such as methyl, ethyl, etc., there is an increased crowding around the central carbon both in the reactant and transition state. Due to steric hindrance of the alkyl groups, the nucleophile finds it more and more difficult to attack the carbon carrying the halogen. Thus, in the reaction of hydrolysis of an alkyl bromide, simultaneous presence of —OH and —Br in the transition state becomes difficult because of overcrowding due to bulky groups. Greater the size of the alkyl groups attached to halogen bearing carbon atom, greater is the difficulty in the transition state formation and thus slower will be the rate of such $SN^2$ reaction. The overcrowding of alkyl groups also leads to strong non-bonded interactions in the transition state in which carbon is bonded to five atoms.

In general, the order of relative reactivities of alkyl halides in $SN^2$ reactions follows the sequence :

$$\text{Methyl halides} > \text{Primary halides} > \text{Secondary halides} > \text{Tertiary halides}$$

**Q. 35. Give the kinetics and stereochemistry of unimolecular nucleophilic substitution in alkyl halides.**

**Or**

**$SN^1$ reaction leads to racemisation. Explain.**

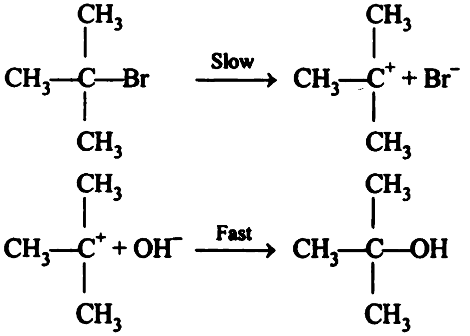
**Ans.** An example of unimoleuclar substituion reacton ($SN^1$) is the hydrolysis of tert, butyl bromide

$$(CH_3)_3\,C-Br + \ddot{O}H^- \longrightarrow (CH_3)_3\,C-OH + Br^-$$

Chemical kinetic studies reveal that the rate of this reaction depends only on the concentration of tert-butyl bromide. Thus,

$$\text{Rate} = k\,[(CH_3)_3\,C-Br]$$

The reaction is of first order and thus it is believed to occur in two steps.



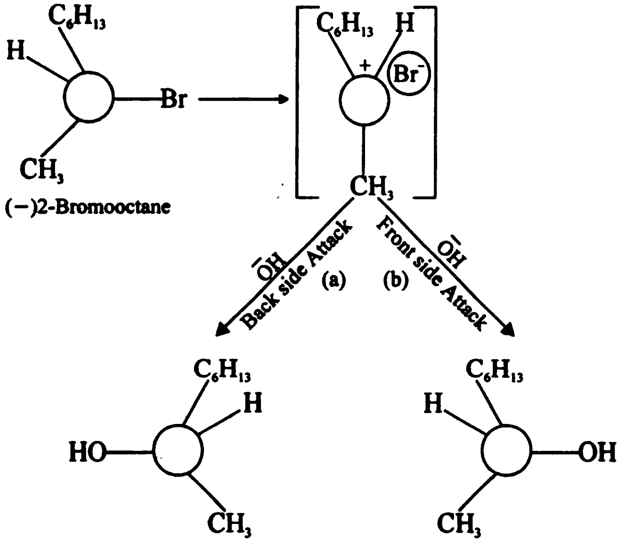
$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-Br \xrightarrow{\text{Slow}} CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C^+}}}} + Br^-$$

$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C^+}}}} + OH^- \xrightarrow{\text{Fast}} CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-OH$$

It is thus clear that the rate determining step of the reaction is the slow ionisation of tert-butyl bromide to form tert-butyl carbocation. The energy required for ionisation is supplied by the formation of many ion-dipole bonds between the ions produced and the polar solvent molecules. The second step involving the combination of carbocation with hydroxide ion to from alcohol is fast.

**Stereochemistry of $SN^1$ reactions :** In unimolecular nucleophilic substituion, the rate determining step involves the formation of a carbocation. The carbon atom in the carbocation is in the $sp^2$ hybridised state. Thus the carbocation has a flat structure in which all the three substituents attached to carbon lie in a plane, making angles of 120° between them. The empty *p*-orbital lies perpendicular to the plane.

The attachment of the nucleophile to the flat carbonium ion can take place with 50% probability from the front and 50% probability from the back of carbonium ion. This may not make a difference in a simple case, but the difference is clearly made when the halogen carrying carbon is chiral *i.e.*, linked to four different groups. Hydrolysis of an alkyl halide in which the halogen bearing carbon is chiral will produce a product which is racemic *i.e.*, it contains 50% each of the *d* and *l* forms. Attachment of the nucleophile from front produces one configuration and that from the back produces the other configiruation. As a result, the final product obtained is expected to be racemic, containing equal number of molecules with retention and inversion of configuration. However, in actual practice, the product as a whole is not racemic. Usually there is a larger proportion of molecules with **inverted configuration** than those of the same configuration. This can be explained on the basis that initial ionisation of alkyl halide does not form a free carboncation. In fact ionisation of alkyl halide leads first to the formation of an **ion pair** in which the departing halide ion is still in close proximity to the carbocation. Consequently, the attack on the front side of the carbocation which leads to a product with retention of configuration is slightly hindered. On the other hand, the attack on the back side leading to a product with inverstion of configuration is somewhat preferred. Thus, the actual product formed is **partially racemised** and the enantiomer with inverted configuration predominates. For example, when (−)-2-bromooctane is hydrolysed under $SN^1$ conditions (low concentration of $OH^-$ ions), a partially racemised product is formed. This is further illustrated as follows :



(−)2-Bromooctane

Enantiomers

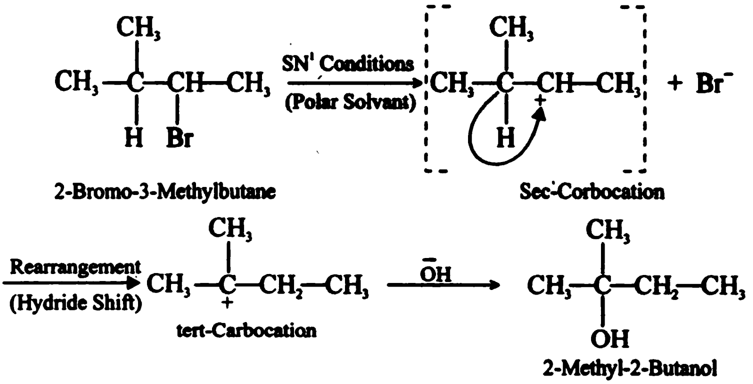
(+)2-Octanol
(*a*) Inversion of confi.
Predominates

(−)2-Octanol
(*b*) Retention of
confi.

(Partial racemisation in $SN^1$ reaction)

**Q. 36. Give evidence for the formation of carbocation intermediates in $SN^1$ reactions ?**

**Ans.** It is well known that carbocations undergo rearrangement to form more stable carbocations wherever possible. Since the carbocations are the intermediates in $SN^1$ reactions, it is expected that these intermediates will undergo rearrangement if the structure permits. As a result, the rearranged substituion product will be obtained. This is actually found to be so. For example, when 2-bromo-3-methylbutane is hydrolysed under $SN^1$ conditions, the formationof rearranged product, 2-methyl-2-butanol and not 3-methyl butanol-2 takes place as shown below :



**Q. 37. Discuss the relative reactivities of alkyl halides in unimolecular nucleophilic substitution ($SN^1$) reactions.**

**Ans. Relative reactivities of alkyl halides.** Formation of the carbocation is the rate determining step in unimolecular nucelophilic substitution ($SN^1$). More the stability, more rapidly is the carbocation formed and hence faster is the reaction. Now the realtive stability of the carbocations follows the sequence :

Benzene, allyl > Tertiary > Secondary > Primary > Methyl carbocations

Therefore, the reactivity of alkyl halides is $SN^1$ reactions follows the same order *i.e.*,

Benzene, allyl > Tertiary > Secondary > Primary > Methyl halides.

**Q. 38. Discuss the effect of polarity of solvent on the rate of $SN^1$ and $SN^2$ reactions.**

**Ans. Effect of solvent in $SN^1$ reactions.** The rate determining step in these reactions involves the ionisation of alkyl halide to form carbocation and halide ion. The energy required for the ionisation is provided by the solvation of these ions. Now polar solvent such as water, alcohols, etc., have a greater capacity as compared to non-polar solvents to solvate the ions and thus liberate considerable amount of energy. The energy released facilitates the ionisation and hence increases the rate of the reaction. It is thus obvious that $SN^1$ reactions are favoured by polar solvents. For example,

$$R{-}X \xrightarrow{\text{Ionization}} R^+ + X^- \quad \text{slow}$$

$$R^+ + OH^- \xrightarrow{\text{Polar solvent}} ROH \qquad \text{fast}$$

**Effect of solvent in SN$^2$ reactions.** SN$^2$ reaction is a concerted process occurring in one step through the intervention of a transition state.

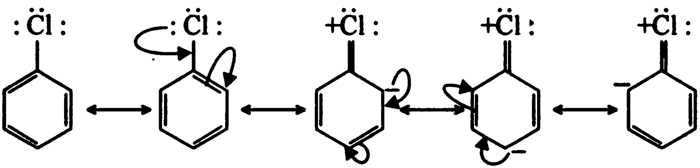
$$Nu^- + R—X \longrightarrow \underset{\text{Transition state}}{\begin{bmatrix} \delta- & & \delta- \\ Nu.....R.....X \end{bmatrix}} \longrightarrow Nu—R + \underset{\text{Halide ion}}{X^-}$$

It is clear that in the transition state, the negative charge is dispersed over nucleophile and halogen while in the reactants, it is concentrated only on the nucleophile. Reactants are thus more polar than the transition state. Evidently polar solvent will solvate the reactants more strongly than the transition state and hence slow down the rate of SN$^2$ reaction. In other words SN$^2$ reactions are favoured by solvents of low polarity.

**Q. 39. Explain giving mechanism low reactivity of chlorobenzene.**

**Ans.** Hydrolysis of $C_2H_5$—Cl is easier because as per the mechanism, C—Cl in this compound is easily broken and a new bond between carbon and the nucleophile OH is formed.

In chlorobenzene C—Cl bond is not easilty broken because chlorobenzene is a resonance hybrid of various contributing structures such as I—V shown below :



I II III IV V

Thus, the molecule of chlorobenzene is resonance stabilised. Moreover, the contribution of structures like III—V imparts a partial double bond character to the carbon halogen bond in the resonance hybrid of the chlorobenzene. Carbon and chlorine are thus held together by little more than a single bond pair of electrons. On the other hand, carbon and chlorine are attached by a single bond in alkyl halides (say $CH_3Cl$). As a result, the carbon-chlorine bond in chlorobenzene is stronger than if it were a pure single bond and hence cannot be easily broken. The low reactivity of aryl halides is also partly due to resonance stabilization of halide which increases the energy of activation ($E_{act}$) for displacement and thus slows down the reaction.

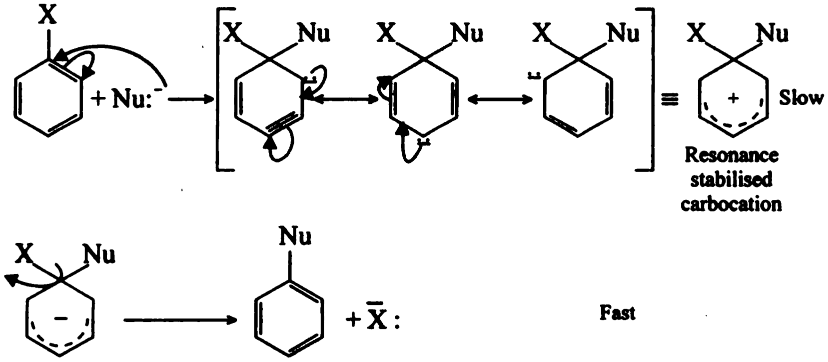
There is an alternative explanation for the low reactivity of aryl halides. The carbon atom attached to the halogen in aryl halides in *sp*$^2$ hybridised while that in alkyl halides is *sp*$^3$ hybridised. Since a *sp*$^2$ hybridised orbital is smaller in size than *sp*$^3$ hybridised orbital, therefore, the C—Cl bond in chlorobenzene is shorter and hence stronger than in methyl chloride.

This has been confirmed by the X-ray analysis which shows that the C—Cl bond in chlorobenzene is 1.69 Å while in $CH_3Cl$ it is 1.77 Å.

**Q. 40. Discuss the bimolecular displacement mechanism for nucleophilic aromatic substitution. Give evidence in support of the proposed mechanism.**

**Ans. Bimolecular displacement mechanism.** According to this mechanism the reaction is believed to proceed in two steps. The first step invovles the attack of the nucleophile on the carbon carrying the halogen. This results in the formation of carbanion which is stabilised by resonance. During the formation of intermediate carbanion, there is a change of hybridisation of the carbon invovled from *sp*$^2$ to *sp*$^3$. As a result the aromatic character of the benzene ring is destroyed. Consequently, this step is slow and hence is the rate determining step of the reaction.

In the second step, the carbon loses the halide ion to form the product in which aromaticity is regenerated. General bimolecular displacement mechanism is represented as :



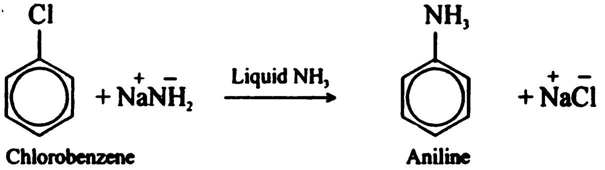
As two molecular species participate in the slow and rate determining step, it is a bimolecular reaction.

It may be mentioned that the above bimolecular mechanism is applicable mainly to activated aryl halides containing electron-withdrawing groups such as —$NO_2$, —C ≡ N, —COOH, etc. at the ortho and para positions.

**Evidence in support of this mechanism.** The rate determining step in bimolecular displacement reactions involves the formation of carbanion in which there is no cleavage of carbon-halogen bond. In other words, the rate of the reaction is independent of the strength of carbon-halogen bond. This has actually been verified by the absence of **element effect.** For example, there is only a little difference in the reactivity of aryl iodides, bromides, chlorides and flourides in nucleophilic aromatic substituion reactions. This lends supports to the proposed mechanism.

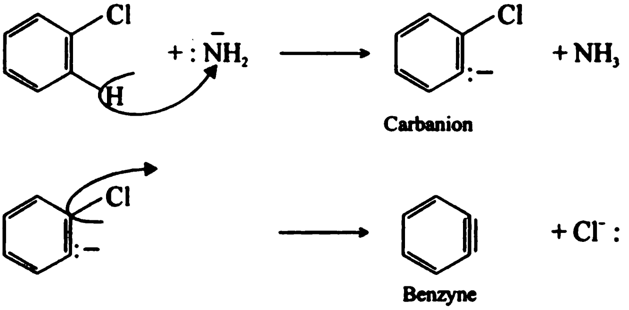
**Q. 41. Describe the benzyne mechanism for nucleophilic aromatic substituion. Give evidence in support of the mechanism.**

**Ans. Benzyne mechanism.** It has been found that electron-withdrawing groups activate the aryl halides towards bimolecular nucleophilic substituion reactions. In the absence of such activation, aryl halides can also be made to undergo nucleophilic substitution in the presence of strong nucleophiles. Thus, when chlorobenzene is treated with very strong nucleophile, *viz* amide ion, it is converted into aniline.

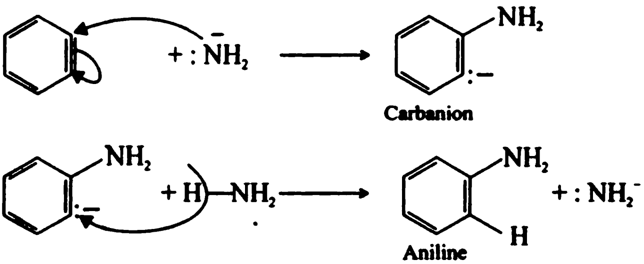


The above type of nucleophilic substitution reaction occurs by benzyne mechanism. In involves both **elimination** and **addition** as represented below:

**(I) Elimination.** In the elimiantion step, the amide ion abstracts a proton from one of the *ortho*-positions with respect to the halogen. The resulting carbanion loses the halide ion to form the benzyne, as illustrated below :

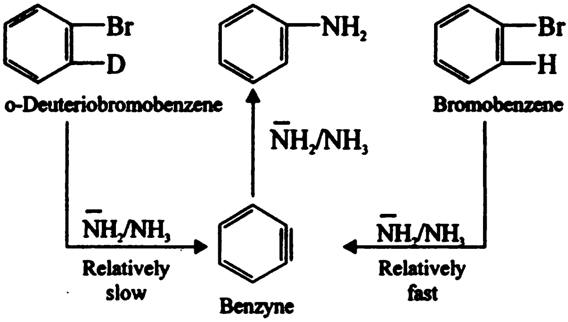


**(II) Addition.** In the addition step, the amide ion attacks the benzyne moelcule to form the carbanion which asbtracts a proton from solvent ammonia to yield the final substituted product. These reactions are give below :

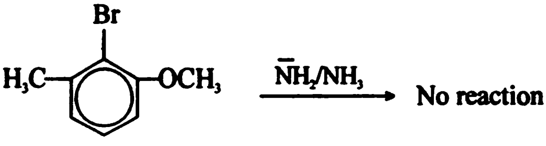


**Evidence in support of benzyne mechanism.** There is ample experimental evidence to prove the truth of benzyne mechanism of aromatic substitution.

(*i*) **Isotope effect.** The amination of *o*-deuteriobromobenzene is slower than that of bromobenzene. This observation indicates that the cleavage of *ortho* hydrogen is involved in the rate determining step during the elimination stage. This can further be illustrated as follows :

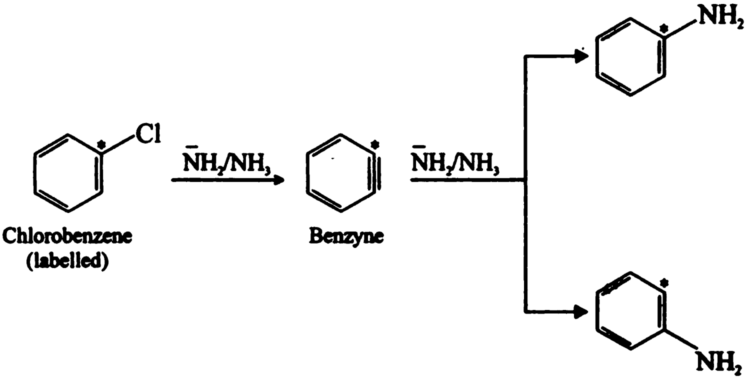


(*ii*) **Absence of ortho hydrogen.** Aryl halides containing two groups ortho to hydrogen, like 2-bromo-3-methylanisol, do not react at all. This is because benzyne intermediate cannot be formed due to the absence of ortho hydrogens with respect to the halogen.



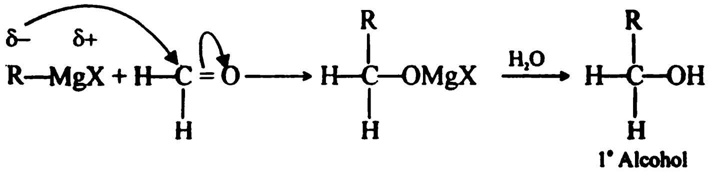
2-Bromo-3-methylanisol

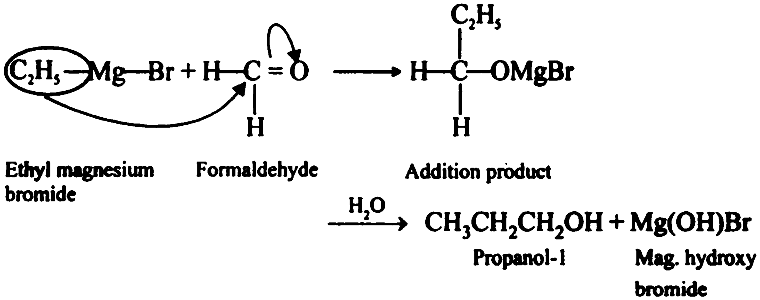
(*iii*) **Tracer studies.** When labelled chlorobenzene in which chlorine is linked to $C^{14}$ isotope $(C^*)$ is allowed to react with amide ion, two types of aniline are formed. In one type, the —$NH_2$ group is bonded to $C^{14}$ while in the other it is attached to carbon *ortho* to the labelled carbon. This can be explained as follows :



**Q. 42. Discuss the mechanism of formation of primary alcohol with the help of Grignard reagent.**

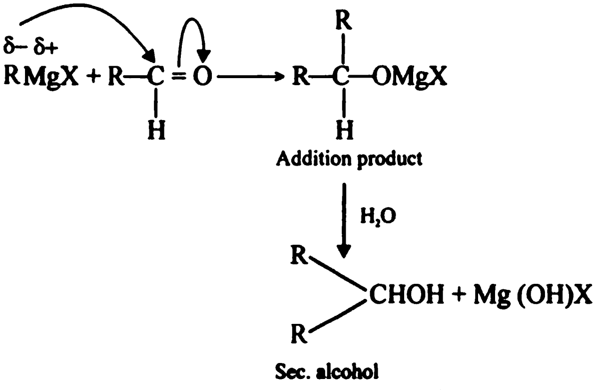
**Ans.** Primary alcohols can be otbained by treating formaldehyde with Grignard reagent followed by decomposition with dilute acid. Alkyl group possesses a slight negative charge. It is a attached to carbonyl carbon. The positive part —Mg X then attaches to oxygen.

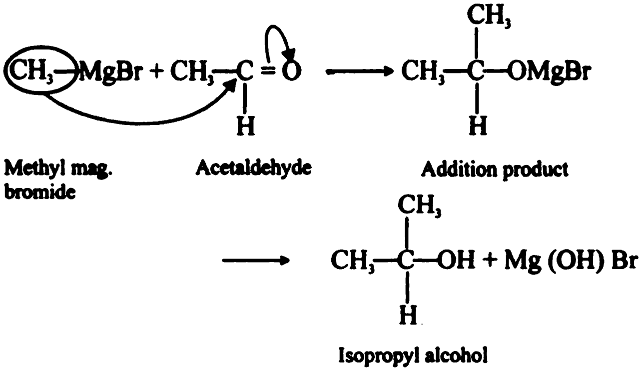




**Q. 43. Explain the mechanism of formation of secondary alcohol using Grignard reagent.**

**Ans.** Secondary alcohols can be obtained by the action of an aldehyde other than formaldehyde followed by hydrolysis. The mechanism is similar to that of formation of primary alcohol and is given as under :

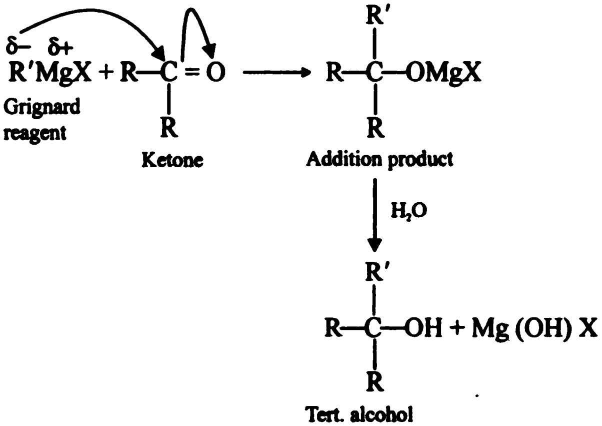




**Q. 44. Explain the mechanism of formation of tertiary alcohol from Grignard reagent.**

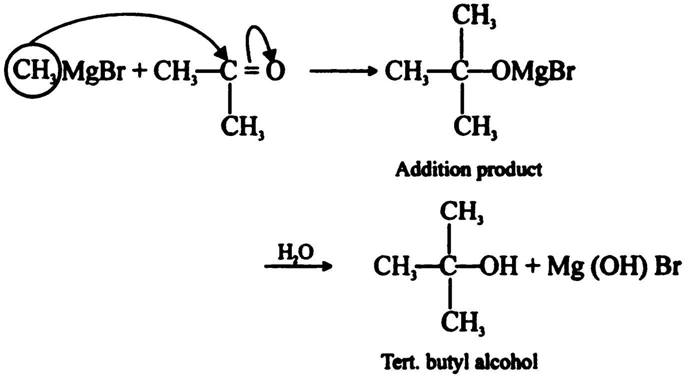
**Ans.** Tertiary alcohols can be obtained from Grignard reagents by :

The action of a ketone with Grignard reagent



$$R'MgX + R_2C{=}O \longrightarrow R_2C(R')OMgX \xrightarrow{H_2O} R_2C(R')OH + Mg(OH)X$$

R and R′ could be same or different.



$$CH_3MgBr + (CH_3)_2C{=}O \longrightarrow (CH_3)_3C{-}OMgBr \xrightarrow{H_2O} (CH_3)_3C{-}OH + Mg(OH)Br$$

**Q. 45. Describe the mechanism of the following reactions**

**(*i*) Reaction of an alcohol with organic acid**

**(*ii*) Reaction of an alcohol with acid halide or acid anhydride**

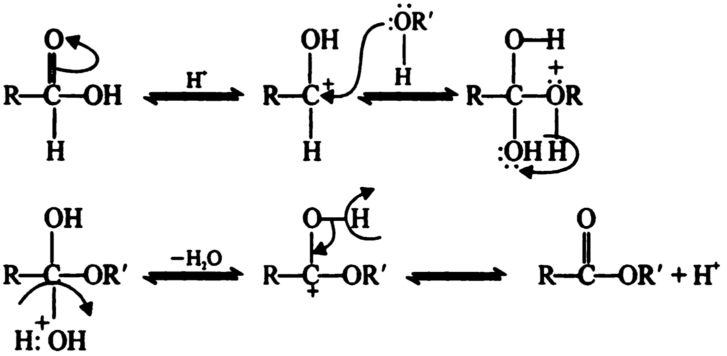
**Ans. (*i*) Reaction with organic acids.** Alcohols react with organic acids to form esters. This reaction is termed as *esterification*. It is generally carried out in the presence of concentrated sulphuric acid or dry hydorgen chloride.

$$\underset{\text{Acid}}{RCOOH} + \underset{\text{Alcohol}}{HOR'} \xrightleftharpoons{\text{Conc. } H_2SO_4} \underset{\text{Ester}}{RCOOR'} + H_2O$$

For example,

$$\underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Ethyl alcohol}}{HOC_2H_5} \rightleftharpoons \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + H_2O$$

**Mechanism.** The reaction is believed to proceed through the following mechanism :

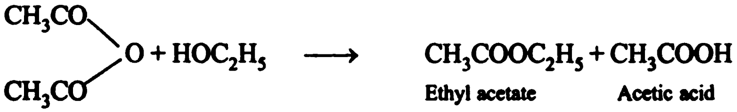


It has been proved beyond doubt by *isotopic tracer tehcnique* that the reaction involves the cleavage of O—H bond of alcohols and the C—OH bond of organic acids.

(*ii*) **Reaction with acid halides or acid anhydrides.** When alcohols are heated with an acid halide or acid anhydride, the hydrogen of —OH group is replaced by acyl group (RCO—) and, once again, an ester is formed. The reaction takes place more rapidly than esterification with carboxylic acids themselves. Thus, we have :

$$CH_3COCl + HOC_2H_5 \longrightarrow CH_3COOC_2H_5 + HCl$$

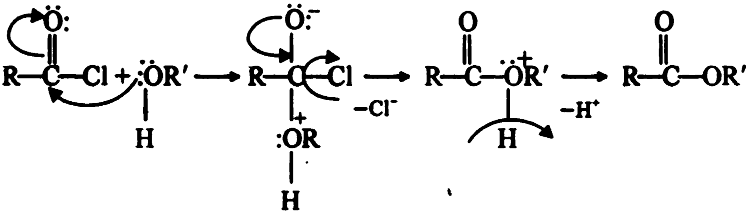
Acetyl chloride — Ethyl acetate



$$(CH_3CO)_2O + HOC_2H_5 \longrightarrow CH_3COOC_2H_5 + CH_3COOH$$

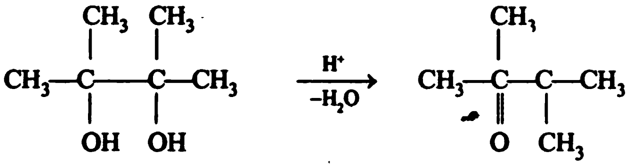
Acetic anhydride — Ethyl acetate — Acetic acid

**Mechanism.** The reaction mechanism may be depicted as follows :



**Q. 46. What is pinacol-pinacolone rearrangement ? Give its mechanism.**

**Ans.** It is found that on treatment with sulphuric acid, pinacol undergoes dehydration with moelcular rearrangement to form methyl *tert*-butyl ketone also known as **pinacolone.**



Pinacol

Methyl tert butyl ketone or Pinacolone

This reaction is known as pinacol-pinacolone rearrangement.

Many other vicinal glycols are now known to undergo similar acid-catalysed reactions. All these reactions are, therefore, collectively known as pinacol rearrangements.

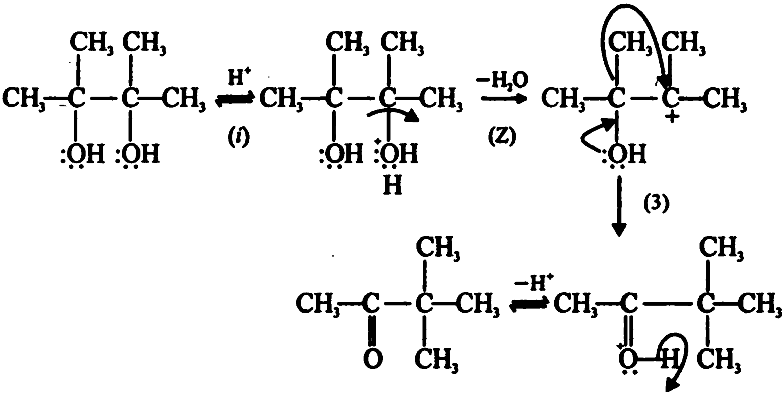
**Mechanism.** The pinacol rearrangement takes place through a stepwise mechansim as depicted below.

**Step 1.** Protonation of pinacol takes place.

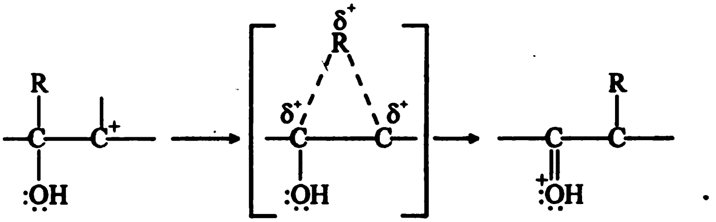
**Step 2.** Protonated pinacol loses a water moelcule to form carbonium ion.

**Step 3.** 1, 2 alkyl shift takes place forming a more stable carbonium ion.

**Step 4.** The carbonium ion loses a hydrogen ion to form the final product. These steps are illustrated as follows :



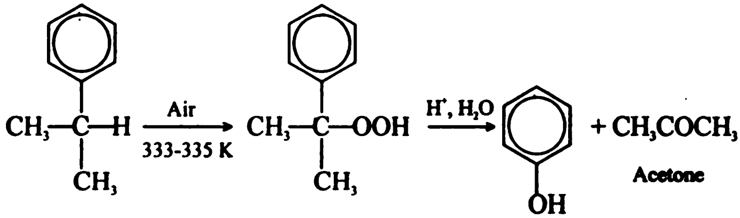
It may be emphasised that the migrating group (*i.e.* methyl group in the above example) is not completely detached from the carbon it is leaving till it has attached itself to the electron-deficient carbon as shown below.



*This would natrually mean that the migrating group in pinacol rearrangement will retain its configuration i.e.,* the new bond formed will have the same relative position as that held previously by the old bond.

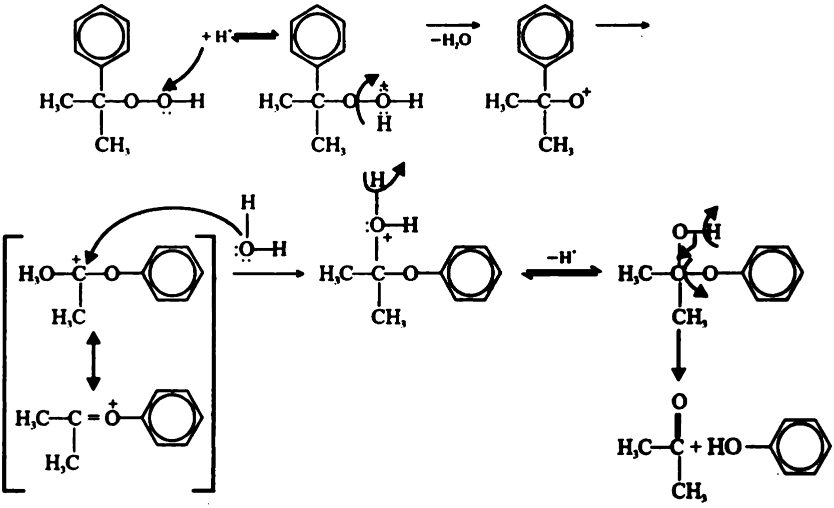
**Q. 47. Describe the mechanism of conversion of cumene hydroperoxide into phenol.**

**Ans.** Cumene is readily oxidised by air to form cumene hydroperoxide which is converted into phenol and acetone by treatment with an aqueous acid



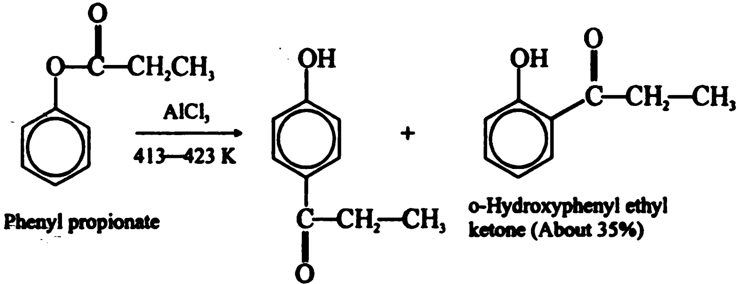
Cumene Cumene hydroperoxide Phenol

The mechanism of conversion of cumene hydroperoxide into phenol involves a sequence of five steps as shown below.



**Q. 48. Give the mechanism of Fries rearrangement.**

**Ans.** If an ester of a phenol is heated with aluminium chloride, the acyl group migrates from the phenolic oxygen to the *ortho* or *para* position on the ring. This is called **Fries rearrangement.** For example :



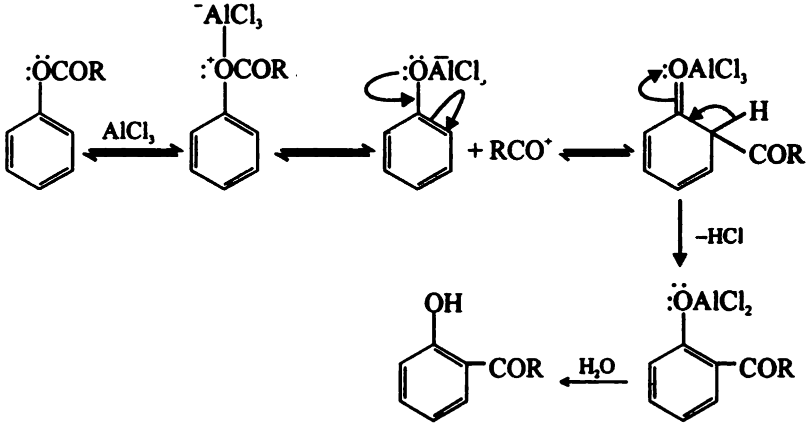
Phenyl propionate

*p*-Hydroxyphenyl ethyl ketone (About 50%)

o-Hydroxyphenyl ethyl ketone (About 35%)

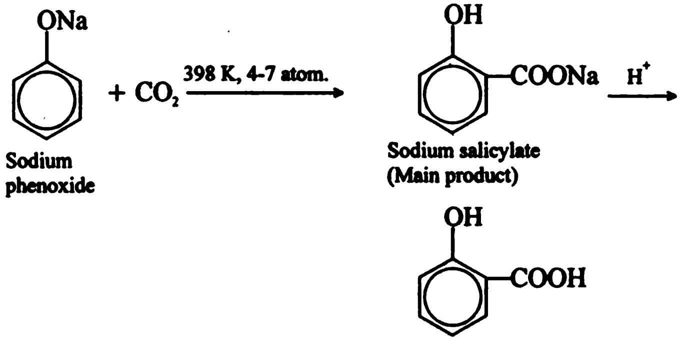
At low temperature, para product predominates while at high temperature ortho isomer is the main product.

**Mechanism.** Fries rearrangement probably involves the formation of an acylium ion ($RCO^+$) which then attacks the aromatic ring as in Friedel-Crafts acylation. The complete mechanism may be summed up as follows :



**Q. 49. Give the mechanism of Kolbe's reaction.**

**Ans. Kolbe's reaction.** When heated with carbon dioxide under pressure, sodium salts of phenols lead to the formation of salts of phenolic acids; the ortho isomers being the main product. For example, when sodium phenoxide is heated with carbon dioxide under pressure, sodium salicylate is obtained as the major product.

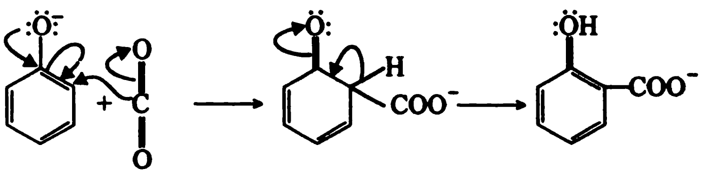


Sodium phenoxide

Sodium salicylate (Main product)

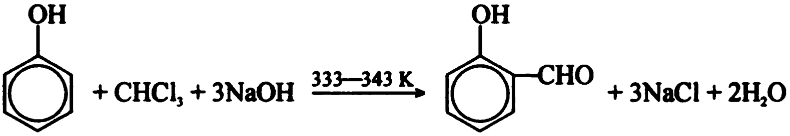
Salicylic acid

**Mechanism.** The mechanism of Kolbe's reaction is believed to involve the electrophilic attack by carbon dioxide on the phenoxide ion as shown below:



**Q. 50. What is Reimer-Tiemann reaction ? Give its mechanism.**

**Ans. Reimer-Tiemann reaction.** On heating with chloroform and an alkali, phenols are converted into phenolic aldehydes ; an aldehyde group is introduced in the aromatic ring generally in *ortho*-position to the —OH group. For example, when phenol is heated with chloroform and aqueous sodium hydroxide, salicylaldehyde is obtained as the main product alongwith a small amount of the *para* isomer.

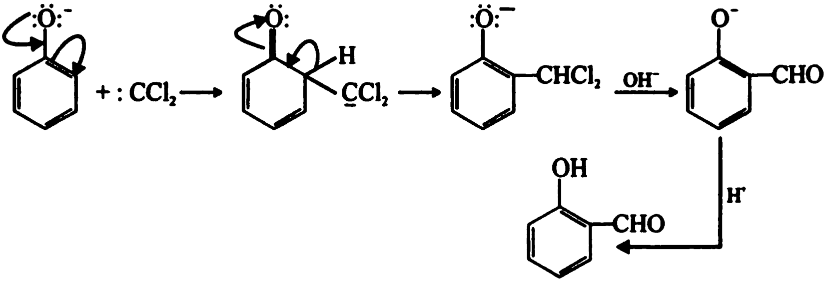


Salicylaldehyde
(Main product)

**Mechanism.** The mechanism of reaction consists of the electrophilic substition of phenoxide ion formed in solution by the action of alkali on phenol. The attacking electrophilic reagent is the electron deficient dichloromethylene; $CCl_2$: a **carbene** generated by the action of alkali on chloroform. Dichloromethylene is electrically neutral but it acts as an electrophilic reagent as the carbon atom present in it is surrounded by only six valence electross. The complete mechanism may be summed up as follows :

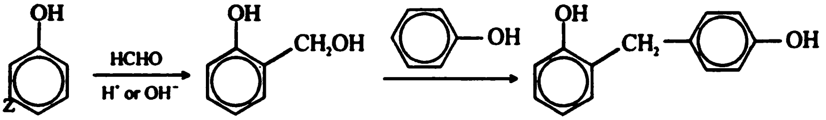
$$CHCl_3 + \bar{O}H \rightleftharpoons :\bar{C}Cl_3 + H_2O$$

$$:\bar{C}Cl_3 \longrightarrow :CCl_2 + Cl^-$$

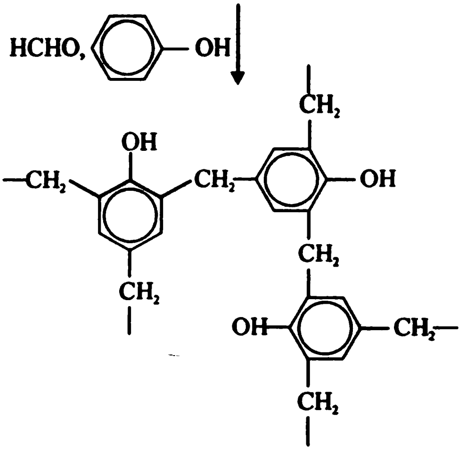


**Q. 51. Give the mechanism of reaction between phenol and formal dehyde.**

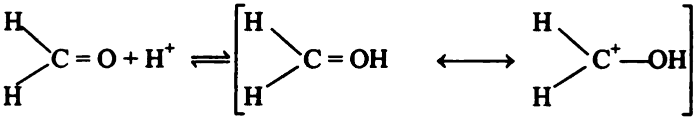
**Ans.** When phenol is treated with formaldehyde in the presence of alkali or acid a resinous polymer, called **bakelite**, is obtained. The process involves the interlinking of many phenol rings by $—CH_2—$ groups in ortho and para positions with respect to the phenolic group as depicted below :



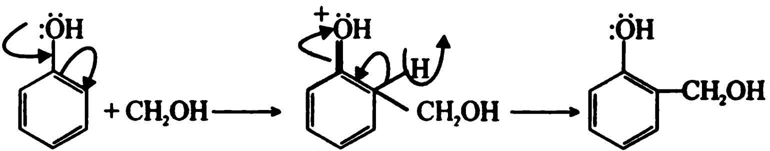
*o*-Hydroxymethyl-
phenol



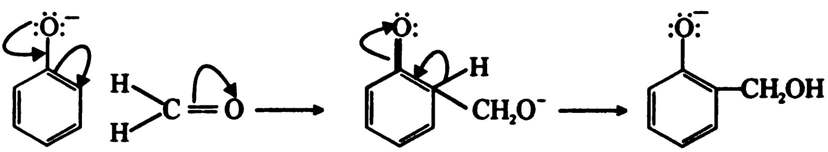
**Mechanism.** The mechanism of the first stage of reaction, *i.e.* formation of *o*-hydroxymethylphenol, involves the electrophilic substitution on the aromatic ring. The reaction may take place between phenol and protonated formaldehyde (*acid catalysis*) or between phenoxide ion and formaldehyde (*base catalysis*) as shown below :



Protonated formaldehyde



Acid catalysis



**Q. 52. Describe with mechanism the preparation of ether by dehydration of alcohols.**

**Ans. Dehydration of alcohols.** When an excess of alcohols is heated with concentrated sulphuric acid (or glacial phosphoric acid) at suitable temperature, two moles of the alcohol lose one mole of water to form a symmetrical ether. Thus, we have :

$$2\,ROH \xrightarrow[413\,K]{H_2SO_4} R{-}O{-}R + H_2O$$

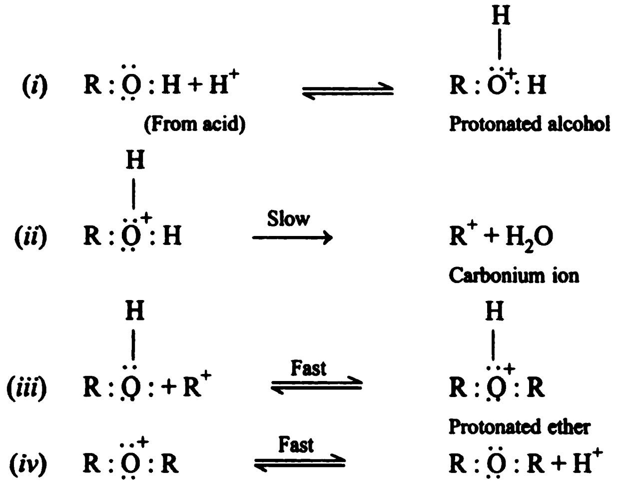
For example,

$$\underset{\text{Ethyl alcohol}}{2C_2H_5OH} \xrightarrow{H_2SO_4,\ 413\ K} \underset{\text{Diethyl ether}}{C_2H_5—O—C_2H_5} + H_2O$$

The formation of alkenes, which is a competing reaction is suppressed by the use of excess of alcohol and regulation of temperature.

**Mechanism.** The mechanism of formation of ethers involves nucleophilic substitution with the protonated alcohol as the substrate and a second molecule of alcohols as nucleophile. The reaction can follow either first order kinetics ($SN^1$) or second order kinetics ($SN^2$) depending upon the nature of alcohol used. In general, secondary and tertiary alcohols react by $SN^1$ mechanism. In both the mechanism, the first step involves the formation of protonated alcohol. This is followed by other steps which differ in the two mechanism as illustrated belows.

**$SN^1$ mechanisms :**



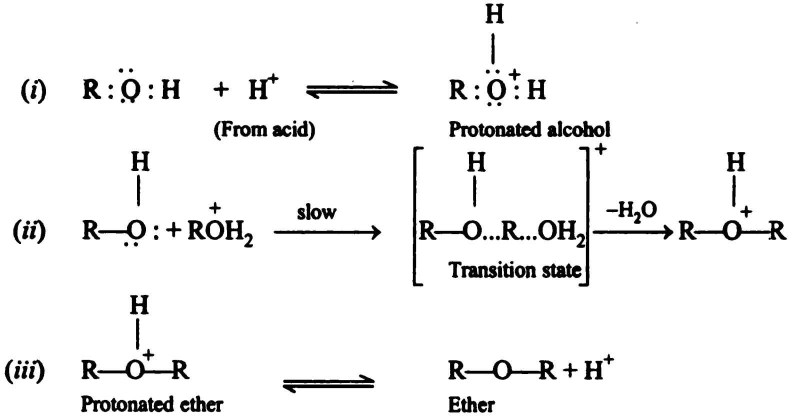
$$(i)\quad R:\underset{\cdot\cdot}{\ddot{O}}:H + \underset{\text{(From acid)}}{H^+} \rightleftharpoons \underset{\text{Protonated alcohol}}{R:\overset{H}{\overset{|}{\ddot{O}^+}}:H}$$

$$(ii)\quad R:\overset{H}{\overset{|}{\underset{\cdot\cdot}{O}^+}}:H \xrightarrow{\text{Slow}} \underset{\text{Carbonium ion}}{R^+ + H_2O}$$

$$(iii)\quad R:\overset{H}{\overset{|}{\underset{\cdot\cdot}{\ddot{O}}}}: + R^+ \overset{\text{Fast}}{\rightleftharpoons} \underset{\text{Protonated ether}}{R:\overset{H}{\overset{|}{\underset{\cdot\cdot}{O}^+}}:R}$$

$$(iv)\quad R:\underset{\cdot\cdot}{\ddot{O}^+}:R \overset{\text{Fast}}{\rightleftharpoons} R:\underset{\cdot\cdot}{\ddot{O}}:R + H^+$$

**$SN^2$ mechanism**



$$(i)\quad R:\underset{\cdot\cdot}{\ddot{O}}:H + \underset{\text{(From acid)}}{H^+} \rightleftharpoons \underset{\text{Protonated alcohol}}{R:\overset{H}{\overset{|}{\underset{\cdot\cdot}{O}^+}}:H}$$

$$(ii)\quad R—\overset{H}{\overset{|}{\underset{\cdot\cdot}{O}}}: + R\overset{+}{O}H_2 \xrightarrow{\text{slow}} \left[\underset{\text{Transition state}}{R—\overset{H}{\overset{|}{O}}...R...OH_2}\right]^+ \xrightarrow{-H_2O} R—\overset{H}{\overset{|}{O^+}}—R$$

$$(iii)\quad \underset{\text{Protonated ether}}{R—\overset{H}{\overset{|}{O^+}}—R} \rightleftharpoons \underset{\text{Ether}}{R—O—R + H^+}$$

**Q. 53. Discuss the mechanism of cleavage of ethers by acids.**

**Ans. Cleavage by acids.** On heating with concentrated acids (particularly hydriodic acid or hydrobromic acid), the ether linkage breaks to form an alcohol or phenol and an alkyl halide.

$$\text{R—O—R}' + \text{HX} \longrightarrow \text{RX} + \text{R}'\text{OH}$$

For example,

$$\underset{\text{Ethyl ether}}{C_2H_5\text{—O—}C_2H_5} + \text{HI} \longrightarrow \underset{\text{Ethyl iodide}}{C_2H_5I} + \underset{\text{Ethyl alcohol}}{C_2H_5OH}$$

The order of reactivity of halogen acids in the reaction is :

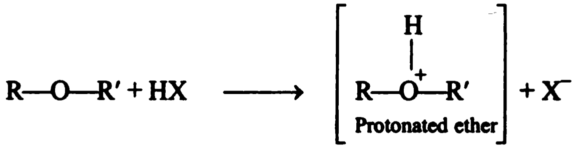
$$\text{HI} > \text{HBr} > \text{HCl}$$

In the presence of excess acids, the alcohol formed reacts with halogen acid to form alkyl halide. Thus in that case the overall reaction may be depicted as :

$$\text{R—O—R}' + 2\text{HX} \longrightarrow \text{RX} + \text{R}'\text{X} + H_2O$$

The **mechanism** of the reaction is believed to be as follows :

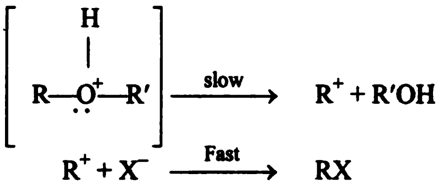
(*a*) Initially the ether reacts with the acid to form a protonated ether as shown below.



$$\text{R—O—R}' + \text{HX} \longrightarrow \left[\underset{\text{Protonated ether}}{\text{R—}\overset{\overset{\text{H}}{|}}{\overset{+}{\text{O}}}\text{—R}'}\right] + \text{X}^-$$

(*b*) The protonated ether is then attacked by the nucleophilic halide ion by $SN^1$ or $SN^2$ mechanism depending upon the nature of R and R′ groups and the reaction conditions. Presence of primary alkyl groups favours $SN^2$ mechanism whereas secondary or tertiary alkyl groups tend to react by $SN^1$ mechanism. Thus, we have :

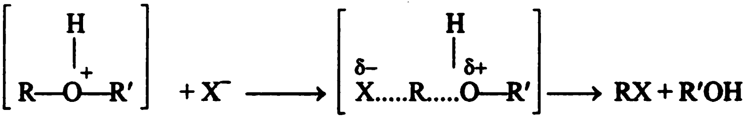
**$SN^1$ mechanism**



$$\left[\text{R—}\overset{\overset{\text{H}}{|}}{\overset{+}{\ddot{\text{O}}}}\text{—R}'\right] \xrightarrow{\text{slow}} \text{R}^+ + \text{R}'\text{OH}$$

$$\text{R}^+ + \text{X}^- \xrightarrow{\text{Fast}} \text{RX}$$

**$SN^2$ mechanism**



$$\left[\text{R—}\overset{\overset{\text{H}}{|}}{\overset{+}{\text{O}}}\text{—R}'\right] + \text{X}^- \longrightarrow \left[\overset{\delta-}{\text{X}}\text{.....R.....}\overset{\overset{\text{H}}{|}}{\overset{\delta+}{\text{O}}}\text{—R}'\right] \longrightarrow \text{RX} + \text{R}'\text{OH}$$

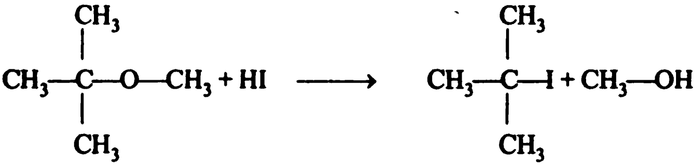
**Point of cleavage.** In case of mixed ethers, the alkyl halide produced depends upon the nature of groups attached to oxygen.

(*i*) If one group is methyl and the other a *primary* or *sec*-alkyl group, it is methyl halide which is produced. For example,

$$CH_3—O—C_2H_5 + HI \longrightarrow CH_3I + C_2H_5OH$$

It is assumed that the reaction proceeds by $SN^2$ mechanism in this case and the halide ion attaches itself to a smaller alkyl group on steric consideration.

(*ii*) When the ether is methyl-*tert*-alkyl ether, we get a *tert*-alkyl halide and methyl alcohol. For example,



$$CH_3—C(CH_3)_2—O—CH_3 + HI \longrightarrow CH_3—C(CH_3)_2—I + CH_3—OH$$

Methyl *tert*-butyl ether *tert*-Butyl iodide

This can be explained by $SN^1$ methchanism, the carbonium ion produced being tert-alkyl because it is more stable than primary carbonium ion.

**Cleavage of alkyl-aryl and diaryl ethers.** In case of an alky-aryl ether, the cleavage of *aromatic* carbon-oxygen bond is much more difficult than the cleavage of *alkyl* carbon-oxygem bond. Thus, the cleavage of such ethers by halogen acids yields a phenol and an alkyl halide. For example,

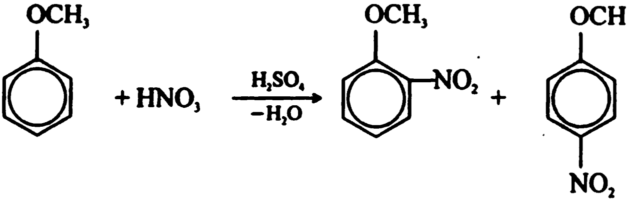
Anisole Phenol

*Diaryl ethers* are very diffciult to cleave as both carbons attached to oxygen are part of aromatic rings. For example, diphenyl ether is not cleaved by HI even at 525 K.

**Q. 54. Explain the ortho-para directing nature of alkoxy group.**

**Ans.** Aromatic ethers such as anisole and phenetole undergo aromatic electrophilic substitution like nitration, halogenation etc. Alkoxy group is moderately activating and *ortho-para* directing.

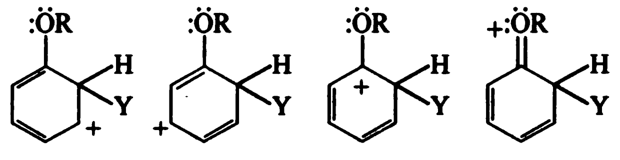
For example,



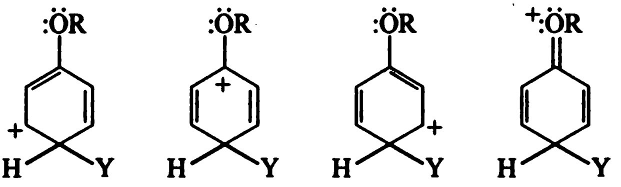
*o*-and *p*-Ntiroanisoles

Alkoxy group has –I inductive effect and + M resonance effect. The latter effect being stronger, there is greater electron density on the ring. This leads to a faster electrophilic substitution.

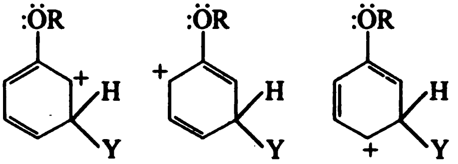
The *ortho-para* directing effect may be explained in terms of the contributing structures of the carbonium ions formed by ortho, para and meta attacks as shown below, taking $Y^+$ as the electrophile :



I*a* I*b* I*c* I*d*



II*a* II*b* II*c* II*d*

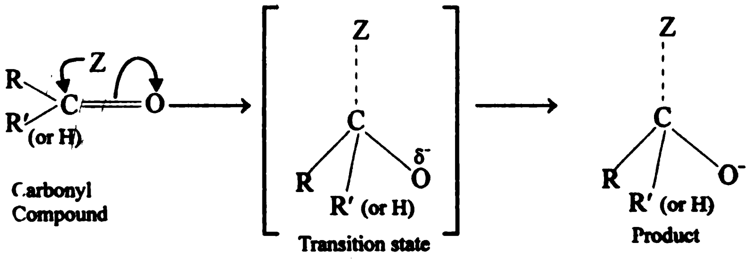


III*a* III*b* III*c*

Carboninum ions formed by ortho and para attacks are more stable than the meta carbonium ion, due to the additional contributions by particularly stable contributing structures I*d* and II*d* respectively. As a result, ortho and para carbonium ions are formed in preference to meta ion so that substitution occurs mostly at ortho and para positions.

**Q. 55. What is a nucleophilic addition reaction ? Describe the mechanism of nucleophilic addition to a carbonyl compound.**

**Ans.** A nucleophilic addition reaction is a reaction in which the addition of a molecule to the carbonyl compound takes place with the initiation of the negative part of the adding molecule *e.g.*, CN in HCN adds first to the positive carbon of the carbonyl group, followed by the attachment of the positive part of the adding moelcule to the negative oxygen of the carbonyl group. The additon of a nucleophile (:Z) to a carbonyl compound may be represented as shown in Figure below :

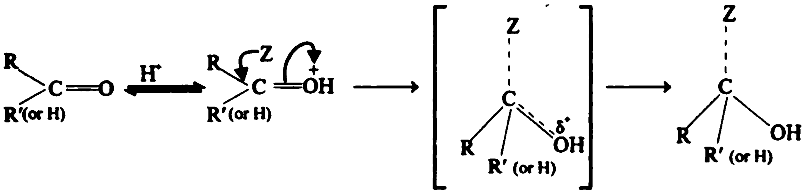


Mechanism of nucleophilic addition

Carbonyl compound has a trigonal configuration. In the transition state, it starts acquiring $sp^3$ configuration which is accomplished in the final product. Ability of oxygen to acquire negative charge is the reason for nucleophilic reactions in carbonyl compounds.

**Q. 56. Why are nucleophilic addition reactions of carbonyl compounds catalysed by protonic acids ?**

**Ans.** It has been observed that a strong nucleophile gets attached to the carbonyl group easily but some difficulty is felt by the weak nucleophile in attaching itself to the carbonyl group. In such cases, the presence of a protonic acid containing ($H^+$) proves helpful as illutrated below.

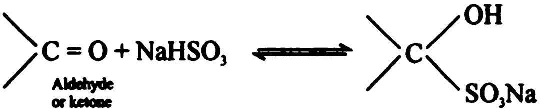


Role of the acid catalyst in nucleophilic reaction.

The proton from the acid attaches itself to the negative oxygen. This paves the way for the attachment of even the weakest nucleophile. The energy of activation for nucleophilic attack is decreased thereby facilitating the reaction.

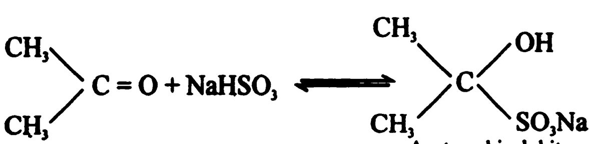
**Q. 57. Describe the mechanism of addition of sodium bisulphite to the carbonyl compound. What is the untility of this reaction ?**

**Ans.** All aldehydes and ketones react with a saturated solution of sodium bisulphite to form the solid bisulphite compound



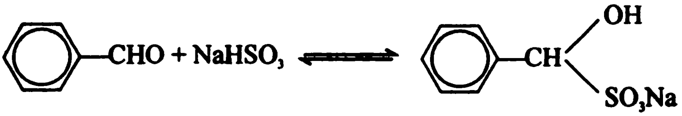
Aldehyde or ketone

Bisulphite compound



Acetone

Acetone bisulphite

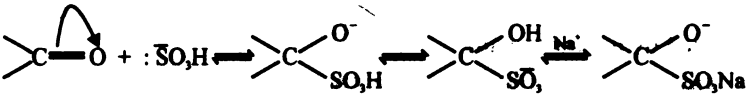


Benzaldehyde bisulphite

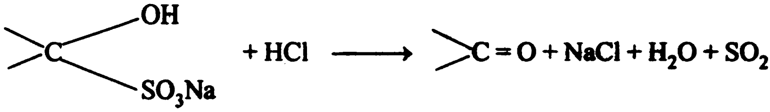
Ketones containing bulky groups fail to give the reaction due to steric hindrance.

**Mechanism of the Reaction**

The reaction is initiated by the attack of the bisulphite ion on the carbonyl carbon followed by the shifting of H to carbonyl oxygen. The complete mechansim is illustrated hereunder :

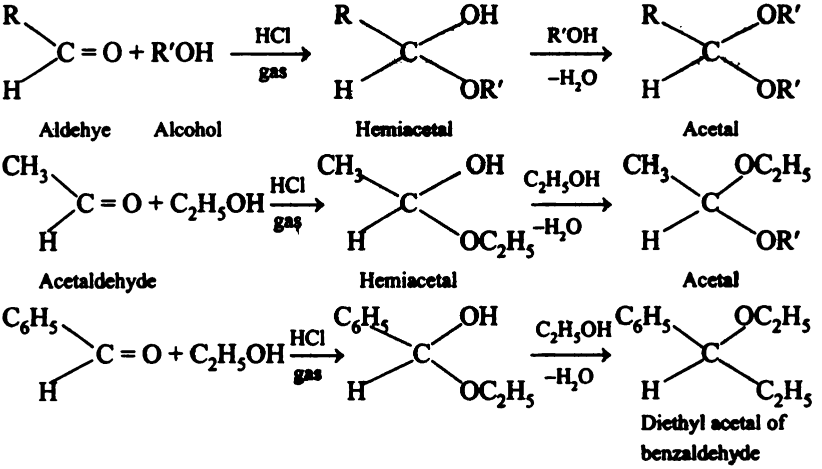


**Utility of the Reaction.** The bisulphite compound as obtained above gets decomposed on treatment with dil. HCl giving back the aldehyde or ketone. Thus reaction can be used to purify or separate the carbonyl compound from impurities.



**Q. 58. Describe with mechanism the addition of alcohol to carbonyl compounds.**

**Ans.** Alcohols added to aldehydic compounds form acetals. Generally the reaction takes place in two steps. In the first step, one molecule of alcohol reacts with the carbonyl compound to form hemiacetal which is generally unstable. Therefore, hemiacetal reacts with the second molecule of alcohol to form acetal. The reaction takes place in the presence of HCl gas. Ketones do not participate in such a reaction.

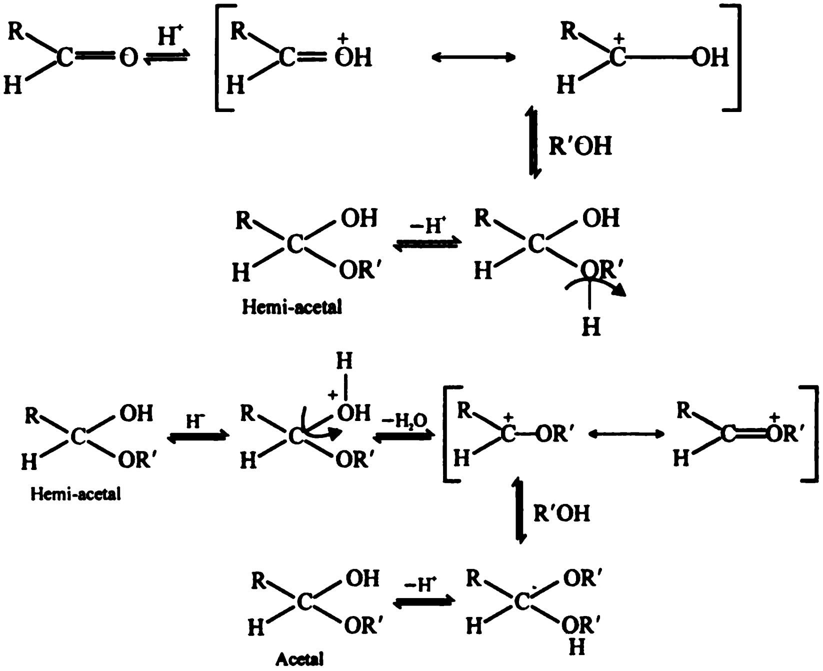


R and R′ in the above reaction stand for alkyl groups.

**Mechanism**

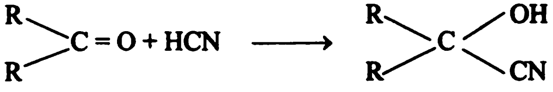
**Step 1.** A molecule of alcohol adds to the carbonyl group to form a hemiacetal. This is made possible by the presence of $H^+$ as it produces a positive centre on the carbonyl carbon. Alcohol molecule approaches this positive centre. $H^+$ is regenerated in this step.

**Step 2.** The proton now removes the —OH group from the hemiacetal, thus reproducing positive centre. This enables the second alcohol molecule to attach itself to the hemiacetal. Finally, the proton is again given out. These steps are illustrated below :



**Q. 59. Illustrate with mechanism the addition of hydrogen cyanide on the carbonyl compounds.**

**Ans.** Hydrogen cyanide adds to aldehydes and ketones to form compounds know as *cyanohydrins*. Cyanohydrin contains an cyano group and a hydroxy group.



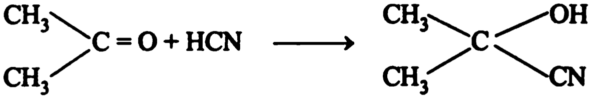
(or H)

Aldehyde or ketone

Cyanohydrin

Acetaldehyde

Acetaldehyde cyanohydrin



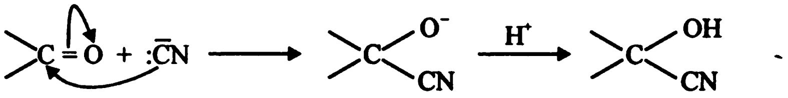
Acetone

Acetone cynohydrin

**Mechanism of the Reaction**

**Step 1.** Cyanide ion attaches itself to the carbonyl carbon by nucleophilic addition process.

**Step 2.** $H^+$ then attaches itself to the oxygen, which carries a negative charge, to produce the final product.



Cyanohydrins are important compounds as they yield α-hydroxy carboxylic compounds

$$CH_3CH(OH)CN \xrightarrow{\text{Hydrolysis}} CH_3CH(OH)COOH$$

Acetaldehyde cyanohydrin → Lactic acid

**Q. 60. Describe with mechanism the reaction of ammonia derivatives with the carbonyl compounds.**

**Ans.** Derivatives of ammonia *viz* hydroxylamine, hydrazine, phenyl hydrazine and semicarbazide react with the carbonyl compounds to give oximes, hydrazones, phenyl hydrazones and semi-carbazones respectively, as shown below :

(*i*) $>C=O + H_2N\,OH \longrightarrow >C=NOH + H_2O$

Hydroxyl amine — Oxime

(*ii*) $>C=O + H_2NNH_2 \longrightarrow >C=NNH_2 + H_2O$

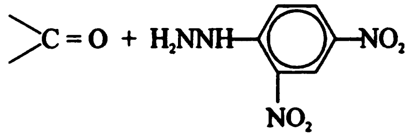
Hydrazine — Hydrazone

(*iii*) $>C=O + H_2N\,NH\,C_6H_5 \longrightarrow >C=N\,NH\,C_6H_5 + H_2O$

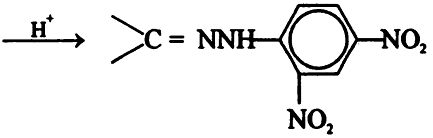
Phenyl hydrazine — Phenyl hydrazone

(*iv*) $>C=O + H_2N\,NHCONH_2 \longrightarrow >C=N\,NHCONH_2 + H_2O$

Semicarbazide — Semicarbazone

(*v*)


2 : 4 Dinotro phenyl hydrazine

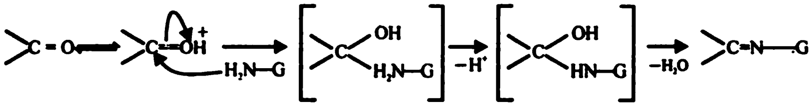


2, 4, Dinitro phenylhydrazone

Reaction (*v*) is particularly used to identify the carbonyl group as it gives yellow derivative *viz* 2, 4 dinitro phenylhydrazone. 2, 4 dinitrophenyl hydrazine is abbreviated as DNPH. Hence this reaction is also known as DNPH Test.

**Mecahnism of Reaction.** Ammonia derivatives may be represented by $H_2NG$. Various steps involved in the reaction may be written as under.

**Step 1. Attack of Proton.** The proton from the acid which is used to catalyse the reaction attaches itself to the electron rich carbonyl oxygen atom as shown below.



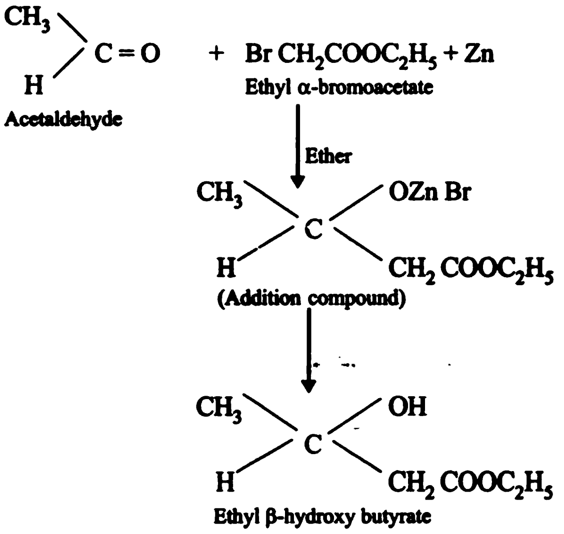
**Step 2. Attack of Nucleophile.** The ammonia derivative in which nitrogen has a lone pair of electrons acts as the nucleophile, attaches itself to the carbonyl carbon atom. This results in a positive charge on nitrogen atom.

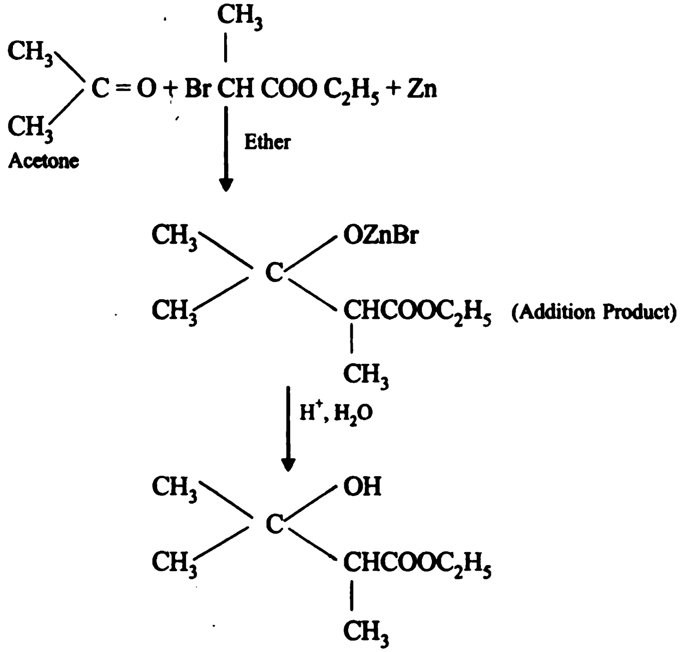
**Step 3. Loss of Proton.** The intermediate formed in step 2 is unstable and loses a proton

**Step 4. Loss of Water Molecule.** The product formed in step 3 loses a water molecule to form a crystalline compound having a double bond between carbonyl carbon and nitrogen ammonia derivative.

**Q. 61. Give account of Roformatsky reaction alongwith its mechanism.**

**Ans.** Reformatsky reaction is performed in order to obtain β-hydroxy esters from aldehydes and ketones using α-bromo ester and zinc in the presence of dry ether. The reactions with an aldehyde and a ketone are depicted below.





Ethyl, 2, 3-dimethyl 3-hydroxy butyrate.

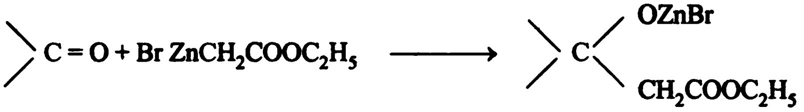
**Mechanism of the Reaction**

The following mechanism has been proposed for the Reformatsky reaction.

**Step 1.** Zinc reacts with the ester to form an organometallic compound

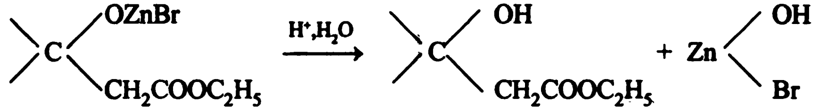
$$Zn + BrCH_2COOC_2H_5 \xrightarrow{\text{Ether}} BrZnCH_2COOC_2H_5$$

**Step 2.** Organometallic compound reacts with the carbonyl compound by nucleophilic addition.



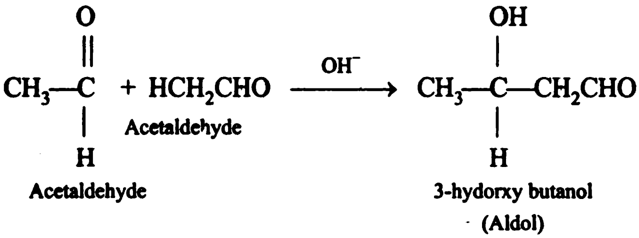
Addition Product

**Step 3.** The addition product formed above gets hydrolysed to give the final product.



**Q. 62. Describe the mechanism of Aldol condensation.**

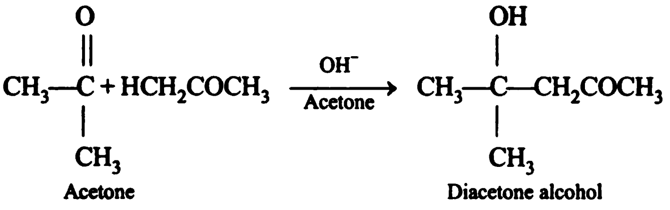
**Ans.** Two molecules of an aldehyde or a ketone having α-hydrogen atom react in the presence of dil. alkali to from β-hydroxyaldehyde or β-hydroxy ketone.



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle H}{|}}{C}} + \underset{\text{Acetaldehyde}}{HCH_2CHO} \xrightarrow{OH^-} CH_3-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-CH_2CHO$$

Acetaldehyde

3-hydorxy butanol (Aldol)



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} + HCH_2COCH_3 \xrightarrow[\text{Acetone}]{OH^-} CH_3-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_2COCH_3$$

Acetone

Diacetone alcohol

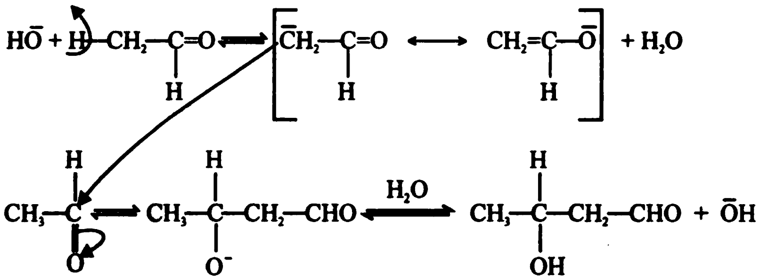
**Mechanism**

**Step 1. Formation of carbanion.** The hydroxide ion from a base removes the proton from the α-carbon atom to give a carbanion. This carbanion gets resonance stabilised.

**Step 2. Attack by carbanion.** The carbanion thus formed attacks the second molecule by nucleophilic addition mechanism to form an alkoxide ion.

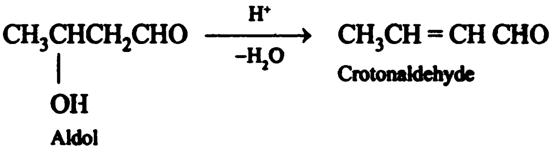
**Step 3. Attachment of a hydrogen.** The alkoxide ion attaches a hydrogen atom removed from water molecule.

These steps as mentioned above are sketched as under :



It may be noted that aldol condensation is a property of aldehydes and ketones having hydrogen atoms attached to α-carbon atoms. Hence this reaction is not observed with compounds like formaldehyde, benzaldehyde which don't process α-hydrogen atoms.

Another fact which may be noted is, that β-hydroxy aldehydes and β-hydroxy ketones which are obtained in the base-catalysed reaction easily get dehydrated on warming with dilute acids to form α-β unsaturated carbonyl compounds.



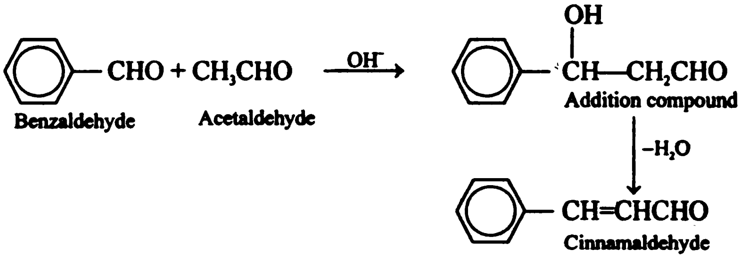
$$\underset{\text{Aldol}}{CH_3\underset{\underset{\displaystyle OH}{|}}{C}HCH_2CHO} \xrightarrow[-H_2O]{H^+} \underset{\text{Crotonaldehyde}}{CH_3CH=CH\,CHO}$$

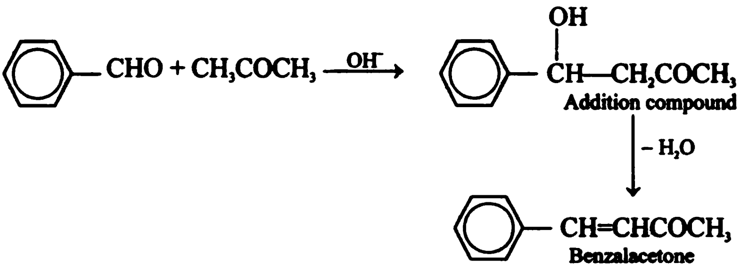
This is the reason we avoid obtaining aldol by acid-catalysed reaction, although, in principle, it is possible to carry out aldol condensation in the presence of an acid.

Aldol reaction provides an important tool in the hands of a chemist to synthesize α, β unsaturated compounds.

**Q. 63. Briefly discuss Claisen-Schmidt reaction.**

**Ans.** This reaction may be considered as a special case of crossed aldol condensation. It involves condensation of aromatic carbonyl compound with an aliphatic carbonyl compound in the presence of a base. Hydroxy derivative first obtained loses a water molecule to yield α, β unsaturated aldehyde or ketone. For example:





**Mechanism.** It involves the following steps :

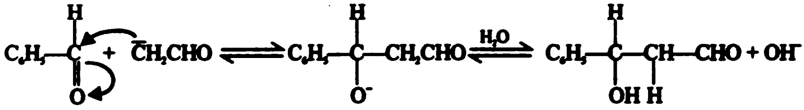
**Step 1. Formation of carbanion.** α-hydrogen of the aliphatic carbonyl compound is removed by the hydroxide ions, thus creating carbanions.

**Step 2. Attack by carbanion on the aromatic carbonyl compound.** The carbanion obtained in step 1 attacks the aromatic carbonyl group by nucleophilic addition mechanism to form the alkoxide ion.

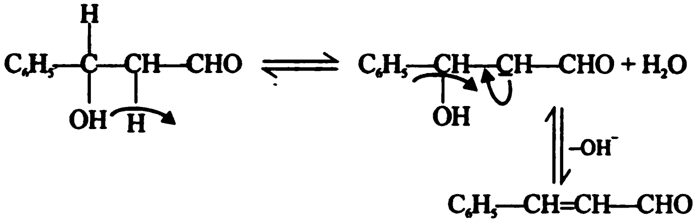
**Step 3. Attachment of a Proton.** The alkoxide ion removes a proton from water and attaches itself to give β-hydroxy compound.

**Step 4.** α-hydrogen atom in the hydroxy compound, is removed by the base followed by the removal of—OH group, thus removing a water molecule finally. The sequence of the above steps in shown below.

$$HO^- + H—CH_2—CHO \rightleftharpoons \bar{C}H_2—CHO + H_2O$$

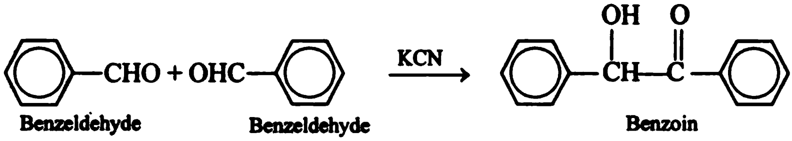


$$C_6H_5—\overset{H}{\underset{O}{\overset{|}{\underset{\|}{C}}}} + \bar{C}H_2CHO \rightleftharpoons C_6H_5—\overset{H}{\underset{O^-}{\overset{|}{\underset{|}{C}}}}—CH_2CHO \overset{H_2O}{\rightleftharpoons} C_6H_5—\overset{H}{\underset{OH}{\overset{|}{\underset{|}{C}}}}—\underset{H}{\underset{|}{C}}H—CHO + OH^-$$



**Q. 64. Write a note on Benzoin Condensation.**

**Ans.** It has been explained earlier that aldol condensation is a property of carbonyl compounds containing α-hydrogen atoms. Thus benzaldehyde which does not contain α-hydrogen is not capable of giving this reaction. Such aromatic aldehydes condense in the presence of KCN (which acts as a base) to yield *benzoins*. This reaction is known as *Benzoin condensation.*

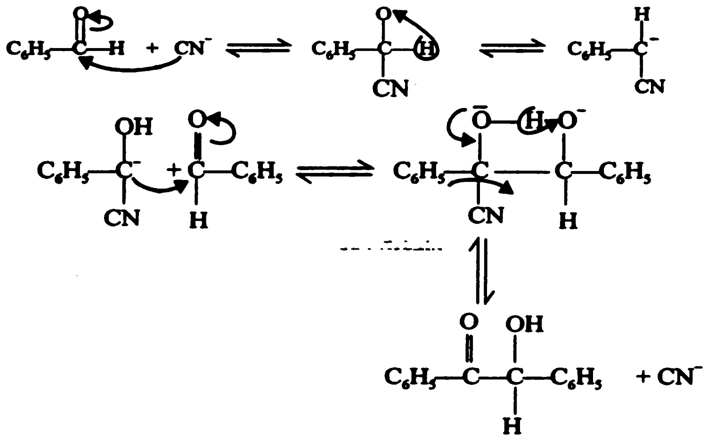


**Mechanism.** It involves the following steps :

**Step 1. Formation of a carbanion.** Direct formation of a carbanion is not possible, as there are no α-hydrogen atoms. Hence this carbanion formation takes place after some rearrangement. It involves attachment of CN– to the carbonyl carbon with simultaneous shifting of electrons to oxygen. Hydrogen is then shifted from carbon to oxygen. This results in the formation ofcarbanion.

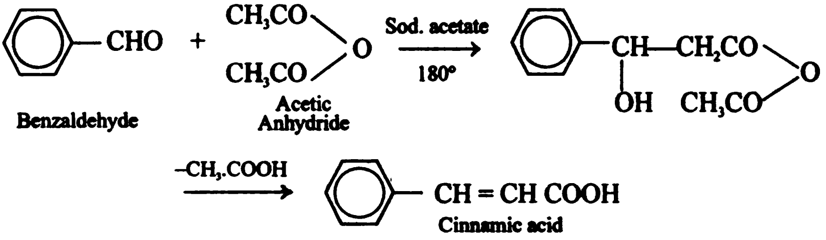
**Step 2. Attack of the carbanion (nucleophile) on the second molecule.** Carbanion obtained in step 1 above attacks the carbonyl group of the second molecule forming an addition product, an alkoxide.

**Step 3. Loss of cyanide ion.** The alkoxide loses cyanide ion with simultaneous loss ofhydrgen from the same carbon atom. Hydrogen combines with the oxygen on the neighbouring carbon atom giving the final products. The sequence of steps is illustrated below :



**Q. 65. Write a note on Perkin's Reaction.**

**Ans.** It is a kind of aldol condensation in which an aromatic aldehyde condenses with acetic anhydride in the presence of sodium acetate to yield unsaturated carboxylic acid. Thus benzaldehyde on treatment with acetic anhydride and sodium acetate yields cinnamic acid



**Mechanism.** It involves the following steps :

**Step 1. Formation of a carbanion.** Acetic anhydride in the presence of acetate ion loses a hydrogen ion forming a carbanion.

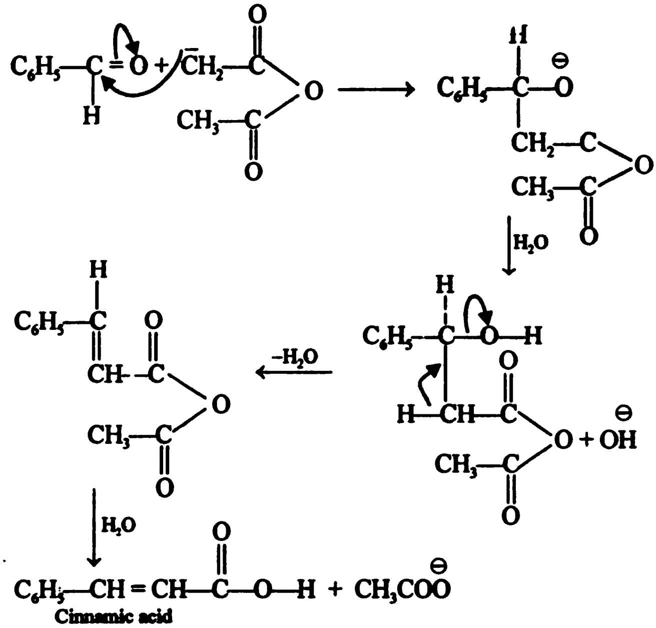
**Step 2. Attack of the carbanion on the carbonyl group.** Carbanion obtained in the above step attacks the carbonyl carbon atom (nucleophilic attack) forming an alkoxide.

**Step 3. Protonation of the alkoxide ion.** Alkoxide gets protonated to form an aldol type compound.

**Step 4. Dehydration.** The hydroxy group and neighbouring hydrogen are removed as water forming an unsaturated product.

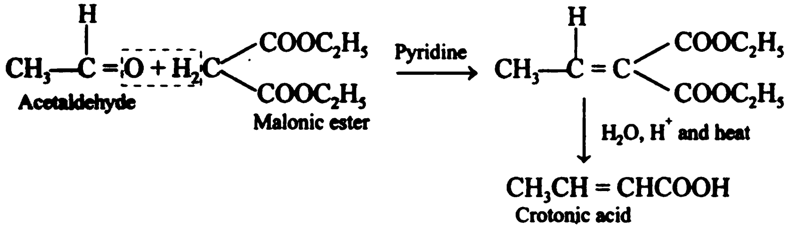
**Step 5. Hydration.** The alkenic compound obtained above gets hydrolysed giving the final product.

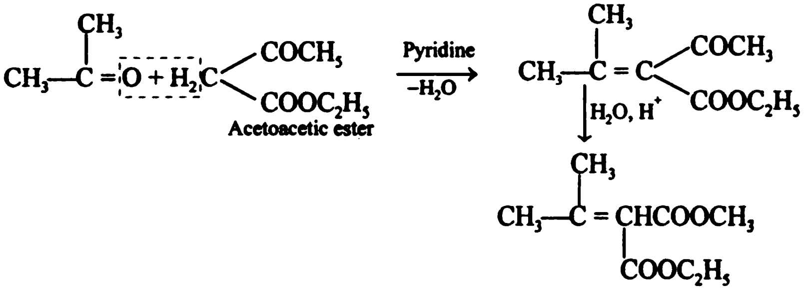
The above steps are illustrated as given below.



**Q. 66. Write a note on Knoevenagal reaction.**

**Ans.** An aldehyde or a ketone on condensation with a compound having an active methylene group (such as malonic ester or acetoacetic ester) in the presence of a base such as pyridine gives an unsaturated compound.





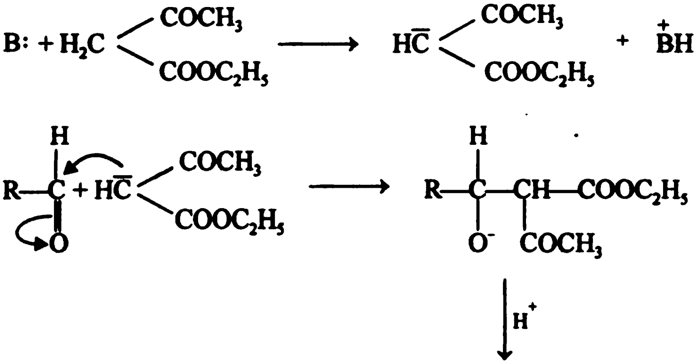
**Mechanism.** Mechanism of the reaction is expained by taking the example of reaction between an aldehyde and aceto acetic ester.

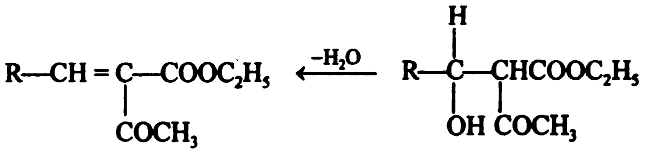
**Step 1. Formation of a carbanion.** The base B : attracts a hydrogen from the acetoacetic ester forming a carbanion.

**Step 2. Attack by the carbanion.** The carbanion as obtained above attacks the carbonyl carbon by nucleophilic chains forming an alkoxide ion.

**Step 3. Protonation.** The alkoxide draws a proton to convert itself into a hydroxy compound.

**Step 4. Dehydration.** Hydroxy and hydrogen from the neighbouring carbon atoms are removed as water, and an unsaturated compound is obtained. The above steps are illustrated as follows :

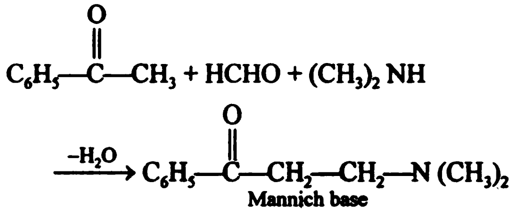




$$R{-}CH{=}\underset{\displaystyle COCH_3}{C}{-}COOC_2H_5 \xleftarrow{-H_2O} R{-}\overset{\displaystyle H}{\underset{\displaystyle OH}{C}}{-}\underset{\displaystyle COCH_3}{C}HCOOC_2H_5$$

### Q. 67. Write a note on Mannich Reaction.

Ans. Formaldehyde on condensation with an amine and an active methylene compound gives a product which is called *Mannich Base.* This reaction is called Mannich reaction.



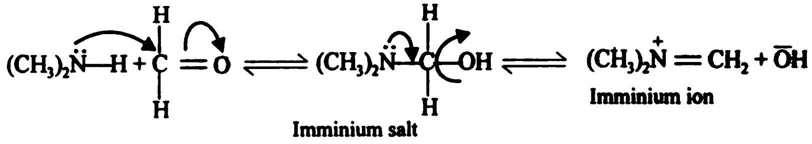
$$C_6H_5{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}CH_3 + HCHO + (CH_3)_2NH \xrightarrow{-H_2O} \underset{\text{Mannich base}}{C_6H_5{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}CH_2{-}CH_2{-}N(CH_3)_2}$$

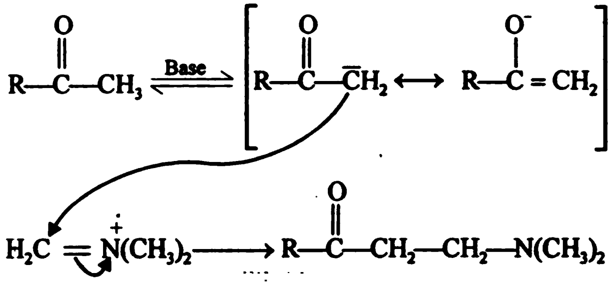
**Mechanism.** It involves the following steps :

**Step 1. Formation of Imminium ion.** Formaldehyde reacts with the amine to form an imminium salt which gives rise to the imminium ion.

**Step 2. Formation of the carbanion.** The active methylene compound in the presence of a base gives the carbanion..

**Step 3. Attack by the carbanion.** Carbanion formed in the above step attacks the imminium ion to give the final product. The above steps are illustrated hereunder :





### 68. Write a note on Wittig's Reaction.

**Ans.** This reaction takes place between an aldehyde or ketone and phosphorus ylides to form substituted alkenes. The phosphorus ylides required in the reaction are obtained by the action of a base on suitable alkyl triphenyl phosphonium halides (prepared from alkyl halide and triphenyl phosphine). For example,

$$(C_6H_5)_3P + CH_3I \longrightarrow [(C_6H_5)_3\overset{+}{P}CH_3]\overset{-}{I} \xrightarrow{C_6H_5Li\ (Base)}$$

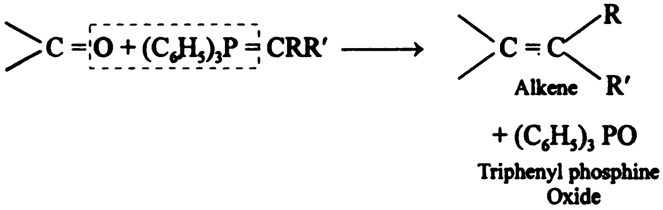
Triphenyl phosphorus + Methyl iodide

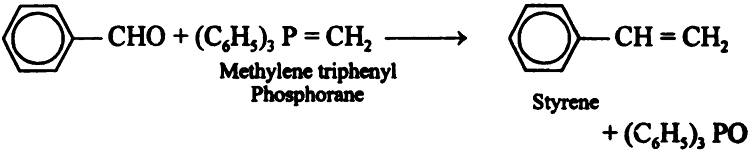
$$(C_6H_5)_3P = CH_2 + C_6H_6 + LiI$$

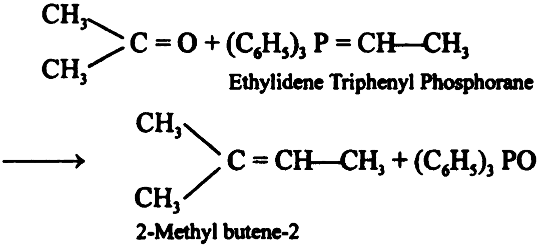
Methylene triphenyl phosphorane (ylide)

The ylides obtained as shown above are not separated but are made to react as such with the aldehydes or ketones in solution.

Some examples of Wittig reaction are given below :







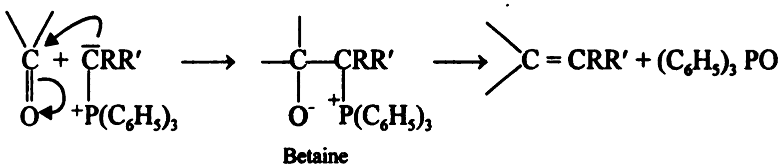
**Mechanism.** The following steps are involved in the reaction.

**Step 1. Attack by ylides.** The phosphorus ylides exists as a resonance hybrid of two structures.

$$\underset{[A]}{(C_6H_5)_3P = CRR'} \longleftrightarrow \underset{[B]}{(C_6H_5)_3\overset{+}{P}—\overset{-}{C}RR'}$$

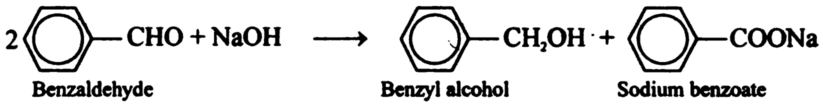
Structure [B] has a negative charge on carbon, thus it acts as a carbanion and initiates the nucleophilic attack on the carbonyl carbon. The resulting addition product is known as *betaine.*

**Step 2. Elimination of Triphenyl phosphine oxide.** Betaine obtained above undergoes elimination of triphenyl phosphine oxide to yield the alkene. The above steps are illustrated hereunder :



**69. Write a note on Cannizzaro reaction.**

**Ans.** Aldehydes having no α-hydrogen like formaldehyde and benzaldehyde undergo self oxidation and reduction. This reaction is given when an aldehyde is treated with a conc. solution of sodum or potasium hydroxide. An alcohol and a salt of carboxylic acid are produced. For example :



$$2HCHO + NaOH \longrightarrow CH_3OH + HCOONa$$

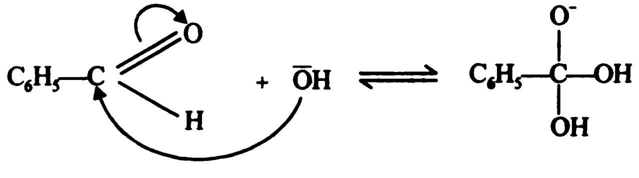
Formaldeyde Methanol Sod. formate

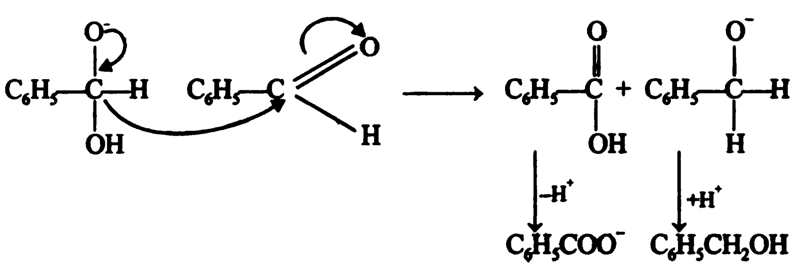
It is evident that one molecule of the aldehyde is oxidised to acid and the second molecule is reduced to alcohol.

**Mechanism.** The following steps are involved :

**Step 1. Attack by OH⁻.** Hydroxide ion attacks the aldehyde molecule to form an anion.

**Step 2. Hydride ion transfer.** Oxidation-reduction takes place between the anion formed in step 1 and the second molecule of aldehyde through transfer of a hydride ion. These two steps are illustrated hereunder :





**Q. 70. Describe with mechanism halogenation of carbonyl compounds.**

**Ans.** The α-hydrogen atoms in the carbonyl compounds can be replaced by halogens in the presence of acids and bases. These are discussed below separately as base-promoted halogenation and acid-promoted halogenation.

**Base-Promoted halogenation.** One or more α hydrogen atoms in the carbonyl compound can be replaced by halogens in the presence of a base like $OH^-$ or $CH_3COO^-$ ions.

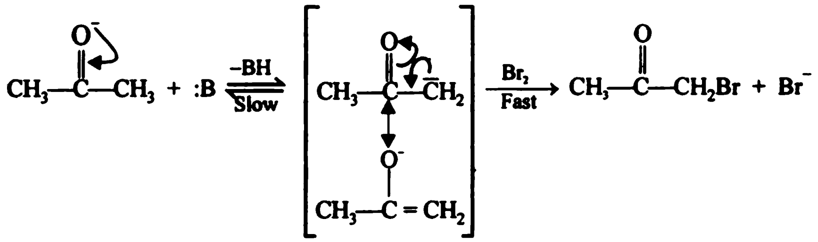
$$\underset{\text{Acetone}}{CH_3\,CO\,CH_3} + Br_2 + OH^- \longrightarrow \underset{\text{Bromo acetone}}{CH_3COCH_2Br} + H_2O + Br^-$$

**Mechanism**

Kinetics studies reveal that the rate of above reaction is proportional to the concentration of the carbonyl compound and the base. It is independent of the concentration of bromine.

Rate of halogenation ∝ [carbonyl compound] × [Base].

This is explained in terms of formtion of a carbanion intermediate as the slow and rate determining step followed by fast bromination process as illustrated hereunder :



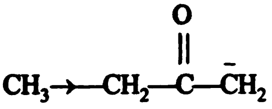
As the base is actually consumed in the rate determining step, we call it base promoted reaction rather then base-catalysed reaction.

Certain observations have been made in respect of base promoted halogenation reaction.

(1) In base promoted halogenation of unsymmetrical ketones (RCOR'), halogenation occurs preferably at the methyl group rather than the methylene group.

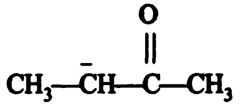
$$CH_3CH_2COCH_3 + Br_2 \xrightarrow{\text{Base}} CH_3CH_2COCH_2\,Br + HBr$$

This is because the electron releasing effect of R alkyl group ($CH_3$—$CH_2$—in the above case) decreases the acidity of the methylene hydrogen atom and prevents the formation of the carbanion. This results in the preferential formation of carbanion (I) which is more stable than the carbanion (II)



$$CH_3 \rightarrow CH_2-\overset{\overset{O}{\|}}{C}-\bar{C}H_2$$

(I)

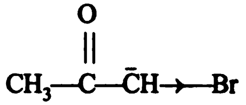


$$CH_3-\bar{C}H-\overset{\overset{O}{\|}}{C}-CH_3$$

(II)

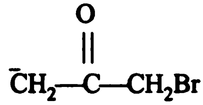
(2) Base promoted halogenation of a monohalogenated ketone takes place preferentially at the carbon already halogenated as long as it has a hydrogen atom. This is becuase the hydrogen atom attached to carbon containing halogen atoms are more acidic and likely to be replaced by halogen as per the above mechanism. The two carbanions resulting from the halogenated ketone

are written below. Obviously carbanion III is more easily formed than IV. Hence fruther halogenation occurs at carbon already halogenated.



$CH_3-\overset{\overset{O}{\|}}{C}-\bar{C}H\rightarrow Br$

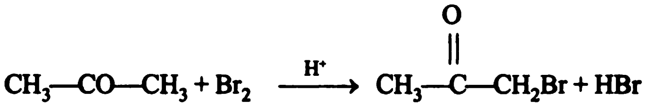
(III)



$\bar{C}H_2-\overset{\overset{O}{\|}}{C}-CH_2Br$

(IV)

**Acid-promoted Halogenation.** Here halogenation of the carbonyl compound takes place in the presence of $H^+$ ions

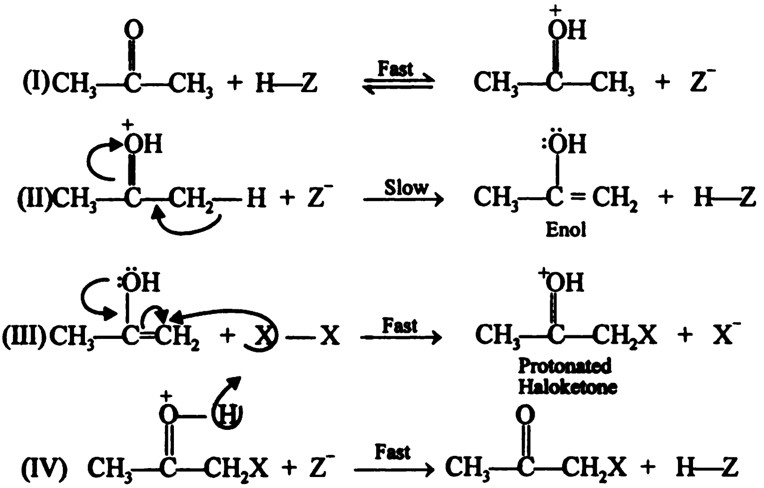


$$CH_3-CO-CH_3 + Br_2 \xrightarrow{H^+} CH_3-\overset{\overset{O}{\|}}{C}-CH_2Br + HBr$$

**Mechanism.** Like in case of base-promoted reaction, here, too, the rate of the reaction is proportional to the concentration of the carbonyl compound and the acid. It is independent of the concentration of the halogen.

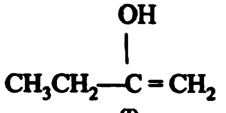
Rate of halogenation ∝ [Carbonyl.compd.] $[H^+]$.

This shows the possibility of formation of intermediate in the rate-determining slow step of the reaction followed by fast attachment of the halogen. The intermediate in acid-promoted halogenation is an *enol*. The steps inovlved in the reaction are reproduced as follows :



Following observations have been made in respect of acid-promoted reactions.

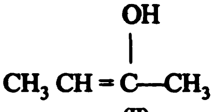
1. In the acid-catalysed halogenation of ketones, halogenation takes place preferably at the methylene group rather than the methyl group. Thus in the compound $CH_3CH_2COCH_3$, halogenation would yield $CH_3$ CHBr $COCH_3$ and not $CH_3CH_2COCH_2Br$. This is explained by the fact that enols which are more branched are more stable. The enols which would be formed with halogenation at the methylene and methyl groups respectively are given below.



$CH_3CH_2-\overset{OH}{\overset{|}{C}}=CH_2$

(I)

Less branched
less stable



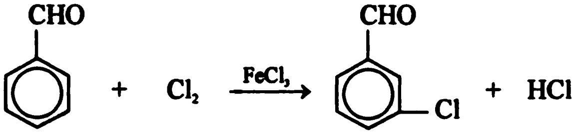
$CH_3CH=\overset{OH}{\overset{|}{C}}-CH_3$

(II)

More branched
more stable

(2) Further halogenation of the monohalogen ketones does not take place readily because the halogen already present tends to withdraw the electrons towards itself. This prevents the attachment of hydrogen ion on the carbonyl oxygen.

Aromatic aldehydes and ketones undergo electrophilic substitution reaction with the halogen in the presence of halogen carriers like $FeX_3$. The halogen enters at the meta position w.r.t. the carbonyl group.



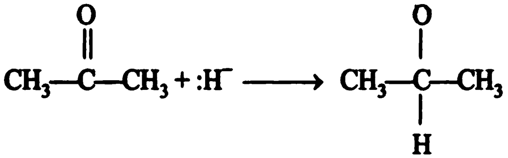
m-chloro
benzaldehyde

**Q. 71. Describe the mechanism of reduction of acetone with Lithium Aluminium hydride.**

**Ans.** It involves the following steps :

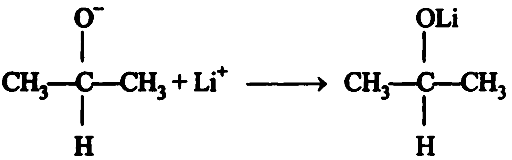
**Step 1. Formation of alkoxide.** Hydride ion from $LiAlH_4$ combines with carbonyl carbon as shown below.

$$LiAlH_4 \longrightarrow Li^+ + Al^{3+} + 4H^-$$



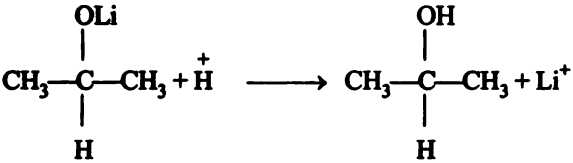
$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + :H^- \longrightarrow CH_3-\underset{\underset{H}{|}}{\overset{\overset{O}{|}}{C}}-CH_3$$

**Step 2.** Lithium ion combines with the alkoxide ion.



$$CH_3-\underset{\underset{H}{|}}{\overset{\overset{O^-}{|}}{C}}-CH_3 + Li^+ \longrightarrow CH_3-\underset{\underset{H}{|}}{\overset{\overset{OLi}{|}}{C}}-CH_3$$

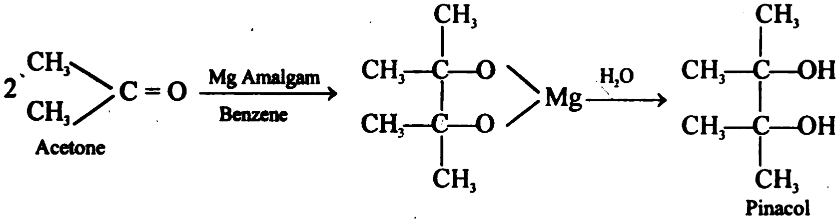
**Step 3.** Lithium alkoxide is changed into alcohol by adding dilute acid



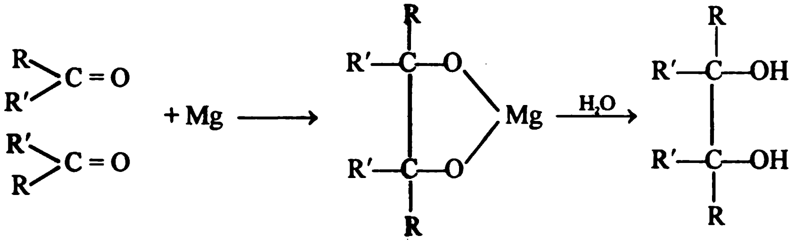
$$CH_3-\underset{\underset{H}{|}}{\overset{\overset{OLi}{|}}{C}}-CH_3 + \overset{+}{H} \longrightarrow CH_3-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3 + Li^+$$

**Q. 72. Give the mechanism of bimolecular reduction of carbonyl compounds.**

**Ans.** Aldehydes and ketones in the presence of Mg amalgam undergo biomolecular reduction to form symmetrical glycols known as **pinacols.**



**Mechanism.** It involves formation of a bond between two carbonyl carbon atoms as shown below :

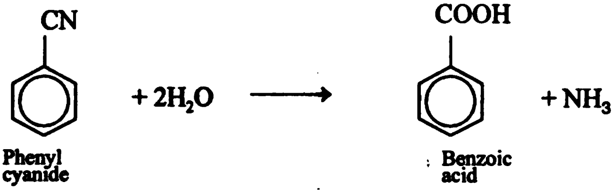


**Q. 73. Give the mechanism of hydrolysis of nitriles or cyanides.**

**Ans.**

$$R{-}CN + 2H_2O \xrightarrow[\text{Alkali}]{\text{Acid or}} R{-}COOH + NH_3$$

$$\underset{\text{Methyl cyanide}}{CH_3{-}CN} + 2H_2O \xrightarrow[\text{Alkali}]{\text{Acid or}} \underset{\text{Acetic acid}}{CH_3COOH} + NH_3$$



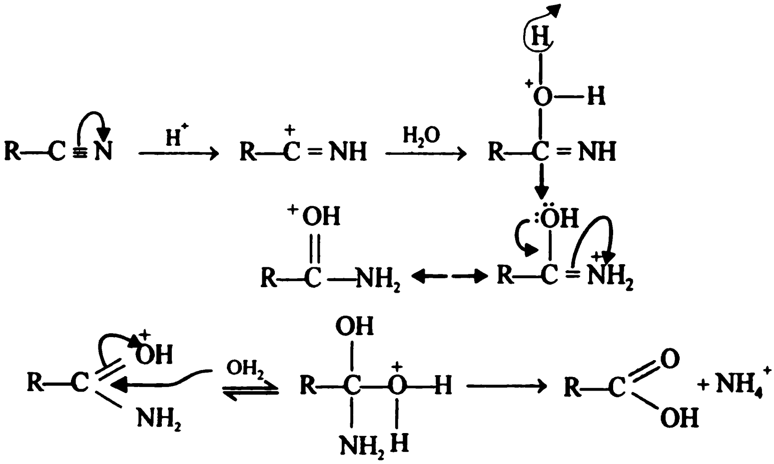
**Mechanism**

**Acidic Hydrolysis**

(*i*) Hydrogen ion attaches itself to the cyano nitrogen atom with the shifting of charge to nitrogen and creation of positive charge on carbon.

(*ii*) Water molecule is attached to the carbonium ion.

The sequence of changes that take palce subsequently is shown hereunder.

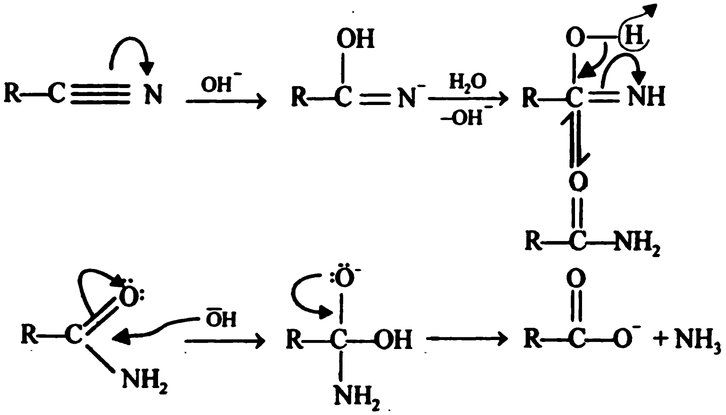


**Alkaline Hydrolysis**

(*i*) Here the electromeric change takes place in the presence of the hydroxyl group. Hydroxyl group is attached to cyano carbon atom with a consequent negative charge on nitrogen.

(*ii*) $H^+$ is attached to negative nitrogen to produce the imine group C = NH.

Sequence of changes is shown below



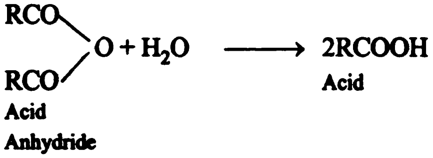
**Q. 74. Give the mechanism of hydrolysis of acid derivatives *viz* acid chlorides, esters, amides and anhydrides.**

**Ans.** The above acid derivatives on hydrolysis in the presence of an acid or alkali produce carboxylic acids

$$\underset{\text{Acid chloride}}{RCOCl} + H_2O \longrightarrow RCOOH + HCl$$

$$\underset{\text{Ester}}{RCOOR'} + H_2O \longrightarrow \underset{\text{Acid}}{RCOOH} + R'OH$$

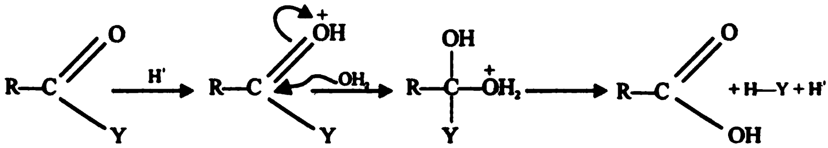
$$RCONH_2 + H_2O \longrightarrow RCOOH + NH_3$$



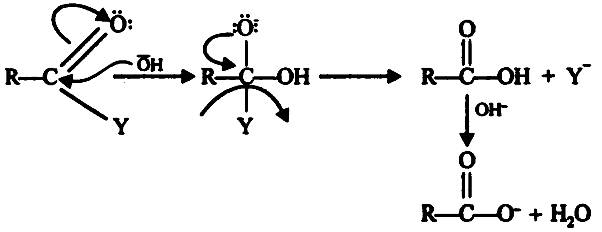
**Mechanism**

An acid derivative could be represented as $R-\overset{\overset{O}{\|}}{C}-Y$ where Y stands for —Cl, —OR′, —$NH_2$ or —OOCR in case of acid chloride, ester, amide or anhydride respectively.

**Acidic hydrolysis**

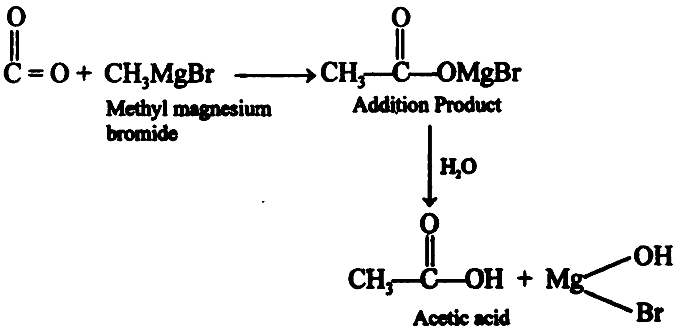


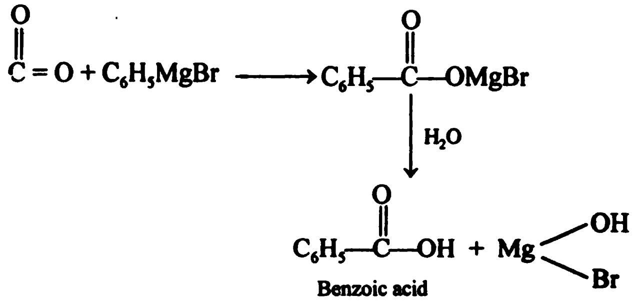
**Alkaline hydrolysis**



**Q. 75. Give the mechanism of reaction between carbon dioxide and alkyl or phenyl magnesium bromide.**

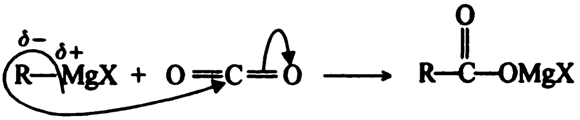
**Ans.** Grignard reagent reacts with carbon dioxide forming an addition product which yields carboxylic acid on hydrolysis





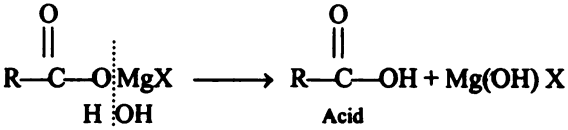
$$\overset{O}{\overset{\|}{C}}=O + C_6H_5MgBr \longrightarrow C_6H_5-\overset{O}{\overset{\|}{C}}-OMgBr \xrightarrow{H_2O} \underset{\text{Benzoic acid}}{C_6H_5-\overset{O}{\overset{\|}{C}}-OH} + Mg\begin{smallmatrix}OH\\Br\end{smallmatrix}$$

**Mechanism.** The nucleophile alkyl group is attached to carbon of the carbon dioxide molecule whereas —MgBr group is attached to one of the two oxygen atoms. This is shown below schematically as under :



$$\overset{\delta-}{R}-\overset{\delta+}{MgX} + O=C=O \longrightarrow R-\overset{O}{\overset{\|}{C}}-OMgX$$

The addition product then hydrolyses to the carboxylic acid



$$R-\overset{O}{\overset{\|}{C}}-\underset{H}{O}\vdots\underset{OH}{MgX} \longrightarrow \underset{\text{Acid}}{R-\overset{O}{\overset{\|}{C}}-OH} + Mg(OH)X$$

**Q. 76. Give the mechanism of estrification of an acid with an alcohol.**

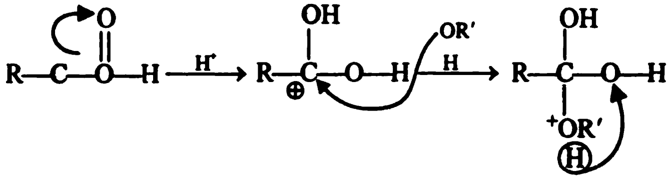
**Ans.** Carboxylic acid on heating with an alcohol in the presence of a strong mineral acid (such as $H_2SO_4$) form **esters.** The reaction is known as **esterification** and is reversible in nature.

$$\underset{\text{Acid}}{RCOOH} + \underset{\text{Alcohol}}{R'OH} \underset{}{\overset{H^+}{\rightleftharpoons}} RCOOR' + H_2O$$

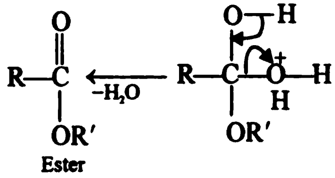
$$\underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Ethanol}}{C_2H_5OH} \overset{H^+}{\rightleftharpoons} \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + H_2O$$

**Mechanism.**

$H^+$ from the mineral acid protonates carbonyl oxygen. As a result, carbon atom becomes positive and undergoes nucleophilic attack by the alcohol molecule. Finally ester is obtained as depicted below :



$$R-\overset{O}{\overset{\|}{C}}-O-H \xrightarrow{H^+} R-\overset{OH}{\overset{|}{\underset{\oplus}{C}}}-O-H \xrightarrow[\text{}]{\overset{OR'}{H}} R-\overset{OH}{\overset{|}{\underset{\underset{\text{(H)}}{^{+}OR'}}{\underset{|}{C}}}}-O-H$$

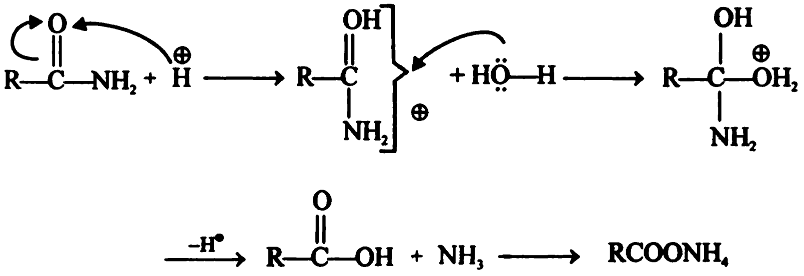


**Q. 77. Give the mechanism of hydrolysis of amides.**

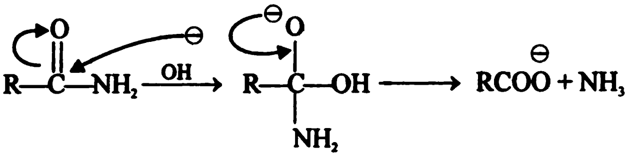
**Ans.** Amides are hydrolysed to parent acids in the presence of a mineral acid or alkali.

$$CH_3CONH_2 + H_2O \xrightarrow[\text{or } OH^-]{H^+} CH_3COOH + NH_3$$

**Mechanism (In the presence of an acid)**



**Mechanism (In the presence of a base)**



**Q. 78. Give the mechanism of following reactions:**

**(*i*) Hydrolysis of acid chlorides**

**(*ii*) Alcoholysis of acid chlorides**

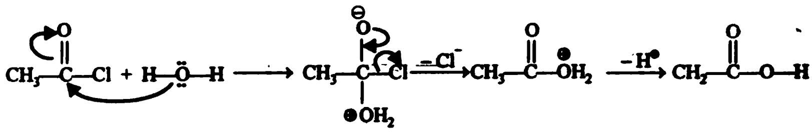
**(*iii*) Ammonolysis of acid chlorides.**

**Ans.** (*i*) **Hydrolysis.** Acid chlorides are hydrolysed by water to form the parent carboxylic acids.

$$\underset{\text{Acetyl chloride}}{CH_3COCl + H_2O} \longrightarrow \underset{\text{Acetic acid}}{CH_3COOH + HCl}$$

$$\underset{\text{Benzoyl chloride}}{C_6H_5COCl + H_2O} \longrightarrow \underset{\text{Benzoic acid}}{C_6H_5COOH + HCl}$$

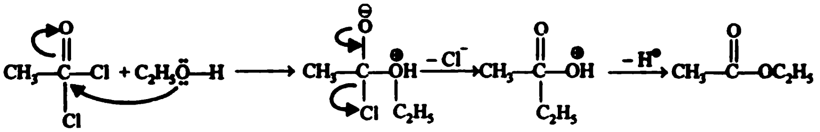
Mechanism of reaction is as follows :



(*ii*) **Alcoholysis.** An acid chloride reacts with alcohol to form an ester

$$CH_3COCl + C_2H_5OH \longrightarrow CH_3COOC_2H_5 + HCl$$

The reaction takes place as a nucleophilic substituion with the following mechanism.

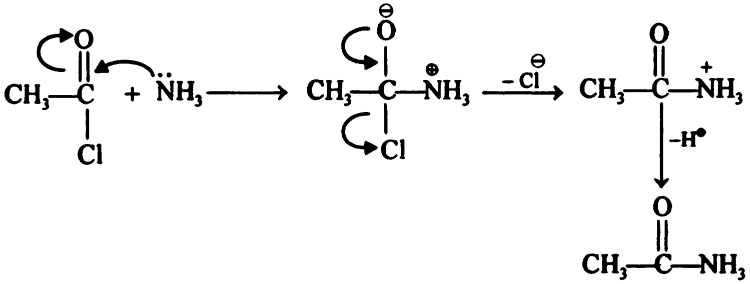


(*iii*) **Ammonolysis.** An acid chlorides reacts with ammonia to form an amide.

$$\underset{\text{Acetyl chloride}}{CH_3COCl} + NH_3 \longrightarrow \underset{\text{Acetamide}}{CH_3CONH_2} + HCl$$

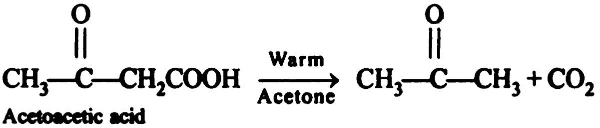
$$\underset{\text{Benzoyl chloride}}{C_6H_5COCl} + NH_3 \longrightarrow \underset{\text{Benzamide}}{C_6H_5CONH_2} + HCl$$

Mechanism of the reaction is given below. It is again a nucleophilic substituion reaction.



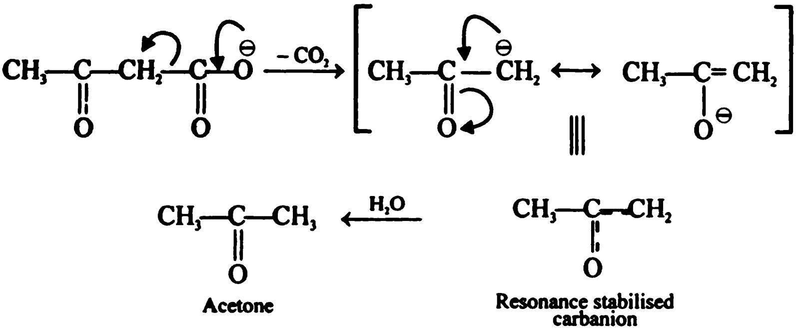
**Q. 79. Give the mechanism of decarboxylation of acetoacetic acid**

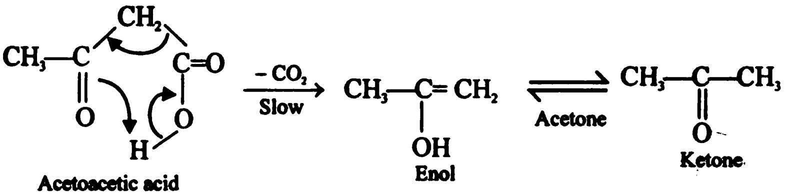
**Ans.** Acetoacetic acid undergoes decarboxylation on warming to give acetone.



$$\underset{\text{Acetoacetic acid}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2COOH} \xrightarrow[\text{Acetone}]{\text{Warm}} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + CO_2$$

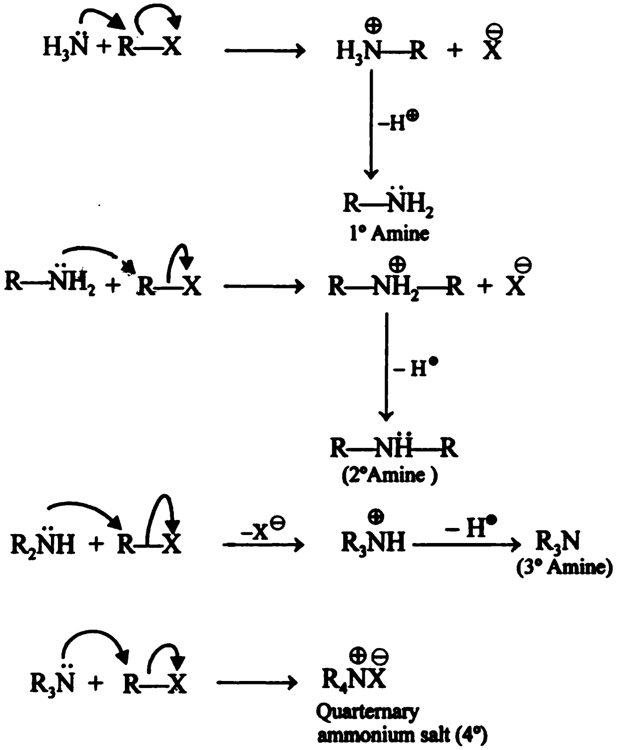
Decarboxylation involves both the carboxylic acid molecule and the carboxylate ion. Mechanism involving both species is given below.





**Q. 80. Give the mechanism of ammonolysis of halogen compounds.**

**Ans.** This reaction involves treating an alkyl halide or an aryl halide of the type $C_6H_5CH_2X$ with ammonia. Ammonia is a nucleophile. It attaches itself with the alkyl group and the halogen is removed as halide to give a molecule of primary amine or 1° amine. But the reaction does not stop here. The primary amine formed acts as a nucleophile and attaches itself to the alkyl halide molecule giving rise to secondary amine or 2° amine. Again secondary amine acts as nucleophile and attaches itself to a molecule of alkyl halide giving rise to tertiary amine or 3° amine. Finally tertiary amine attaches itself to the alkyl halide molecule to form the quarternary ammonium salt (4°). These reactions are explained as under :

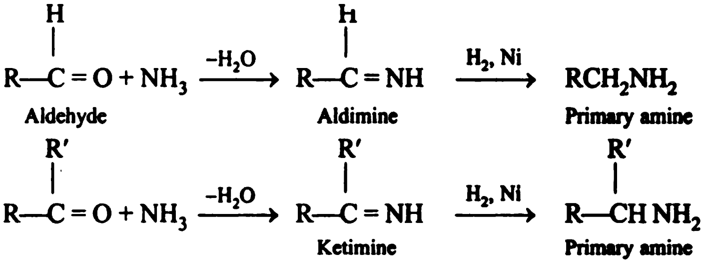


$$CH_3{-}Cl + NH_3 \xrightarrow{-\,HCl} \underset{\text{Methyl amine}}{CH_3NH_2} \xrightarrow[-\,HCl]{CH_3Cl} \underset{\text{Dimethylamine}}{(CH_3)_2NH}$$

$$\xrightarrow[-\text{HCl}]{CH_3Cl} \underset{\text{Trimethyl amine}}{(CH_3)_3N} \xrightarrow{CH_3Cl} \underset{\text{Tetramethyl ammonium chloride}}{(CH_3)_4N^+Cl^-}$$

**Q. 81. Give the mechanism of reductive amination of aldehydes and ketones.**

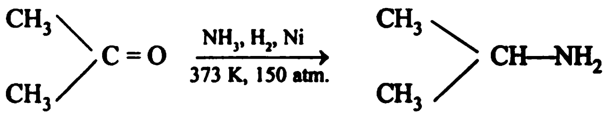
**Ans.** Aldehyes and ketones on reduction with hydrogen and ammonia change into primary amines at 373 K, 150 atm. pressure and in the presence of nickel as catalyst



$$\underset{\text{Aldehyde}}{R-\overset{H}{C}=O} + NH_3 \xrightarrow{-H_2O} \underset{\text{Aldimine}}{R-\overset{H}{C}=NH} \xrightarrow{H_2,\ Ni} \underset{\text{Primary amine}}{RCH_2NH_2}$$

$$R-\overset{R'}{C}=O + NH_3 \xrightarrow{-H_2O} \underset{\text{Ketimine}}{R-\overset{R'}{C}=NH} \xrightarrow{H_2,\ Ni} \underset{\text{Primary amine}}{R-\overset{R'}{C}H\,NH_2}$$

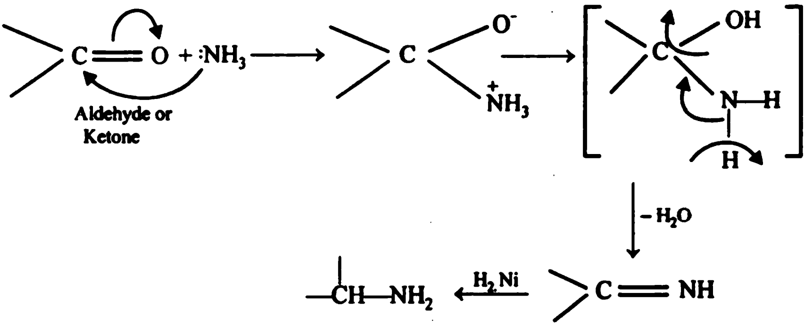
$$\underset{\text{Propanal}}{CH_3CH_2CHO} \longrightarrow \underset{\text{Propyl amine}}{CH_3CH_2CH_2NH_2}$$



Isopropyl amine

**Mechanism**

Reductive amination involves the formation of amine as an intermediate and proceeds through the following mechanism :



**Q. 82. Give the mechanism of Hofmann's degradation of amides.**

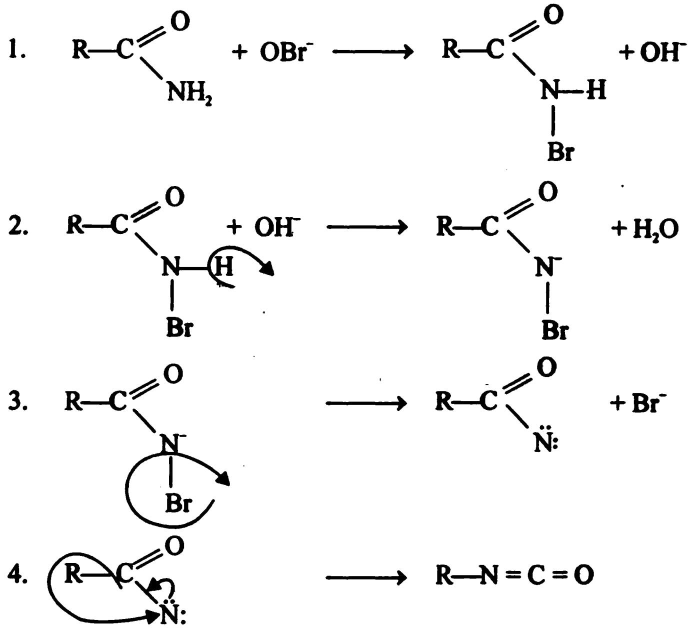
**Ans.** On treatment with bromine and potassium hydroxide, amides are converted into amines.

$$\underset{\text{Amide}}{R-\overset{O}{\overset{\|}{C}}NH_2} + Br_2 + 4KOH \longrightarrow \underset{\text{Amine}}{RNH_2} + K_2CO_3 + 2KBr + 2H_2O$$

$$\underset{\text{Acetamide}}{CH_3CONH_2} + Br_2 + 4KOH \longrightarrow \underset{\text{Methyl amine}}{CH_3NH_2} + K_2CO_3 + 2KBr + 2H_2O$$

**Mechanism**

The hypobromite ion $OBr^-$ produced by alkaline solution of $Br_2$ attacks the amide molecule. Various steps which are involved are illustrated hereunder.



5. $R—N=C=O + 2OH^- \longrightarrow R—NH_2 + CO_3^{2-}$

**Q. 83. Give the mechanism of acetylation of amines.**

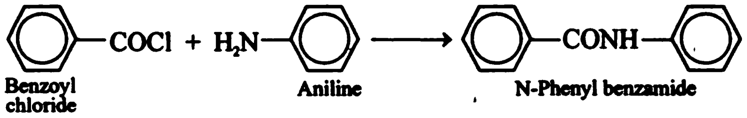
**Ans.** Primary and secondary amines on treatment with acetyl chloride or acetic anhydride undergo acylation to give N-substituted amides.

$$RCOCl + R'NH_2 \longrightarrow \underset{\text{N-alkyl amide}}{RCONHR'} + HCl$$

$$RCOCl + R'_2NH \longrightarrow \underset{\text{N,N dialkyl amide}}{RCONR'_2} + HCl$$

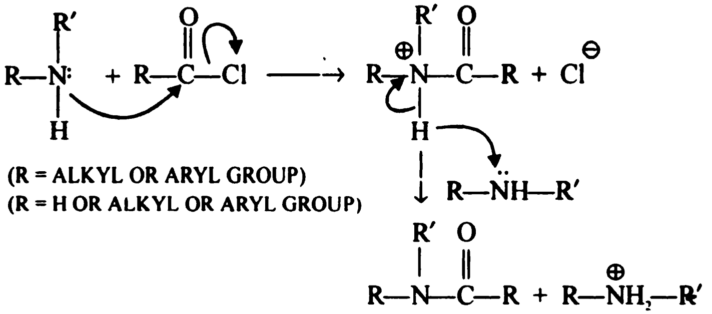
Tertiary amine has no hydrogen and as such it does not participate in acylation.

In case the acid chloride or anhydride is aromatic, the reaction is known as **Schotten-Baumann's reaction** as given below :



Benzoyl chloride — Aniline — N-Phenyl benzamide

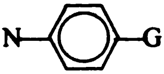
The mechanism of the reaction is as follows :

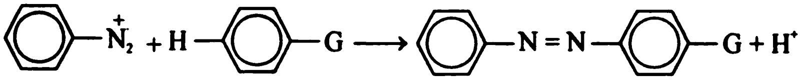


(R = ALKYL OR ARYL GROUP)
(R = H OR ALKYL OR ARYL GROUP)

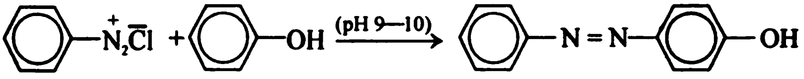
Since tertiary amines cannot lose the proton after attachment to carbon, they do not react.

**Q. 84. Give the mechanism of coupling reactions.**

**Ans.** It is an important reaction of diazonium salts and involves reaction of diazonium ions which act as electrophilic agents, with aromatic compounds containing strong electron releasing groups such as —OH, —NH$_2$, —NHR and —NHR$_2$. The reaction is known as coupling and leads to the formation of **azo compounds** having the general formula $C_6H_5$—N = NG where G is one of above mentioned electron releasing groups. The coupling reaction in general may be written as



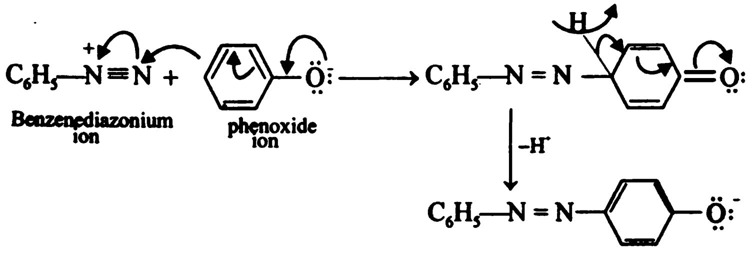
(*a*) **Coupling with phenol.** Benzene diazonium salt reacts with phenol in weakly alkaline solution to form hydroxyazo compound



p-hydroxyazobenzene + HCl

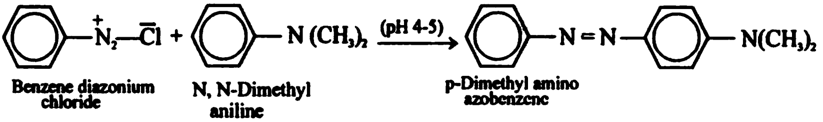
**Mechanism of reaction**

It involves the electrophilic attack of diazonium ion on phenoxide ion as shown below :

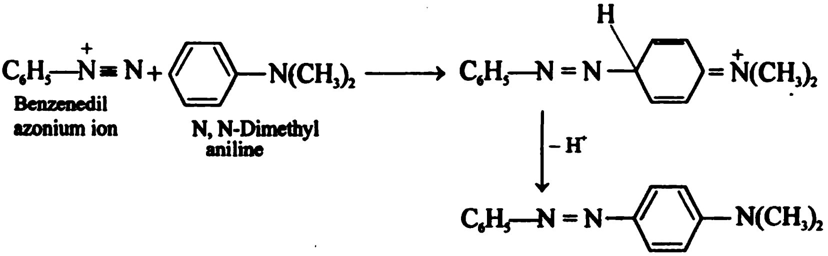


(b) **Coupling with tertiary amine.** This coupling takes place in acidic

**solution.** Diazonium salt reacts with tertiary amine to form dialkylamino azo compound.

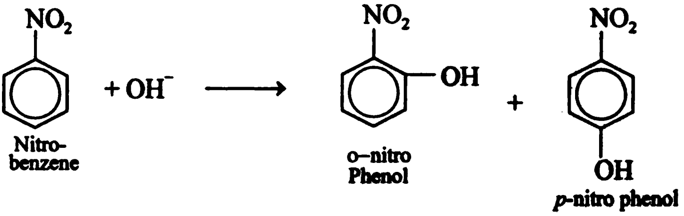


The mechanism of the reaction is as follows :

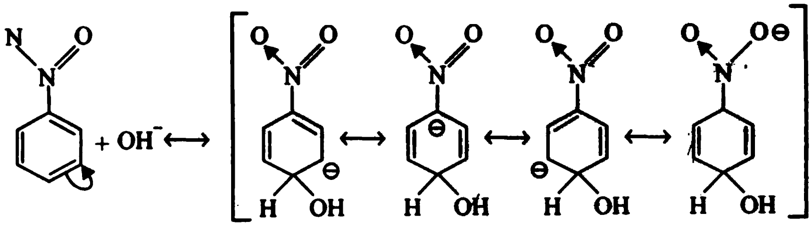


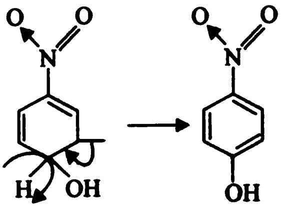
**Q. 85. Give the mechanism of nucleophilic substitution in nitrobenzene.**

**Ans.** Nitro compounds easily undergo nucleophilic substituion reaction because of positive charge on the ring, as a result of electron withdrawing effect of nitro group.



The mechanism of this reaction (taking the case of *p*-nitrophenol) is as follows :

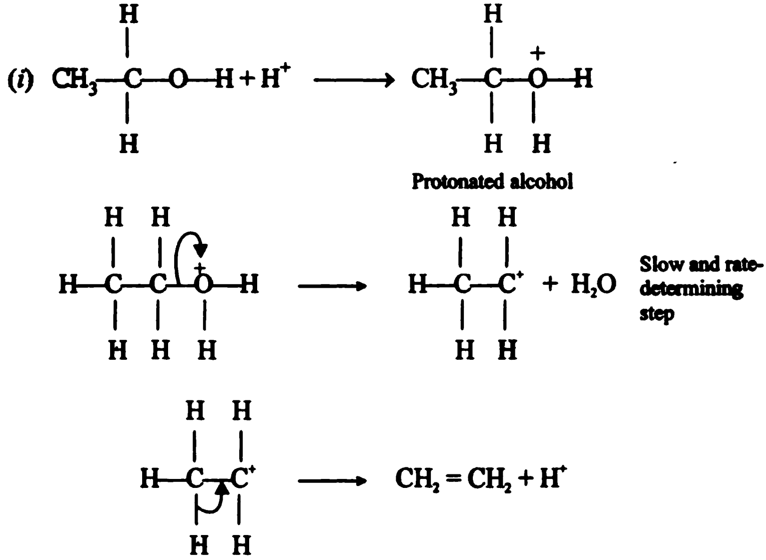




**Q. 86. What are $E_1$ and $E_2$ reactions. Explain the mechanism of the reactions giving examples.**

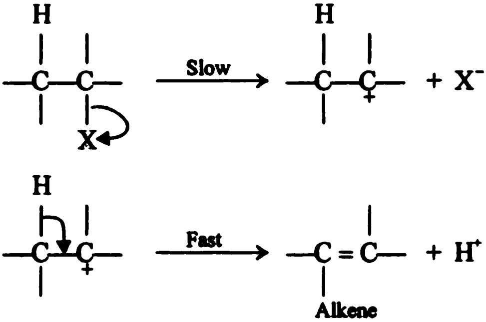
**Ans.** ***$E_1$ reactions*** **(Elimination reaction of the first order)**

These are the reactions in which only one substance is involved in the slow rate deteriming step. Dehydration of an alcohol in the presence of conc. $H_2SO_4$ is an example of $E_1$ reaction. The mechanism is explained as under



In the second and rate-determining step, only one substance is involved, therefore, it is $E_1$ reaction. The concentration of the acid does not influence the rate of reaction.

Commonly, an $E_1$ reaction can be represented as under :

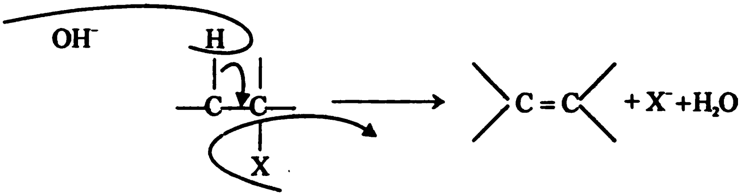


***$E_2$ reactions*** **(Elimination reactions of the second order)**

These reactions follow a second order kinetics *i.e.*, two species are involved in the slow and rate-detemrining step of the reaction. An example of this reaction is dehydrohalogenation of alkyl halide in the presence of alcoholic solution of potassium hydroxide.

$$CH_3CH_2Cl + KOH\,(alc.) \longrightarrow CH_2{=}CH_2 + KCl + H_2O$$

Mechanism of the reaction is as follows :



It is a single step concerted mechanism. Removal of proton and halide ion take place in the same step. Here the rate of the reaction depends upon both the concentration of the alkyl halide and the base. Hence this is a second-order or $E_2$ reaction.

**Q. 87. What happens when ethanol is heated with concentrated sulphuric acid at 453 K ? Explain the mechanism of this reaction.** ***(A.I.S.B. 2004)***

**Ans.** Ethanol is converted into ethene

$$CH_3CH_2OH \xrightarrow[453K]{H_2SO_4} CH_2{=}CH_2 + H_2O$$

For mechanism of the reaction, refer to Q.3 in this chapter.

**Q. 88. Write the mode of free radical addition polymerization of an alkene. Clearly indicate the role of an initiator in it.** ***(A.I.S.B. 2004)***

**Ans.** Refer to Q. 17.

# 9

# Problems Based upon Organic Reactions

Solving a structural problem is an interesting job. What is required to accomplish this work is the thorough knowledge of organic reactions. Before that, it is required to determine the molecular formula of the compound by making use of percentage of elements and molecular mass data. Given below is the summary of various relations used and sequence of investigation made.

(*a*) **Estimation of the elements.**

$$\text{Percentage of C} = \frac{12 \times \text{wt. of } CO_2 \times 100}{44 \times \text{wt. of compd.}}$$

$$\text{Percentage of H} = \frac{2 \times \text{wt. of } H_2O \times 100}{18 \times \text{wt. of compd.}}$$

$$\text{Percentage of N} = \frac{\text{wt. of } N_2 \times 100}{\text{wt. of compd.}}$$

$$= \frac{\text{Vol. of } N_2 \text{ at N.T.P.} \times 28 \times 100}{22400 \times \text{wt. of compd.}}$$

(*Duma's Method*)

$$= \frac{1.4 \times \text{Normality of acid} \times \text{Vol. of acid used}}{\text{wt. of compound}} \times 100$$

(*Kjeldahl's Method*)

$$\text{Percentage of Cl} = \frac{35.5 \times \text{wt. of AgCl} \times 100}{143.5 \times \text{wt. of compd.}}$$

(*Carius Method*)

(*b*) **Calculation of empirical formula** *i.e.* the simplest ratio between the atoms of various elements.

(*c*) **Determination of molecular formula** which is *n* times the empirical formula where

$$n = \frac{\text{Molecular weight}}{\text{Empirical weight}}$$

(*i*) *Mol. wt. of acid* = Eq. wt. of acid × basicity.

Eq. wt. of acid is generally determined by silver salt method.

$$\text{Eq. wt acid} = \frac{\text{wt. of Ag salt} \times 108}{\text{wt. of Ag}} - 107$$

(*ii*) *Mol. wt. of Base* = Eq. wt. of base × Acidity

Eq. wt of base is determined by platinic chloride method.

$$\frac{\text{wt. of chloroplatinate}}{\text{wt. of Pt}} = \frac{2B + 410}{195}$$

(where B is the eq. wt. of the base)

**Molecular weight by cryoscopic method**

This method involves the measurement of depression of freezing point by dissolving a known amount of an organic substance in a definite quantity of solvent. The depression of freezing point is related to its molal depression constant, $K_f$, as follows :

$$\text{Molecular weight} = \frac{1000 \times K_f \times \text{weight of the sample}}{\Delta T_f \times \text{weight of solvent}}$$

where $\Delta T_f$ = depression of freezing point

and $K_f$ = molal depression constant.

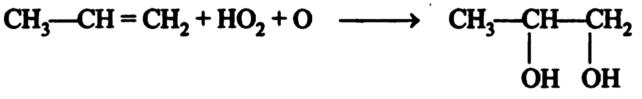
**(*d*) Determination of structural formulae**

*Remember these points for aliphatic compounds*

**(i) An unsaturation** in a compound is indicated by addition of bromine (*i.e.*, bromine water decolourized) and also by oxidation with 1% alk. $KMnO_4$ soln. (decolourised).

$$CH_3—CH = CH_2 + Br_2 \longrightarrow CH_3CHBr.CH_2Br$$

Propylene  Propylene dibromide



$$CH_3—CH = CH_2 + HO_2 + O \longrightarrow CH_3—\underset{OH}{CH}—\underset{OH}{CH_2}$$

Propylene glycol

**(*ii*) A compound containing C, H and O, if it**

(*a*) gives violet colur with Schiff's reagent or

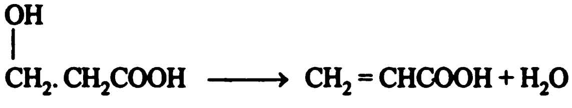
(*b*) gives silver mirror with Tollen's reagent and red ppt. with Fehling's solution, it contains —CHO group (*Aldehyde*).

(*c*) forms oxime, phenyl hydrazone, but does not reduce Fehling's solution, it contains ketonic >C = O group (*Ketones*).

(*d*) gives an aldehyde on oxidation, it contains primary alcoholic $—CH_2OH$ group and if yields ketone, it contains secondary alcoholic >CHOH group (*Alcoholic*).

(*e*) gives effervescence with $NaHCO_3$, it contains —COOH group (*Acids*).

**(*iii*) If a hydroxy acid on heating loses water, it contains** —OH group on β-carbon atom.

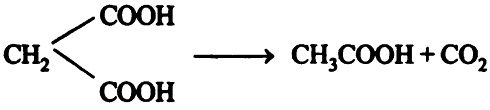


$$\overset{\text{OH}}{\overset{|}{\text{CH}_2}}.\,\text{CH}_2\text{COOH} \longrightarrow \text{CH}_2=\text{CHCOOH}+\text{H}_2\text{O}$$

β-Hydroxy propionic acid Acrylic acid

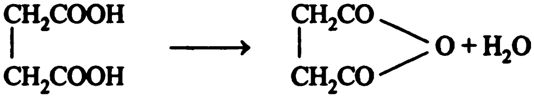
**(*iv*) A dibasic acid on heating**

(*a*) If evolves $CO_2$, the two —COOH groups are present on same C-atom.



Malonic acid

(*b*) If loses water, the two —COOH groups are present on adjacent C-atom (*i.e.* succinic acid).

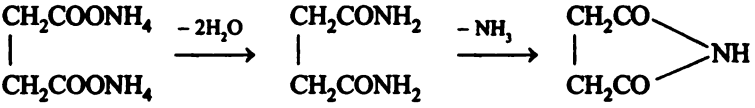


Succinic acid Succinic anhydride

**(*v*) A compound containing C, H, N and O if it**

(*a*) Loses $NH_3$ on heating, it may be an amide, ammonium salt of an acid or urea.

$$\text{NH}_2\text{CONH}\boxed{\text{H}+\text{H}_2\text{N}}\text{CONH}_2 \longrightarrow \text{NH}_2\text{CONHCONH}_2+\text{NH}_3$$



Amm. succinate Succinamide Succinimide

(*b*) Gives primary amine with $Br_2$ and KOH, it contains —$CONH_2$ group or (*Amide*).

(*c*) On heating with NaOH gives off $NH_3$, it contains amide group or is ammonium salt.

$$\underset{\text{Acetamide}}{\text{CH}_3\text{CONH}_2}+\text{NaOH} \longrightarrow \underset{\text{Sod. acetate}}{\text{CH}_3\text{COONa}}+\text{NH}_3$$

(*d*) Gives an amine on reduction, it is nitro compound and if it gives alcohol and $NH_3$, it is alkyl nitrite.

$$\underset{\text{Nitroethane}}{\text{C}_2\text{H}_5\text{NO}_2}+6\text{H} \longrightarrow \underset{\text{Ethylamine}}{\text{C}_2\text{H}_5\text{NH}_2}+2\text{H}_2\text{O}$$

$$\underset{\text{Ethyl nitrite}}{\text{C}_2\text{H}_5\text{ONO}}+6\text{H} \longrightarrow \underset{\text{Ethyl alcohol}}{\text{C}_2\text{H}_5\text{OH}}+\text{NH}_3+\text{H}_2\text{O}$$

**(*vi*) A compound containing C, H and N only** may be either amine (Prim, sec., tert), cyanide or isocyanide.

(*a*) If it is soluble in dil. HCl, it may be amine.

(*b*) If on hydrolysis with dil. HCl yields acid and $NH_3$, it is cyanide but if gives amine and formic acid, it is isocyanide.

$$\underset{\text{Methyl cayanide}}{CH_3CN} + 2H_2O \longrightarrow \underset{\text{Acetic acid}}{CH_3COOH} + NH_3$$

$$\underset{\text{Methyl isocyanide}}{CH_3NC} + 2H_2O \longrightarrow \underset{\text{Methylamine}}{CH_2NH_2} + HCOOH$$

(*c*) If on reduction yields primary amine, it is cyanide and if yields secondary amine, it is isocyanide.

$$\underset{\text{Methyl cyanide}}{CH_3\,CN} + 4H \longrightarrow \underset{\text{Ethyl amine}}{CH_3CH_2NH_2}$$

$$\underset{\text{Methyl isocyanide}}{CH_3NC} + 4H \longrightarrow \underset{\text{Dimethyl amine}}{CH_3\,NHCH_3}$$

**(*vii*) A compound containing asymmetric C atom is optically active.**

*Remember these points for aromatic compounds*

**(*i*) Compounds containing C and H**

(*a*) On oxidation, if it gives a carboxylic acid, it contains side chain.

(*b*) On oxidation, if it gives dicarboxylic acid, it contains two side chains.

(c) If the compound decolourises alk. $KMnO_4$ solution and gives precipitate with decolourisation with $Br_2$ water, it contains unsaturation in the side-chain.

**(*ii*) Compounds containing C, H and O**

(*a*) If it turns blue litmus red, it could be a carboxy or phenolic compound.

(*b*) It turns blue litmus red but does ont give effervescence with $NaHCO_3$, phenolic group is present.

(*c*) It gives a red, blue, green or violet colour with $FeCl_3$-phenolic group is present.

(*d*) It undergoes Reimer-Tiemann, Kolbe's-Schmidt reaction-phenolic group is present.

(*e*) It decomposes $NaHCO_3$—Carboxy group is present.

(*f*) Its sodium salt distilled with soda-lime, undergoes decarboxylation, carboxy group present.

(*g*) On heating, it loses a water molecule—Two carboxylic groups are present in *o*-position.

(*h*) It is neutral to litmus, gives hydrogen gas with sodium metal and forms sweet smelling ester with organic acid, —OH (alc) group is present.

(*i*) It reacts with HCN, $NaHSO_3$ and $NH_2NH_2$ ; $> C = O$ group (ketone or aldehyde) is present.

(*j*) It gives Fehling solution and Tollen's reagent tests and restores the pink colour of Schiff's reagent, —CHO group is present.

(*k*) Give Cannizzaro reaction, —CHO group is present.

(*l*) It gives reaction with acetic anhydride and sodium acetate (Perkin's reaction) to give unsaturated acid, —CHO group is present.

(*m*) Compound with pleasant smell, hydrolysed to a mixture of carboxylic acid and alcohol —ester is present.

(*n*) Burning sugar smell on heating, gives Molisch's test—carbohydrate is present.

**(*iii*) Compounds containing C, H, O and N**

(*a*) Neutral compound, when heated with NaOH it gives carboxy acid and $NH_3$,—$CONH_2$ group indicated.

(*b*) It gives primary amine with one carbon less with $Br_2$ + KOH (Hoffmann Bromamide reaction), —$CONH_2$ group indicated.

(*c*) It gives amine and carboxylic acid on hydrolysis, —NHCOR group is present.

(*d*) On redcution with metal and mineral acid, it gives amine, —$NO_2$ group is present.

**(*iv*) Compounds containing C, H and N**

(*a*) It turns red litmus blue, soluble in HCl, —$NH_2$ group is present.

(*b*) It gives unpleastant smell with $CHCl_3$ and NaOH (carbylamine test) —$NH_2$ group is present.

(*c*) It gives diazotisation with $NaNO_2$ and HCl followed by coupling reaction with phenols, —$NH_2$ group is present.

(*d*) With $HNO_2$, $N_2$ is evolved with the formation of alcohol, —$NH_2$ in the side-chain.

(*e*) It produces ammonia and an acid on hydrolysis and on reduction it gives a primary amine, —CN group.

(*f*) It gives a sec. amine on reduction, —NC group is present.

**(*v*) Compounds containing C, H and Cl**

(*i*) It igves easily substitution reactions with $NH_3$, NaOH and NaCN, —Cl group in the side-chain.

(*ii*) Oxidation of compound gives an acid not containing chlorine, —Cl present in the side-chain.

(*iii*) Oxidation of compound gives an acid containing chlorine, —Cl attached to benzene nucleus.

**(*vi*) Compounds contaning C, H, O, S**

(*i*) It is acidic to litmus, reacts with $PCl_5$ and $SOCl_2$, —$SO_3H$ group is present.

(*ii*) On fusion with NaOH, it forms phenol, —$SO_3$ group is present.

(*iii*) When heated with dil. mineral acid in the presence of steam, aromatic hydrocarbon is produced, —$SO_3H$ group is present.

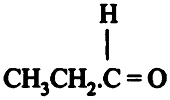
## ALIPHATIC COMPOUNDS WITH MOL. FORMULAE

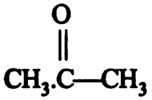
(*i*) **$C_2H_6O$**

$CH_3.CH_2.OH$
Ethyl alcohol

$CH_3.O.CH_3$
Dimethyl ether

(*ii*) **$C_3H_6O$**


$CH_3CH_2.\overset{\displaystyle H}{\overset{|}{C}}=O$
Propionaldehyde


$CH_3.\overset{\displaystyle O}{\overset{\|}{C}}—CH_3$
Acetotne

$CH_2=CH—CH_2OH$
Allyl aalcohol

(*iii*) **$C_3H_6O_2$**

$C_2H_5COOH$
Propionic acid

$H.COOC_2H_5$
Ethyl formate

$CH_3.COOCH_3$
Methyl acetate

(*iv*) **$C_3H_6O_3$**

$(HCHO)_3$
Metaformaldehyde

$CH_3.CHOH—COOH$
α-Hydroxy propionic acid

$CH_2OH.CH_2.COOH$
β-Hydroxy propionic acid

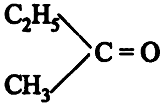
(*v*) **$C_3H_8O$**

$CH_3.CH_2.CH_2OH$
*n*-Propyl alcohol

$CH_3CHOHCH_3$
iso-Propyl alcohol

$CH_3—O—CH_2.CH_3$
Methyl ethyl ether

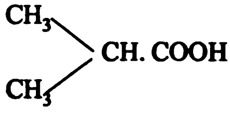
(*vi*) **$C_4H_8O$**


Methyl ethyl ketone

$C_3H_7CHO$
Butyraldehyde

(*vii*) **$C_4H_8O_2$**

$CH_3.CH_2.CH_2COOH$


Iso-butyric acid

*Esters*

$HCOOC_3H_7$
Propyl formate

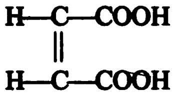
$CH_3COOC_2H_5$
Ethyl acetate

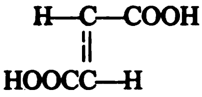
$C_2H_5COOCH_3$
Methyl propionate

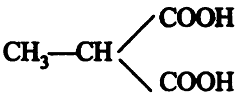
*Aldol*

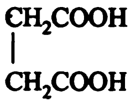
$CH_3.CHOH.CH_2CHO$
(β-hydroxy butryic aldehyde)

(*viii*) **$C_4H_6O_4$**


$$\begin{array}{l} H—C—COOH \\ \quad\;\; \| \\ H—C—COOH \end{array}$$
Maleic acid


$$\begin{array}{l} \quad\;\; H—C—COOH \\ \qquad\quad\;\; \| \\ HOOCC—H \end{array}$$
Fumaric acid


Iso-succinic acid
(Methylmalonic acid)


$$\begin{array}{l} CH_2COOH \\ | \\ CH_2COOH \end{array}$$
Succinic acid

(*ix*) **$C_4H_{10}O$**

$C_2H_5—O—C_2H_5$
Diethyl ether

$CH_3—O—C_3H_7$
Methyl propyl ether

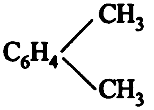
(*x*) $C_2H_7N$ — $CH_3—NH—CH_3$ Dimethylamine — $C_2H_5NH_2$ Ethylamine

(*xi*) $C_3H_5N$ — $C_2H_5—C \equiv N$ Ethyl cyanide — $C_2H_5 \overset{=}{\rightarrow} NC$ Ethyl isocyaznide

## AROMATIC COMPOUNDS WITH MOL. FORMULAE

### 1. Hydrocarbons

(*i*) $C_8C_{10}$ (5 isomers)



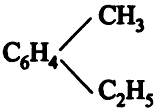
$C_6H_4(CH_3)_2$

*o*-, *m*-, *p*-Xylenes

$C_6H_5C_2H_5$ Ethylbenzene

(*ii*) $C_9H_{12}$ (8 isomers)

$C_6H_3(CH_3)_3$ Trimethylbenzenes (1,2,3- ; 1, 3, 4- ; 1, 3, 5-)



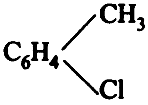
$C_6H_4(CH_3)(C_2H_5)$

*o*-, *m*-, *p*- Methyl ethylbenzenes

$C_6H_5CH_2CH_2CH_3$ *n*-Propylbenzene

$C_6H_5CH(CH_3)_2$ iso-Propylbenzene

### 2. Halogenated hydrocarbons, *e.g.* $C_7H_7Cl$ (4 isomers).

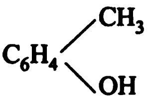


$C_6H_4(CH_3)(Cl)$

*o*-, *m*-, *p*- Chlorotoluenes

$C_6H_5CH_2Cl$ Benzyl chloride

### 3. Phenols, e.g. $C_7H_8O$ (5 isomers).



$C_6H_4(CH_3)(OH)$

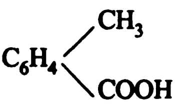
*o*-, *m*-, *p*- Cresols

$C_6H_5CH_2OH$ Benzyl alcohol

$C_6H_5.O.CH_3$ Anisole

### 4. Carboxylic acids

(*i*) $C_8H_8O$ (4 isomers)



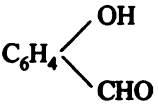
$C_6H_4(CH_3)(COOH)$

*o*-, *m*-, *p*- Toluic acids

$C_6H_5CH_2COOH$ Phenylacetic acid

### 5. Aldehydes

(*i*) $C_7H_6O_2$ (4 isomers)

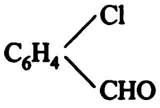


$C_6H_4(OH)(CHO)$

*o*-, *m*-, *p*- hydroxy benzaldehydes

$C_6H_5COOH$ Benzoic acid

(*ii*) $C_7H_5ClO$ (4 isomers)

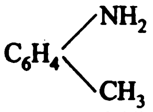


*o*-, *m*-, *p*-, Chloro benzaldehydes

$C_6H_5COCl$ Benzoyl chloride

**6. Amines**

(*i*) $C_7H_9N$ (5 isomers)



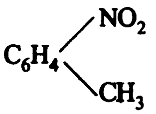
*o*-, *m*-, *p* Toluidines

$C_6H_5CH_2NH_2$ Benzylamine

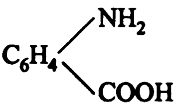
$C_6H_5NHCH_3$ N-Methylaniline

**7. Nitro compounds**

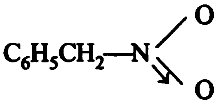
(*i*) $C_7H_7O_2$ (8 isomers)



*o*-, *m*-, *p*-Nitrotoluenes



*o*-, *m*-, *p*- Aminobenzoic acids



Phenylnitromethane

$C_6H_5CH_2—O—N=O$ Benzyl nitrite

**8. Nitriles and Isonitriles**

$C_7H_5N$ (2 isomers)

$C_6H_5\,C\equiv N$ Phenyl cyanide

$C_6H_5—NC$ Phenyl isocyanide

## REAGENTS IN ORGANIC REACTIONS

Sometimes the reagent used to effect a particular reaction furnishes a vital information about the reaction. The important reagents in relation to a characteristic reaction are given in Table 9.1 :

### TABLE 9.1

| | *Reagent* | *Kind of Reaction* |
|---|---|---|
| 1. | Alkyl halide and $AlCl_3$ | Friedel-Crafts alkylation |
| 2. | Acyl halide and $AlCl_3$ | Friedel-Crafts acylation |
| 3. | Acetic anhydride and $AlCl_3$ | Friedel-Crafts acylation |
| 4. | Conc. $H_2SO_4$ | Dehydration of alcohol |
| 5. | Lucas reagent (a mixture of anhydrous $ZnCl_2$ and conc. HCl) at room temp. | 3° alcohol reacts most rapidly<br>2° alcohol does in 5 min.<br>1° alcohol does not react. |
| 6. | Aqueous NaOH/aq. KOH/ moist $Ag_2O$ | Hydrolysis |

| | | |
|---|---|---|
| 7. | Mercuric sulphate (or $Hg^{++}$) and $H_2SO_4$ | Hydration of alkyne. |
| 8. | (CaO)/Sodalime | Decarboxylation. |
| 9. | Sodamide, $NaNH_2$ in conc. $NH_3$ | *a.* Presence of $—C \equiv C—H$,<br>*b.* Dehydrohalogenation |
| 10. | Raney Ni—$H_2$/Pd—$H_2$<br>Pt—$H_2$/Na and alcohol/<br>$LiAlH_4$/Sn and conc. HCl | Reduction |
| 11. | $PCl_5/SOCl_2$ | — OH group of an alcohol or a carboxylic acid changes to —Cl, |
| 12. | Ammoniacal $AgNO_3$ (Tollen's reagent) | *a.* Reducing property of HCOOH<br>*b.* Presence of an aldehydic group<br>*c.* Presence of $C \equiv C—H$. |
| 13. | Zn-Hg and conc. HCl | Clemmensen reduction. |
| 14. | Sodium hypoiodite (NaOI), NaOH and $I_2$<br>Sodium hypohalite | Iodoform reaction.<br>Haloform reaction. |
| 15. | Nitrous acid ($NaNO_2$ + HCl) | *a.* Diazotisation reaction of primary aromatic amine<br>*b.* Formation of alcohol from primay aliphatic amine. |
| 16. | $H_2SO_4$ followed by water | Hydration of alkene. |
| 17. | CuCl and HCl<br>CuBr and HBr<br>CuCN and KCN | Sandmeyer reaction. |
| 18. | Acetic anhydride and sodium acetate | Perkin reaction, (Benzaldehyde gives cinnamic acid). |
| 19. | Alkaline $KMnO_4/CrO_3$ in acetic acid/acid dichromate | Oxidation. |
| 20. | Alcoholic KOH/ $C_2H_5ONa$ | *a.* Dehydrohalogenation<br>*b.* In synthesis of ether. |

## SOLVED PROBLEMS

**Example 1. An alkene A on ozonolysis followed by treatment with zinc powder yields besides OHC. $CH_2$. CHO two other products B and C. B on oxidation yields a monocarboxylic acid, the calcium salt of which on strong heating yields propanone. C reduces Tollen's reagent and on treatment with concentrated alkali, it gives a mixture consisting of methanoic acid (as salt) and methanol, write down the structures of A, B and C.**

(*MLNR 1991*)

**Sol.** Since compound B on oxidation yields a monocarboxylic acid, the calcium salt of which on strong heating yields propanone, *i.e.*, $CH_3COCH_3$, the monocarboxylic acid is, ethanoic acid, $CH_3COOH$ and the compound B ethanal $CH_3CHO$. Reactions are explained as under :

$$\underset{\text{Ethanal } B}{CH_3CHO} \xrightarrow{[O]} \underset{\text{Ethanoic acid}}{CH_3COOH} \xrightarrow{Ca(OH)_2} \underset{\text{Calcium ethanoate}}{(CH_3COO)_2Ca}$$

$$\xrightarrow{\text{Heat}} \underset{\text{Propanone}}{CH_3COCH_3} + CaCO_3$$

The compound *C* reduces Tollen's reagent hence is an aldehyde. Further on treatment with concentrated alkali it gives a mixture of methanoic acid, HCOOH (as salt) and methanol, $CH_3OH$. This reaction is an example of Cannizzaro reaction and, therefore, the compound *C* is methanal, HCHO

$$\underset{\text{Methanal C}}{2HCHO} \longrightarrow \underset{\text{Methanol}}{HCH_2OH} + \underset{\text{Methanoic acid}}{HCOOH}$$

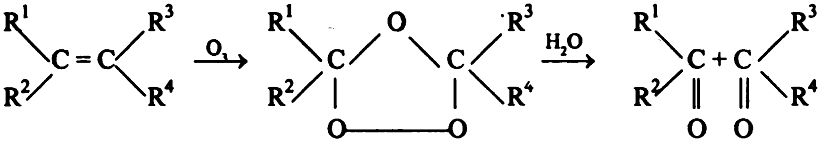
Alkene *A* gives on ozonolysis $OHC.CH_2.CHO$, $CH_3CHO$ (B) and HCHO (C). Only structure that is possible for A is :

$$CH_3CH = CHCH_2CH = CH_2$$

Hex-1, 4-diene

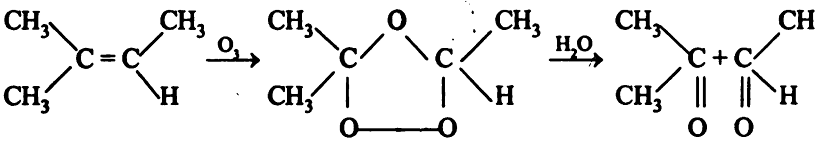
**Example 2. A ketone (A) gives idoform on reacting with iodine and sodium hydroxide. (A) on reduction gives B which on heating with sulphuric acid gives (C). (C) on ozonolysis gives acetaldehyde and acetone. Identify (A), B and (C).** (*M.L.N.R. 1992*)

**Sol.** According to general equation of ozonolysis :

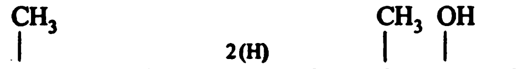


where $R_1$, $R_2$ $R_3$ and $R_4$ represent alkyl groups linked to the double bond.

By putting the values of $R_1$, $R_2$, $R_3$ and $R_4$ as given in the problem, the alkene (C) is found to be *2-methyl butene-2*

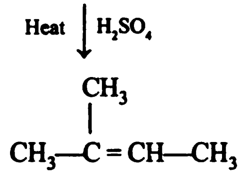


(C) is obtained by heating (B) with sulphuric acid (dehydration) and (B) is obtained on reduction of ketone (A), hence (B) is 3-*methyl butanol*-2 and (A) is 3-*methyl butanone*-2



$$\underset{\text{3-Methyl butanone-2}}{CH_3-\overset{\overset{\large CH_3}{|}}{C}H-CO-CH_3} \xrightarrow{2(H)} \underset{\text{3-Methyl butanol-2}}{CH_3-\overset{\overset{\large CH_3}{|}}{C}H-\overset{\overset{\large OH}{|}}{C}H-CH_3}$$

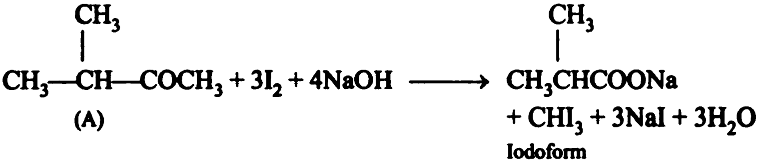
(A) (B)



$$\xrightarrow[\text{Heat}]{H_2SO_4} CH_3-\overset{\overset{CH_3}{|}}{C}=CH-CH_3$$

(*C*)

That (A) is 3-methyl butanone-2 is further confirmed by iodoform reaction.



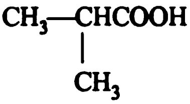
$$\underset{(A)}{CH_3-\overset{\overset{CH_3}{|}}{CH}-COCH_3} + 3I_2 + 4NaOH \longrightarrow CH_3\overset{\overset{CH_3}{|}}{C}HCOONa + \underset{\text{Iodoform}}{CHI_3} + 3NaI + 3H_2O$$

**Example 3. An alkyne with five carbon atoms per molecule when passed through dilute sulphuric acid containing mercuric sulphate gives a compound which forms an oxime, but has no effect on Fehling's solution. The compound on oxidation gives dimethylacetic acid and reacts with sodamide to form a hydrocarbon. What is the structure of the alkyne?**

(*M.L.N.R. Allahabad, 1996*)

**Solution.** (*i*) The compound obtained on passing the alkyne through dilute sulphuric acid containing mercuric sulphate must be a ketone. This is because it does not react with Fehling solution but, forms an oxime (aldehydes form the oxime as well as give the reaction with Fehling's solution).

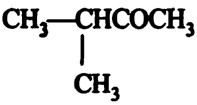
(*ii*) The ketonic compound on oxidation gives dimethylacetic acid. Cleavage of the ketone takes place at the ketonic group.



$$CH_3-\underset{\underset{CH_3}{|}}{C}HCOOH$$

Dimethylacetic acid

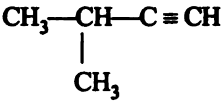
The ketone has the probable structure as follows :



$$CH_3-\underset{\underset{CH_3}{|}}{C}HCOCH_3$$

3-methyl butanone-2

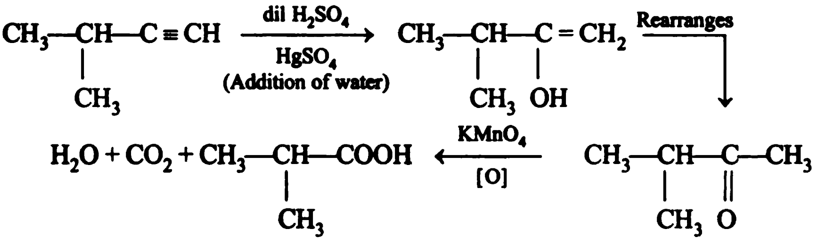
(*iii*) Keeping in view the structure of the ketone, the alkyne must have the structure as given below :



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

3-methyl butyne-1

The reaction can be explained as under :



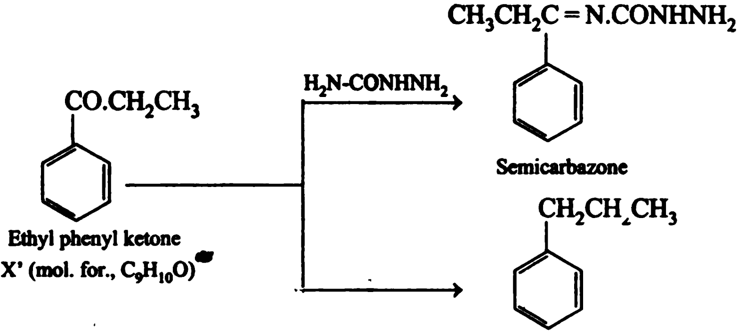
$$CH_3-\underset{\underset{CH_3}{|}}{CH}-C\equiv CH \xrightarrow[\text{HgSO}_4\ \text{(Addition of water)}]{\text{dil } H_2SO_4} CH_3-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{OH}{|}}{C}=CH_2 \xrightarrow{\text{Rearranges}} CH_3-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{O}{\|}}{C}-CH_3$$

$$H_2O+CO_2+CH_3-\underset{\underset{CH_3}{|}}{CH}-COOH \xleftarrow[\text{[O]}]{KMnO_4} CH_3-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{O}{\|}}{C}-CH_3$$

Dimethyl acetic acid

**Example 4. Compound 'X' with molecular formula $C_9H_{10}O$ forms a semicarbazone and gives negative Tollens and idoform tests. On reduction, it gives *n*-propylbenzene. Deduce the structure of 'X'.** (*MLNR 1997*)

**Sol.** Compound 'X' forms semicarbozone, hence it is a carbonyl compound, 'X' gives negative Tollen's test, hence it is a ketone (not an aldehyde). 'X' gives negative iodoform test, hence cannot be a methyl ketone. On reduction 'X' gives *n*-propylbenzene. It has, therefore, a benzene ring and a side chain of 3-carbon atoms which also has the ketonic group. 'X' is, thus found to be ethyl phenyl ketone. The reactions are explained as under :

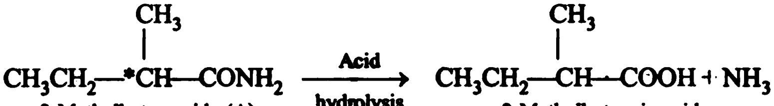


*n*-Propylbenzene

**Example 5. An optically active compound (A), $C_5H_{11}NO$ on acid hydrolysis gives an acid and $NH_3$. When A is treated with bromine/KOH, a compound is obtained which upon treatment with $HNO_2$ yields an optically active alcohol and nitrogen. The alcohol gives a +ve iodoform test. What is the structure of (A), and write the reactions involved.**

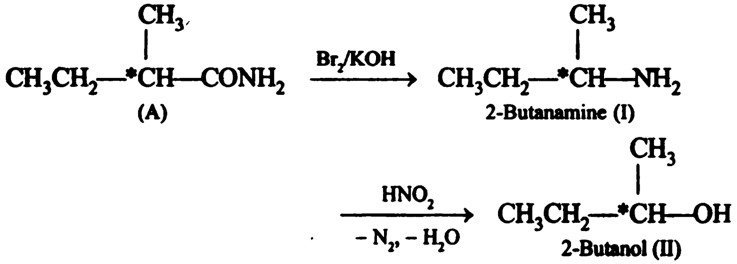
(*P.S.B. 1994*)

**Sol.** (*i*) Since compound (A), $C_5H_{11}NO$ on acid hydrolysis gives an acid and $NH_3$, (A) must be an *amide*. Further since (A) is optically active, it must be *2-methylbutanamide*.



$$CH_3CH_2-\overset{\overset{CH_3}{|}}{^*CH}-CONH_2 \xrightarrow[\text{hydrolysis}]{\text{Acid}} CH_3CH_2-\overset{\overset{CH_3}{|}}{CH}-COOH+NH_3$$

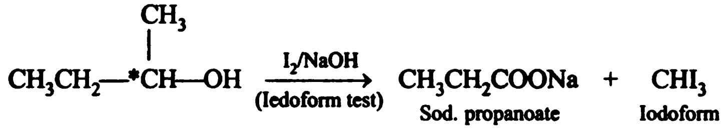
2-Methylbutanamide (A) 2-Methylbutanoic acid (*ii*) Since (A) — an optically active amide, on treatment with $Br_2/KOH$ (*Hofmann bromamide reaction*), gives another compound (I) which upon further treatment with $HNO_2$ gives an optically active alcohol (II), compound (I) must be an 2-*butanamine* and therefore optically active alcohol must be 2-butanol (II).



$$\underset{\text{(A)}}{CH_3CH_2-\overset{CH_3}{\overset{|}{^*CH}}-CONH_2} \xrightarrow{Br_2/KOH} \underset{\text{2-Butanamine (I)}}{CH_3CH_2-\overset{CH_3}{\overset{|}{^*CH}}-NH_2}$$

$$\xrightarrow[-N_2,\ -H_2O]{HNO_2} \underset{\text{2-Butanol (II)}}{CH_3CH_2-\overset{CH_3}{\overset{|}{^*CH}}-OH}$$

(*iii*) Since the optically active alcohol, *i.e.*, 2-butanol contains the grouping —$CHOHCH_3$, it gives positive iodoform test.



$$CH_3CH_2-\overset{CH_3}{\overset{|}{^*CH}}-OH \xrightarrow[\text{(Iodoform test)}]{I_2/NaOH} \underset{\text{Sod. propanoate}}{CH_3CH_2COONa} + \underset{\text{Iodoform}}{CHI_3}$$

Thus, the optically active compound A, $C_5H_{11}NO$ is 2-methylbutanamide.

**Example 6. Two organic compounds A and B containing C, H and O have the same percentage composition ; C = 40,% H = 6.6%. The vapour density of A is 15 and that of B is 30. A reduces ammoniacal silver nitrate solution but B gives a red colour with neutral solution of ferric chloride. Find out the molecular formula of both the compounds and give their names.** (*U.P. 1991*)

**Sol. Calculation of empirical formula of A and B**

Percentage of oxygen = 100 – (40 + 6.6) = 53.4

$$C = 40/12 = 3.33/3.33 = 1$$
$$H = 6.6/1 = 6.6/3.33 = 2$$
$$O = 53.4/16 = 3.33/3.33 = 1$$

Hence, the empirical formula is $CH_2O$ and the empirical formula weight is 12 + 1 × 2 + 16 = 30

Molecular weight of A = Vapour density × 2 = 15 × 2 = 30

As the empirical and molecular weights are same, the molecular formula would also be $CH_2O$

Molecular weight of B = Vapour density × 2 = 30 × 2 = 60

Molecular formula = Empirical formula × *n*

$$n = \frac{\text{Mol. wt.}}{\text{Emp. wt.}} = \frac{60}{30} = 2$$

Molecular formula of B is $CH_2O \times 2 = C_2H_4O_2$

Since A reduces ammoniacal silver nitrate it is an aldehyde. Wtih molecular formula $CH_2O$ it can only be formaldehyde, HCHO.

B gives red colour with neutral solution of ferric chloride, hence B is acetic acid. $CH_3COOH$.

Reactions are explained as under :

$$\underset{A}{HCHO} + Ag_2O \longrightarrow HCOOH + \underset{Mirror}{2\,Ag}$$

$$CH_3COOH + \text{Neutral solution of } FeCl_3 \longrightarrow \underset{\text{(Red colour)}}{\text{Ferric acetate}}$$

**Example 7. A chloro compound (A) showed the following properties:**

**(*i*) Decolorised bromine in $CCl_4$.**

**(*ii*) Absorbed hydrogen catalytically.**

**(*iii*) Gave a precipitate with ammoniacal cuprous chloride.**

**(*iv*) When vapourised 1·49 g of (A) gave 448 ml of vapour at STP. Identify (A) and write down the equation at step (*iii*).** **(*Roorkee 1991*)**

**Sol. Calculation of molecular weight of (A)**

448 ml of vapour at STP is obtained from 1·49 g of (A)

∴ 22400 ml of vapour at STP would be obtained from

$$\frac{1\cdot 49 \times 22400}{448} \text{ g of (A)} = 74\cdot 5 \text{ g.}$$

Hence, the molecular weight of (A) = 74·5.

Since (A) decolorises bromine in $CCl_4$ as well as absorbs hydrogen catalytically, it is an *unsaturated compound.*

(*iii*) (A) gives a precipitate with ammoniacal cuprous chloride, (A) is, therefore, a terminal alkyne *i.e.* $-C \equiv CH$.

(A), a chloro dervative (with molecular weight 74.5) can have only one chlorine (35.5) atom and it contains $-C \equiv CH$ (12 + 12 + 1 = 25) group, hence the residual part would have mass 74.5 – (35.5 + 25) = 14 which accounts for $CH_2$. Compound (A), therefore, is $ClCH_2-C \equiv CH$, 3-chloropropyne-1.

The reaction is explained as under :

$$ClCH_2C \equiv CH + AgNO_3 + NH_4OH \longrightarrow \underset{ppt.}{ClCH_2C \equiv C.Ag} + NH_4NO_3 + H_2O$$

**Example 8. When 0·0088 g of compound (A) was dissolved in 0·50 g of camphor the melting point of the camphor was lowered by 8°C. Analysis of (A) gave 68·18% C and 13.16% H. Compound (A) showed the following reactions :**

**(*i*) It reacted with acetyl chloride and evolved hydrogen with sodium.**

**(*ii*) When reacted with HCl + $ZnCl_2$ a dense oily layer separated out immediately. Compound (A) was passed over $Al_2O_3$ at 350°C to give compound (B). (B) on ozonolysis followed by hydrolysis gave two neutral compounds (C) and (D), which gave positive tests with carbonyl reagents**

**but only (C) gave a positive test with Fehling solution and resinous substance with NaOH. Identify (A), (B), (C) and (D) with proper reasoning.**

**$K_f$ of camphor = 40 K mole$^{-1}$ kg.** (*Roorkee 1991*)

**Sol. Calculation of molecular weight of (A)**

The formula used is written as under :

$$\text{Mol. wt. [M]} = \frac{1000 \times K_f \times w}{\Delta T \times W}$$

here $K_f = 40$, $w = 0.0088$ g, $\Delta T = 8°C$, $W = 0{\cdot}50$ g.

$$M = \frac{100 \times 40 \times 0{\cdot}0088}{8 \times 0{\cdot}50} = 88.$$

**Calculation of molecular formula of (A)**

Percentage of oxygen = 100 – [68·18 + 13·16] = 18.66

$C = 68{\cdot}18/12 = 5{\cdot}68/1{\cdot}16 = 4{\cdot}89 = 5$

$H = 13{\cdot}16/1 = 13{\cdot}16/1{\cdot}16 = 11{\cdot}34 = 12$

$O = 18{\cdot}66/16 = 1{\cdot}16/1{\cdot}16 = 1 = 1$

Empirical formula of (A) = $C_5H_{12}O$.

Empirical formula weight of (A) = 12 × 5 + 1 × 12 + 16 = 88.

As the empirical weight and molecular weight (calculated) are same, therefore, the molecular formula is $\mathbf{C_5H_{12}O}$.

(*i*) Since the compound (A) reacts with acetyl chloride and evolves hydrogen with sodium it must be an alcohol, $\mathbf{C_5H_{11}OH}$.

(*ii*) As the compound (A) immediately gives a dense oily layer, it is a tertiary alcohol.

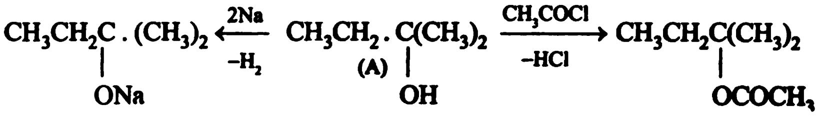
(*iii*) Compound (A) when passed over $Al_2O_3$ at 350°C gives a compound (B). As the reaction is dehydration, compound (B) must be an alkene.

(*iv*) (B), an alkene, on ozonolysis gives two neutral compound (C) and (D), both of them gives positive test with carbonyl reagents. Hence both (C) and (D) are carbonyl compounds.

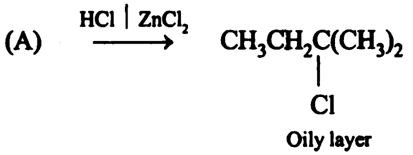
As only (C) gives positive test with Fehling solution, it is an aldehyde, whereas (D) is a ketone. As (C) gives resinous substance with NaOH, it cannot be formaldehyde (which gives Cannizzaro's reaction with NaOH).

Compound (A) is, therefore, $CH_3CH_2C(OH)(CH_3)_2$, *2-methyl butanol-2*; (B) is $CH_3CH = C(CH_3)_2$, *2-methyl butene-2*; (C) is $CH_3CHO$, *acetaldehyde*; and (*D*) is $(CH_3)_2CO$, *acetone*.

Reactions are explained as under :

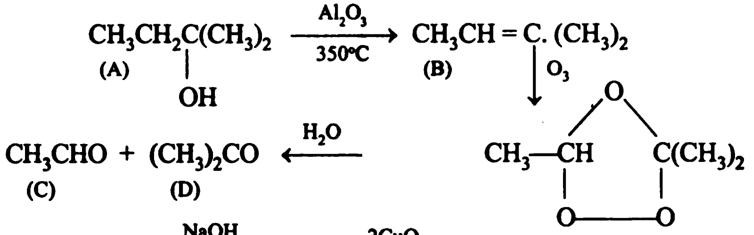


$$\begin{array}{c}CH_3CH_2C\,.\,(CH_3)_2\\ |\\ ONa\end{array} \xleftarrow[-H_2]{2Na} \begin{array}{c}CH_3CH_2\,.\,C(CH_3)_2\\ (A)\ |\\ OH\end{array} \xrightarrow[-HCl]{CH_3COCl} \begin{array}{c}CH_3CH_2C(CH_3)_2\\ |\\ OCOCH_3\end{array}$$



$$(A) \xrightarrow{HCl\ |\ ZnCl_2} CH_3CH_2\underset{\underset{Cl}{|}}{C}(CH_3)_2$$

Oily layer



$$\underset{(A)}{CH_3CH_2\underset{\underset{OH}{|}}{C}(CH_3)_2} \xrightarrow[350°C]{Al_2O_3} \underset{(B)}{CH_3CH=C.(CH_3)_2} \xrightarrow{O_3}$$

$$\underset{(C)}{CH_3CHO} + \underset{(D)}{(CH_3)_2CO} \xleftarrow{H_2O}$$

$$\text{Resinous substance} \xleftarrow{NaOH} CH_3CHO \xrightarrow[\text{Fehling sol.}]{2CuO} CH_3COOH + \underset{\text{Red ppt}}{Cu_2O}.$$

**Example 9. A hydrocarbon (A) (C = 90·56%, vapour density 53) was subjected to vigorous oxidation to give a dibasic acid (B). 0·10 g of (B) required 24.1 ml of 0·05 N NaOH for complete neutralization. Nitration of (B) gave a single mono nitro derivative. When (B) was heated strongly with sodalime it gave benzene. Identify (A) and (B) with proper reasoning and also give their structures.** (*Roorkee 1991*)

**Sol. Calculation of molecular formula of (A)**

Percentage of hydrogen = 100 − 90·56 = 9·44

C = 90·56/12 = 7·545/7·545 = 1 × 8 = 8

H = 9·44/1 = 9·44/7·545 = 1·25 × 8 = 10

The empirical formula of (A) = $C_8H_{10}$

and the empirical formula weight of (A) = 12 × 8 + 1 × 10 = 106

Molecular weight of (A) = 2 × Vapour density

= 2 × 53 = 106

As the molecular and empirical formula weights are same, the molecular formula for A is, $C_8H_{10}$.

Since (A) on vigorous oxidation gives a dibasic acid and on strong heating with soda lime gives benzene, it is a dialkyl benzene, *i.e.*, dimethyl benzene $C_6H_4(CH_3)_2$.

**Calculation of molecular weight of (B)**

24·1 ml of 0·05 N NaOH neutralizes 0·10 g of acid

∴ 1000 ml of N NaOH neutralizes

$$= \frac{0\cdot10 \times 1000 \times 1}{24\cdot1 \times 0\cdot05} = 88 \text{ g acid}$$

∴ Equivalent weight of dibasic acid B is 88.

The molecular weight of dibasic acid

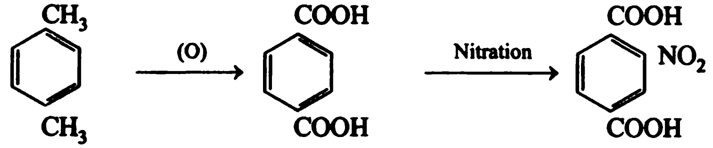
$$= \text{Equivalent weight} \times \text{Basicity}$$
$$= 88 \times 2 = \mathbf{166}$$

This indicates it to be a *benzene dicarboxylic acid,* $C_6H_4(COOH)_2$. Molecular weight $= 12 \times 6 + 1 \times 4 + (12 + 16 + 16 + 1)_2$

$$= 166.$$

Since (B) gives only one mono nitro derivative on nitration it is a para-isomer, *i.e.,* terephthalic acid and (A) is, therefore, *p-xylene.*

Reactions are explained as under :



*p*-xylene (A)   Terephthalic acid (B)   Nitroterephthalic acid

**Exmaple 10. One mole of an organic amide (A) upon alkaline hydrolysis gives one mole of $NH_3$ and one mole of a monobasic acid of equivalent weight 74. What is the molecular weight of (A) ?** (*Roorkee 1992*)

**Sol.** Since the acid obtained by the hydrolysis of amide (A) is monobasic, its molecular weight and the equivalent weight are the same.

The monobasic acid may be respresented as R.COOH. The molecular weight of the acid R.COOH = 74.

$$R + 12 + 16 + 16 + 1[45] = 74$$
$$R = 74 - 45 = 29$$

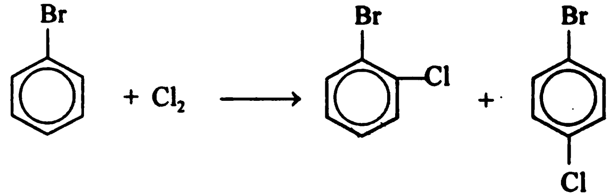
The alkyl group R is thus —$C_2H_5$ $(12 \times 2 + 1 \times 5 = 29)$, hence the monobasic acid is **propionic acid, $C_2H_5$ COOH.**

As one mole of acid and one mole of ammonia are obtained by alkaline hydrolysis of an organic amide (A), the amide is **propionamide, $C_2H_5CONH_2$.** The following reaction illustrates this.

$$\underset{\text{Propionamide (A)}}{C_2H_5CONH_2} + H_2O \xrightarrow{OH^-} \underset{\text{Propionic acid}}{C_2H_5COOH} + NH_3$$

**Example 11. When bromobenzene is monochlorinated two isomeric compounds (A) and (B) are obtained. Monobromination of (A) gives several isomeric products of molecular formula, $C_6H_3ClBr_2$ while monobromination of (B) yields only two isomers (C) and (D). Compound (C) is identical with one of the compounds obtained from the bromination of (A), however, (D) is totally different from any of the isomeric compounds obtained from the bromination of (A). Give the structures of (A), (B), (C) and (D) and also structures of four isomeric monobrominated products of (A). Support your answer with reasoning.** (*Roorkee 1992*)

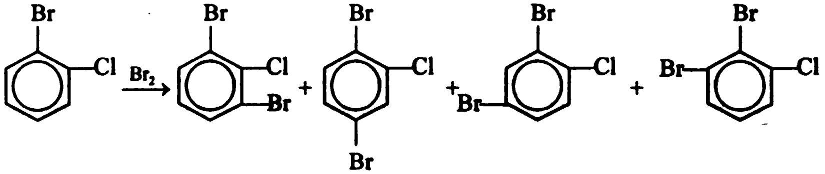
**Sol.** Bromobenzene on monochlorination will give ortho and para-chlorobromobenzene out of which para-isomer is compound (B) as its gives only two isomeric products of molecular formula, $C_6H_3ClBr_2$, on further bromination. (A) is, therefore, the ortho-isomer as on monobromination, it gives four isomeric products of molecular formula, $C_6H_3ClBr_2$. The following reactions explain the observations.



Bromobenzene

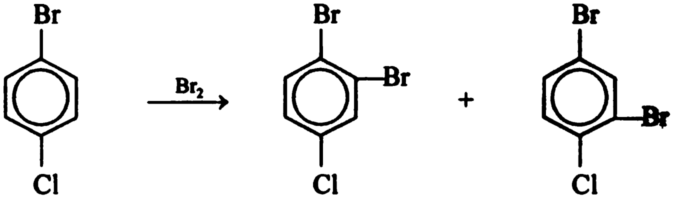
*o*-Chloro-Bromobenzene (A)

*p*-Chloro-Bromobenzene (B)



2, 6- 2, 5- 2, 4- 2, 3-

Dibromochlorobenzenes



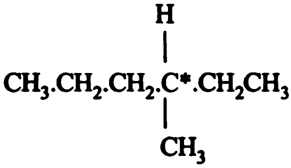
(B) 3, 4 - (D) 2, 4 - (C)

Dibromochlorobenzenes

**Example 12. There are six different alkenes (A), (B), (C), (D), (E) and (F). Each on addition of one molecule of hydrogen gives (G) which is the lowest molecular weight hydrocarbon containing only one asymmetric carbon atom. None of the above alkenes gives acetone as a product on ozonolysis. Give the structures of (A), (B), (C), (D), (E) and (F). Identify the alkene which is likely to give a ketone containing more than five carbon atoms on treatment with a warm concentrated solution of alkaline $KMnO_4$. Show various configurations of (G) in Fischer projection.**

*(Roorkee 1992)*

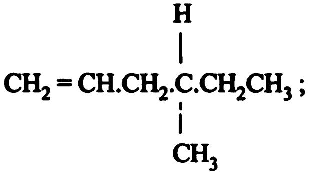
**Sol.** Since the six alkenes give an alkane of lowest molecular weight with one asymmetric carbon atom and none of the alkene gives acetone on ozonolysis, the only possible structure for (G) is :



$$CH_3.CH_2.CH_2.\overset{\displaystyle H}{\underset{\displaystyle CH_3}{C^*}}.CH_2CH_3$$

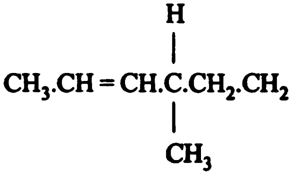
3-Methylhexane (G)

Thus, the six alkenes forming the alkane (G) by addition of one molecule of hydrogen can be represented as under :



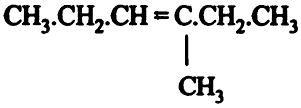
$$CH_2=CH.CH_2.\overset{\displaystyle H}{\underset{\displaystyle CH_3}{C}}.CH_2CH_3\ ;$$

4-Methylhexene-1 (A)



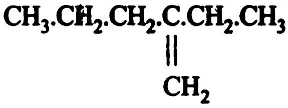
$$CH_3.CH=CH.\overset{\displaystyle H}{\underset{\displaystyle CH_3}{C}}.CH_2.CH_2$$

4-Methylhexene-2 (B)



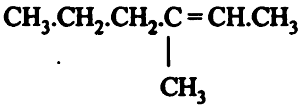
$$CH_3.CH_2.CH=\underset{\displaystyle CH_3}{C}.CH_2.CH_3$$

3-Methylhexene-3 (C)



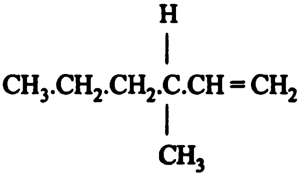
$$CH_3.CH_2.CH_2.\underset{\displaystyle CH_2}{\underset{\parallel}{C}}.CH_2.CH_3$$

2-Ethylpentene-1 (D)



$$CH_3.CH_2.CH_2.\underset{\displaystyle CH_3}{C}=CH.CH_3$$

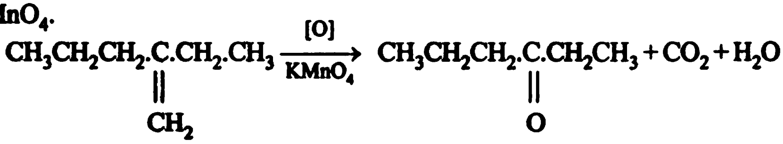
3-Methylhexene-2 (E),



$$CH_3.CH_2.CH_2.\overset{\displaystyle H}{\underset{\displaystyle CH_3}{C}}.CH=CH_2$$

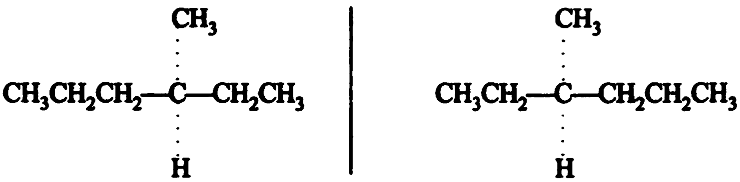
3-Methylhexene-1 (F)

It is (*D*), 2-ethyl pentene-1 which will give a ketone containing more than five carbon atoms on treatment with a warm concentrated solution of alkaline $KMnO_4$.



$$CH_3CH_2CH_2.\underset{\displaystyle CH_2}{\underset{\parallel}{C}}.CH_2.CH_3 \xrightarrow[KMnO_4]{[O]} CH_3CH_2CH_2.\underset{\displaystyle O}{\underset{\parallel}{C}}.CH_2CH_3+CO_2+H_2O$$

(D) Hexanone-3



$$CH_3CH_2CH_2—\overset{\displaystyle CH_3}{\underset{\displaystyle H}{C}}—CH_2CH_3 \qquad \Bigg| \qquad CH_3CH_2—\overset{\displaystyle CH_3}{\underset{\displaystyle H}{C}}—CH_2CH_2CH_3$$

Configurations of (G) in Fischer projection formula

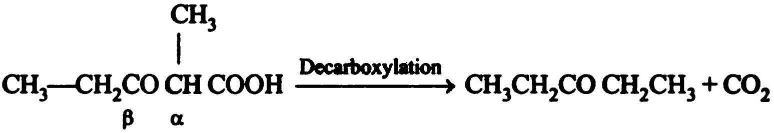
**Example 13. Two molecules of an ester (A) are condensed in the presence of sodium ethoxide to give a β-keto ester (B) and ethanol. On heat-**

**ing in an acidic solution (B) gives ethanol and a β-keto acid (C). On decarboxylation (C) gives 3-pentanone. Identify (A), (B) and (C) with proper reasoning. Name the reactions involved in the conversion of (A) to (B).**

*(Roorkee 1992)*

**Sol.** Condensation of an ester in presence of sodium ethoxide to form a β-keto ester is an example of *Claisen condensation.*

As the β-keto acid (C), formed by acidic hydrolysis of β-keto ester (B), on decarboxylation gives 3-pentanone, (C) can have the following structure.

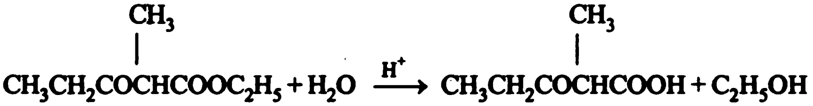


$$CH_3-CH_2\underset{\beta}{CO}\,\underset{\alpha}{\overset{\overset{CH_3}{|}}{CH}}\,COOH \xrightarrow{\text{Decarboxylation}} CH_3CH_2CO\,CH_2CH_3 + CO_2$$

α-Methyl-β-keto valeric acid (C)

3-Pentanone

As the β-keto ester (B) on acid-hydrolysis gives the β-keto acid (C) and ethanol, it is an ethyl ester of (C). This is explained by the following reaction.

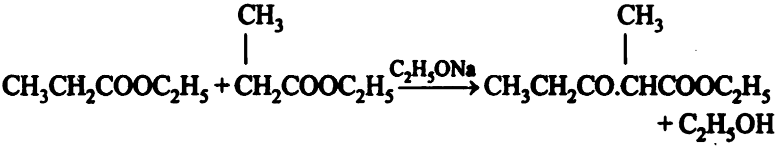


$$CH_3CH_2CO\overset{\overset{CH_3}{|}}{CH}COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3CH_2CO\overset{\overset{CH_3}{|}}{CH}COOH + C_2H_5OH$$

Ethyl ester (B)

(C)

(B) is obtained by Claisen-condensation of (A), therefore, (A) is ethyl propionate, $CH_3CH_2COOC_2H_5$.



$$CH_3CH_2COOC_2H_5 + \overset{\overset{CH_3}{|}}{CH_2}COOC_2H_5 \xrightarrow{C_2H_5ONa} CH_3CH_2CO.\overset{\overset{CH_3}{|}}{CH}COOC_2H_5 + C_2H_5OH$$

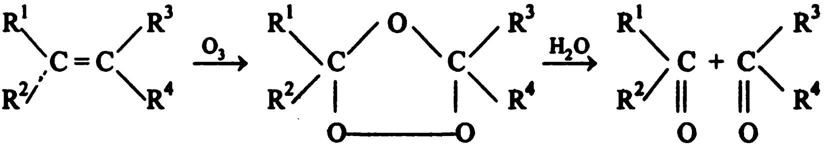
Ethyl propionate. (A, 2 moles)

(B)

**Example 14. An unsaturated hydrocarbon (A) $C_6H_{10}$ readily gives a monosodium compound on treatment with $NaNH_2$ in liquid $NH_3$. When (B) is allowed to react with 1-chloropropane a compound (C) is obtained, on partial hydrogenation in the presence of Lindlar catalyst (C) gives (D), $C_9H_{18}$. On ozonolysis, (D) gives 2,2-dimethyl propanal and 1-butanal. With proper reasoning give the structures of (A), (B), (C) and (D).**

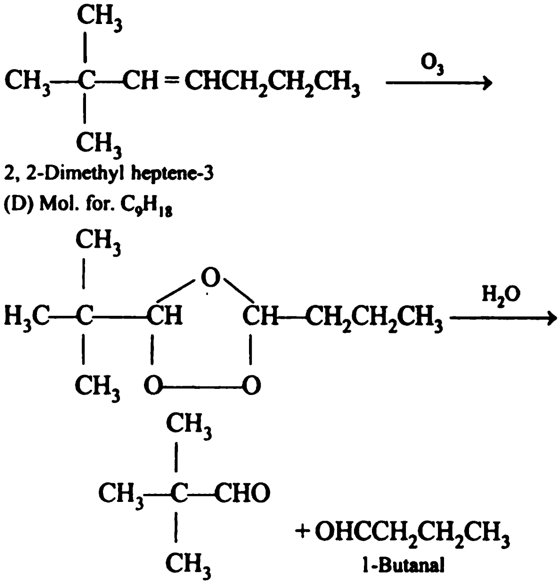
*(Roorkee 1992)*

**Sol.** A general ozonolysis reaction may be represented as :



By putting the values of $R^1$, $R^2$, $R^3$ and $R^4$ in the product as given in the problem, the alkene (D) comes out to be 2, 2-dimethyl heptene-3.

The following reaction illustrates this point.



2, 2-Dimethyl heptene-3

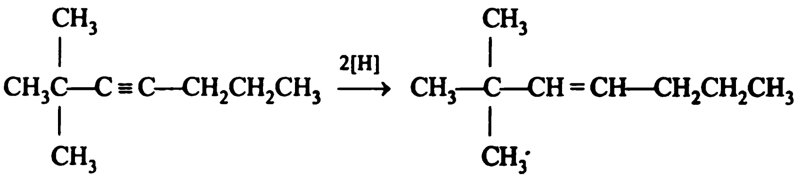
(D) Mol. for. $C_9H_{18}$

2,2-Dimethyl-propanal

1-Butanal

$$CH_3C(CH_3)_2CH=CHCH_2CH_2CH_3 \xrightarrow{O_3} \text{ozonide} \xrightarrow{H_2O} CH_3C(CH_3)_2CHO + OHCCH_2CH_2CH_3$$

Since (D) is obtained by partial hydrogenation of (C) in presence of Lindlar catalyst, (C) is 2, 2-dimethyl heptyne-3

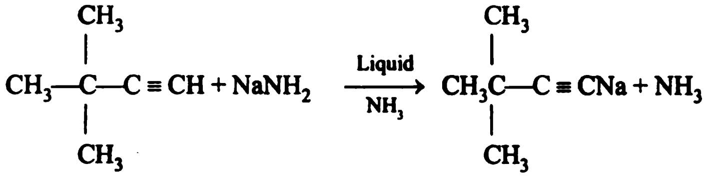


$$CH_3C(CH_3)_2—C\equiv C—CH_2CH_2CH_3 \xrightarrow{2[H]} CH_3—C(CH_3)_2—CH=CH—CH_2CH_2CH_3$$

2, 2-Dimethyl heptyne-3 (C)

(D)

As compound (A) reacts with $NaNH_2$ in liquid $NH_3$, it must be an alkyne 1. The molecular formula ($C_6H_{10}$) also agrees with the general molecular formula of alkynes ($C_nH_{2n-2}$). Further as (A) forms a sodium compound (B) with $NaNH_2$, in liquid $NH_3$ which on reacting with 1-chloropropane (a straight chain compound) gives (C), *i.e.*, 2, 2-dimethyl heptyne-3. (A) must be 3, 3, dimethyl 1-butyne and (B) is the monosodium compound. The following reactions explain the points:

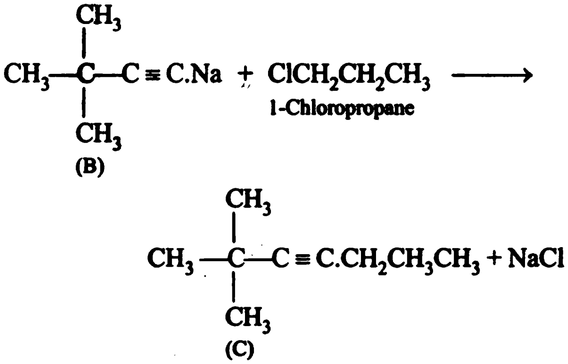


$$CH_3—C(CH_3)_2—C\equiv CH + NaNH_2 \xrightarrow[NH_3]{Liquid} CH_3C(CH_3)_2—C\equiv CNa + NH_3$$

3, 3-Dimethyl butyne-1 (A)

Mol. for. $C_6H_{10}$

Sodium *tert.* butyl acetylenide (B)



$$\underset{\text{(B)}}{\mathrm{CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-C\equiv C.Na}} + \underset{\text{1-Chloropropane}}{\mathrm{ClCH_2CH_2CH_3}} \longrightarrow$$

$$\underset{\text{(C)}}{\mathrm{CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-C\equiv C.CH_2CH_3CH_3}} + \mathrm{NaCl}$$

**Example 15. 0.450 g of an aromatic organic compound (A), on ignition gives 0.905 g $CO_2$ and 0.185 g $H_2O$. 0.350 g of (A) on boiling with $HNO_3$ and adding $AgNO_3$ solution gives 0.574 g of AgCl. The vapour density of A is 87.5. (A) on hydrolysis with $Ca(OH)_2$ yields (B) which on mild reduction gives an optically active compound (C). On heating (C) with $I_2$ and NaOH iodoform is produced along with (D). With HCl (D) gives a solid which is markedly more soluble in hot water than in cold. Identify (A) to (D) with proper explanation.** (*Roorkee 1993*)

**Sol. Calculation of percentage composition**

$$\text{Percentage of C} = \frac{12}{44} \times \frac{0.905}{0.450} \times 100 = 54.84$$

$$\text{Percentage of H} = \frac{2}{18} \times \frac{0.185}{0.450} \times 100 = 4.56$$

$$\text{Percentage of Cl} = \frac{35.5}{143.5} \times \frac{0.574}{0.350} \times 100 = 40.57$$

**Calculation of empirical formula**

| *Element* | *Percentage/Atomic Weight* | *Relative number/Simple ratio of atoms* |
|---|---|---|
| C | $\frac{54.84}{12} = 4.56$ | $= \frac{4.56}{1.14} = 4$ |
| H | $\frac{4.56}{1} = 4.56$ | $= \frac{4.56}{1.14} = 4$ |
| Cl | $\frac{40.57}{35.5} = 1.14$ | $= \frac{1.14}{1.14} = 1$ |

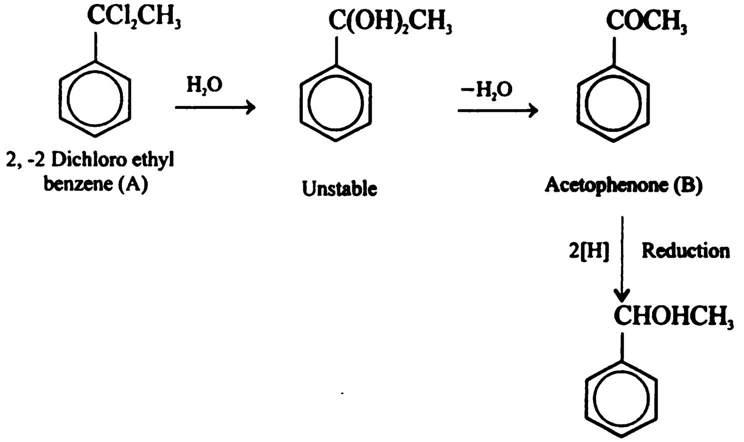
Hence the empirical formula of (A) is $C_4H_4Cl$

Empirical formula weight = 48 + 4 + 35.5 = 87.5

Its V.D. is 87.5 (given)

Hence its moelcular formula would be $C_4H_4Cl \times 2 = C_8H_8Cl_2$

(A) on hydrolysis gives (B) which on mild reduction gives an optically active compound (C) which also gives iodoform test. (C) is an alkanol-2 and (B) must be an alkanone-2. Hence (A) has to be a *gem* dihalide (with two Cl atoms attached to the same C-atom). These two atoms must be attached with 2nd C-atom, only then alkanone-2 would be formed on hydrolysis. Hence (A) is 2,2-dichloroethyl benzene. The following reactions illustrate the observations :

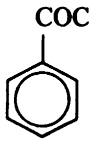


2, -2 Dichloro ethyl benzene (A)

Unstable

Acetophenone (B)

Methyl phenyl carbinol (C) (optically active)



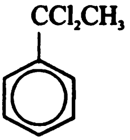
$\xrightarrow{I_2/NaOH}$ $CHI_3 + C_6H_5COONa$

Iodoform (D)

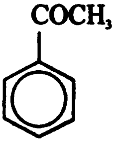
$$C_6H_5COONa \xrightarrow[H^+]{HCl} C_6H_5COOH$$

Benzoic acid

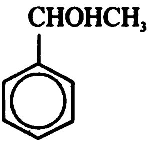
Benzoic acid is markedly more soluble in hot water than in cold. Hence (A), (B), (C) and (D) are given as follows :



(A)



(B)

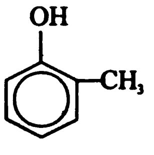


(C)

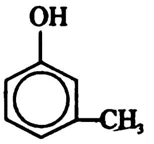
(D)

**Example 16. An organic compound (A), $C_7H_8O$ is insoluble in aqueous $NaHCO_3$ but soluble in NaOH. A on treatment with bromine water rapdily forms compound (B), $C_7H_5OBr_3$. (*i*) Give structures for (A) and (B). (*ii*) What will be (A) if it does not dissolve in NaOH but shows reactions gives above ? Give answers with proper reasoning.** (*Roorkee 1993*)

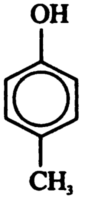
**Sol.** Since compound (A) is soluble in NaOH but insoluble in aqueous $NaHCO_3$, it is weakly acidic, hence (A) is phenol. The molecular formula $C_7H_8O$ points to the possibility of a methyl substituted phenol. Three probable structures are :



ortho

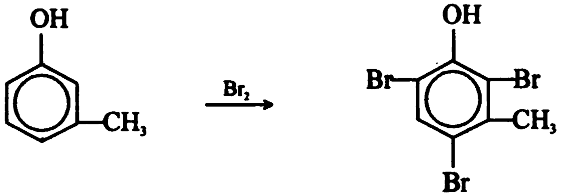


meta



para cresols

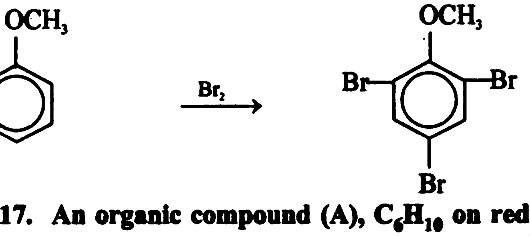
Since (A) readily reacts with bromine water to give (B) $C_7H_5OBr_3$, it can be meta isomer only.



[A] [B]

2, 4, 6-Tribromo-3-methyl phenol

(*ii*) If (A) does not dissolve in NaOH, it may be anisole.



**Example 17. 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 the acid (F), $C_4H_8O_2$. Determine the structures of the compounds (A) to (F) with proper reasoning.** (*Roorkee 1993*)

**Sol.** (A) with molecular formula $C_6H_{10}(C_n H_{2n-2})$ is either an alkyne or diene. Since it gives on ozonolysis two aldehydes, it must be a diene. Moreover (B) on oxidation with acidified $KMnO_4$ gives $C_4H_8O_2$, it shows that four C-atoms are on one side of the double bond. It means that (B) is 2-hexene;

(C), $C_6H_{14}$ is hexane. Hence (A), (B) and (C) are represented as under :

$$CH_3CH = CH - CH = CHCH_3 \qquad (A)$$

Hexa-2, 4-diene

$$\downarrow H_2$$

$$CH_3CH = CH - CH_2CH_2CH_3 \qquad (B)$$

2-Hexene

$$\downarrow H_2$$

$$CH_3CH_2CH_2CH_2CH_2CH_3 \qquad (C)$$

*n*-Hexane

Ozonolysis and oxidation reactions are explained as under :

$$CH_3CH = CH - CH = CHCH_3 \qquad (A)$$

Hexa-2, 4-diene

$$O_3 \downarrow H_2O$$

$$2CH_3CHO + \begin{array}{c} CHO \\ | \\ CHO \end{array}$$

Ethanal Glyoxal

(D) (E)

$$CH_3CH = CH - CH_2CH_2CH_3$$

$$[O] \downarrow \text{Acidified } KMnO_4$$

$$CH_3COOH + HOOC.\,CH_2CH_2CH_3$$

Butanoic acid (F)

Hence (A) to (F) are

(A) $CH_3CH = CH - CH = CHCH_3$
Hexa-2, 4-diene

(B) $CH_3CH = CH - CH_2 - CH_2CH_3$
2-Hexene

(C) $CH_3CH_2CH_2CH_2CH_2CH_3$
Hexane

(D) $CH_3CHO$
Ethanal

(E) $CHO\,.\,CHO$
Glyoxal

(F) $CH_3CH_2CH_2COOH$
Butanoic acid

**Example 18. 0.037 g of an alcohol, was added to $CH_3MgI$ and the gas evolved measured 11·2 cm$^3$ at STP. What is the molecular weight of ROH ? On dehydration, ROH gives an alkene which on ozonolysis gives acetone as one of the products. ROH on oxidation easily gives an acid containing the same number of carbon atoms. Give the structures of ROH and the acid with proper reasoning.** (*Roorkee 1994*)

**Sol.** (*i*) A Griguard reagent reacts with a compound containing active hydrogen to liberate hydrogen gas.

Consider the equation,

$$ROH + CH_3MgI \longrightarrow CH_4 + Mg(OR)I$$

11·2 cm$^3$ of $CH_4$ are produced from = 0.037 g ROH

$\therefore$ 22,400 cm$^3$ of $CH_4$ are produced from $= \frac{0 \cdot 037}{11 \cdot 2} \times 22400 = 74$ **g ROH**

$\therefore$ Mol. wt. of alcohol (ROH) = 74

(*ii*) The four possible isomeric alcohols having the moecular weight 74 are :

$CH_3CH_2CH_2CH_2OH$ **1-Butanol (I)**

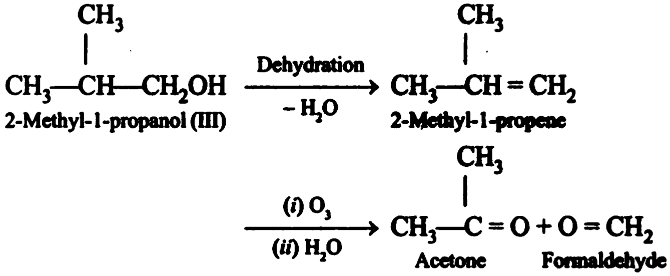
$CH_3CHOHCH_2CH_3$ **2-Butanol (II)**

$(CH_3)_2CHCH_2OH$ **2-Methyl-1-propanol (III)**

$(CH_3)_3COH$ **2-Methyl-2-Propanal (IV)**

(*iii*) Since the alcohol (ROH) on oxidation gives an acid containing the same number of carbon atoms, *it must be a* 1° *alcohol.* Out of the four alcohols listed above, the two 1° alcohols are : 1-butanol (I) and 2-methyl-1-propanol (III). Thus structures (II) and (IV) are ruled out.

(*iv*) Further since the alcohol (ROH) on dehydration gives an alkene which on ozonolysis gives acetone as one of the products, alcohol (ROH) must be 2-methyl-1-propanol (III). The reactions are explained as under :



$$\underset{\textbf{2-Methyl-1-propanol (III)}}{CH_3-\overset{\overset{CH_3}{|}}{C}H-CH_2OH} \xrightarrow[-H_2O]{\textbf{Dehydration}} \underset{\textbf{2-Methyl-1-propene}}{CH_3-\overset{\overset{CH_3}{|}}{C}H=CH_2}$$

$$\xrightarrow[(ii)\ H_2O]{(i)\ O_3} \underset{\textbf{Acetone}}{CH_3-\overset{\overset{CH_3}{|}}{C}=O} + \underset{\textbf{Formaldehyde}}{O=CH_2}$$

Thus, alcohol (ROH) is 2-methyl-1-propanol or isobutyl alcohol. $(CH_3)_2CH-CH_2OH$.

**Example 19. An alkane (A), $C_5H_{12}$ on chlorination at 300°C gives a mixture of four different monochlorinated derivatives, (B), (C), (D) and (E). Two of these derivatives give the same alkene (F) on**

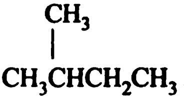
**dehydrohalogenation. On oxidation with alkaline $KMnO_4$, followed by acidification, (F) gives two products (G) and (H). Give structures of (A) to (H) with proper reasoning.** (*Roorkee 1995*)

**Sol.** With the molecular formula $C_5H_{12}$ of alkane (A), following three compounds are possible :

$CH_3CH_2CH_2CH_2CH_3$ ;

I

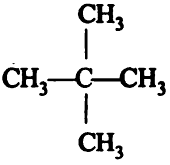
Pentane



$CH_3\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_2CH_3$ ;

II

2-Methyl butane

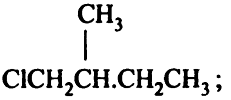


$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_3$

III

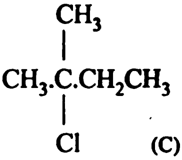
2,2-Dimethyl propane

Out of three compounds only II would give four different monochlorinated derivatives, as given below :



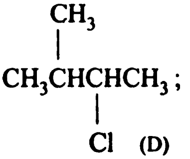
$ClCH_2\overset{\overset{\displaystyle CH_3}{|}}{C}H.CH_2CH_3$ ;

(B)



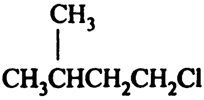
$CH_3.\underset{\underset{\displaystyle Cl}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}.CH_2CH_3$

(C)



$CH_3\overset{\overset{\displaystyle CH_3}{|}}{C}H\underset{\underset{\displaystyle Cl}{|}}{C}HCH_3$ ;

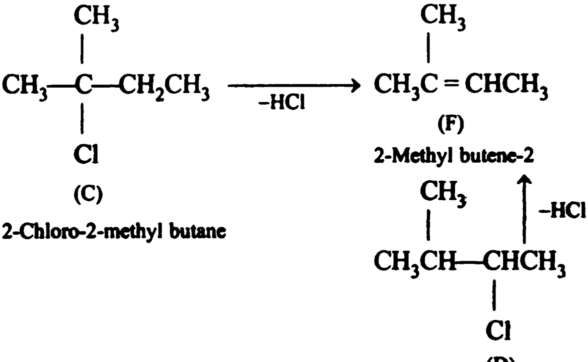
(D)



$CH_3\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_2CH_2Cl$

(E)

Out of the four derivatives only two give the same stable alkene (F) on dehydrohalogenation. These derivatives are : (C) and (D).



$$CH_3-\underset{\underset{\displaystyle Cl}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_2CH_3 \xrightarrow[-HCl]{} CH_3\overset{\overset{\displaystyle CH_3}{|}}{C}=CHCH_3 \xleftarrow[-HCl]{} CH_3\overset{\overset{\displaystyle CH_3}{|}}{C}H-\underset{\underset{\displaystyle Cl}{|}}{C}HCH_3$$

(C)

2-Chloro-2-methyl butane

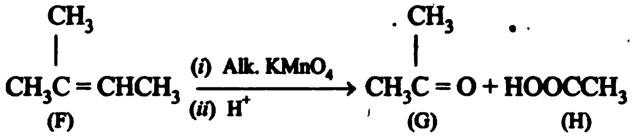
(F)

2-Methyl butene-2

(D)

2-Chloro-3-methyl butane

On oxidation with alkaline $KMnO_4$ followed by acidification, alkene (F) gives acetone (G) and acetic acid (H).



$$\underset{(F)}{CH_3\overset{\displaystyle CH_3}{\overset{|}{C}}=CHCH_3} \xrightarrow[(ii)\ H^+]{(i)\ \text{Alk. KMnO}_4} \underset{(G)}{CH_3\overset{\displaystyle CH_3}{\overset{|}{C}}=O} + \underset{(H)}{HOOCCH_3}$$

Acetone Acetic acid

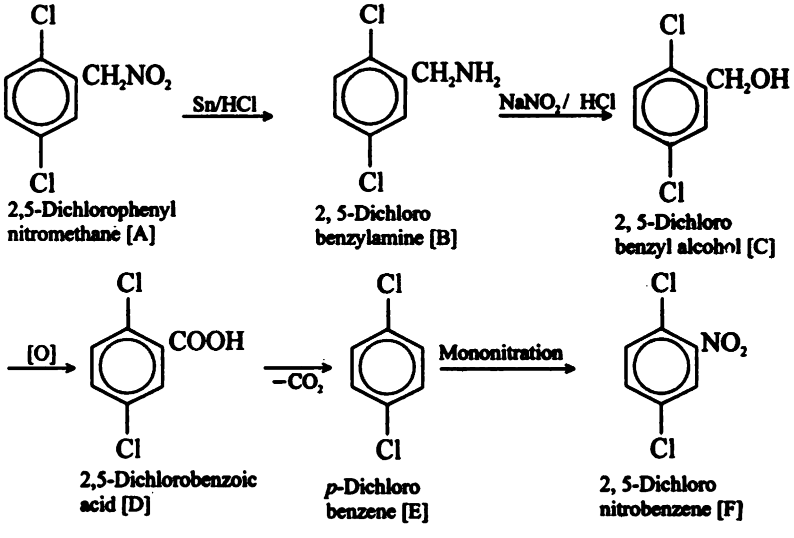
**Example 20. An aromatic compound (A), $C_7H_5NO_2Cl_2$ on reduction with Sn/HCl gives (B) which on reaction with $NaNO_2$/HCl gives (C). Compound (B) does not form a dye with β-naphthol. However, (C) gives red colour with ceric ammonium nitrate and on oxidation gives an acid (D) of equivalent weight 191. Decarboxylation of (D) gives (E) which forms a single mononitro derivative (F) on nitration. Give structures of (A) to (F) with proper reasoniug.** (*Roorkee 1995*)

Sol. Since the compound (C) gives red colour with ceric ammonium nitrate, it is an alcohol, *i.e.*, the —OH group is present in the side chain of aromatic compound. (C) is obtained by the action of $NaNO_2$/HCl on (B), hence (B) is an amine with the amino group attached to the side chain. Further since (B) an amine, is obtained by reduction of an aromatic compound (A) by Sn/HCl, (A) must be a nitro compound with the nitro group in side chain.

Following structures for compounds (A), (B) and (C) explain the reactions :

$$\underset{[A]}{Cl_2C_6H_3CH_2NO_2}\ ; \quad \underset{[B]}{Cl_2C_6H_3CH_2NH_2}\ ; \quad \underset{[C]}{Cl_2C_6H_3CH_2OH}$$

(C) on oxidation gives an acid (D) with equivalent weight 191, it can be $Cl_2C_6H_3COOH$ (molecular weight 191, being monocarboxylic acid its equivalent weight is equal to molecular weight). (D) on decarboxylation gives a compound (E) which forms only a single mononitro derivative (F), therefore, (E) can only be *p*-dichloro benzene. All the observations are explained as under :

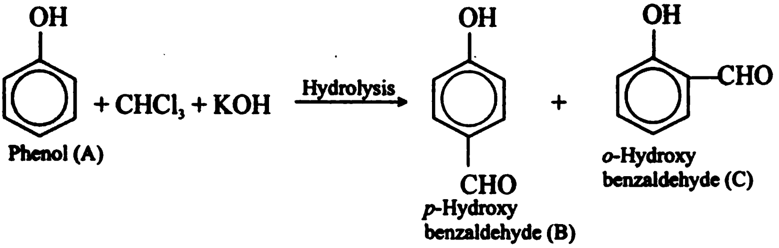


**Example 21. An organic compound (A) gives posistive Libermann reaction and on treatment with $CHCl_3/KOH$ followed by hydrolysis gives (B) and (C). Compound (B) gives colour with Schiff's reagent but not (C), which is steam volatile. (C) on treatment with $LiAlH_4$ gives (D), $C_7H_8O_2$ which on oxidation gives (E). Compound (E) reacts with $(CH_3CO)_2O/CH_3COOH$ to give a pain reliever (F). Give structures of (A) to (F) with proper reasoning.** (*Roorkee 1995*)

**Sol.** (*i*) Compound (A) gives positive Libermann reaction, it is, therefore, a phenol.

(*ii*) (A) gives two compounds (B) and (C) on treatment with $CHCl_3/KOH$ (Reimer-Tiemann reaction), (B) and (C) are thus aromatic hydroxy aldehydes, *i.e.*, ortho and para isomers. Compound (C) on reduction with $LiAlH_4$ gives a compound (D), which would be an alcohol. With moelcular formula $C_7H_8O_2$, it could be $C_6H_4(OH)CH_2OH$. Thus (A) is phenol, $C_6H_5OH$.

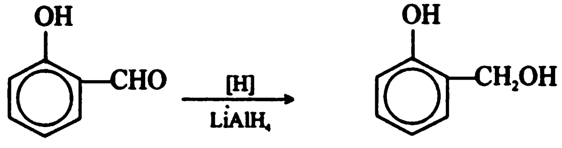
(*iii*) Since (B) gives test with Schiff's reagent, it is the para isomer and (C) which is steam volatile (due to intramolecular H-bond) must be ortho-isomer. The reactions are explained with the help of following structures of (A), (B), (C) and (D).



Phenol (A)

*p*-Hydroxy benzaldehyde (B)

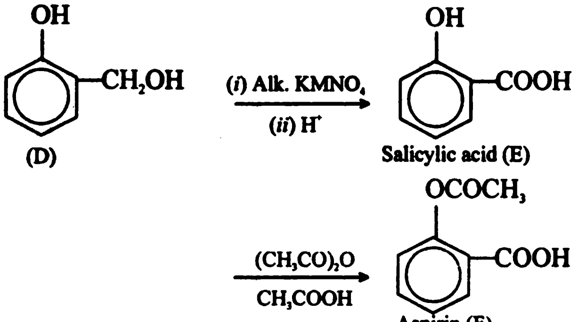
*o*-Hydroxy benzaldehyde (C)



(C)

*o*-Hydroxy benzyl alcohol ($C_7H_8O_2$) (D)

(*iv*) (D) on oxidation gives an acid (E) which should be salicylic acid. (E) on treatment with $(CH_3CO)_2O/CH_3COOH$ gives (F), a pain-reliever, which must be acetyl salicylic acid (aspirin).



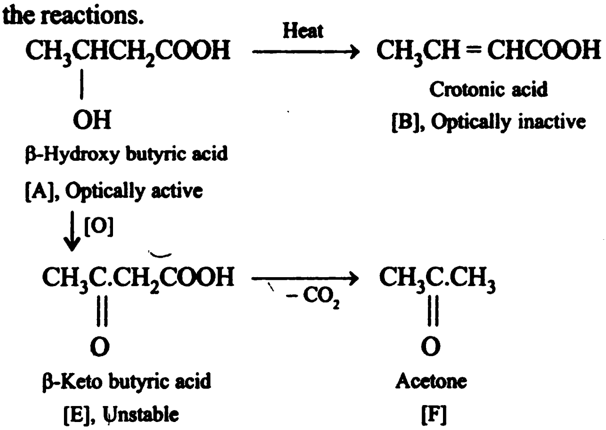
(D)

Salicylic acid (E)

Aspirin (F)

**Example 22. An acidic compound (A), $C_4H_8O_3$ loses its optical activity on strong heating yielding (B), $C_4H_6O_2$ which reacts readily with $KMnO_4$. (B) forms a derivative (C) with $SOCl_2$, which on reaction with $(CH_3)_2$ NH gives (D). The compound (A) on oxidation with dilute chromic acid gives an unstable compound (E) which decarboxylates readily to give (F), $C_3H_6O$. The compound (F) gives a hydrocarbon (G) on treatment with amalgamated Zn and HCl. Give structures of (A) to (G) with proper reasoning.** (*Roorkee 1995*)

**Sol.** (*i*) The acidic compound (A), $C_4H_8O_3$ on heating yields a compound (B), $C_4H_6O_2$. It is a hydroxy acid. On heating of (A), a molecule of water is lost ($C_4H_8O_3$—$C_4H_6O_2$ = $H_2O$). Compound (B) is an unsaturated compound since it reacts readily with $KMnO_4$. Further oxidation of (A) gives an unstable compound (E) which decarboxylates readily, (E) must be a β-keto acid, thus (A) is a β-hydroxy acid. Following structures for the compounds (A) to (G) explain the reactions.



$$\underset{\text{OH}}{\overset{|}{\text{CH}_3\text{CHCH}_2\text{COOH}}} \xrightarrow{\text{Heat}} \text{CH}_3\text{CH}=\text{CHCOOH}$$

β-Hydroxy butyric acid [A], Optically active; Crotonic acid [B], Optically inactive

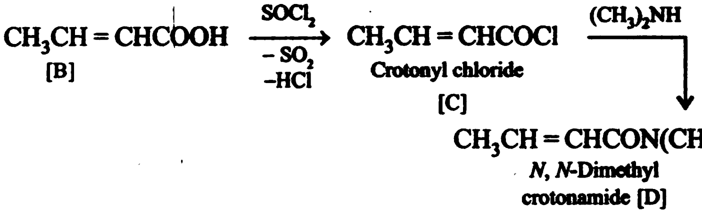
$$\downarrow [\text{O}]$$

$$\underset{\text{O}}{\overset{\|}{\text{CH}_3\text{C.CH}_2\text{COOH}}} \xrightarrow[-\text{CO}_2]{} \underset{\text{O}}{\overset{\|}{\text{CH}_3\text{C.CH}_3}}$$

β-Keto butyric acid [E], Unstable; Acetone [F]

Since (F) is acetone, its reduction with amalgamated Zn/HCl would give propane, $CH_3CH_2CH_3$ (G).

Reaction of (B) with $SOCl_2$ produces acid chloride (C) which gives a substituted amide (D) on treatment with $(CH_3)_2NH$

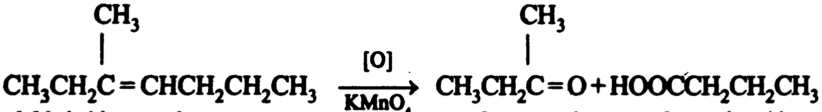


$$\underset{[\text{B}]}{\text{CH}_3\text{CH}=\text{CHCOOH}} \xrightarrow[-\text{SO}_2,\ -\text{HCl}]{\text{SOCl}_2} \underset{\text{Crotonyl chloride [C]}}{\text{CH}_3\text{CH}=\text{CHCOCl}} \xrightarrow{(\text{CH}_3)_2\text{NH}} \underset{N,N\text{-Dimethyl crotonamide [D]}}{\text{CH}_3\text{CH}=\text{CHCON(CH}_3)_2}$$

**Example 23. 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 structures of (A) to (G) with proper reasoning.** (*Roorkee 1995*)

**Sol.** (*i*) Since the two compounds (D) (A carbonyl compound) and (E) (an acid) obtained on vigorous oxidation of alkene (A), contain 4—C atoms each, alkene (A) contains a total of 8—C atoms.

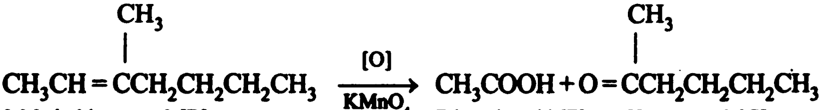
(*ii*) Oxidation of (A) gives a carbonyl compound and an acid. It must have a side chain at one of the two C-atoms atttached through the double bond. It is this part which will give a carbonyl compound. On both sides of the double bond there are 4-carbon atoms each in alkene (A). The side with the branching would give carbonyl compound on oxidation and the other side with a straight chain of C-atoms would give the acid. Hence alkene (A) has the structure as given below and tthe oxidation reaction is explained as under :



$$CH_3CH_2\overset{\overset{CH_3}{|}}{C}=CHCH_2CH_2CH_3 \xrightarrow[KMnO_4]{[O]} CH_3CH_2\overset{\overset{CH_3}{|}}{C}=O + HOOCCH_2CH_2CH_3$$

3-Methyl heptene-3 [A] Butanone-2 [D] Butanoic acid [E]

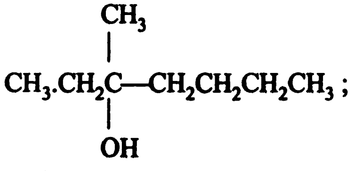
(*iii*) Since alkenes (A) and (B) give the same alcohol on hydration, (B) would also have 8—C atoms with the change in the position of double bond. Alkene (B) on oxidation gives a carbonyl compound which has no two identical groups attached. It would, therefore, have two C-atoms on one side of the double bond and 5-C-atoms including the branch on the other side of the double bond. (B) Thus has the structure as given below and oxidation takes place as follows :



$$CH_3CH=\overset{\overset{CH_3}{|}}{C}CH_2CH_2CH_2CH_3 \xrightarrow[KMnO_4]{[O]} CH_3COOH + O=\overset{\overset{CH_3}{|}}{C}CH_2CH_2CH_2CH_3$$

3-Methyl heptene-2 [B] Ethanoic acid [F] Hexanone-2 [G]

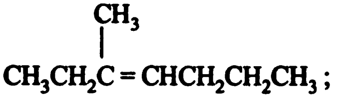
Compound (C) obtained on hydration of (A) and (B) is :



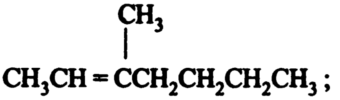
$$CH_3.CH_2\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}—CH_2CH_2CH_2CH_3\ ;$$

3-Methyl heptanol-3

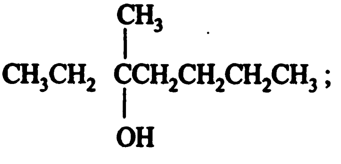
Thus the various compounds can be represented as under :

(A) 

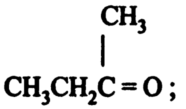
$CH_3CH_2\overset{\overset{CH_3}{|}}{C}=CHCH_2CH_2CH_3$ ; 3-Methyl heptene-3

(B) 

$CH_3CH=\overset{\overset{CH_3}{|}}{C}CH_2CH_2CH_2CH_3$ ; 3-Methyl heptene-2

(C) 

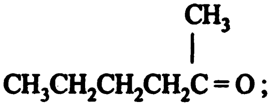
$CH_3CH_2\ \underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}CH_2CH_2CH_2CH_3$ ; 3-Methyl heptanol-3

(D) 

$CH_3CH_2C(CH_3)=O$ ; **Butanone-2**

(E) $CH_3CH_2CH_2COOH$ ; **Butanoic acid**

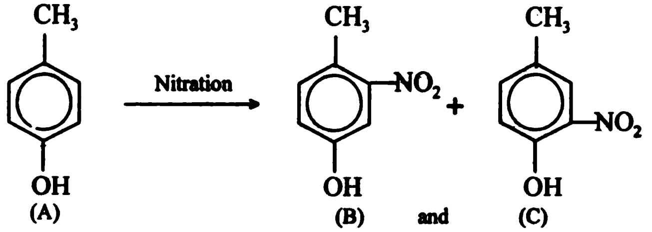
(F) $CH_3COOH$ ; **Ethanoic acid**

(G) 

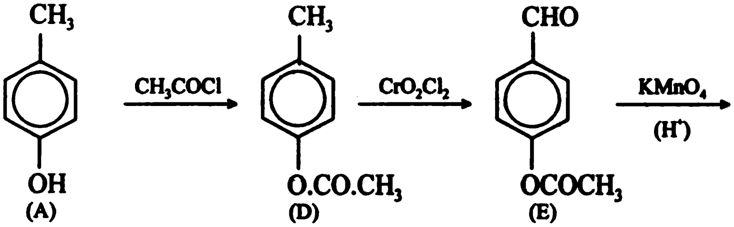
$CH_3CH_2CH_2CH_2C(CH_3)=O$ ; **Hexanone-2**

**Example 24. Two isomeric mononitro derivatives (B) and (C) are obtained by the nitration of an organic compound (A) $C_7H_8O$. Treatment of (A) with acetyl chloride produces (D) which on reaction with $CrO_2Cl_2$ gives (E) whose oxidation with neutral $KMnO_4$ followed by acidification gives (F). he compound (F) on heating gives phenol. (A) on treatment with alkaline $C_6H_5SO_2Cl$ produces (G) which on oxidation with $KMnO_4$ gives (H). Hydrolysis of (H) also gives (F). Give structures of (A) to (H) with proper reasoning.** *(Roorkee 1996)*

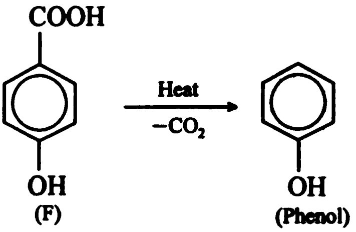
Sol. Since the compound (F) on heating gives phenol, the compound (A) contains—OH group. The molecular formula of (A) is $C_7H_8O$. Therefore, compound (A) is a cresol, $CH_3.C_6H_4.OH$. This cresol gives two isomers on nitration, therefore, it should be *p*-cresol. Different reactions may be presented as under :



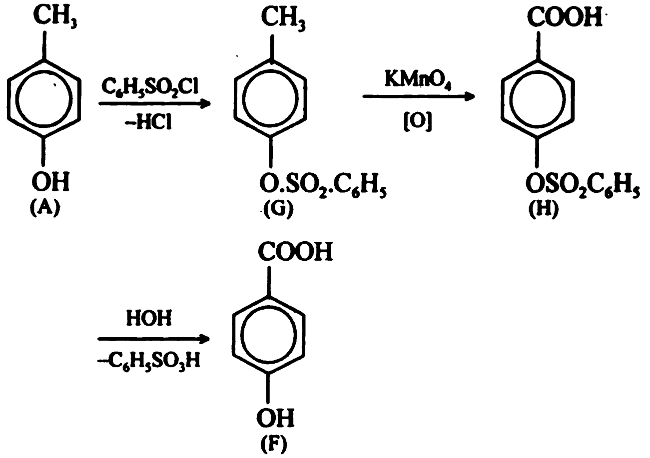
(A) (B) and (C)



(A) (D) (E)



(F) (Phenol)



**Example 25. An organic compound (A) composed of C, H and O gives characteristic colour with ceric ammonium nitrate. Treatment of (A) with $PCl_5$ gives (B) which reacts with KCN to form (C). The reducion 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 nitrobenzene. Give structures of (A) to (E) with proper reasoning.**

(*Roorkee 1996*)

**Sol.** Since compound (A) gives characteristic colour with ceric ammonium nitrate, it should be an alcohol.

The final product is pyridine $C_5H_5N$. It contains five carbon atoms and is obtained by the evolution of $NH_3$. Therefore, the compound 'D' should contain two nitrogen atoms which is obtained after the reactions with $PCl_5$, KCN and reduction. Therefore, 'A' contains three carbon atoms with two —OH groups at the terminal.

On the basis of above observations 'A' should have the structure :

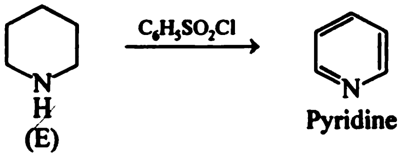
$HO—CH_2.CH_2.CH_2.OH$.

The reactions are as follows :

$$\underset{(A)}{HO.CH_2.CH_2.CH_2.OH} \xrightarrow[-2POCl_3,\ -2HCl]{2PCl_5} \underset{(B)}{Cl.CH_2.CH_2.CH_2.Cl}$$

$$\xrightarrow[-2KCl]{2KCN} \underset{(C)}{NC.CH_2.CH_2.CH_2.CN} \xrightarrow{Na/C_2H_5OH}$$

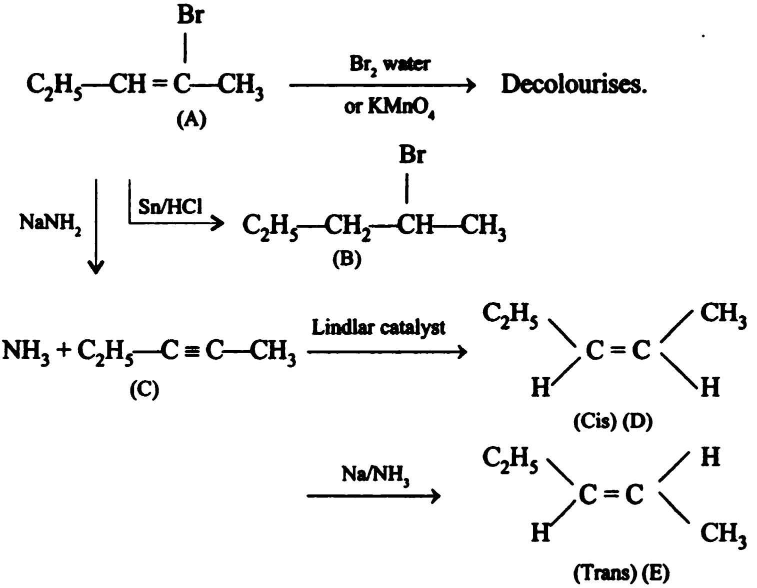
$$\underset{(D)}{H_2N.CH_2.CH_2.CH_2.CH_2.NH_2} \xrightarrow[-NH_3]{Heat}$$



**Example 26. An organic compound (A) $C_5H_9Br$ which readily decolourises 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 catalyst to give (D) and on reaction with Na/liq. $NH_3$ produces (E). Both the compounds (D) and (E) are isomeric. Give structures of (A) to (E) with proper reasoning.** (*Roorkee 1996*)

**Sol.** Since the compound (A) decolourised bromine water and $KMnO_4$ solution, it should be unsaturated. But with Sn/HCl it ($C_5H_9Br$) changes to $C_5H_{11}Br$, *i.e.*, two hydrogen atoms are added, therefore, there should be one double bond in (A). Because the compound (C) gives two isomers (cis and trans), therefore, in (C) the triple bond should be at second carbon atom. In other words, the double bond in (A) should be at second C-atom.

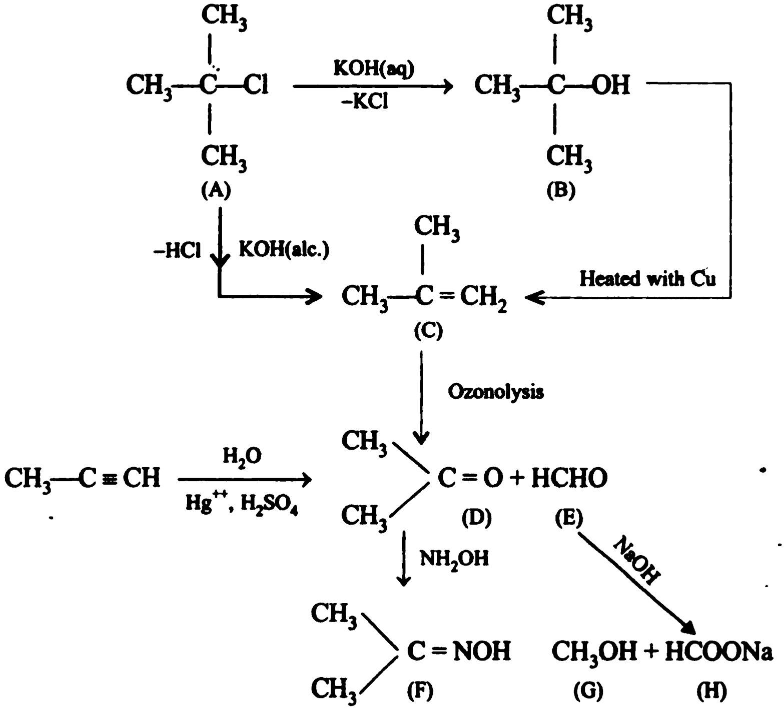
Following structures for different compounds explain the reactions.



**Example 27. An organic compound (A) $C_4H_9Cl$ on reacting with 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 decolourises bromine water. Ozonolysis of (C) gives two compounds (D) and (E). Compound (D) reacts with $NH_2OH$ to give (F) and the compound (E) which 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.** (*Roorkee 1996*)

**Sol.** Since the compound (E) reacts with NaOH to form alcohol and sodium salt of an acid, it should be HCHO. Compound (D) is formed by propyne and $H_2O$ in the presence of $Hg^{2+}$ and $H_2SO_4$, therefore, (D) is acetone. Compounds (D) and (E) are obtained by the ozonolysis of (C). Hence the compound (C) should be $(CH_3)_2.C=CH_2$. (A) is, therefore, tertiary butyl chloride.

Different compounds and their reactions are given as under :



**Example 28. The percentage of carbon, hydrogen and nitrogen in a disubstituted aromatic compound (A) is 71.11, 6.67 and 10.37 respectively. Its molecule contains a single atom of nitrogen. Compound (A) evolves $NH_3$ when heated with NaOH to form at salt (B), from which an acid (C) is obtained on acidification. If an electrophilic substitution is carried on (C), an entering electrophile can occupy either of the two identical positions available in the ring. Acid (C) on heating with $PCl_5$ gives (D) which reacts with (B) to give an organic product (E). Give structures of (A) to (E) with proper reasoning.** *(Roorkee 1996)*

**Sol.** Empirical formula of compound 'A' may be arrived as under :

| *Element* | *Percentage* | *At. mass* | *Atomic ratio* | *Simple ratio* |
|---|---|---|---|---|
| C | 71.11 | 12 | $\frac{71.11}{12}=5.92$ | $\frac{5.92}{0.74}=8$ |
| H | 6.67 | 1 | $\frac{6.67}{1}=6.67$ | $\frac{6.67}{0.74}=9$ |

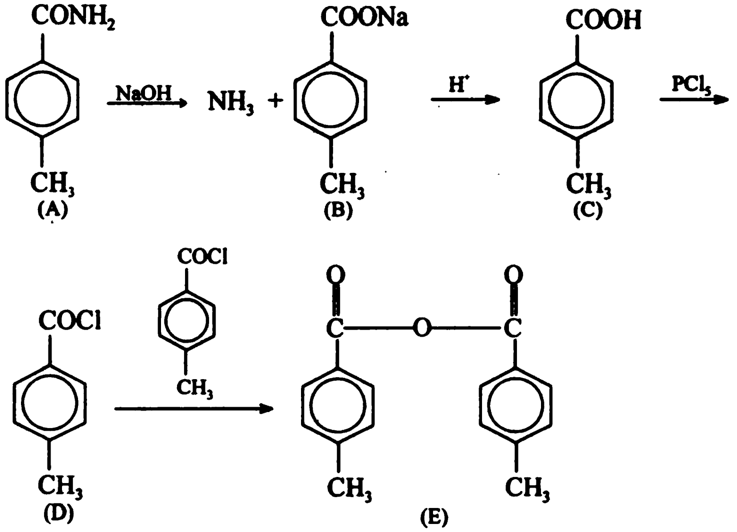
| | | | | |
|---|---|---|---|---|
| N | 10.37 | 14 | $\frac{10.37}{14} = 0.74$ | $\frac{0.74}{0.74} = 1$ |
| O | 11.85 | 16 | $\frac{11.85}{16} = 0.74$ | $\frac{0.74}{0.74} = 1$ |

Empirical formula of 'A' = $C_8H_9NO$

Since the molecule 'A' contains a single atom of nitrogen hence the molecular formula of 'A' is $C_8H_9NO$.

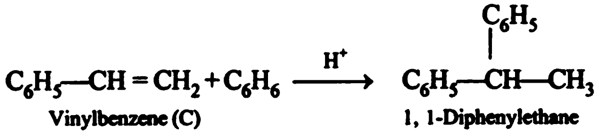
As the compound 'A' on heating with NaOH evolves $NH_3$ gas, it contains —$CONH_2$ group. Compound 'C' obtained from 'A' has ring structure, therefore, 'A' too has a ring structure.

Structures for different compounds and their reactions are given below :



**Example 29. Dehydrobromination of compound (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. Hydrolysis 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 strucures of (A) to (E) with reasons.** (*Roorkee 1997*)

Sol. (*i*) 1, 1-diphenylethane is obtained on reaction of (C), an alkene with benzene in presence of $H^+$. Alkene (C) is, therefore, vinylbenzene.



$$\underset{\text{Vinylbenzene (C)}}{C_6H_5{-}CH{=}CH_2} + C_6H_6 \xrightarrow{H^+} \underset{\text{1, 1-Diphenylethane}}{C_6H_5{-}\overset{\overset{\displaystyle C_6H_5}{|}}{C}H{-}CH_3}$$

(*ii*) Alkene (C) on addition of HBr forms (A) acid (B) in presence and in absence of peroxide, respectively. The formation of (A) and (B) may be shown as :

$$C_6H_5—CH = CH_2 + HBr \xrightarrow{\text{Peroxide}} C_6H_5—CH_2CH_2Br$$

(A) (C) β-Bromoethylbenzene

$$C_6H_5—CH = CH_2 + HBr \xrightarrow[\text{Markownikoff rule}]{\text{According to}} C_6H_5—CHBr.CH_3$$

α-Bromoethylbenzene (B)

Hydrolysis of (A) and (B) gives isomeric alcohols as shown below :

$$C_6H_5CH_2CH_2Br \xrightarrow{H_2O/OH^-} C_6H_6CH_2CH_2OH$$

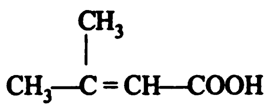
(A) 2-Phenyl ethanol (D)

$$C_6H_5CHBrCH_3 \xrightarrow{H_2O/OH^-} C_6H_5CHOH.CH_3$$

(B) 1-Phenyl ethanol (E)

**Example 30. An organic acid (A), $C_5H_{10}O_2$ reacts with $Br_2$ in the presence of phosphorous to give (B). Compound (B) contains an asymmetric carbon atom and yields (C) on dehydrobromination. Compound (C) does not show geometrical 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.** (*Roorkee 1997*)

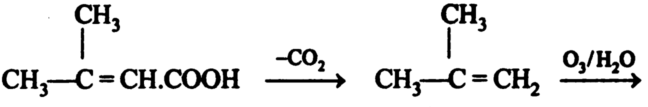
Sol. (A) $C_5H_{10}O_2$ is an organic acid, it may, therefore, be written as, $C_4H_9COOH$. On treatment with $Br_2$ in presence of phosphorous it gives α-bromo acid, (B) (Hell-Volhard Zelinsky reaction). (B) may be represented as $C_4H_8BrCOOH$. Dehydrobromination of (B) gives (C) which would be $C_4H_7COOH$. The hydrocarbon part $—C_4H_7$ will thus have a double bond. Since (C) does not show geometrical isomerism, one of the double bonded carbon atoms will have identical groups or atoms. The acid (C) thus has the structure :



$$CH_3—\overset{\overset{\displaystyle CH_3}{|}}{C} = CH—COOH$$

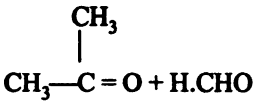
3-Methyl-2-butenoic acid (C)

The above structure of (C) is further confirmed as on decarboxylation followed by ozonolysis, it gives an aldehyde (E) which gives positive Schiff test and a compound (F) which does not give Schiff's test and hence is a ketone. Structure of different compounds and the reactions are as given below :



$$CH_3—\overset{\overset{\displaystyle CH_3}{|}}{C} = CH.COOH \xrightarrow{-CO_2} CH_3—\overset{\overset{\displaystyle CH_3}{|}}{C} = CH_2 \xrightarrow{O_3/H_2O}$$

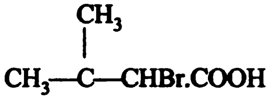
(C) 2-Methyl propene (D)



$$CH_3-\overset{\overset{CH_3}{|}}{C}=O + H.CHO$$

Acetone (F) Formaldehyde (E)

With the structure of (C) as above, the compound (B) would be :

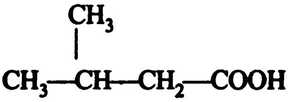


$$CH_3-\overset{\overset{CH_3}{|}}{C}-CHBr.COOH$$

2-Bromo 3-methyl butanoic acid

(An α-bromo acid with one asymmetric C-atom)

(A), therefore, has the structure :

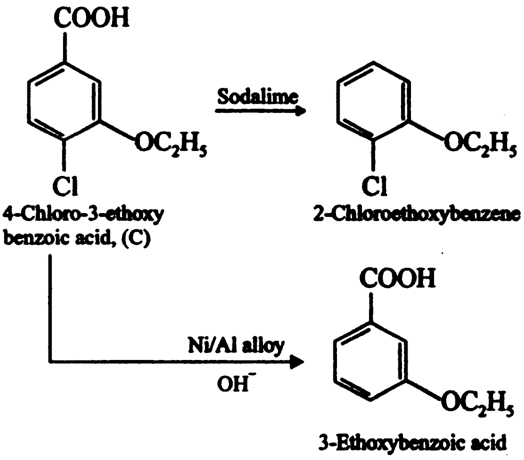


$$CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_2-COOH$$

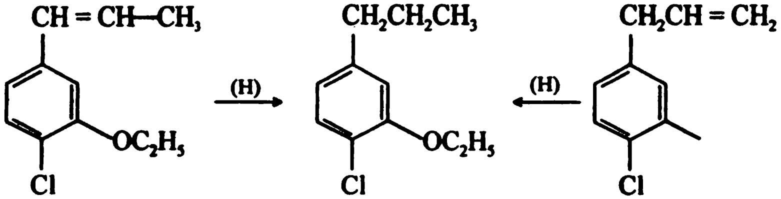
3-Methyl butanoic acid

**Example 31. Two isomeric forms of an organic compound (A), $C_{11}H_{13}OCl$ readily decolourise bromine water and give same compound (B) on catalytic hydrogenation. Both the isomeric forms, on vigorous oxidation, give (C) which on treatment with sodalime gives 2-chloroethoxybenzene. However, (C) on treatment with Ni/Al alloy in alkaline medium gives 3-ethoxybenzoic acid. Only one of the isomers of (A) gives geometrical isomers (D)and (E). Identify (A) to (E) with proper reasoning.** (*Roorkee 1997*)

**Sol.** Compound (A) on oxidation gives (C) which on treatment with sodalime gives 2-chloroethoxybenzene. Since treatment with sodalime decarboxylate an acid, (C) must be 2-chloroethoxybenzoic acid. Further (C) on treatment with Ni/Al alloy in alkaline medium gives 3-ethoxybenzoic acid, a reduction reaction in which chlorine is removed. As the compound, 3-ethoxybenzoic acid is obtained, the ethoxy group is meta to carboxylic group. (C) gives 2-chloroethoxybenzene, therefore, chlorine in (C) is ortho to ethoxy group. (C), therefore, is 4-chloro-3-ethoxybenzoic acid.



(A) with molecular formula $C_{11}H_{13}OCl$ decolourise, bromine water, hence it has a double bond in the side chain which on oxidation produces (C). (A) with molecular formula $C_{11}H_{13}OCl$ can have following two isomeric structures. I and II. Both I and II on reduction give the same compound B.

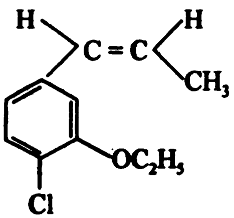


2-Chloro-5-propenyl ethoxybenzene (A)
I

2-Chloro-5-propyl ethoxybenzene (B)

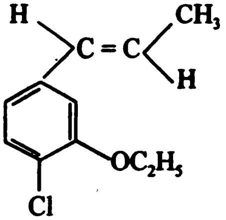
2-Chloro-5-prop-2-enyl ethoxybenzene (A)
II

Geometrical isomers (D) and (E) of structure I of compound A are :



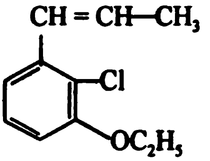
(D) *Cis* form

and

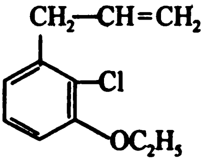


(E) *Trans* form

Other possible isomers of (A) are :

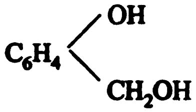


and



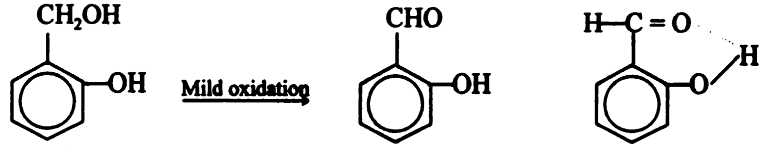
**Example 32. A phenolic compound (A), $C_7H_8O_2$ on mild oxidation gives a highly volatile oil (B). (A) forms (C) on reaction with dimethyl sulphate in alkali. Oxidation of (C) with hot $KMnO_4$ gives (D) which then reacts with bromine water to give (E) containing about 72% bromine. Give structures of (A) to (E) with proper reasoning.** (*Roorkee 1997*)

**Sol.** (*i*) Compound (A) has a phenolic group, the other oxygen atom present in the compound (A), $C_7H_8O_2$ must either be in the form of an alcoholic group or an ethereal group. However, (A) can be oxidized with a mild oxidizing agent. Hence (A) should have an alcoholic group. (A) may be represtented as :



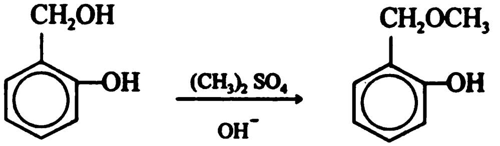
$$C_6H_4\begin{cases} OH \\ CH_2OH \end{cases} \quad (A)$$

(*ii*) Mild oxidation of (A) results in oxidation of —$CH_2OH$ group to —CHO group. Since the compound (B) formed is highly volatile, the phenolic and aldehydic groups in (B) must be ortho to each other, so that they can form H—bond.



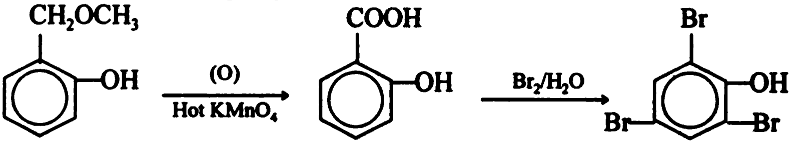
*o*-Hydroxybenzyl alcohol (A)  Salicylaldehyde (B), (Highly volatile)  H-bond (Intramolecular hydrogen bonding)

(*iii*) (A) forms (C) with dimethyl sulphate in alkali. The reaction may be shown as :



(A)  (C)

(*iv*) (C) on oxidation with hot $KMnO_4$ forms salicylic acid (D) which on treatment with bromine water will form 2, 4, 6-tribromophenol (E) with the removal of carboxylic group.



(C)  Salicylic acid (D)  2,4,6-Tribromophenol (E)

Molecular weight of (E), $C_6H_3OBr_3 = 72 + 3 + 16 + 240 = 331$

331 g of E has bromine $= 240$ g

100 g of E would have bromine $= \frac{240 \times 100}{331} = 72\%$

Percentage of bromine in (E) is thus verified

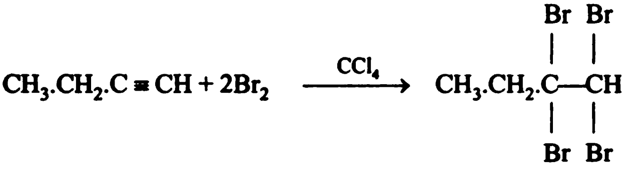
**Example 33. A hydrocarbon (A) of molecular weight 54 reacts with an excess of $Br_2$ in $CCl_4$ to give a compound (B) whose molecular weight is 593% more than that of (A). However, on catalytic hydrogenation with excess of hydrogen, (A) forms (C) whose molecular weight is only 7.4% more than that 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 reasons.** (*Roorkee 1997*)

Sol. Hydrocarbon (A) reacts with $CH_3CH_2Br$ in the presence of $NaNH_2$ to give another hydrocarbon, a reaction given by terminal alkynes. The only possible alkyne is butyne-1 as its molecular weight is given as 54.

$CH_3.CH_2C \equiv CH = 12 \times 4 + 1 \times 6 = = 54$

Butyne-1 (A)

Butyne-1 will add four bromine atoms with excess of bromine in $CCl_4$ to form a tetrabromide.



$$CH_3.CH_2.C \equiv CH + 2Br_2 \xrightarrow{CCl_4} CH_3.CH_2.\overset{Br}{\underset{Br}{C}}-\overset{Br}{\underset{Br}{C}}H$$

(A) 1,1,2,2-Tetrabromobutane (mol. wt. = 374)

An increase of 593% in the molecular weight takes place.

Hydrogenation of (A) with excess of hydrogen forms (C) which would be butane.

$$\underset{(A)}{CH_3.CH_2.C \equiv CH} + 2H_2 \longrightarrow \underset{\text{Butane (C) (mol. wt = 58)}}{CH_3.CH_2CH_2.CH_3}$$

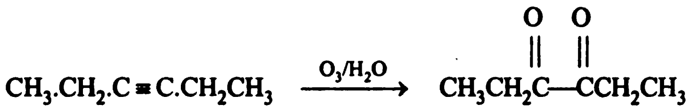
An increase of 7.4% in molecular weight occurs.

Hydrocarbon (D) obtained by treating butyne-1 (A) with $CH_3CH_2Br/NaNH_2$ would thus be hexyne-3.

$$\underset{(A)}{CH_3.CH_2.C \equiv CH} \xrightarrow{NaNH_2} CH_3.CH_2.C \equiv C.Na$$

$$\xrightarrow{CH_3CH_2Br} \underset{\text{Hexyne-3 (D)}}{CH_3.CH_2.C \equiv C.CH_2.CH_3}$$

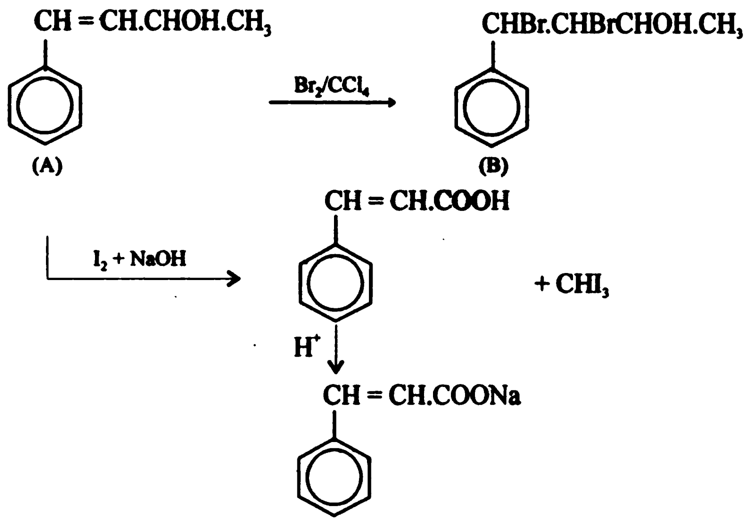
Hexyne-3, on ozonolysis, will give hexane-3, 4-dione, a diketone (E).



$$\underset{(D)}{CH_3.CH_2.C \equiv C.CH_2CH_3} \xrightarrow{O_3/H_2O} \underset{\text{Hexane-3,4-dione (E)}}{CH_3CH_2\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}CH_2CH_3}$$

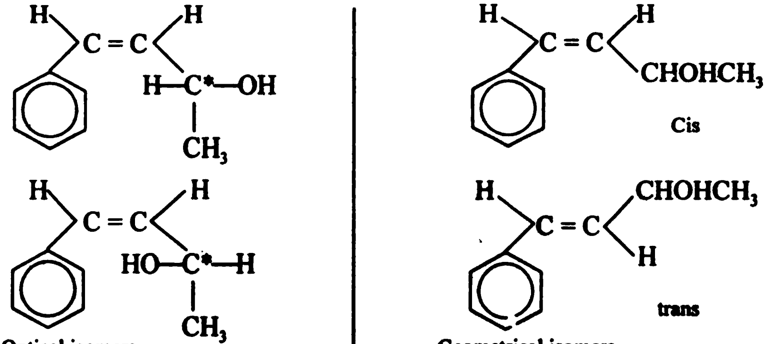
**Example 34. Compound (A), $C_{10}H_{12}O$ gives off hydrogen on treatment with sodium metal and also decolourises $Br_2$ in $CCl_4$ to give (B), $C_{10}H_{12}OBr_2$. (A) on treatment with $I_2$ in NaOH gives iodoform and an acid (C) after acidification. Give structures of (A) to (C) and also of all the geometrical and optical isomers of (A).** (*Roorkee 1997*)

**Sol.** Compound (A), $C_{10}H_{12}O$ liberates hydrogen on treatment with sodium metal, hence it is an alcohol. (A) also gives iodoform reaction. Therefore, it contains $CH_3CHOH$— group, *i.e.*, it is a secondary alcohol. Further (A) decolourises $Br_2$ in $CCl_4$ to give a compound (B) with molecular formula $C_{10}H_{12}OBr_2$, hence it has a double bond also. With molecular formula, $C_{10}H_{12}O$, a double bond and a secondary alcoholic group, (A) can only be a benzene derivative. (A) also shows geometrical and optical isomerism, hence the possible structure of (A) is :



(C), Cinnamic acid

Optical and geometrical isomers of (A) are represented as under :



Optical isomers | Geometrical isomers

**Example 35. A mixture of an acid anhydride (A) and a monobasic acid (B) on heating produces another monobasic acid (C) of equivalent weight 74 and an anhydride (D). The acids and anhydrides remain in equilibrium. The anhydride (D) contains two identical fluoroalkyl groups. The acid (B) contains a trifluoromethyl group and has an equivalent weight of 128.**

**Give structures of (A) to (D) with proper reasoning. (Atomic weight of fluorine = 19).** *(Roorkee 1998)*

**Sol.** Acid anhydride, A + Monobasic acid, B $\rightleftharpoons$ Monobasic acid, C + Anhydride, D

Eq. wt. = 128 Eq. wt. = 74

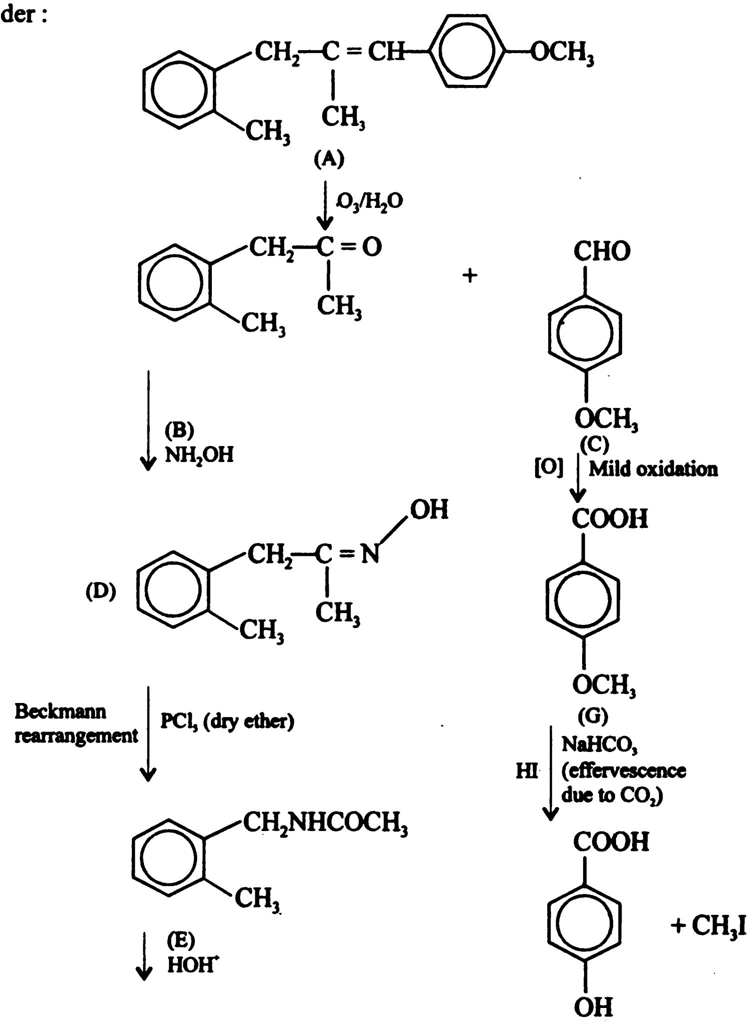
(*i*) Since B has one $F_3C$ group, its probable formula is $F_3C.(CH_2)_n$ COOH ($r = 0, 1, 2, 3$). However, its eq. wt. 128 coincides with the molecular formula $F_3C.CH_2COOH$. So the anhydride D should be $(F_3C.CH_2.CO)_2O$.

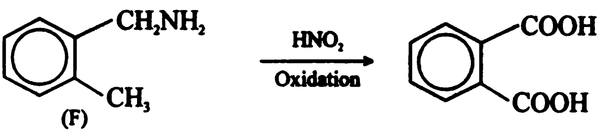
(*ii*) The monobasic acid C, $CH_3(CH_2)_n$ COOH with eq. wt. 74 should be $CH_3CH_2COOH$. The reaction can be shown as under :

$$\underset{A}{(CH_3CH_2CO)_2O} + \underset{B}{F_3C.CH_2COOH} = \underset{C}{CH_3CH_2COOH} + \underset{D}{(F_3C.CH_2.CO)_2O}$$

**Example 36. An organic compound (A), $C_{18}H_{20}O$ on ozonolysis gives (B), $C_{10}H_{12}O$ and (C), $C_8H_8O_2$. Compound (B) gives iodoform reaction and produces an oxime (D), $C_{10}H_{13}ON$ on treatment with $NH_2OH$. Compound (D) reacts with $PCl_5$ in dry ether to give (E) which on hydrolysis gives (F), $C_8H_{11}N$ and acetic acid. (F) on treatment with $HNO_2$ followed by oxidation gives phthalic acid. Compound (C) on mild oxidation gives (G) which gives effervescence with $NaHCO_3$. (G) on treatment with HI produces *p*-hydroxybenzoic acid and $CH_3I$. Give structures of (A) to (G) with proper reasoning.** (*Roorkee 1998*)

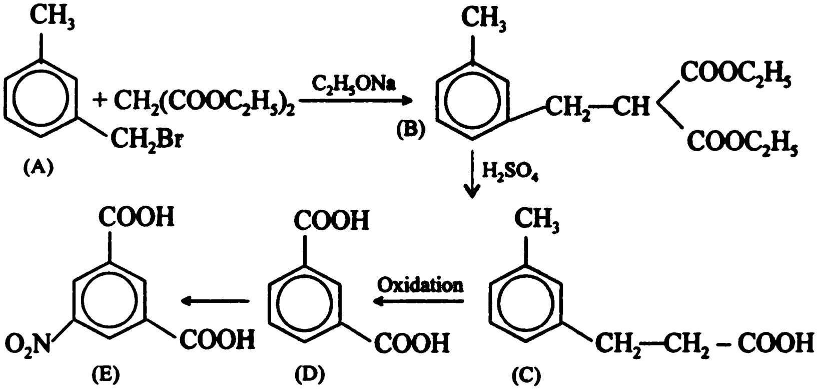
**Sol.** Structures of various compounds and their reactions are given as under :





**Example 37. An aromatic compound (A), $C_8H_9Br$ reacts with $H_2C(COOC_2H_5)_2$ in the presence of $C_2H_5ONa$ to give (B). Compound (B) on refluxing with dilute $H_2SO_4$ gives (C) which on vigorous oxidation gives (D). The compound (D) is a dibasic acid but on heating does not give an anhydride. It forms a mononitro derivative (E), in which all the substituents are equidistant from one another. Give structures of (A) to (E) with proper reasoning.** (*Roorkee 1998*)

**Sol.** Structures of various compounds acid their reactions are given as under :

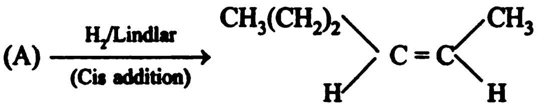


**Example 38. Hydrocarbon (A), $C_6H_{10}$ on treatment with $H_2$/Ni, $H_2$/ Lindlar catalyst and Na/liquid ammonia forms three reduction products (B), (C) and (D) respectively. (A) does not form any salt with ammoniacal $AgNO_3$ solution, but forms a salt (E) on heating with $NaNH_2$ in inert solvent. Compound (E) reacts with $CH_3I$ to give (F). Compound (D) on oxidative ozonolysis gives *n*-butanoic acid along with other product.**

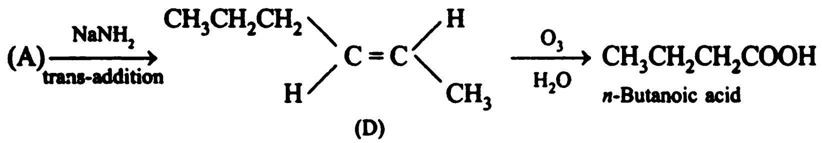
**Give structures of (A) to (F) with proper reasoning.** (*Roorkee 1998*)

**Sol.** Structures of (A) to (F) and their reactions are given as under :

$$\underset{(B)}{CH_3(CH_2)_4CH_3} \xleftarrow{H_2/Ni} \underset{(A)}{CH_3CH_2CH_2C \equiv C.CH_3}$$



(C)



$$\underset{(A)}{CH_3CH_2CH_2C \equiv C.CH_3} \xrightarrow[\text{Inert solvent}]{NaNH_2} \underset{(E)}{CH_3CH_2CH_2CH_2C \equiv C.Na}$$

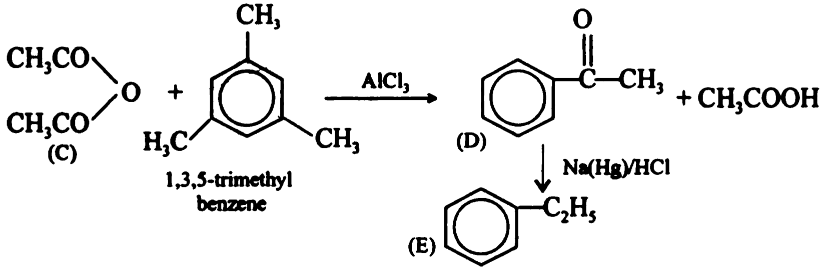
$$\xrightarrow{CH_3I} \underset{(F)}{CH_3CH_2CH_2CH_2C \equiv C.CH_3}$$

**Example 39. An organic acid (A) on heating with $AlPO_4$ at 700°C forms (B). Compound (B) also reacts with (A) to give (C). Compound (C) on reaction with 1, 3, 5-trimethyl benzene in presence of $AlCl_3$ gives a ketone (D) and $CH_3COOH$. (D) on treatment with Na (Hg)/HCl gives an aromatic hydrocarbon (E).**

**Give structures of (A) to (E) with proper reasoning.** (*Roorkee 1998*)

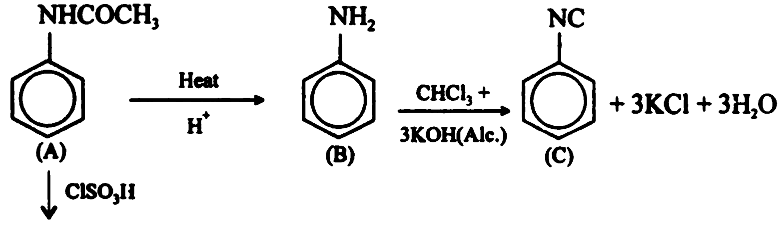
**Sol.** Structures of compounds (A) to (E) and their reactions are given as under :

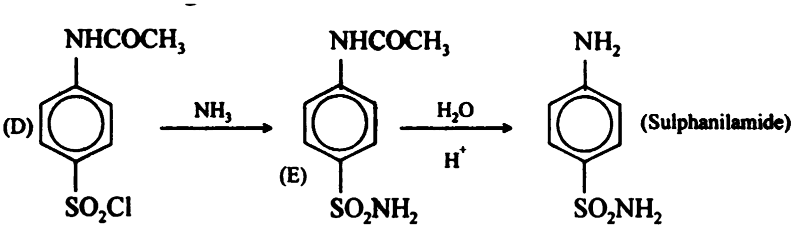
$$\underset{(A)}{CH_3COOH} \xrightarrow[700^\circ C]{AlPO_4} \underset{\text{Keten (B)}}{CH_2=C=O} \xrightarrow{+CH_3COOH} \underset{(C)}{CH_3COOCOCH_3}$$



**Example 40. A colourless substance (A) is sparingly soluble in water and gives (B) on heating with mineral acids. Compound (B) on reaction with $CHCl_3$ and alcoholic potash produces an obnoxious smell of carbylamine due to the formation of (C). Compound (A) on reaction with chlorosulfonic acid gives (D) which on treatment with ammonia gives (E). Compound (E) on acid hydrolysis gives sulfanilamide, a well known drug. Give structures of (A) to (E) with proper reasoning.**

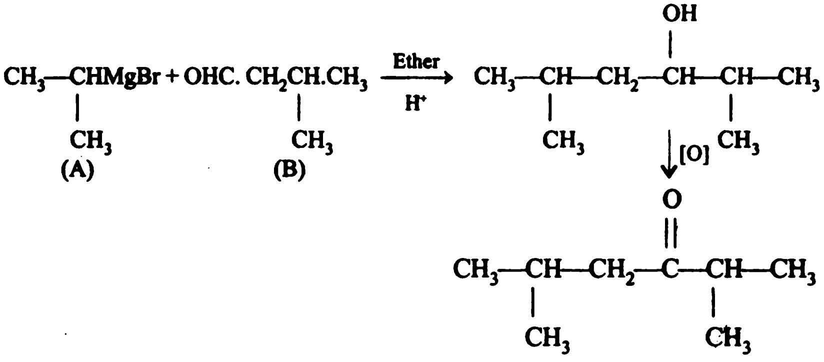
**Sol.** Structures of compounds (A) to (E) and their reactions are given as under :





**Example 41. Compound (A) and (B) on reaction in ether medium and subsequent acidification and oxidation give 2, 5-dimethyl-3-hexanone. What are (A) and (B) ?** (*Roorkee 1998*)

**Sol.** Structures of (A) and (B) and their reactions are given as under :



$$\underset{(A)}{CH_3-\underset{CH_3}{\underset{|}{C}}HMgBr} + \underset{(B)}{OHC.CH_2\underset{CH_3}{\underset{|}{C}}H.CH_3} \xrightarrow[H^+]{Ether} CH_3-\underset{CH_3}{\underset{|}{C}}H-CH_2-\overset{OH}{\overset{|}{C}}H-\underset{CH_3}{\underset{|}{C}}H-CH_3$$

$$\big\downarrow [O]$$

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

2, 5-Dimethyl-3-hexanone

**Example 42. An organic compound containing C, H and O exists in two isomeric froms '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 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.** (*I.I.T. 1991*)

**Sol. Calculation of empirical formula**

$$\text{Percentage of C} = \frac{12}{44} \times \frac{\text{Wt. of } CO_2 \times 100}{\text{Wt. of compound}}$$

$$= \frac{12 \times 0 \cdot 308 \times 100}{44 \times 0 \cdot 108} = 77.77$$

$$\text{Percentage of H} = \frac{2}{18} \times \frac{\text{Wt. of } H_2O \times 100}{\text{Wt. of Compound}}$$

$$= \frac{2 \times 0 \cdot 072 \times 100}{18 \times 0 \cdot 108} = 7 \cdot 40.$$

Percentage of O = 100 – (77.77 + 7·40) = **14·83.**

(By difference)

C = 77.77/12 = 6·48/0·926 = 7

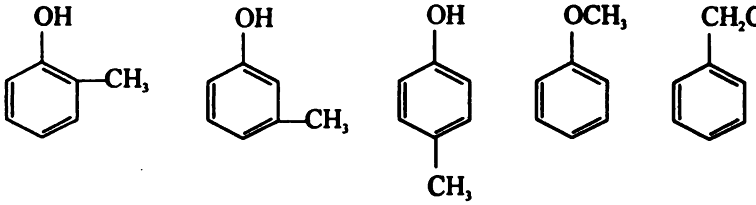
H = 7·40/1 = 7·40/0·926 = 8

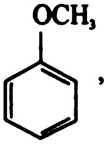
O = 14·83/16 = 0·926/0·926 = 1

The empirical formula of 'A' and 'B' is **$C_7H_8O$.**

Since 'B' gives on bromination $C_7H_5OBr_3$, the three H-atoms being replaced by three Br-atoms, the molecular formula of 'A' and 'B' is **$C_7H_8O$.**

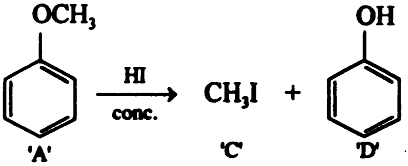
The various possible isomers with the moelcular formula $C_7H_8O$ are given below :



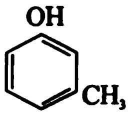
As 'A' is insoluble in NaOH and $NaHCO_3$, it can be  , anisole.

Other compounds are ruled out. They would react with NaOH and $NaHCO_3$.

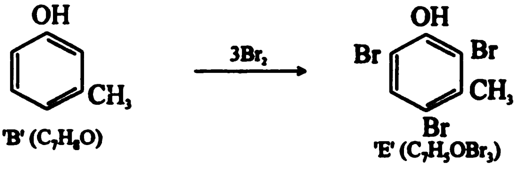
'A' reacts with conc. HI to give compounds 'C' and 'D'. As 'C' is soluble in ethanolic $AgNO_3$ it is methyl iodide $CH_3I$ and 'D' which is soluble in NaOH must be phenol, $C_6H_5OH$.



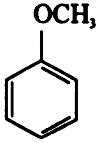
'B' is soluble in NaOH, hence it can be one of the cresols. As the 'B' gives a tribromo derivative on bromination it has to be *m*-cresol.

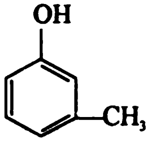


(other cresols do not give a tribromo derivative)



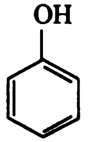
Structures of compounds (A) to (E) are given as under :

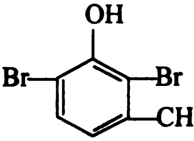

Anisole 'A'


*m*.Cresol 'B'

$CH_3I$

Methyl iodide 'C'


Phenol 'D'


Tribromo *m*-cresol 'E'

**Example 43. A compound '*x*' containing chlorine on treatment with strong ammonia gave a solid '*y*' which is free from chlorine, '*y*' is analysed as C = 49·31% H = 9·59% and N = 19·18% and reacts with $Br_2$ in caustic soda to give a basic compound '*z*', '*z*' reacts with $HNO_2$ to give ethanol. Suggest structures for '*x*', '*y*' and '*z*'.** (*I.I.T. 1992*)

**Sol. Calculations for empirical and molecular formulae of 'y'.**

Percentage of oxygen = 100 − (49·31 + 9·59 + 19·18) = 21.12 (By difference)

$$\begin{aligned} C &= 49{\cdot}31/12 = 4{\cdot}11/1{\cdot}37 = 3 \\ H &= 9{\cdot}59/1 = 9{\cdot}59/1{\cdot}37 = 7 \\ N &= 19{\cdot}18/14 = 1{\cdot}37/1{\cdot}37 = 1 \\ O &= 21{\cdot}92/16 = 1{\cdot}37/1{\cdot}37 = 1 \end{aligned}$$

Thus the empirical formula of '*y*' is $C_3H_7NO$. Since the compound finally gives ethanol its molecualr formula is also $C_3H_7NO$

As '*y*' reacts with $Br_2$ and caustic soda Hofmann's bromamide reaction] to give a basic compound '*z*', it must be an amide and '*z*' is, therefore, a primary amine. The only possible amide with the molecular formula $C_3H_7NO$ is $CH_3CH_2CONH_2$, propionamide and thus the amine '*z*' is $CH_3CH_2NH_2$, ethylamine. That '*z*' is ethylamine, is further confirmed as it gives ethanol, $CH_3CH_2OH$, on treatment with $HNO_2$, as shown by the following reactions.

$$\underset{\text{Propionamide 'y'}}{CH_3CH_2CONH_2} + Br_2 + 4NaOH \longrightarrow \underset{\text{Ethylamine 'z'}}{CH_3CH_2NH_2} + Na_2CO_3 + 2NaBr + 2H_2O$$

$$\underset{\text{'z'}}{CH_3CH_2NH_2} + HNO_2 \longrightarrow \underset{\text{Ethanol}}{CH_3CH_2OH} + N_2 + H_2O$$

Hence, compound '*x*' is propionyl chloride, $CH_3CH_2COCl$ as noticed from the following reaction.

$$\underset{\text{Propionyl chloride 'x'}}{CH_3CH_2COCl} + NH_3 \longrightarrow \underset{\text{'y'}}{CH_3CH_2CONH_2} + HCl$$

**Example 44. Compound '*x*' (molecular formula, $C_5H_8O$) does not react appreciably with Lucas reagent at room temperature but gives a precipitate with ammoniacal 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*-butane. Suggest structure for '*x*' and write the equation involved.** (*I.I.T. 1992*)

**Sol.** As the compound '*x*' does not react appreciably with Lucas reagent at room temperature, it is a primary alcohol (—$CH_2OH$). Further its 0·42 g (the molecular weight of compound '*x*' with molecular formula $C_5H_8O = 12 \times 5 + 8 + 16 = 84$) gives 224 ml of $CH_4$ at STP with MeMgBr, hence the compound must possess two active hydrogens. Since its also gives a precipitate with ammoniacal silver nitrate the compound '*x*' must contain an acetylenic hydrogen. Thus '*x*' has the following structure.

4-pentynol-1, $HC \equiv C.CH_2CH_2CH_2OH$.

$$\underset{\text{'}x\text{', Mol. Wt.} = 84}{HC \equiv C.CH_2CH_2CH_2OH} + 2MeMgBr \longrightarrow$$

$$BrMgC \equiv C.CH_2CH_2CH_2OMgBr \; + \; 2CH_4 (2 \times 22{,}400 \text{ ml})$$

Thus, $2 \times 22400$ ml of methane is obtained from = 84 g of '*x*'

∴ 224 ml of methane will be obtained from

$$= \frac{84 \times 224}{2 \times 22{,}400} = 0{\cdot}42 \text{ g of '}x\text{'}.$$

The compound '*x*' gives *n*-pentane on treatment with $H_2$ in presence of Pt(saturation of triple bond) followed by boiling with HI (reduction of —OH group). These reactions can be explained by above structure.

**Example 45. 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'.** (*I.I.T. 1992*)

**Sol.** (*i*) Since 'E' forms a 2, 4-dinitrophenyl hydrazone but does not give Tollen's test and does not reduce Fehling's solution, 'E' is a ketone with molecular formula, $C_3H_6O$, the only possible ketone is acetone, $CH_3COCH_3$.

(*ii*) Acetone 'E' is formed by heating carboxylic acid 'B' with $Ca(OH)_2$, thus 'B' is acetic acid, $CH_3COOH$ as shown by the following reaction.

$$\underset{\text{Acetic acid 'B'}}{2\,CH_3COOH} + Ca(OH)_2 \longrightarrow \underset{\text{Calcium acetate}}{(CH_3COO)_2Ca} + 2H_2O$$

$$(CH_3COO)_2Ca \xrightarrow{\text{Heat}} \underset{\text{Acetone 'E'}}{CH_3COCH_3} + CaCO_3$$

(*iii*) As compound 'C' on acidic hydrolysis gives 'B' and 'D' and 'D' on oxidation with $KMnO_4$ gives 'B' ; 'D' is ethyl alcohol, $CH_3CH_2OH$ and 'C' is ethyl acetate, $CH_3COOC_2H_5$.

$$\underset{\text{Ethyl acetate, 'C'}}{CH_3COOC_2H_5} + H_2O \xrightarrow{H^+} \underset{\text{Acetic acid 'B'}}{CH_3COOH} \; + \; \underset{\text{Ethyl alcohol 'D'}}{C_2H_5OH}$$

$$\underset{\text{'D'}}{\mathrm{CH_3CH_2OH}} + [\mathrm{O}] \xrightarrow{\mathrm{KMnO_4}} \underset{\text{'B'}}{\mathrm{CH_3COOH}} + \mathrm{H_2O}$$

Since 'B', acetic acid and 'C', ethyl acetate are obtained by treatment of 'A' with ethyl alcohol, 'A' must be acetic anhydride, $(\mathrm{CH_3CO})_2\mathrm{O}$.

$$\underset{\substack{\text{Acetic anhydride}\\ \text{'A'}}}{(\mathrm{CH_3.CO})_2\mathrm{O}} + \mathrm{C_2H_5OH} \longrightarrow \underset{\text{'B'}}{\mathrm{CH_3COOH}} + \underset{\text{'C'}}{\mathrm{CH_3COOC_2H_5}}$$

**Example 46. Give the structures of A,B,C, and D. (Explanations are not required).**

**(*i*) A ($C_3H_9N$) reacts with benzene sulphonyl chloride to give a solid insoluble in alkali.**

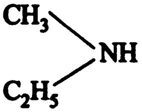
**(*ii*) B ($C_4H_8$) which adds on HBr in the presence and in the absence of peroxide to give the same product, $C_4H_9Br$.**

**(*iii*) C ($C_4H_8$) which when treated with $H_2O$, $H_2SO_4$, gives $C_4H_{10}O$ which can not be resolved into optical isomers.**

**(*iv*) D($C_6H_{12}$), and optically active hydrocarbon which on catalytic hydrogenation gives an optically inactive compound, $C_6H_{14}$.** (*I.I.T. 1993*)

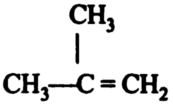
Sol. Structures of compounds A to D are given below :

A. ($C_3H_9N$)



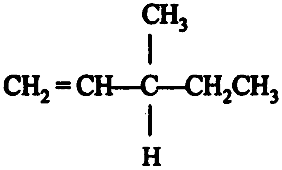
B. $C_4H_8$ $\quad \mathrm{CH_3CH=CHCH_3}$

C. $C_4H_8$



$$\mathrm{CH_3{-}\overset{\overset{\displaystyle CH_3}{|}}{C}{=}CH_2}$$

D. $C_6H_{12}$



$$\mathrm{CH_2{=}CH{-}\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}{-}CH_2CH_3}$$

**Example 47. A basic, volatile, nitrogen compound gave a found smelling gas when treated with chloroform and alcoholic potash. 0.295 g sample of the substance, dissolved in aq. HCl and treated with $NaNO_2$ solution at 0°C, liberated a colourless, odourless gas whose volume corresponded 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.** (*I.I.T. 1993*)

**Sol.** Since the nitrogen compound gives a foul smelling gas with chloroform and alcoholic potash (carbylamine reaction) it should be a primary amine.

**Calculation of molecular formula of amine**

112 ml of gas is evolved from = 0.295 g of amine

$$\therefore \quad 22{,}400 \text{ ml of gas will be evolved from } = \frac{2.95 \times 22400}{112}$$

$$= 59 \text{ g}$$

Hence the molecular weight of amine = 59

Size of the alkyl group can be computed as follows :

$$R.NH_2 = 59$$

$$R + (14 + 1 \times 2) = 59 \text{ or } R + 16 = 59$$

or, $R = 59 - 16 = 43$

Thus R (alkyl group) in amine must be $C_3H_7-$

$$C_3H_7(12 \times 3 + 1 \times 7) = 43$$

There are two possibilities for the compound as given below :

$CH_3CH_2CH_2NH_2$ (*n*-Propylamine) (I) or $(CH_3)_2\,CHNH_2$ (Isopropylamine) (II)

But the compound is isopropylamine since on reaction with $NaNO_2$ and dil. HCl, it would give isopropyl alcohol which gives iodoform test, as stated in the question. *n*-propylamine on the other hand would give *n*-propyl alcohol which does not give iodoform test.

Reactions are given as under :

$$\underset{\text{Isopropylamine}}{(CH_3)_2\,CHNH_2} + CHCl_3 + \underset{\text{Alc.}}{3KOH} \longrightarrow \underset{\substack{\text{Isopropyl isocyanide}\\ \text{(foul smelling)}}}{(CH_3)_2\,CHNC} + 3\,KCl + 3H_2O$$

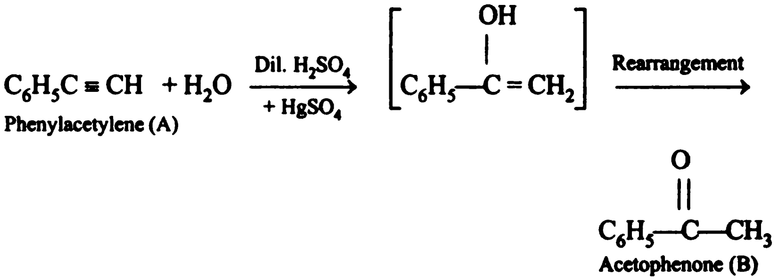
$$(CH_3)_2CHNH_2 + NaNO_2 + HCl \longrightarrow (CH_3)_2CHOH + NaCl + N_2 + H_2O$$

$$(CH_3)_2CHOH + 4\,I_2 + 6\,NaOH \longrightarrow CH_3COONa + 5\,NaI + 5\,H_2O + \underset{\text{Iodoform}}{CHI_3}$$

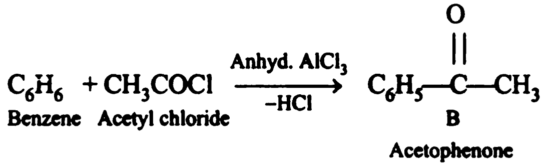
**Example 48. An organic compound A, $C_8H_6$, on treatment with dilute sulphuric acid containing mercuric sulphate gives a compound B, which can also be obtained from a reaction of benzene with an acid chloride in the presence of anhydrous aluminium chloride. The compound B when treated with iodine in aqueous KOH, yields C and a yellow compound D. Identify A, B, C and D with justification. Show how B is obtained from A ?** (*I.I.T. 1994*)

**Sol.** (*i*) Since compound B is obtained by Friedel-Crafts reaction of benzene with an acid chloride, therefore, B *must be an aromatic ketone.*

(*ii*) Since an aromatic ketone B is obtained from A after treatment with dil. $H_2SO_4$ in presence of $HgSO_4$, therefore, A must be an aromatic acetylene. The only aromatic acetylene possible with mol. formula $C_8H_6$ is phenylacetylene. If A is phenylacetylene then B must be acetophenone as shown by the following reaction.



$$\underset{\text{Phenylacetylene (A)}}{C_6H_5C\equiv CH} + H_2O \xrightarrow[+\,HgSO_4]{\text{Dil. } H_2SO_4} \left[C_6H_5-\overset{\overset{\displaystyle OH}{|}}{C}=CH_2\right] \xrightarrow{\text{Rearrangement}} \underset{\text{Acetophenone (B)}}{C_6H_5-\overset{\overset{\displaystyle O}{||}}{C}-CH_3}$$



$$\underset{\text{Benzene}}{C_6H_6} + \underset{\text{Acetyl chloride}}{CH_3COCl} \xrightarrow[-HCl]{\text{Anhyd. } AlCl_3} \underset{\substack{B\\ \text{Acetophenone}}}{C_6H_5-\overset{\overset{\displaystyle O}{||}}{C}-CH_3}$$

(*iii*) Since acetophenone B is obtained by Friedel-Crafts reaction of benzene with an acid chloride, the acid chloride must be acetyl chloride, $CH_3COCl$

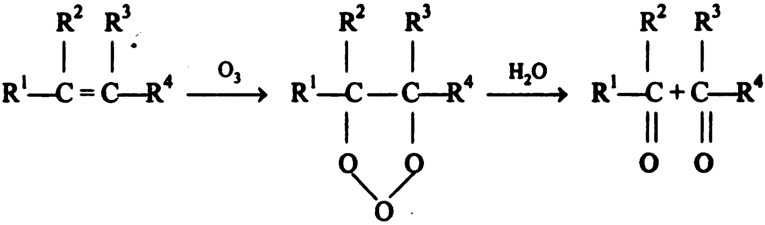
(*iv*) Since acetophenone B, a methyl ketone on treatment with $I_2$ and aqueous KOH gives C and a yellow compound D, therefore, C must be potassium benzoate and D must be iodoform as shown below :

$$\underset{\substack{B\\ \text{Acetophenone}}}{C_6H_5COCH_3} + 3I_2 + 4KOH \longrightarrow \underset{\substack{(C)\\ \text{Pot. benzoate}}}{C_6H_5COOK} + \underset{\text{Iodoform}}{CHI_3} + 3KI + 2H_2O$$

Thus, A is phenylacetylene, B is acetophenone. C is pot. benzoate and D is iodoform.

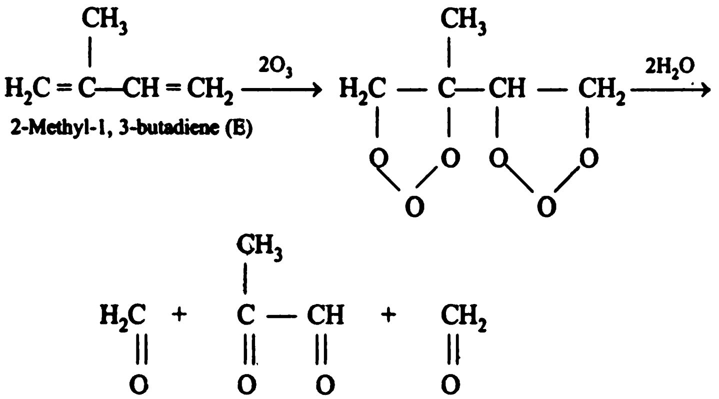
**Example 49. An organic compound E ($C_5H_8$) on hydrogenation gives compound F($C_5H_{12}$). Compound E on ozonolysis gives formaldehyde and 2-ketopropanal. Deduce the structure of compound E.** (*I.I.T. 1995*)

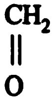
**Sol.** Ozonolysis of an alkene may in general be represented as :



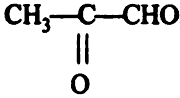
where $R^1$, $R^2$, $R^3$ and $R^4$ represented alkyl groups attached to the double bond.

Since compound E ($C_5H_8$) gives formaldehyde and 2-ketopropanal on ozonolysis, it must contain two double bonds. From the ozonolysis products it is found to be 2-methyl-1, 3-butadiene as explained by the following reaction :



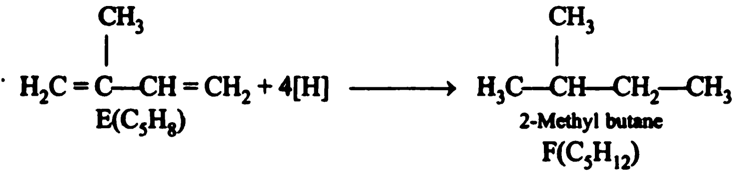


$\underset{\underset{\displaystyle O}{\|}}{CH_2}$ or HCHO, Formaldehyde and



$CH_3-\underset{\underset{\displaystyle O}{\|}}{C}-CHO$, 2-Keto propanal.

F, obtained by hydrogenation of E would be 2-methyl butane.

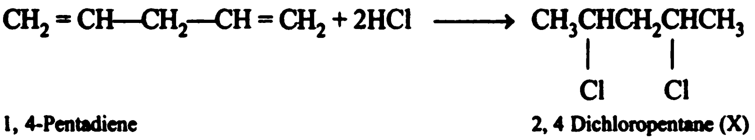


$$H_2C=\overset{\overset{\displaystyle CH_3}{|}}{C}-CH=CH_2+4[H]\longrightarrow H_3C-\overset{\overset{\displaystyle CH_3}{|}}{C}H-CH_2-CH_3$$

$E(C_5H_8)$ 2-Methyl butane $F(C_5H_{12})$

**Example 50. 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.** *(I.I.T. 1995)*

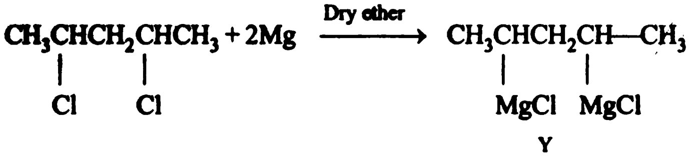
**Sol.** Addition of excess of HCl, *i.e.*, addition of two molecules of HCl on two double bonds of 1, 4 pentadiene would take place according to Markownikoff's rule, since presence of peroxide does not effect the addition of HCl.



$$CH_2=CH-CH_2-CH=CH_2+2HCl\longrightarrow CH_3\underset{\underset{\displaystyle Cl}{|}}{C}HCH_2\underset{\underset{\displaystyle Cl}{|}}{C}HCH_3$$

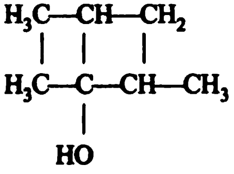
1, 4-Pentadiene 2, 4 Dichloropentane (X)

X with excess of Mg in dry ether will form Grignard's reagent, *i.e.*, Y.

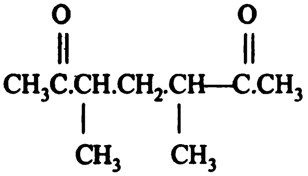


$$CH_3\underset{\substack{|\\ Cl}}{CH}CH_2\underset{\substack{|\\ Cl}}{CH}CH_3 + 2Mg \xrightarrow{\text{Dry ether}} \underset{Y}{CH_3\underset{\substack{|\\ MgCl}}{CH}CH_2\underset{\substack{|\\ MgCl}}{CH}—CH_3}$$

Treatment of Y with ethyl acetate followed by dilute acid yields Z which may be,

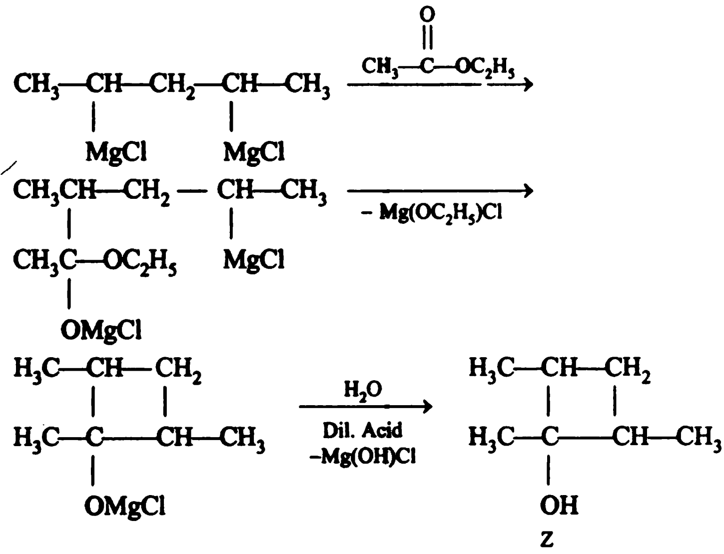


or

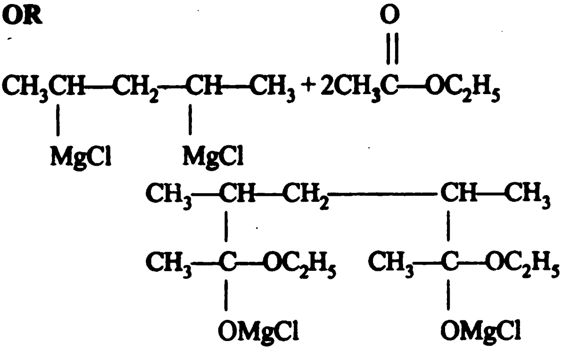


$$CH_3\overset{\substack{O\\ \|}}{C}.\underset{\substack{|\\ CH_3}}{CH}.CH_2.\underset{\substack{|\\ CH_3}}{CH}—\overset{\substack{O\\ \|}}{C}.CH_3$$

Formation of Z on treatment of Y with ethyl acetate is explained as under:

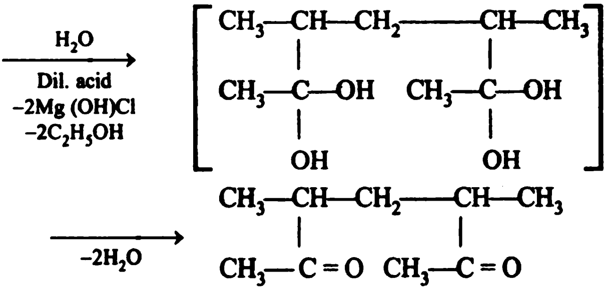


**OR**



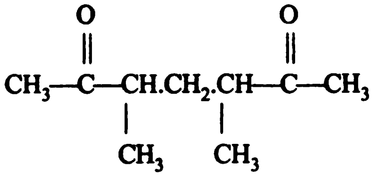
$$CH_3\underset{\substack{|\\ MgCl}}{CH}—CH_2—\underset{\substack{|\\ MgCl}}{CH}—CH_3 + 2CH_3\overset{\substack{O\\ \|}}{C}—OC_2H_5$$

$$CH_3—\underset{\substack{|\\ CH_3—\underset{\substack{|\\ OMgCl}}{C}—OC_2H_5}}{CH}—CH_2———\underset{\substack{|\\ CH_3—\underset{\substack{|\\ OMgCl}}{C}—OC_2H_5}}{CH}—CH_3$$



$$\xrightarrow[\substack{\text{Dil. acid}\\ -2Mg(OH)Cl\\ -2C_2H_5OH}]{H_2O}\left[CH_3-\underset{\underset{\underset{OH}{|}}{CH_3-C-OH}}{\underset{|}{CH}}-CH_2-\underset{\underset{\underset{OH}{|}}{CH_3-C-OH}}{\underset{|}{CH}}-CH_3\right]\xrightarrow{-2H_2O}CH_3-\underset{\underset{CH_3-C=O}{|}}{CH}-CH_2-\underset{\underset{CH_3-C=O}{|}}{CH}-CH_3$$

**OR**



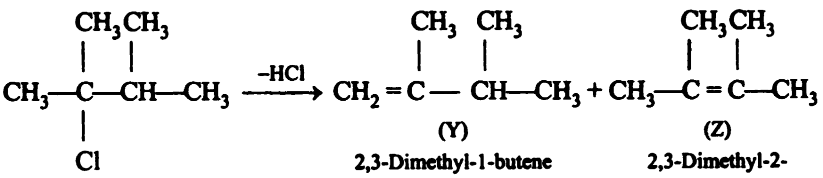
$$CH_3-\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{CH}.CH_2.\underset{\underset{CH_3}{|}}{CH}-\overset{\overset{O}{\|}}{C}-CH_3$$

Z

**Example 51. 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.** (*I.I.T. 1996*)

**Sol.** Since the alkenes Y and Z ($C_6H_{12}$) on hydrogenation give 2,3-diethyl butane, two methyl groups in the alkenes Y and Z should be at 2nd and 3rd carbon atoms. It is clear from the molecular formulae of Y and Z that there is only one double bond.

The compounds Y and Z are obtained by the reaction of $C_6H_{13}Cl$ and potassium teritary butaoxide. Therefore, in compound X there are two methyl gtroups at 2nd and 3rd carbon atoms and one of them is bonded with Cl group. Structures of X, Y and Z and the reactions are given as under :

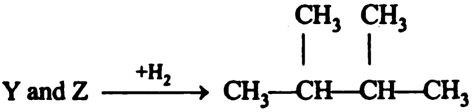


$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{Cl}{|}}{C}}-\overset{\overset{CH_3}{|}}{CH}-CH_3\xrightarrow{-HCl}CH_2=\overset{\overset{CH_3}{|}}{C}-\overset{\overset{CH_3}{|}}{CH}-CH_3+CH_3-\overset{\overset{CH_3}{|}}{C}=\overset{\overset{CH_3}{|}}{C}-CH_3$$

(X) 2-Chloro-2, 3-dimethyl butane

(Y) 2,3-Dimethyl-1-butene

(Z) 2,3-Dimethyl-2-butene



$$\text{Y and Z}\xrightarrow{+H_2}CH_3-\overset{\overset{CH_3}{|}}{CH}-\overset{\overset{CH_3}{|}}{CH}-CH_3$$

2, 3-Dimethyl butane

**Example 52. 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.** *(I.I.T. 1996)*

**Sol.** Since the compound 'D' $C_8H_{10}O$ gives yellow precipitate. with $I_2$ and NaOH (iodoform test), 'D' contains $CH_3CHOH$—group. Keeping in view the mol. formula, 'D' may be $C_6H_5.CHOH.CH_3$ which gives the reactions as given in the problem.

$$\underset{(D)}{C_6H_5.CHOH.CH_3} \xrightarrow{I_2/NaOH} \underset{Yellow}{CHI_3\downarrow} + C_6H_5COONa$$

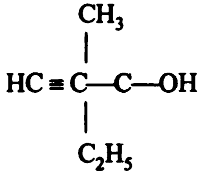
$$C_6H_5COONa \xrightarrow{H^+} \underset{(E)\ White\ solid}{C_6H_5COOH} + Na^+$$

Thus,

$$D = C_6H_5.CHOH.CH_3$$
$$E = C_6H_5COOH$$

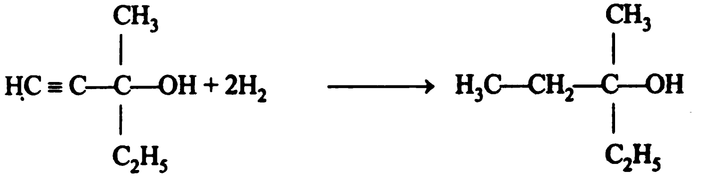
**53. An optically active alcohol A ($C_6H_{10}O$) absorbs two moles of hydrogen per mole of A upon catalytic hydrogenation and gives a product B. The compound B is resistant to oxidation by $CrO_3$ and does not show any optical activity. Deduce the structures of A and B.** *(I.I.T. 1996)*

**Sol.** Since the alcohol 'A' is optically active, the carbon carrying the alcoholic group (—OH) must be linked to four different groups, one being —OH group. The following structure for A explains the reactions.



$$HC\equiv C-\underset{\underset{C_2H_5}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH$$

(A)



$$HC\equiv C-\underset{\underset{C_2H_5}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH + 2H_2 \longrightarrow H_3C-CH_2-\underset{\underset{C_2H_5}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH$$

3-methyl-pentyne-1-ol-3 (A) Optically active

3-methyl pentanol-3 (B) Optically inactive

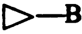
Since the compound 'B' is a tertiary alcohol, it is resistant to oxidation by $CrO_3$.

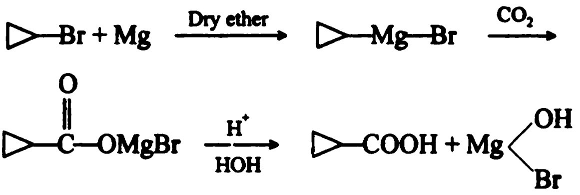
**Example 54. A hydrocarbon A of the formula $C_8H_{10}$ on ozonolysis gives compound B ($C_4H_6O_2$) only. The compound B can also be obtained from the alkyl bromide, C ($C_3H_5Br$) upon treatment with magnesium in dry ether, followed by carbon dioxide and acidification. Identify A, B, and C and also give equations for the reactions.** *(I.I.T. 1996)*

**Sol.** Since the hydrocarbon ($C_8H_{10}$) 'A' on ozonolysis gives only compound 'B' ($C_4H_6O_2$), there should be only one triple bond in the molecule which is centrally located. At the same time, number of hydrogen atoms is quite less. Therefore, the hydrocarbon should be a cyclic compound.

On the above basis the compound 'A' may be  and B may be .

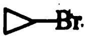
Since the compound 'B' may be obtained by the treatment of $C_3H_5Br$ (C) and Mg in ether followed by $CO_2$ and acidification, 'C' may be

 and its reaction may be represented as :



Therefore, A = 

B = 

C = 

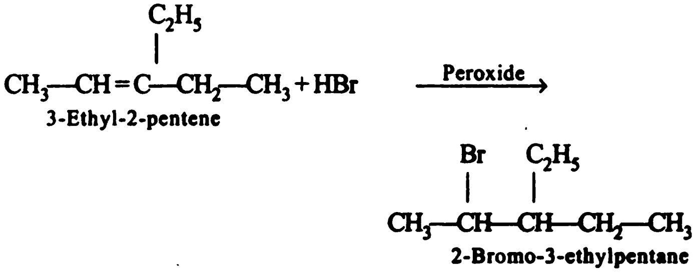
**55. Give the structures of the major organic products from 3-ethyl-2-pentene under each of the given reaction conditions :**

(*a*) **HBr in the presence of peroxide**

(*b*) **$Br_2/H_2O$**

(*c*) **$Hg(OAC)_2/H_2O$ ; $NaBH_4$** (*I.I.T. 1996*)

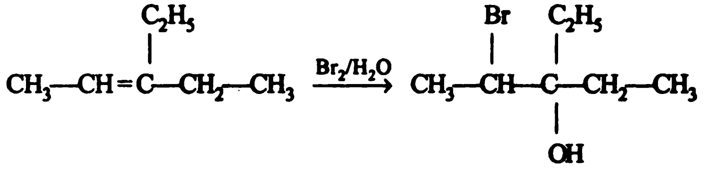
**Sol.**

(*a*) 

$$CH_3-CH=\overset{\overset{\large C_2H_5}{|}}{C}-CH_2-CH_3+HBr\xrightarrow{\text{Peroxide}}CH_3-\overset{\overset{\large Br}{|}}{CH}-\overset{\overset{\large C_2H_5}{|}}{CH}-CH_2-CH_3$$

3-Ethyl-2-pentene

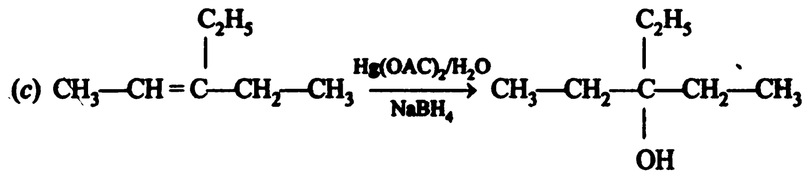
2-Bromo-3-ethylpentane

(*b*) 

$$CH_3-CH=\overset{\overset{\large C_2H_5}{|}}{C}-CH_2-CH_3\xrightarrow{Br_2/H_2O}CH_3-\overset{\overset{\large Br}{|}}{CH}-\underset{\underset{\large OH}{|}}{\overset{\overset{\large C_2H_5}{|}}{C}}-CH_2-CH_3$$

($Br_2+H_2O\rightarrow HOBr+HBr$)

4-Bromo-3-ethyl pentanol-3



$$(c)\ CH_3-CH=\overset{\overset{\Large C_2H_5}{|}}{C}-CH_2-CH_3 \xrightarrow[NaBH_4]{Hg(OAC)_2/H_2O} CH_3-CH_2-\underset{\underset{\Large OH}{|}}{\overset{\overset{\Large C_2H_5}{|}}{C}}-CH_2-CH_3$$

3-Ethyl-3-pentanol

**Example 56. The hydrocarbon 'A' adds one mole of hydrogen in presence of a platinum catalyst to form *n*-hexane. When 'A' is oxidised vigorously with $KMnO_4$, a single carboxylic acid containing three carbon atoms, is isolated. Give the structure of 'A' and explain.** (*I.I.T. 1997*)

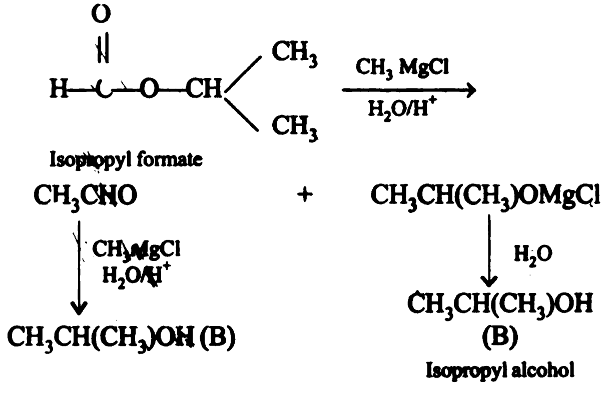
**Sol.** The hydrocarbon 'A' adds one mole of hydrogen to form *n*-hexane, hence hydrocarbon 'A' is straight chain hexene.

'A', on oxidation with $KMnO_4$ gives a single carboxylic acid with three carbon atoms, hence the double bond in hexene must be present between 3rd and 4th carbon atoms. Thus A is 3-hexene.

$$\begin{tikzcd}
\underset{\text{3-Hexene (A)}}{CH_3.CH_2.CH=CH.CH_2.CH_3} \arrow[r, "H_2/Pt"] \arrow[d, "KMnO_4"', "{[O]}"] & \underset{n\text{-Hexene}}{CH_3.CH_2.CH_2-CH_2.CH_2.CH_3} \\
\underset{\text{Propionic acid}}{2\,CH_3.CH_2COOH} &
\end{tikzcd}$$

**Example 57. An ester A ($C_4H_8O_2$), on treatment with excess methyl magnessium 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.** (*I.I.T. 1998*)

**Ans.** Structures of A and B and the reactions are given as under :



Isopropyl formate

$$\begin{tikzcd}
H-\overset{\overset{O}{\|}}{C}-O-CH(CH_3)_2 \arrow[r, "CH_3\,MgCl", "H_2O/H^+"'] & {} \\
CH_3CHO \arrow[d, "CH_3MgCl", "H_2O/H^+"'] & + & CH_3CH(CH_3)OMgCl \arrow[d, "H_2O"] \\
CH_3CH(CH_3)OH\ (B) & & \underset{\text{(B)}}{CH_3CH(CH_3)OH}
\end{tikzcd}$$

Isopropyl alcohol

$$CH_3—CH(CH_3)OH \xrightarrow{NaOCl} CHCl_3 + CH_3COONa \xrightarrow{H_2O/H^+} \underset{\text{Acetic acid}}{CH_3COOH}$$

**Example 58. An aldehyde A ($C_{11}H_8O$), which does not undergo self aldol condensation, gives benzaldehyde and two moles or B on ozonolysis. Compound B, on oxidation with silver ion gives oxalic acid. Identify the compounds A and B.** (*I.I.T. 1998*)

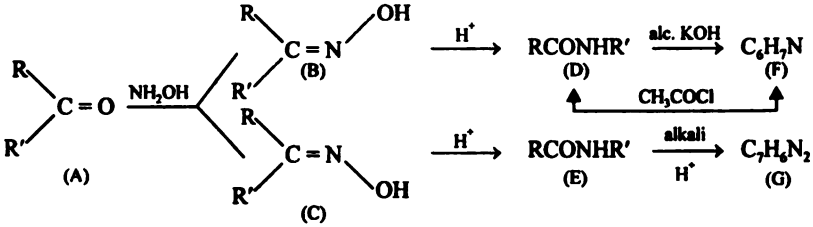
**Ans.** Structures of A and B and their reactions are given as under :

$$C_6H_5CH{=}CH—C{\equiv}C—CHO \xrightarrow[Zn/CH_3COOH]{O_3} C_6H_5CHO + \underset{\text{(B) Glyoxalic acid}}{2OHC—COOH}$$

$$\xrightarrow[\text{[O]}]{Ag} \underset{\text{oxalic acid}}{2HOOC—COOH}$$

**Example 59. 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.** (*I.I.T. 1999*)

**Ans.** As A combines with hydroxylamine hydrochloride, it must be a keto compound. Let it be represented by RCOR′. Reactions given in the problem may be represented as under :

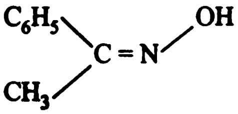


Reaction (B) to (D) and (C) to (E) are Beckmann reactions which give substituted amides due to the migration of R group in the *anti* position.

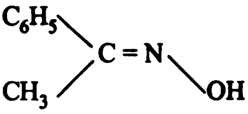
The following structures for A to G explain the reactions.

(A) $C_6H_5COCH_3$

(B)



(C)



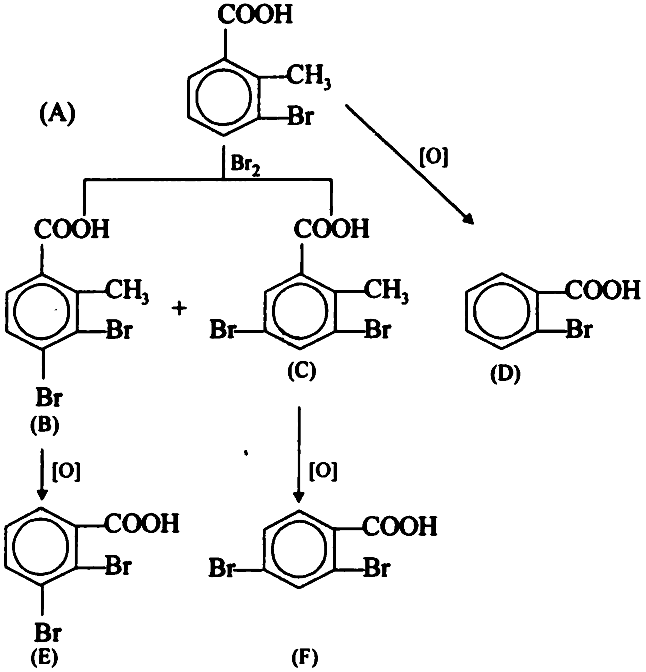
(D) $CH_3CONHC_6H_5$ (E) $C_6H_5CONHCH_3$

(F) $C_6H_5NH_2$ (G) $C_6H_5COOH$

**Example 60. An acid (A), $C_8H_7O_2Br$ on bromination in the presence of $FeBr_3$ gives two isomers, (B) and (C) of formula $C_8H_6O_2Br_2$. Vigorous**

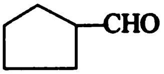
**oxidation of (A), (B) and (C) gives acids (D), (E) and (F) respectively. (D), $C_7H_5O_2Br$ is the strongest acid among all of its isomers, whereas (E) and (F) each has a molecular formula of $C_7H_4O_2Br_2$. Give structures of (A) to (F) with justification.** (*Roorkee 2000*)

**Ans.** Structures of (A), (B) and (C) are as under :

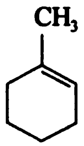


**Example 61. An organic compound A, $C_6H_{10}O$, on reaction with $CH_3MgBr$ followed by acid treatment gives compound B. The compound B on ozonolysis gives compound C, which is the presence of a base gives 1-acetyl cyclopentene, D. The compound B on reaction with HBr gives compound E. Write the structures of A, B, C and E. Show how D is formed from C.** (*I.I.T. 2000*)

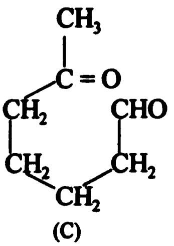
**Ans.** The following structures of A, B, C, D and *l* explain the observations



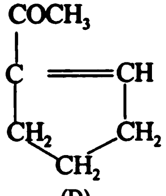
(A)



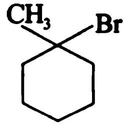
(B)



(C)



(D)

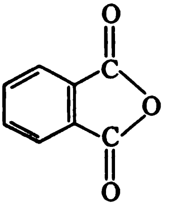


(E)

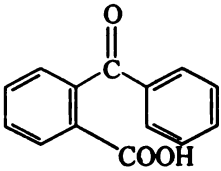
**Example 62. An organic compound A, $C_8H_4O_3$, in dry benzene in the presence of anhydrous $AlCl_3$ gives compound B. The compound B on treatment with $PCl_5$, followed by reaction with $H_2$/Pd ($BaSO_4$) gives compound C, which on reaction with hydrazine gives a cyclised compound D ($C_{14}H_{10}N_2$). Identify A, B, C and D. Explain the formation of D from C.**

*(I.I.T. 2000)*

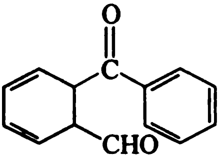
**Ans.** The following structures of A, B, C and D explain the observations.



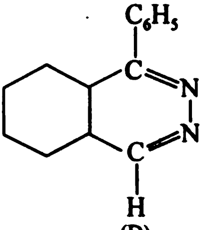
(A)



(B)



(C)



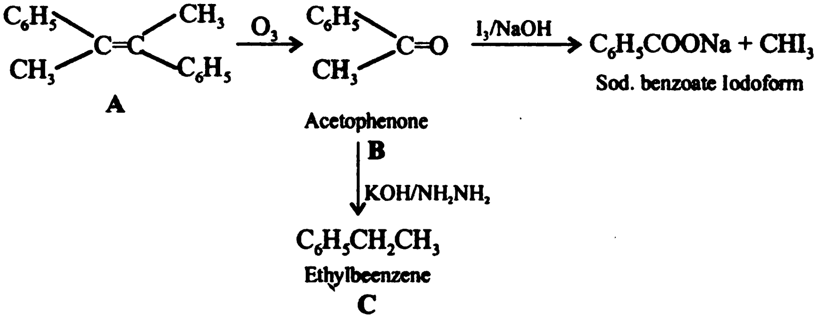
(D)

$$C \xrightarrow[-2H_2O]{NH_2—NH_2} D$$

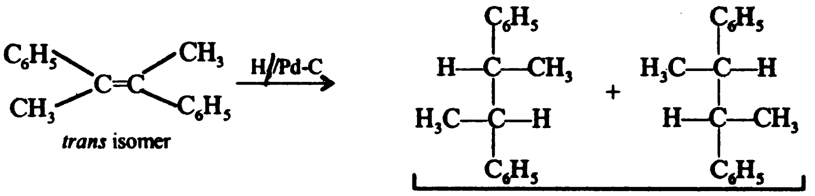
**Example 63.** ***An alkene A*** **($C_{16}H_{16}$) on ozonolysis gives only one product** ***B*** **($C_8H_8O$). Compound B on reaction with NaOH/$I_2$ yields sodium benzoate. Compound** ***B*** **reacts with KOH/$NH_2NH_2$ yielding a hydrocarbon C($C_8H_{10}$). Write the structures of compounds** ***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.** ***(I.I.T. 2001)***

**Ans.** Since A on ozonolysis gives only one product B, the alkene must be symmetrical.

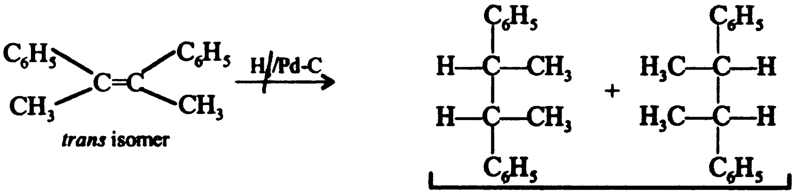
Again, B gives sodium benzoate on treatment with $I_2$/NaOH. Therefore, one of the groups attached to the double bond must be $C_6H_5$ and the other, of course, is $CH_3$. The reactions can be represented as under :



The alkene A occurs in two isomers. Catalytic hydrogenation involves *syn* addition of hydrogens. The *trans* isomer gives racemic mixture while *cis* isomer gives *meso* compound.



Racemic mixture



*Meso* compound

**Example 64. 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 :**

**(*a*) On hydrogenation, Bombykol gives a compound A, $C_{16}H_{34}O$ which reacts with acetic anhydride to give an ester.**

**(*b*) Bombykol also reacts with acetic anhydride to give another ester, which on oxidative 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 ?** ***(I.I.T. 2002)***

Ans. 1. Bombykol takes up four hydrogen atoms to form the compound A. Hence,bombykol contains either one triple bond or two double bonds.

2. The possibility of the triple bond is ruled out because the ester of bombykol gives three products on ozonolysis. Hence, the presence of two double bonds in bombykol is established.

$$\begin{tikzcd} \underset{\text{Bombykol}}{C_{16}H_{30}O} \arrow[r, "(CH_3CO)_2O"] & \underset{\text{Ester of Bombykol}}{C_{16}H_{30}OCOCH_3} \arrow[d, "O_3"] \\ & {} \end{tikzcd}$$

$$\underset{\text{Butanoic acid}}{CH_3CH_2CH_2COOH} + \underset{\text{Oxalic acid}}{HOOC—COOH} + \underset{\text{10-Acetoxy decanoic acid}}{HOOC—CH_2(CH_2)_7CH_2OCOCH_3}$$

Structure of bombykol acetate (ester) is

$CH_3CH_2CH_2CH{=}CH—CH{=}CH—CH_2(CH_2)_7CH_2OCOCH_3$

The structure of bombykol therefore is

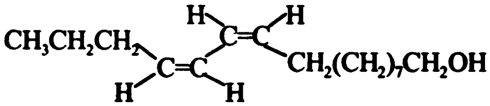
$CH_3CH_2CH_2CH{=}CH—CH{=}CH—CH_2(CH_2)_7CH_2OH$

Structure of compound A is

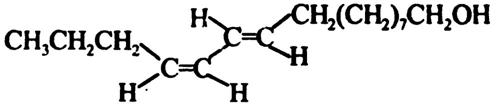
$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2(CH_2)_7CH_2OH$ or $CH_3(CH_2)_{14}CH_2OH$

Due to the presence of two double bonds, bombykol exists in four geometric forms given below.

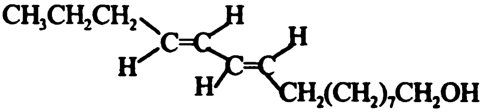
(*i*)



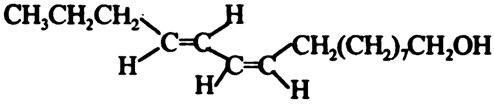
(*ii*)



(*iii*)



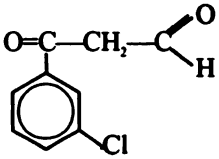
(*iv*)

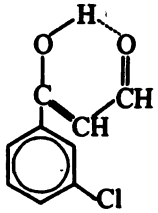


**Example 65. An organic compound $C_9H_7ClO_2$ exists in two forms (A), keto form and predominant (B), an enol form. On oxidation, one of the products is *m*-chlorobenzoic acid. Give the structures of (A) and (B).**

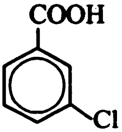
***(I.I.T. 2003)***

**Ans.** The two forms are :


Keto form
(A)


Enol form
(B)

Both the forms on oxidation will give *m*-chlorobenzoic acid as one of the products.


*m*-chlorobenzoic acid

# 10

# Conceptual (Reasoning) Questions

**Q. 1. The boiling points of alkanes increase with increase in molecular weight. Explain.**

**Ans.** With increase in molecular weight the surface area of the compound gradually increases, thus increasing the van der Waals' force between molecules. Hence increase in boiling point, takes place.

**Q. 2. The boiling points of isomeric alkanes decrease with increase in branching. Explain.**

**Ans.** Molecules tend to possess smaller surface area with increase in branching. As surface area and hence area of contact between molecules decreases, van der Waals force also decreases resulting in lower boiling point.

**Q. 3. Methane does not react with chlorine in dark at room temperature. explain.** *[I.I.T]*

**Ans.** Dark condition does not provide energy. Energy in the form of ultraviolet light or high temperature for dissociation of chlorine molecules, $Cl_2$, into chlorine radicals, $Cl\cdot$ is required for the reaction to takes place.

$$Cl_2 \xrightarrow[\text{Energy}]{h\nu} 2Cl\cdot$$

**Q. 4. Methane does not react with iodine. Explain.**

**Ans.** The reaction $CH_4 + I_2 \longrightarrow CH_3I + HI$ is highly endothermic, that is, requires lot of energy to occur. In contrast, the reverse reaction takes place in a smooth manner.

**Q. 5. *n*-Alkanes with an even number of carbon atoms have slightly higher melting point than the next higher homologue. Explain.**

**Ans.** The end carbons of the *n*-alkanes with even number of carbon atoms are on opposite sides resulting in a greater intermolecular attraction due to closer packing of the molecules. Hence they show a higher melting point.

**Q. 6. In Wurtz synthesis the alkyl halide must be primary, not secondary or tertiary. Explain.**

**Ans.** The Wurtz reaction proceeds through an intermediate alkylsodium.

$$RX + 2\,Na \longrightarrow RNa + NaX$$

Alkylsodium ($R^-Na^+$) is a strong base which results in dehydrohalogenation of alkyl halide to the alkene. Formation of alkane occurs when the reaction

**takes place between alkylsodium and alkyl halide which is a nucleophilic substitution reaction.**

$$RNa + RX \longrightarrow R{-}R + NaX$$

This substitution reaction works best for primary alkyl halides. Tertiary alkyl halides give rise to alkenes under the condition.

**Q. 7. Members of a homologous series show identical chemical properties. Explain.**

**Ans.** Properties depend on the fuctional group present in the compound and all memebers of a homologous series possess the same functional group. Thus they show identical chemical properties.

**Q. 8. Excess methane is required in the chlorination of methane to produce methyl chloride as the chief product. Explain.**

**Ans.** The greater the concentration of methane, the greater is the chance of collision of methane molecules with chlorine radicals hence the greater is the yield of methyl chloride. If the amount of methane is kept low, di, tri or tetrahalogen products may be obtained.

**Q. 9. Bromination is preferred to chlorination in the halogenation of an alkane. Explain.**

**Ans.** Bromination often gives a pure alkyl bromide in high yield, whereas chlorination yields a mixture of isomeric alkyl chlorides. This character of bromine is due to its great size and low reactivity compared with chlorine. Again, bromine removes only the hydrogen of an alkane that is weakly bonded to a carbon atom, because $-\overset{|}{\underset{|}{C}}-H + Br^{\bullet} \longrightarrow -\overset{|\,\bullet}{\underset{|}{C}} + HBr$ is endothermic.

**Q. 10. Propagation of a free radical chain reaction is often inhibited by rapid cambination of two radicals. Explain why it is possible to carry out chain reaction despite that fact.**

**Ans.** Even a low concentration of free radical is enough to keep the chain reaction going. There is higher probability of a free radical species reacting with the high concentration of reactants to propagate the chain rather than with another radical in very low concentration.

**Q. 11. When methane is treated with $Cl_2$ in the presence of ultraviolet light, small amounts of ethane and ethyl chloride are also produced. Explain.**

**Ans.** According to mechanism of chlorination of methane, methyl radical, $\dot{C}H_3$, combines with $Cl_2$ molecule to form methyl chloride. Methyl radical also has a chance to dimerise itself to produce ethane, When it happens, ethane begins to take part in the reaction leading to the formation of ethyl chloride.

$$\dot{C}H_3 + Cl_2 \longrightarrow CH_3Cl + \dot{C}l$$

$$\dot{C}H_3 + \dot{C}H_3 \longrightarrow CH_3{-}CH_3 \text{ (ethane)}$$

$$CH_3—CH_3 + \dot{Cl} \longrightarrow CH_3—CH_2 + HCl$$

$$CH_3—\dot{C}H_2 + Cl_2 \longrightarrow \underset{\text{Ethyl chloride}}{CH_3CH_2Cl} + \dot{Cl}$$

**Q. 12. A σ (sigma) bond is stronger than a π (pi) bond. Explain.**

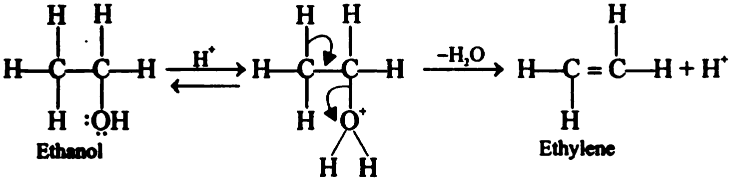
**Ans.** The lateral overlap of *p*-orbital that occurs in the formation of a pi bond is less effective than the axial overlap that occurs in the formation of a sigma bond. Hence σ bond is stronger than π bond.

**Q. 13. Why is alcoholic KOH and not aqueous KOH used for dehydrohalogenation of an alhyl halide to an alkene. Explain.**

**Ans.** Dehydrohalogenation of an alkyl halide takes place in the presence of a stronger base. Alcoholic KOH, (a solution of KOH in 100% ethonal) contains a small amount of ethoxide ion, $C_2H_5—O^-$, which is a stronger base than hydroxide ion, $OH^-$, present in the aqueous KOH solution. It removes the proton from the alkyl halide with simultaneous removal of halide ion.

**Q. 14. Dehydration of an alcohol to produce an alkene takes place in the presence of an acid catalyst. Explain.**

**Ans.** By combining with a proton from an acid, —O—H functional group of the alcohol molecule is converted to water, H—O—H, which leaves the molecules. It generates a carbocation which subsequently loses a proton to form alkene.



**Q. 15. Alkenes undergo addition reactions. Explain.**

**Ans.** A carbon-carbon double bond in alkenes contains a week π bond. Hence they add to produce saturated compounds. If substitution reaction is to take place, it will be required to break higher-energy σ bonds.

**Q. 16. Ethylene, not ethane, is soluble in conc. $H_2SO_4$. Explain.**

**Ans.** Ethylene, an unsaturated compound, reacts with conc. $H_2SO_4$ to form addition product ethyl hydrogen sulphate which is soluble. Conc. $H_2SO_4$ ordinarily has no effect on ethane.

$$CH_2=CH_2 + H_2SO_4\,(\text{conc.}) \longrightarrow \underset{\text{Ethyl hydrogen sulphate}}{CH_3—CH_2—O—SO_2—OH}$$

**Q. 17. Ethylene is much more reactive than ethane. Explain.** [*B.I.T*]

**Ans.** Ethylene contains a weaker π bond (bond energy: 65 kcal/mol, less than the bond energy of C—C bond in alkanes). It is easier to break the π bond than the σ bond. Hence ethylene is more reactive than ethane.

**Q. 18. Dehydration of 1-butanol gives 2-butene as the chief product, though the expected product is 1-butene. Explain.**

**Ans.** *n*-Butyl carbocation, $CH_3CH_2CH_2\overset{+}{C}H_2$, formed by protonation of 1-butanol followed by loss of water, soon changes to more stable sec-butyl cation, $CH_3CH_2\overset{+}{C}HCH_3$ which, on losing a proton yields 2-butene as the chief product according to Saytzeff rule.

$$\underset{\text{1-Butanol}}{CH_3{-}CH_2{-}CH_2{-}CH_2OH} \xrightarrow{H^+} CH_3CH_2CH_2\overset{+}{O}H_2 \xrightarrow{-H_2O}$$

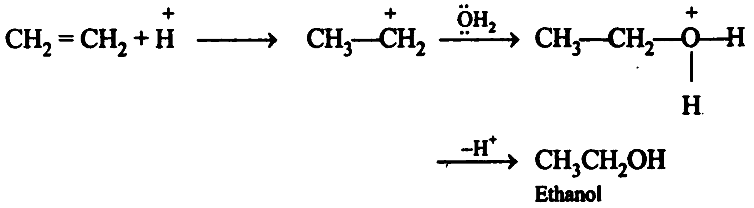
$$CH_3{-}CH_2{-}CH_2{-}\overset{+}{C}H_2 \xrightarrow[\text{1, 2-hydride shift}]{\text{isomeries}} \underset{\textit{sec-}\text{Butyl cation}}{CH_3CH_2\overset{+}{C}HCH_3} \xrightarrow{-H^+} \underset{\text{2-Butene}}{CH_3CH{=}CHCH_3}$$

**Q. 19. Alkenes react with electrophilic reagents. Explain.**

**Ans.** Overlapping of electron orbitals in $\pi$ bond is incomplete. Less tightly held electron cloud in alkenes is available to the reagents which can accept these electrons. Such reagents are electron-deficient species, *i.e.*, electrophiles.

**Q. 20. Hydration of an alkene to an alcohol is catalysed by an acid. Explain.**

**Ans.** Ethylene and water do not react together. The proton from the acid converts ethylene to a reactive ethyl cation $CH_3\overset{+}{C}H_2$, which soon takes up water present in excess resulting in the formation of ethanol.



$$CH_2=CH_2+\overset{+}{H} \longrightarrow CH_3{-}\overset{+}{C}H_2 \xrightarrow{\ddot{O}H_2} CH_3{-}CH_2{-}\underset{\displaystyle H}{\overset{+}{O}}{-}H$$

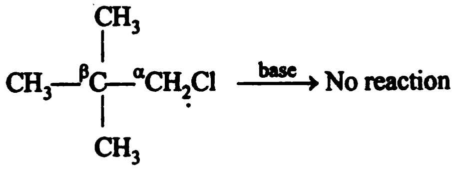
$$\xrightarrow{-H^+} \underset{\text{Ethanol}}{CH_3CH_2OH}$$

**Q. 21. Alkenes are also called olefins. Explain.**

**Ans.** The lower-molecular weight alkenes yield "oily" products on treatment with chlorine or bromine, hence the term olefins (oil-formers) is used for alkenes, in general.

**Q. 22. Neopentyl chloride does not undergo dehydrohalogenation in presence of a base. Explain.**

**Ans.** There must be a hydrogen at β-position in the alkyl halide, which is to be lost as a proton when a base approaches the alkyl halide for dehydrohalogenation. Neopentyl chloride does not have a β-hydrogen and hence does not undergo dehydrohalogenation.



$$CH_3{-}{}^{\beta}\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}{-}{}^{\alpha}CH_2Cl \xrightarrow{\text{base}} \text{No reaction}$$

**Q. 23. Conc. $H_2SO_4$ is used to dry ethane, not ethylene. Explain.**

**Ans.** Ethylene being an unsaturated and reactive compound reacts with conc. $H_2SO_4$ to give ethyl hydrogen sulphate. Conc. $H_2SO_4$ does not react with ethane and hence can be used to dry ethane.

$$\underset{\text{Ethylene}}{CH_2=CH_2} + H_2SO_4\,(\text{conc.}) \longrightarrow \underset{\text{Ethyl hydrogen sulphate}}{CH_3-CH_2-O-SO_2-OH}$$

$$\underset{\text{Ethane}}{CH_3-CH_3} \xrightarrow{\text{Conc. } H_2SO_4} \text{No reaction}$$

**Q. 24. Addition of HCl to propene gives 2-chloropropane, not 1-chloropropane. Explain.**

**Ans.** The addition is electrophilic. The electrophilic $H^+$ from HCl adds to propene to form more stable isopropyl cation, $CH_3\,\overset{+}{C}H-CH_3$ (and not $CH_3-CH_2-\overset{+}{C}H_2$) which combines with $Cl^-$ ion to give isopropyl chloride (2-chloropropane). This is also known as Markownikoff's rule.

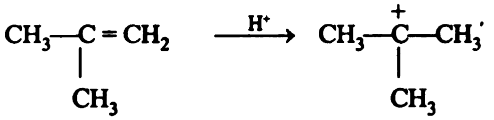
$$\underset{\text{Propene}}{CH_3-CH=CH_2} \xrightarrow{H^+} \underset{\text{Isopropyl cation}}{CH_3-\overset{+}{C}H-CH_3} \xrightarrow{Cl^-} \underset{\text{2-Chloropropane}}{CH_3-CHCl-CH_3}$$

**Q. 25. Dehydrohalogenation of isopropyl bromide, which requires several hours of refluxing in alcoholic KOH, is brought about in less than a minute at room temperature by potassium tert-butoxide in dimethyl sulphoxide. Explain.**

**Ans.** tert-Butoxide ion, $BuO^-$, in dimethyl suphoxide is not solvated via hydrogen bonding and hence is a much stronger base than highly solvated hydroxide ion in alcohol.

**Q. 26. The acid-catalysed hydration of isobutylene is considerably faster than hydration of propylene under similar conditions, Explain.**

**Ans.** The addition of hydrogen ion, $H^+$ takes place more readily to the alkene which produces a more stable carbocation. *tert*-Butyl cation is more stable than isopropyl cation (a 2° carbocation). Hence the hydration of isobutylene takes place faster. This is explaned with the help of following reaction



$$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{C}=CH_2 \xrightarrow{H^+} CH_3-\overset{+}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_3$$

(3° carbocation, more stable)

$$CH_3-CH=CH_2 \xrightarrow{H^+} CH_3-\overset{+}{C}H-CH_3$$

3° carbocation is more stable than 2° carbocation. (2° Carbocation)

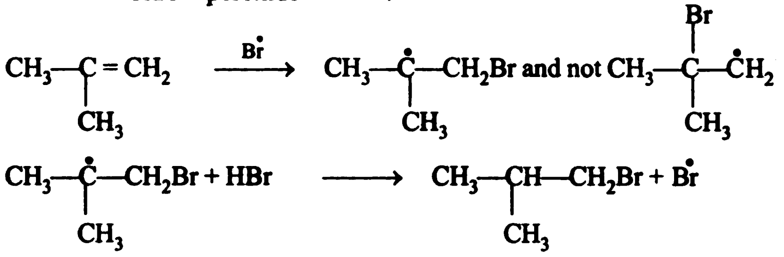
**Q. 27. The rate of catalytic hydrogenation of ethylene is the fastest of all the other homologues. Explain.**

**Ans.** Smaller the number and size of the substituents that are attached to the double bond, more easily the compound will fit on to the catalytic surface, and the faster will be the rate of hydrogenation. Ethylene being the simplest and smallest alkene is hydrogenated at the fastest rate.

**Q. 28. 2-Methylpropene can be converted to isobutyl bromide by HBr in the presence of a peroxide. Explain.**

**Ans.** This reaction takes place by free-radical mechanism. The peroxide generates bromine radical, $\dot{Br}$ from HBr, which combines with 2-methylpropene to form a more stable radical which subsequently yields isobutyl bromide.

$$HBr + \text{peroxide} \longrightarrow \dot{Br}$$



$$CH_3-\underset{\substack{|\\CH_3}}{C}=CH_2 \xrightarrow{\dot{Br}} CH_3-\underset{\substack{|\\CH_3}}{\dot{C}}-CH_2Br \text{ and not } CH_3-\overset{\substack{Br\\|}}{\underset{\substack{|\\CH_3}}{C}}-\dot{C}H_2$$

$$CH_3-\underset{\substack{|\\CH_3}}{\dot{C}}-CH_2Br + HBr \longrightarrow CH_3-\underset{\substack{|\\CH_3}}{CH}-CH_2Br + \dot{Br}$$

Isobutyl bromide

Stability of radicals follows the order $3° > 2° > 1° > \dot{C}H_3$

**Q. 29. Only HBr, not HCl and HI, gives the anti-Markownikoff's product, when it reacts with an alkene. Explain.**

**Ans.** The C—I bond is so weak that the addition of iodine atoms to double bond is endothermic.

$$R—CH = CH_2 + \dot{I} \longrightarrow R\dot{C}H\ CH_2I,\ \Delta H° = +5 \text{ kcal/mole}$$

The H—Cl bond is a strong bond and requires a large amount of energy to break.

$$R\,\dot{C}HCH_2Cl + HCl \longrightarrow RCH_2CH_2Cl + \dot{C}l,\ \Delta H° = +8 \text{ kcal/mole}$$

With HBr however, propogation steps are exothermic.

**Q. 30. Deep brown colour of bromine solution in carbon tetrachloride vanishes when it is treated with excess of ethylene. Explain.**

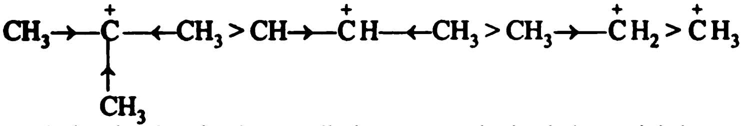
**Ans.** Ethylene is an unsaturated compound which reacts with $Br_2$ to give the product 1, 2-dibromoethane, which is colourless.

$$CH_2 = CH_2 + Br_2 \xrightarrow{CCl_4} CH_2Br—CH_2Br$$

Ethylene dibromide (colourless)

**Q. 31. The stability of carbocation follows the order: $3° > 2° > 1° > CH_3^+$. Explain.**

**Ans.** Alkyl groups are electron-donating groups. It means more the alkyl groups on the positive carbon of the cation, more stable the cation, because electron-donating alkyl groups neutralize the positive charge on carbon, making it more stable.



$$CH_3\rightarrow\underset{\underset{\displaystyle CH_3}{\uparrow}}{\overset{+}{C}}\leftarrow CH_3 > CH\rightarrow\overset{+}{C}H\leftarrow CH_3 > CH_3\rightarrow\overset{+}{C}H_2 > \overset{+}{C}H_3$$

Methyl carbonium ion has no alkyl group attached to it, hence it is least stable.

**Q. 32. A reducing agent is often used during hydrolysis of alkene ozonides to the carbonyl compounds. Explain.**

**Ans.** Hydrogn peroxide obtained as a by-product during hydrolysis of alkene ozonide is destroyed by the reducing agent, otherwise $H_2O_2$ will oxidise the carbonyl compounds, particularly the aldehydes which are more sensitive.

**Q. 33. Markownikoff's rule is observed only when an unsymmetrical alkene reacts with an unsymmetrical reagent. Explain.**

**Ans.** When either the alkene or reagent is symmetrical, only one product is theoretically possible. In case of unsymmetrical alkene and unsymmetrical reagent two products are possible. One product will dominate according to Markownikoff's rule as illustrated below.

$$\underset{\text{Sym}}{CH_3—CH = CH—CH_3} + \underset{\text{Unsym}}{HCl} \longrightarrow \underset{\text{2-Chlorobutane (only product)}}{CH_3—CH_2—CHCl—CH_3}$$

$$\underset{\text{Unsym}}{CH_3—CH = CH_2} \xrightarrow{HCl} \begin{cases} CH_3CH_2CH_2Cl \\ CH_3 — CHCl — CH_3 \text{ (the major product)} \end{cases}$$

**Q. 34. Sulphuric acid or phosphoric acid is preferred as an acid catalyst for hydration of an alkene. Explain.**

**Ans.** Conjugate bases $HSO_4^-$ and $H_2PO_4^-$ of sulphuric and phosphoric acids are poor nucleophiles and do not interfere in the reaction.

**Q. 35. Acetylenic hydrogen, $\equiv$ C—H, is acidic. Explain.**

**Ans.** The hybrid orbital *sp* of acetylenic carbon possesses 50% *s* character. Electron in *s* orbital resides much closer to the nucleus than a *p* or *d*-orbital. Acetylenic carbon thus becomes electronegative, and the carbon-hydrogen bond becomes polar, $\equiv \overset{\delta-}{C} — \overset{\delta+}{H}$. A much stronger base such as sodamide knocks out hydrogen as a proton.

$$\equiv C — H \xrightarrow{NaNH_2} \equiv \overset{-}{C}\overset{+}{Na} + NH_3$$

**Q. 36. Acetylene forms metal acetylides, but dimethylacetylene does not. Explain.**

**Ans.** Dimethylacetylene, $CH_3C \equiv C—CH_3$, does not contain acidic hydrogen, hence dimethylacetylene with does not react with ammoniacal CuCl or $AgNO_3$ solution.

**Q. 37. Acetylene reacts with an ammoniacal cuprous chloride solution, to give a red precipitate, ethylene does not. Explain.**

**Ans.** Due to the presence of acetylenic hydrogen (which is acidic in nature) acetylene reacts with amm. CuCl to give a red precipitate of copper acetylide. Ethylene does not have such acidic hydrogen, hence no precipitate is obtained.

$$\underset{\text{Acetylene}}{H—C \equiv C—H} + 2CuCl \longrightarrow \underset{\text{Copper acetylide (Red ppt.)}}{Cu—C \equiv C—Cu}$$

$$CH_2 = CH_2 \xrightarrow{\text{Amm, CuCl}} \text{No reaction}$$

**Q. 38. Acetylene is less reactive than ethylene towards electrophilic reagents. Explain.**

**Ans.** The $\pi$-electrons in a carbon-carbon triple bond are more tightly held and, therefore, are less easily available to an electrophile compared to $\pi$-electrons in alkenes. Again, on protonation, acetylene forms a less stable *sp*-hybrid carbocation.

**Q. 39. Though acetylenic hydrogen is acidic, it does not react with sodium hydroxide solution. Explain.**

**Ans.** The acetylenic hydrogen, $\equiv$ C—H, is not so acidic as to react with NaOH. A base stronger than NaOH, *e.g.*, sodium amide ($NaNH_2$) does react. Note that acetylene is a weaker acid than water.

**Q. 40. Acetylene is a linear molecule. Explain.**

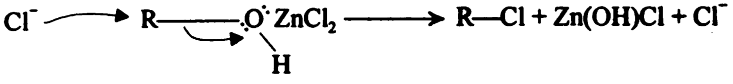
**Ans.** Both carbons in acetylene have *sp*-hybrid orbitals. The two *sp*-hybrid orbitals on each carbon are oriented at an angle of 180° to minimise repulsive force between those orbitals. A strong $\sigma$-bond is formed by the linear overlap of *sp*-orbital of carbon with *s*-orbital of hydrogen, also carbon—carbon $\sigma$ bond is formed when *sp* orbitals of each carbon overlap along the internuclear axis. As a result, all four atoms in acetylene form a straight line.

**Q. 41. Oxyacetylene flame is used for cutting and welding metals. Explain.** *[B.I.T]*

**Ans.** Oxidation of acetylene is a highly exothermic reaction. The oxyacetylene flame liberates enormous heat (temperature > 3000°C) enough to liquefy a metal. Hence it is used for cutting and welding metals.

**Q. 42. Anhydrous $ZnCl_2$ is used in the preparation of alkyl chloride from alcohols and conc. HCl. Explain.**

**Ans.** $Cl^-$ ion is a poor nucleophile and anhydrous $ZnCl_2$ is a Lewis acid. $ZnCl_2$ attaches to the oxygen of hydroxy group, and helps in the removal of OH group. Thus alkyl chloride is formed easily.



$$Cl^- \longrightarrow R—\underset{\substack{\backslash \\ H}}{\dot{O}}\cdot ZnCl_2 \longrightarrow R—Cl + Zn(OH)Cl + Cl^-$$

**Q. 43. $PCl_5$ is preferred to $PCl_3$ in the preparation of alkyl chlorides from alcohols. Explain.**

**Ans.** Some trialkyl phosphite is also formed when an alcohol reacts with $PCl_3$ as shown by the following equation.

$$3ROH + PCl_3 \longrightarrow (RO)_3P + 3\,HCl$$

**Q. 44. Conc. HI is not preferred in the preparation of an alkyl iodide from an alcohol. Explain.**

**Ans.** Conc. HI is a strong reducing agent. A part of alkyl iodide formed is reduced to the alkane. Hence it is not preferred in the preparation of alkyl iodide.

$$R\text{—}OH + HI\,(conc.) \longrightarrow RI + H_2O; \quad R\text{—}I + HI \longrightarrow RH + I_2$$

**Q. 45. Alkyl iodides turn brown in light on long standing. Explain.**

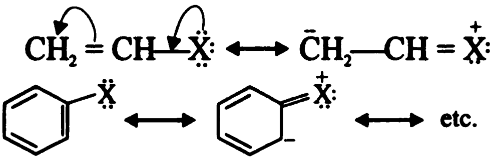
**Ans.** They decompose to liberate free iodine which imparts brown colour to the entire mass. Weak C—I bond accounts for this decomposition.

**Q. 46. Alkyl halides undergo nucleophilic substitution ($S_N$) reactions. Explain.**

**Ans.** Due to greater electronegativity of halogen the carbon of carbon-halogen bond in the alkyl halide acquires a slight positive charge (δ+) This positive centre is attacked by a nucleophile which displaces halogen as a halide ion.

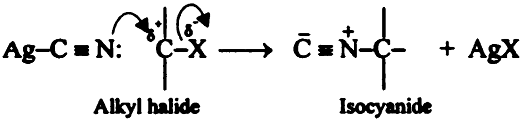
**Q. 47. Vinyl halides and aryl halides are less reactive, hence they do not undergo hydrolysis smoothly, and are not used in Williamson synthesis. Explain.**

**Ans.** Carbon-halogen bond in vinyl halides and aryl halides is relatively stronger than that in alkyl halides. This is because carbon-halogen bond possesses a double bond character due to resonance.



**Q. 48. Reaction of an alkyl halide with alcoholic AgCN gives as a major product alkyl isocyanide, not alkyl cyanide. Explain.**

**Ans.** Silver cyanide, Ag—C ≡ N, is predominantly a covalent compound. Alkyl halides undergo nucleophilic substitution reactions. Nitrogen with its lone pair approaches positively charged carbon of the carbon-halogen portion of the alkyl halide, and a new nitrogen-carbon is formed. It is due to direct bond between nitrogen and carbon, that isocyanide is formed.

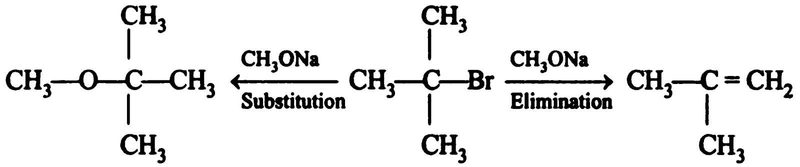


**Q. 49. Alkyl iodide is the most reactive of alkyl halides. Explain.**

**Ans.** Carbon-iodine bond is the weakest of all the carbon-halogen bonds. Hence alkyl iodide is most reactive.

**Q. 50. Tertiary alkyl halides are not used in Williamson synthesis. Explain.**

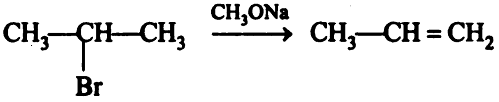
**Ans.** Tertiary alkyl halides undergo elimination of hydrogen halide to give an alkene in the presence of a strong base in preference to substitution. The reaction uses R—ONa which is a much stronger base.



$$CH_3-O-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 \xleftarrow[\text{Substitution}]{CH_3ONa} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Br \xrightarrow[\text{Elimination}]{CH_3ONa} CH_3-\underset{CH_3}{C}=CH_2$$

**Q. 51. There are two possible ways of preparing isopropyl methyl ether by Williamson synthesis, which is the preferred one and why ?**

**Ans.** The two possible ways of preparing methyl isopropyl ether by Williamson synthesis are (*i*) reaction between methyl bromide and sodium isopropoxide and (*ii*) reaction between sodium methoxide and isopropyl bromide. The first combination gives better results. $CH_3ONa$ is a strong base and isopropyl bromide, a secondary halide is more reactive in elimination. Hence the second combination predominantly leads to the elimination product, propene.



$$\underset{\text{2-Bromopropene}}{CH_3-\underset{Br}{CH}-CH_3} \xrightarrow{CH_3ONa} \underset{\text{Propene}}{CH_3-CH=CH_2}$$

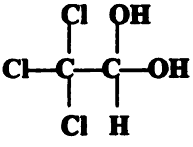
**Q. 52. Tertiary alkyl halide is most reactive of primary, secondary and tertiary alkyl halides in $SN^1$ reactions. Explain.**

**Ans.** Tertiary carbocation, $(CH_3)_3C^+$, is the most stable and most readily formed, hence tertiary alkyl halide dissociates readily and reacts rapidly to give $SN^1$ reaction.

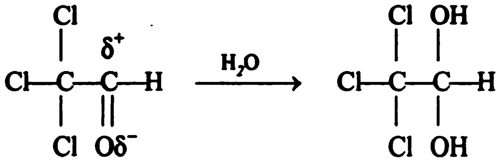
**Q. 53. Chloroform is stored in dark-coloured bottles. Explain.**

**Ans.** Dark colour of the bottles cuts off active part of sunlight which retards oxidation of chloroform to phosgene gas.

$$CHCl_3 + O \xrightarrow{\text{Sunlight}} COCl_2 + HCl$$

**Q. 54. Chloral hydrate**  $Cl-\underset{Cl}{\overset{Cl}{C}}-\underset{H}{\overset{OH}{C}}-OH$ **contains two —OH groups on the same carbon, yet it is quite stable. Explain.**

**Ans.** There are three strong electron-attracting chlorine atoms attached to the α-carbon is chloral. This increases the electron-seeking character of carbonyl carbon which gets readily attached to the nucleophile water, H—O—H.



$$Cl-\underset{Cl}{\overset{Cl}{C}}-\overset{\delta^+}{\underset{O\delta^-}{\overset{}{C}}}-H \xrightarrow{H_2O} Cl-\underset{Cl}{\overset{Cl}{C}}-\underset{OH}{\overset{OH}{C}}-H$$

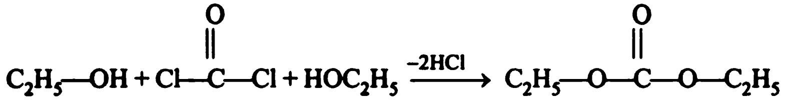
chloral chloral hydrate

**Q. 55. Chloroform may be used as an anaesthetic. Explain.**

**Ans.** Chloroform brings about physical changes in the fatty material of the nerve tissue when it dissolves fats by inhalation.

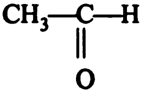
**Q. 56. 1% Ethanol is added to chloroform for its preservation. Explain.**

**Ans.** Ethanol prevents oxidation of chloroform. Also it combines with highly poisonous phosgene gas, if it does form, to non-poisonous diethyl carbonate.



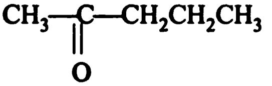
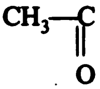
$$C_2H_5-OH + Cl-\overset{\overset{O}{\|}}{C}-Cl + HOC_2H_5 \xrightarrow{-2HCl} C_2H_5-O-\overset{\overset{O}{\|}}{C}-O-C_2H_5$$

**Q. 57. Ethanol responds to iodoform test, methanol does not. Explain.**

**Ans.** A compound containing $CH_3CO$— or $CH_3CHOH$— group responds. to iodoform test. Under the reaction condition ethanol is first oxidised to acetaldehyde,  $CH_3-\underset{\underset{O}{\|}}{C}-H$

which later forms iodoform; methanol does not have such grouping.

**Q. 58. 2-Pentanone gives iodoform test, 3-pentanone does not. Explain.**

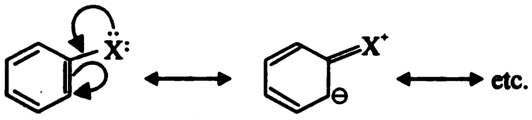
**Ans.** 2-Pentanone,  $CH_3-\underset{\underset{O}{\|}}{C}-CH_2CH_2CH_3$ possesses the characteristic  $CH_3-\underset{\underset{O}{\|}}{C}$ group required for the compound to undergo haloform reaction, 3-pentanone does not contain such group. Hence it does not give the test.

**Q. 59. Acetaldehyde gives iodoform test, formaldehyde does not. Explain.**

**Ans.** Formaldehyde does not have a $CH_3$ CO— group or a group that can be readily oxidised to this group. Hence it does not give this test.

**Q. 60. Aryl halides are less reactive than alkyl halides. Explain.**

**Ans.** There is a stronger carbon-halogen bond in aryl halides. This is attributed to its double bond character due to resonance.



As the C—X bond cannot be broken easily, aryl halide is less reactive than alkyl halide.

**Q. 61. Reaction of a primary aliphatic amine with nitrous acid is not a useful synthetic method for preparation of alcohol. Explain.**

**Ans.** The reaction proceeds through an intermediate alkanediazonium ion which can lead to a number of products, *viz.*, alcohol (1°, 2°, 3°), alkenes, alkyl nitrates, alkyl chlorides, etc.

**Q. 62. Methanol is a liquid and ethane is a gas at room temperature though their molecular weight is almost the same. Explain.**

**Ans.** Ethane molecules do not exhibit hydrogen bonding. Hydrogen bonding is possible in methanol leading to associated molecules having a higher boiling point.

**Q. 63. Glycerol is a viscous water-soluble liquid with a very high boiling point. Explain.**

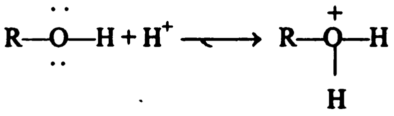
**Ans.** The three hydroxyl groups in glycerol account for a significant degree of hydrogen bonding which increases intermolecular attraction. This explains viscosity and high boiling point of glycerol. It is water soluble because it forms hydrogen bond with water also.

**Q. 64. The alcohol may act as an acid and a base. Explain.**

**Ans.** An alcohol may dissociate to alkoxide ion and hydrogen ion.

$$R{-}O{-}H \rightleftarrows \underset{\text{Alkoxide ion}}{R{-}O^-} + H^+ \qquad \text{(As an acid)}$$

An alcohol may accept a proton due to the presence of the lone pair of electrons on oxygen atom.



$$R{-}\underset{\cdot\cdot}{\ddot{O}}{-}H + H^+ \longrightarrow R{-}\overset{+}{\underset{\displaystyle H}{O}}{-}H$$

Protonated alcohol (As a base)

**Q. 65. Molecular weights of ethanol and dimethyl ether are the same. However ethanol is a liquid at room temperature, but dimethyl ether is a gas. Explain.**

**Ans.** Ethanol molecules are associated through hydrogen bonding which raises the boiling point of ethanol. That is why it is a liquid at room temperature. No hydrogen bond exists between ether molecules.

**Q. 66. Pure and dry ethanol cannot be obtained by fractional distillation of a mixture of water and ethanol. Give reasons.**

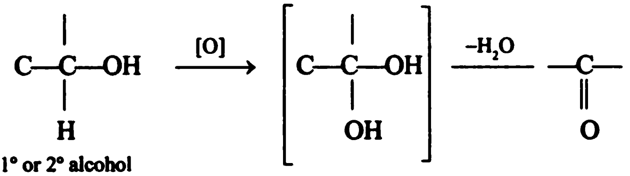
**Ans.** A mixture of ethanol and water of composition 95.6% ethanol and 4.4% water by weight forms an azeotropic (constant boiling) mixture with b.p. 78.25°. Hence the mixture of this boiling point distills over, and the components cannot be separated completely.

**Q. 67. Tertiary butyl alcohol reacts less vigorously with sodium than a primary alcohol. Explain.**

**Ans.** The greater the acid strenth, the greater is the reactivity of an alcohol with sodium. Tertiary butyl alcohol is less acidic than a primary alcohol due to electron donating effect of methyl groups which prevents the removal of hydrogen from the alcoholic group.

**Q. 68. Tertiary butyl alcohol is oxidised with difficulty. Explain.**

**Ans.** Alcohols in which carbon attached to —OH is also attached to hydrogen directly are easily oxidised. Tertiary alcohol does not have such C—H bond and hence is oxidised with difficulty.



**Q. 69. Tertiary alcohol is more repidly dehydrated by an acid than a primary or secondary alcohol. Explain.**

**Ans.** Dehydration of an alcohol involves formation of carbocation. Stability of carbocation follows the order : 3° > 2° > 1° and the rate of dehydration of an alcohol depends on the ease of formation of carbocations. Tertiary alcohols form such ions quite rapidly and get dehydrated.

**Q. 70. Anhydrous $CaCl_2$ is not used for drying ethanol containing traces of water. Explain.**

**Ans.** Anhydrous $CaCl_2$ absorbs not only water but also ethanol forming $CaCl_2 . 4C_2H_5OH$, in which alcohol is present as alcohol of crystallization.

**Q. 71. Tertiary alcohol does not give a positive Victor Meyer test for alcohols. Explain.**

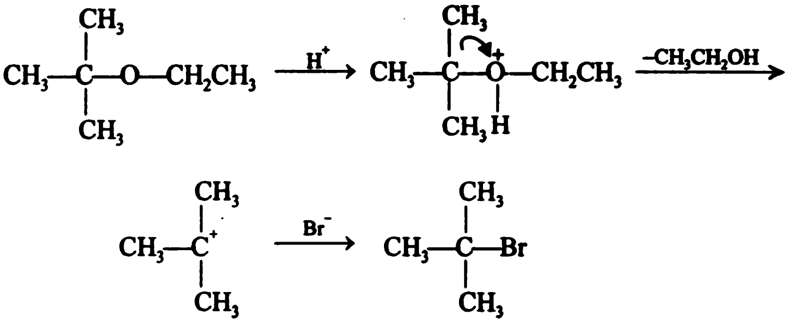
**Ans.** Victor Meyer test involves reaction of an alcohol with HI, $AgNO_2$ and $HNO_2$ successively. Reaction with $HNO_2$ in the reaction takes place with the alcohol containing hydrogen joined to hydroxy-bearing carbon. Such hydrogen does not exist in tertiary alcohols. Therefore, they do not give the test.

**Q. 72. Ethylene glycol is used as an antifreeze in automobiles. Explain.**

**Ans.** Due to high boiling point, low freezing point and high solubility in water, ethylene glycol is used as an antifreeze. Also the freezing point of a solvent (water) gets lowered by addition of glycol (impurity)

**Q. 73. Tert-Butyl ethyl ether is cleaved readily by HBr to give primarily tert-butyl bromide and ethyl alcohol, not tert-butyl alcohol and ethyl bromide. Explain**

**Ans.** As per the mechanism of cleavage, *tert*-butyl ethyl ether is first protonated and then ionisation occurs to give the tert-butyl cation as it is more stable compared to ethyl carbocation. Thus tert-butyl bromide and ethanol are the products.



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-O-CH_2CH_3 \xrightarrow{H^+} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-\underset{\underset{H}{|}}{\overset{+}{O}}-CH_2CH_3 \xrightarrow{-CH_3CH_2OH}$$

$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C^+}} \xrightarrow{Br^-} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-Br$$

**Q. 74. Sodium is used for drying diethyl ether, not ethanol. Explain.**

**Ans.** Diethyl ether does not react with sodium, but ethanol does.

**Q. 75. Diethyl ether is partially soluble in water. Explain.**

**Ans.** Hydrogen bonding between ether and water molecules takes place to some extent making ether partially soluble in water.

**Q. 76. Williamson synthesis is superior to other methods of preparation of ethers. Explain.**

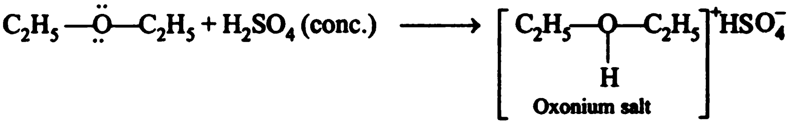
**Ans.** Symmetrical and unsymmetrical ethers both can conveniently be synthesised by William method.

$$R-ONa + X-R_1 \longrightarrow \underset{\text{Ether}}{R-O-R_1}$$

Dehydration of alcohol produces only symmetrical ethers.

**Q. 77. Diethyl ether dissolves in conc. $H_2SO_4$. Explain.** (*B.I.T*)

**Ans.** Diethyl ether gets protonated to form the oxonium ion which is soluble under the conditions.

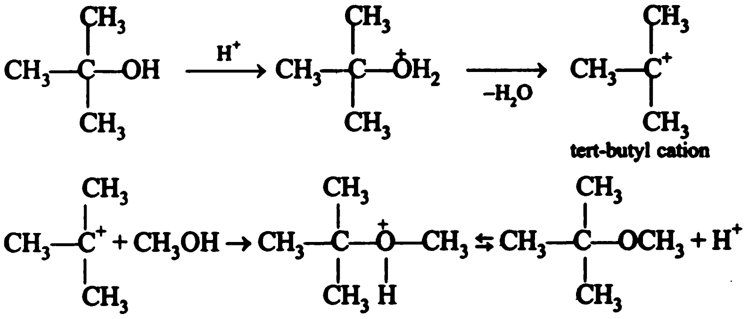


$$C_2H_5-\overset{..}{\underset{..}{O}}-C_2H_5 + H_2SO_4\,(\text{conc.}) \longrightarrow \left[C_2H_5-\underset{\underset{H}{|}}{O}-C_2H_5\right]^+ HSO_4^-$$

Oxonium salt

**Q. 78. When *tert*-butyl alcohol is heated in methanol containing $H_2SO_4$, good yield of *tert*-butyl methyl ether is formed. Explain.**

**Ans.** *tert*-butyl alcohol readily forms a stable *tert*-butyl cation which reacts readily with methanol to yield *tert*-butyl methyl ether. Following equations explain the reaction.



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH \xrightarrow{H^+} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-\overset{+}{O}H_2 \xrightarrow[-H_2O]{} \underset{\text{tert-butyl cation}}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C^+}}}$$

$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C^+}} + CH_3OH \rightarrow CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-\underset{\underset{H}{|}}{\overset{+}{O}}-CH_3 \rightleftharpoons CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OCH_3 + H^+$$

**Q. 79. Unsymmetrical ethers are generally not prepared by heating two alcohols with sulphuric acid. Explain.**

**Ans.** With two different alcohols, a mixture of three ethers is obtained as shown by the following equation.

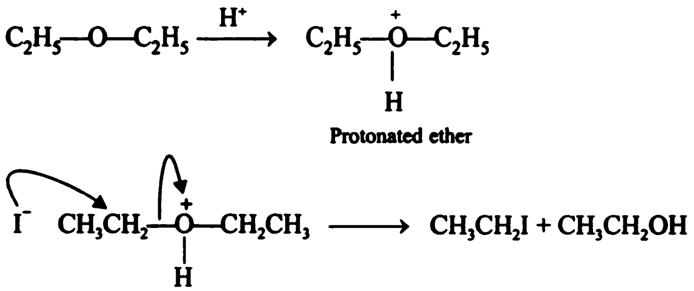
$$R'CH_2{-}OH + R''CH_2{-}OH \xrightarrow{H_2SO_4} R'CH_2{-}O{-}CH_2R'$$
$$+ R'CH_2{-}O{-}CH_2R'' + R''CH_2{-}O{-}CH_2R''$$

**Q. 80. An ether-fire is not extinguieshed by water. Explain.**

**Ans.** Ether is lighter than and insoluble in water. As a result, ether continues to burn even by pouring water over it.

**Q. 81. Conc. HI is preferably used in the cleavage of ether linkage. Explain.**

**Ans.** Conc. HI is a very strong acid and hence ether gets protonated readily, Also iodine ion is a good nucleophile.



$$C_2H_5{-}O{-}C_2H_5 \xrightarrow{H^+} C_2H_5{-}\overset{+}{\underset{H}{O}}{-}C_2H_5$$

$$I^- \; CH_3CH_2{-}\overset{+}{\underset{H}{O}}{-}CH_2CH_3 \longrightarrow CH_3CH_2I + CH_3CH_2OH$$

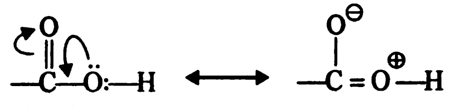
**Q. 82. The boiling points of aldehydes and ketones lie between those of alkanes and alcohols of comparable molecular weights. Explain.**

**Ans.** There is association of alcohol molecules due to large scale hydrogen bonding, but no hydrogen bonding exists in alkanes, aldehydes and ketones. Carbon-oxygen bond of the carbonyl groups is polar on account of electronegativity difference between carbon and oxygen. Due to dipole-dipole attraction, molecules of aldehydes and ketones boil at higher temperature compared to alkanes. Neither hydrogen bonding nor dipole-dipole attraction takes place in alkane. They have the lowest boiling points.

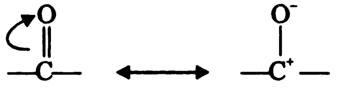
**Q. 83. Carbonyl part of the carboxyl group does not react with hydroxylamine or hydrazines as do aldehydes and ketones. Explain.**

**Ans.** Carbonyl carbon of aldehydes and ketones is slightly positive due to electronegativity difference between carbon and oxygen. Nucleophiles like hydroxylamine and hydrazines attack this positive carbon and the derivatives are obtained.

Carbonyl carbon of the carboxyl group is not so positive as to attract nucleophiles like $NH_2OH$, hydrazines, etc. Due to resonance, the positive charge on the carbonyl carbon decreases as shown below.



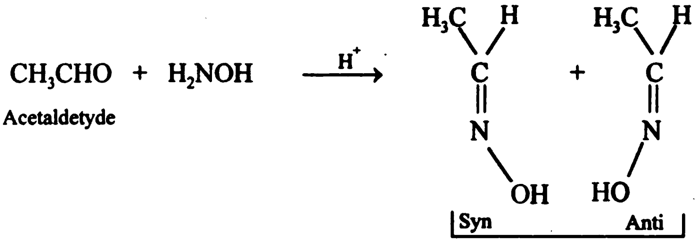
Carboxyl group



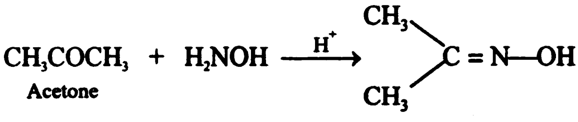
Carbonyl group

**Q. 84. Acetone reacts with hydroxylamine to form only one product but acetaldehyde reacts with hydroxyamine to form two products. Why?**

**Ans.** Acetaldehyde reacts with hydroxylamine to form syn-and anti-acetaldoxime which being geometrical isomers are different products but acetoxime is a single product as it does not exhibit geometrical isomerism.



Acetaldoxime



Acetoxime

**Q. 85. Poisoned catalyst is used in Rosenmund reduction. Explain.**

**Ans.** The aldehyde obtained as a product of the reaction may be further reduced to the primary alcohol when the active catalyst palladium alone is used. To prevent this, the catalyst is poisoned or weakened.

**Q. 86. Saturated sodium bisulphite solution is used while preparing addition bisulphite compound of an aldehyde or ketone. Explain.**

**Ans.** The addition bisulphite compound of an aldehyde or ketone is the sodium salt which is water-soluble, hence the saturated solution of sodium bisulphate is used in order to get it as a precipitate.

**Q. 87. Predict which is a better method for the preparation of acetone: The treatment of acetyl chloride with methyl cadmium chloride or the treatment of acetyl chloride with methyl magnesium chloride.**

**Ans.** Acetone can be better prepared by treating acetyl chloride with methyl cadmium chloride as acetone formed in the latter case further reacts with methyl magnesium chloride to form *tert*-butyl alcohol.

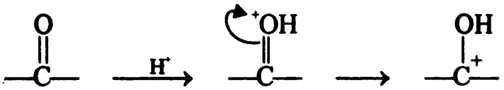
$$(i)\quad \underset{\substack{\text{Acetyl}\\ \text{chloride}}}{CH_3COCl} + \underset{\substack{\text{Methyl}\\ \text{cadmium chloride}}}{CH_3CdCl} \longrightarrow \underset{\text{Acetone}}{CH_3COCH_3} + CdCl_2$$

$$(ii)\quad CH_3COCl + CH_3MgCl \longrightarrow CH_3COCH_3 + MgCl_2$$

$$CH_3COCH_3 + CH_3MgCl \xrightarrow{H_3O^+} \underset{\textit{tert}\text{-butyl alcohol}}{(CH_3)_3COH} + Mg\,(OH)Cl$$

**Q. 88. Hydrazones of aldehydes and ketones are not prepared in highly acidic medium. Explain.** *[I.I.T]*

**Ans.** High concentration of the acid enhances the electrophilic character of carbonyl carbon of aldehydes or ketones. But it destroys the nucleophilic character of nucleophiles like $NH_3$, $NH_2—NH_2$, etc. due to protonation with the lone pair. Thus the nucleophile is not able to approach the carbonyl compound.



$$\overset{O}{\overset{\|}{—C—}} \xrightarrow{H^+} \overset{{}^+OH}{\overset{\|}{—C—}} \longrightarrow \overset{OH}{\overset{|}{—\overset{+}{C}—}}$$

Carbonyl group

$$\underset{\text{Hydrazines}}{\ddot{G}—NH_2} \xrightarrow{H^+} G—NH_3$$

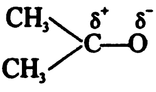
**Q. 89. Treatment of benzaldehyde with HCN gives a mixture of isomers which cannot be separated by physical methods. Why ?**

**Ans.** On treating benzaldehyde with HCN, a pair of isomers (enantiomers) of benzaldehyde cyanohydrin are formed. These enantiomers cannot be separated by physical methods such as fractional distillation, Fractional crystalllization, chromatography etc.

$$C_6H_5CHO + HCN \longrightarrow \underset{\text{Benzaldebyde cyanohydrin}}{C_6H_5CH(OH)CH}$$

**Q. 90. Acetone is less reactive than acetaldehyde. Explain.**

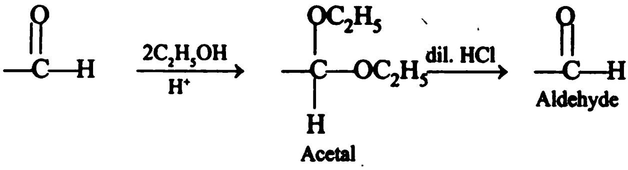
**Ans.** Carbonyl carbon in acetaldehyde is joined to one methyl group, and that in acetone to two methyl groups. Neutralization of positive character of carbonyl carbon in acetone is more due to two electron-donating methyl groups compared to one in acetaldehyde. Hence the result.



$$(CH_3)_2\overset{\delta^+}{C}—\overset{\delta^-}{O}$$

**Q. 91. Acetal formation is often used for the protection of a carbonyl group of aldehydes and ketones. Explain.**

**Ans.** Acetal is obtained when an aldehyde reacts with an alcohol in the presence of dry HCl. The acetal is stable to the alkaline condition, but unstable in acid medium, and thus regenerating the aldehyde group when required.



Acetal

Aldehyde

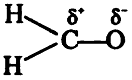
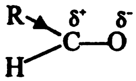
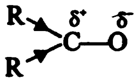
**Q. 92. Pure HCN fails to react with carbonyl compounds. Why ?**

**Ans.** HCN being a weak electrolyte undergoes ionization upto a very small extent and thus fails to react with carbonyl compounds. However, its ionization can be facilitated in the presence of a base.

$$\bar{O}H + HCN \longrightarrow H_2O + \bar{C}N$$

**Q. 93. Formaldehyde is more reactive towards nucleophiles than acetaldehyde or acetone. Explain.**

**Ans.** Aldehydes and ketones react with nucleophilic reagents. Greater the positive character of carbonyl carbon, the greater is the reactivity of aldehydes and ketones. The electron-donating ability of methyl group is greater than hydrogen, and hence the degree of positive character of the carbonyl carbon in formaldehyde is relatively higher than that in acetaldehyde and acetone. Again, formaldehyde is a smaller molecule in size, and hence offers least steric hindrance.

**Q. 94. Aldehydes undergo nucleophilic addition more readily than ketones. Explain.**

**Ans.** Carbonyl carbons of the ketones are linked to one more alkyl group than that of the aldehydes, hence ketones offer more steric hindrance and are thus less reactive. Again, neutralization of positive character of carbonyl carbon in ketones is more, compared with that in aldehydes on account of one more electron-releasing alkyl group present in acetone, Hence ketones are less reactive towards nucleophiles compared to aldehydes.

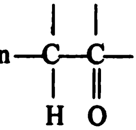
**Q. 95. The most common reactions of aldehydes and ketones are nucleophilic addition. Explain.**

**Ans.** Due to difference in electronegativity between carbon and oxygen in the carbonyl group, carbon acquires a slight positive charge, and hence it is prone to be attacked by nucleophiles. Again, the π bond in carbonyl group leads to the additon product. Hence the overall reaction is nucleophilic addition. The reaction is initiated by a nuclephile.

**Q. 96. Benzaldehyde does not react with Benedict's reagent. Explain.**

**Ans.** The oxidation potential of copper ion of the Benedict's reagent has just the right value to oxidise aliphatic aldehydes, but not aromatic aldehydes like benzaldehyde.

**Q. 97. Formaldehyde does not undergo aldol condensation. Explain.**

**Ans.** An aldehyde or ketone contains an α-hydrogen  $-\underset{H}{\overset{|}{\underset{|}{C}}}-\underset{O}{\underset{\|}{\overset{|}{C}}}-$ a condition for aldol condensation. Formaldehyde does not possess an α-carbon, hence aldol condensation does not take place.

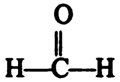
**Q. 98. Though silver oxide, $Ag_2O$, is able to oxidise an aldehydic group to a carboxylic acid, ammoniacal $AgNO_3$ solution is used for the test of an aldehyde. Explain.**

**Ans.** For production of a bright silver mirror on the walls of the inner vessel the reduction of silver ion must take place slowly. This condition is provided by the ammoniacal $AgNO_3$ solution which contains silver ion as the ammine complex. $Ag(NH_3)_2^+$. Silver oxide alone does oxidise the aldehydic group, but silver mirror is not formed as the reaction takes place repidly.

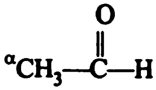
$$AgNO_3 + 2NH_3(aq.) \rightarrow [Ag(NH_3)_2]^+ NO_3^- + H_2O$$

**Q. Formaldehyde undergoes Cannizzaro reaction, acetaldehyde does not. Explain.**

**Ans.** Only those aldehydes which do not have an α–hydrogen (i.e. hydrogen joined to an α–carbon) undergo Cannizzaro reaction. Acetaldehyde possesses α–hydrogens, hance Cannizzaro reaction does not take place.


$H-\overset{\overset{O}{\|}}{C}-H$

Formaldehyde.


${}^{\alpha}CH_3-\overset{\overset{O}{\|}}{C}-H$

Acetaldehyde

**Q. 100. Explain the function of sodium potassium tartrate in Fehling's solution.**

**Ans.** The solution formed by mixing aqueous copper sulphate solution (Fehling's solution 1) and alkaline sodium potassium tartrate solution (Fehling's solution 2) is the Fehling's solution. Sodium potassium tartrate forms a soluble complex with insoluble copper hydroxide which is produced from reaction of $CuSO_4$ solution with alkali. The soluble complex helps in making reduction of cupric ion to cuprous state a smooth process.

**Q. 101. Aldehydes exhibit reducing properties, ketones do not. Explain.**

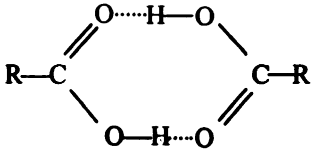
**Ans.** Carbon-hydrogen bond in the aldehydic group is easier to be oxidised to C—OH than the C—C bond in ketones which cannot be oxidised without breaking C—C bond. The substance which gets oxidised in a reaction is a reducing agent. Hence aldehydes show reducing properties.

**Q. 102. 2, 4-Dinitrophenylhydrazine is most frequently employed for the test of a carbonyl group in aldehydes and ketones. Explain.**

**Ans.** 2, 4-Dinitrophenylhydrazine (DNP) is a deep orange-coloured solid with high melting point. The DNP solution reacts with an aldehyde or ketone (in solution) to yield a bright coloured crystalline product of high melting point. Hence it is a preferred reagent to test carbonyl group.

**Q. 103. Boiling points of carboxylic acids are higher than those of alcohols of comparable molecular weights. Explain.**

**Ans.** Most carboxylic acids exist as cyclic dimers through hydrogen bonding as shown below.

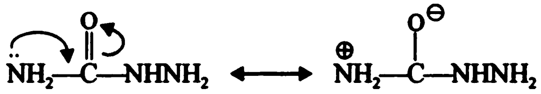


(Dimer of the carboxylic acid)

Hence acids have much higher boiling points than alcohols.

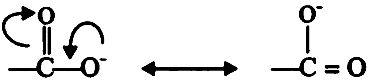
**Q. 104. In semicarbazide $\overset{II}{N}H_2$—CO—NH$\overset{I}{N}H_2$, the amino group marked (I) reacts with acetone to form semicarbazone, but the amino group marked (II) does not participate. Explain.**

**Ans.** The electron pair on the nitrogen atom of $NH_2$ (II) is delocalised due to electron—withdrawing effect of carbonyl group and therefore availability of the electrons decreases. As a result, the $NH_2$ is much less nucleophilic. No such situation exists with $NH_2$ (I).

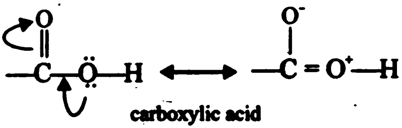


**Q. 105. Resonance is more important in the carboxylate ion than in the carboxyl group itself. Explain.**

**Ans.** Two resonance forms of carboxylate ion have identical energy. The same is not true for carboxyl group in which one is of higher energy due to charge separation.



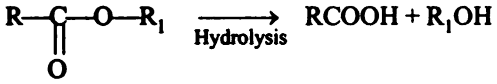
carboxylate ion



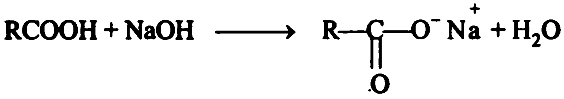
carboxylic acid

**Q. 106. Alkaline hydrolysis of an ester is called saponification. Explain.**

**Ans.** The hydrolysis of an ester yields a carboxylic acid which reacts with the alkali in the reaction mixture to form a salt. A soap is the sodium or potassium salt of a fatty acid (monocarboxylic acid). That is why alkaline hydrolysis of an ester is termed saponification hydrolysis of an ester is termed saponification



$$R{-}\underset{\underset{O}{\|}}{C}{-}O{-}R_1 \xrightarrow[\text{Hydrolysis}]{} RCOOH + R_1OH$$

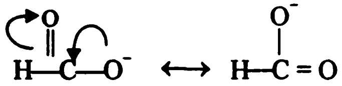


$$RCOOH + NaOH \longrightarrow R{-}\underset{\underset{O}{\|}}{C}{-}O^-\overset{+}{Na} + H_2O$$

(soap)

**Q. 107. Both carbon-oxygen bonds in formate ion (as in sodium formate) are of equal length, but they are different in formic acid. Explain.**

**Ans.** Due to resonance in formate ion the carbon-oxygen bonds are of equal length, and the bond length is intermediate between C = O and C—O bond lengths. (Both the structures are alike).



Formate ion

The resonating structures of formic acid are different and have different C—O bond length.

**Q. 108. Which is a weaker acid and why : formic acid or benzoic acid ?**

**Ans.** Benzoic acid is a weaker acid than formic acid. This is because + R effect of phenyl group ($C_6H_5$—) of benzoic acid overpowers its — I effect and thus oxygen atom linked to H possesses less partial + ve charges and thus weakens the ionization.

**Q. 109. 100% pure acetic acid is called "glacial" acetic acid. Explain.**

**Ans.** Acetic acid freezes at 16.5°C and forms an ice-like crystalline solid, hence the name glacial acetic acid. Glacial means ice-like.

**Q. 110. Good yield of the hydrolysis product of an ester is obtained in alkaline medium. Explain.**

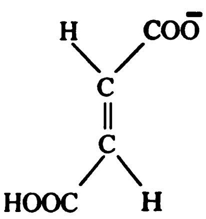
**Ans.** As the ester gets hydrolysed to the carboxylic acid, the latter at once reacts with alkali in the medium to form a salt. The carboxylate ion in the salt is very stable and does not react with alcohol to give back ester.

$$RCOOR' + H_2O \xrightarrow{NaOH} RCOOH + R'OH$$
$$RCOOH + NaOH \longrightarrow RCOONa + H_2O$$

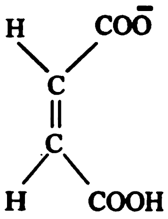
**Q. 111. $K_2$ for fumaric acid is more than that of maleic acid. Why ?**

**Ans.** Both the acids are dibasic acids due to the presence of two replaceable hydrogen atoms. After the release of first H as $H^+$, the meleate ion exhibits intramolecular H bonding but fumerate ion does not.

Thus more energy is required for the release of second H as $H^+$ from maleate ion. Thus $K_2$ for maleic acid is less than that of fumaric acid. Therefore, $K_2$ for fumaric acid is more than that of maleic acid.



Fumerate ion



Maleate ion

**Q. 112. More than one equivalent of alkali is necessary for the hydrolysis of an ester. Explain.**

**Ans.** The carboxylic acid obtained as the hydrolysis product consumes at once the alkali present in the medium to form the salt and therefore some extra amount of alkali must be there to catalyse the reaction. Therefore more than one equivalent of the alkali is necessary to effect hydrolysis in the alkaline medium.

**Q. 113. Formic acid reduces mercuric chloride, $HgCl_2$ solution, acetic acid does not. Explain.**

**Ans.** Formic acid easily is oxidised to $CO_2$ and thus behaves as a reducing agent. Oxidising agents $KMnO_4$, $AgNO_3$ and $HgCl_2$ are reduced.

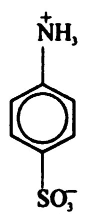
$$2HgCl_2 + HCOOH \longrightarrow \underset{\text{(White)}}{Hg_2Cl_2} + CO_2 + 2HCl$$

$$HgCl_2 + HCOOH \longrightarrow Hg + 2HCl + CO_2$$

$$HCOOH \xrightarrow{AgNO_3} \underset{\text{Silver formate}}{HCOOAg} \longrightarrow Ag + CO_2$$

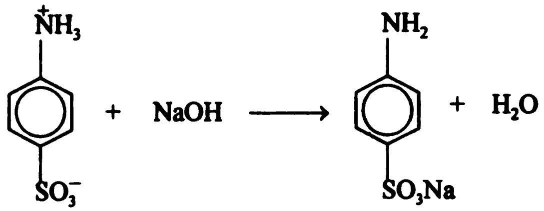
**Q. 114. Account for the fact that sulphanilic acid is insoluble in water and acid but soluble in caustic alkali. Why ?**

**Ans.** Sulphanilic acid exists as a Zwitter ion and exhibits strong dipole-dipole interaction. Therefore, it is water insoluble.



Zwitter ion of sulphanilic acid

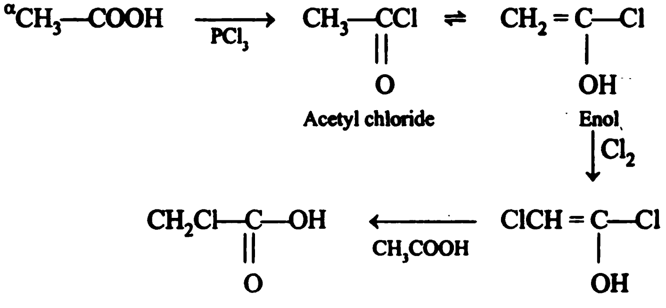
On adding acid, the $SO_3^-$ fails to accept $H^+$ ions to form —$SO_3H$ group and thus suplhanilic acid is also insoluble in acid. However, it is soluble in caustic alkali. This is because the strongly basic hydroxyl ion can abstract a proton from —$\overset{+}{N}H_3$ to form water soluble salt.



Sodium p-aminodbenzenesulphonate

**Q. 115. Acetic acid undergoes chlorination with chlorine in the presence of red phosphorus, formic acid does not. Explain.** [*I.I.T*]

**Ans.** There must be an α-hydrogen for enolisation of the acid chloride formed from the carboxylic acid, and the enol undergoes chlorination. Formic acid does not have the α-hydrogen, hence no chlorination takes place.

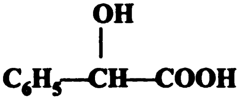


$$^{\alpha}CH_3—COOH \xrightarrow[PCl_3]{} \underset{\text{Acetyl chloride}}{CH_3—\underset{\underset{O}{\|}}{C}Cl} \rightleftharpoons \underset{\text{Enol}}{CH_2=\underset{\underset{OH}{|}}{C}—Cl} \xrightarrow{Cl_2} ClCH=\underset{\underset{OH}{|}}{C}—Cl \xrightarrow[CH_3COOH]{} \underset{\text{Chloroacetic acid}}{CH_2Cl—\underset{\underset{O}{\|}}{C}—OH}$$

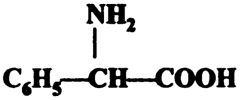
**Q. 116. Which of the following carboxylic acids undergoes decarboxylation easily ?**

(*i*) $C_6H_5—CO—CH_2—COOH$

(*ii*) $C_6H_5—CO—COOH$

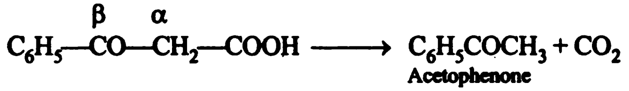


(*iii*) $C_6H_5—\overset{\overset{OH}{|}}{CH}—COOH$



(*iv*) $C_6H_5—\overset{\overset{NH_2}{|}}{CH}—COOH$ (*I.I.T 1995*)

**Ans.** (*i*) being β-keto acid (unstable) undergoes decarboxylation readily



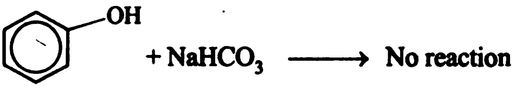
$$C_6H_5—\overset{\beta}{CO}—\overset{\alpha}{CH_2}—COOH \longrightarrow \underset{\text{Acetophenone}}{C_6H_5COCH_3} + CO_2$$

**Q. 117. Carboxylic acid gives effervescence of $CO_2$ with sodium bicarbonate solution, phenol does not. Explain.**

**Ans.** Phenol is a weak acid. It is not strong enough to decompose sodium bicarbonate, whereas a carboxy acid reacts with $NaHCO_3$ to liberate $CO_2$.

$$R{-}COOH + NaHCO_3 \longrightarrow RCOONa + H_2CO_3$$

$$H_2CO_3 \longrightarrow CO_2 + H_2O$$



$+ NaHCO_3 \longrightarrow$ No reaction

Phenol

**Q. 118. Iodoform acts as an antiseptic. Explain.**

**Ans.** The antiseptic action of iodoform is due to iodine which is liberated slowly by the decomposition of iodoform.

**Q. 119. Boiling points of alcohols are much greater than those of alkanes of comparable molecular weight. Explain.**

Ans. Alcohol molecules are associated due to intermolecular hydrogen bonding. Greater energy is needed to overcome the force arising out of hydrogen bonding, hence greater boiling point. Alkanes do not exhibit hydrogen bonding.

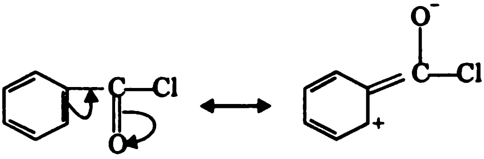
**Q. 120. Thionyl chloride, $SOCl_2$ is often preferred for the preparation of an acid chloride from a carboxylic acid. Explain.**

**Ans.** The by-products of the reaction *viz.*, $SO_2$ and HCl are gases and hence they escape from the reaction vessel as soon as they are formed, and the purification of acid chloride is easy.

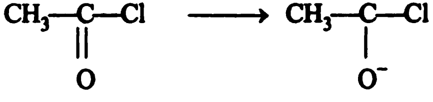
$$RCOOH + SOCl_2 \longrightarrow RCOCl + SO_2 + HCl$$

**Q. 121. Benzoyl chloride is much slowly decomposed by water than acetyl chloride. Explain.**

**Ans.** The electron-releasing phenyl group in benzoyl chloride decreases the positive charges on carbonyl carbon. Hence the reactivity of benzoyl chloride is much less than that of acetyl chloride.



Benzoyl chloride



$$CH_3{-}\underset{\underset{O}{\|}}{C}{-}Cl \longrightarrow CH_3{-}\overset{+}{\underset{\underset{O^-}{|}}{C}}{-}Cl$$

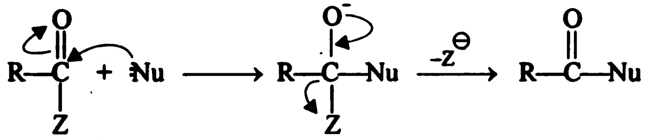
Acetyl chloride

**Q. 122. Carbon tetrachloride is used as a fire extinguisher and marketed as pyrene. Explain.**

**Ans.** Due to lower boiling point (76°C), high density (1.63) and non-inflammability of carbon tetrachloride its vapours envelope the region around fire and cut off air. Fire is ultimately extinguished.

**Q. 123. Amongst acid derivatives, *viz*, acid chloride, acid anhydride ester and amide, acid chloride is the most reactive towards nucleophiles. Explain.**

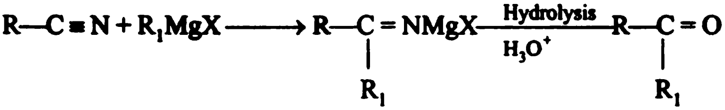
**Ans.** The halide ion, $X^-$, is the weakest base among halide ion, carboxylate ion ($RCOO^-$), alkoxide ion ($R—O^-$) and amide ion $NH_2^-$ as hydrogen halide is the strongest acid of their conjugate acids HX, RCOOH, and $NH_3$. The halide ion is therefore, displaced most readily. As a result, the acid chloride is most reactive.



(Z = X, OCOR, OR, $NH_2$)

**Q. 124. The Grignard reagent does not add to the carbonyl group when a ketone is prepared by addition of the Grignard regent to a nitrile. Explain.**

**Ans.** The nitrile-Grignard addition product forms a ketone only after the hydrolysis step. Any unreacted Grignard reagent is destroyed in the hydrolysis step. Therefore Grignard reagent is not left for reaction with carbonyl group.

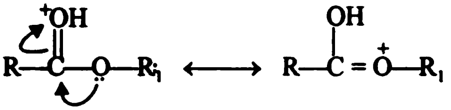


$$R—C\equiv N + R_1MgX \longrightarrow \underset{\displaystyle R_1}{R—\overset{}{C}}=NMgX \xrightarrow[H_3O^+]{\text{Hydrolysis}} \underset{\displaystyle R_1}{R—C}=O$$

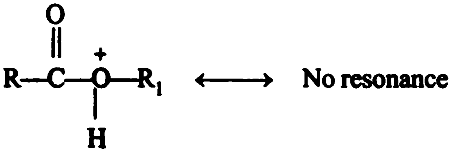
kettone

**Q. 125. The carbonyl-oxygen of an ester is more basic than alkoxy oxygen of an ester. Explain.**

**Ans.** The ester protonated at the carbonyl oxygen is stabilised by resonance. Similar stabilisation in the alcohol-oxygen protonated species does not take place.



Protonated carbonyl-oxygen



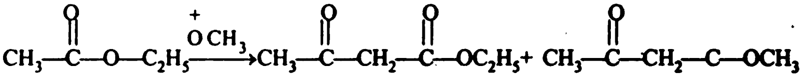
Protonated alcoholic-oxygen

**Q. 126. The Schotten-Baumann method for preparing phenyl esters consists of mixing the acid chloride and alcohol in aqueous sodium hydroxide. Explain why the yields tend to be higher when the ester formed is insoluble in water.**

**Ans.** Ester formed as a result of Schotten Baumann reaction hydrolyses and undergoes saponification in the aqueous base. If the ester is not soluble in the basic solution the saponification reaction is markedly decreased resulting to the high yield of ester.

**Q. 127. Why is the alkoxide base used in the Claisen ester condensation reaction usually the conjugate base of the alcohol portion of the ester, that is, methoxide used with methyl ester, ethoxide with ethyl ester etc. ?**

**Ans.** It is used to avoid any possibility of trans-esterification which would give a mixture of ester products as illustrated below.



$$CH_3-\overset{O}{\overset{\|}{C}}-O-C_2H_5 \xrightarrow{\overset{+}{O}CH_3} CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OC_2H_5 + CH_3-\overset{O}{\overset{\|}{C}}-CH_2-C-OCH_3$$

Ethyl acetate Ethyl acetoacetate Methyl acetoacetate

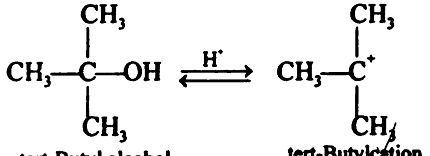
**Q. 128. The Wurtz reaction between two different alkyl halides (for example, methyl iodide and ethyl iodide) is of no synthetic value. Explain.**

**Ans.** A mixture of three different alkanes is obtained. The components differ very little in their boiling point, hence they are difficult to be separated from one another. With methyl iodide and ethyl iodide the product is a mixture of ethane, propane and *n*-butane.

$$CH_3I + 2Na + ICH_3 \longrightarrow CH_3-CH_3 + 2NaI$$
$$CH_3I + 2Na + IC_2H_5 \longrightarrow CH_3-CH_2CH_3 + 2NaI$$
$$CH_3CH_2I + 2Na + IC_2H_5 \longrightarrow CH_3-CH_2CH_2CH_3 + 2NaI$$

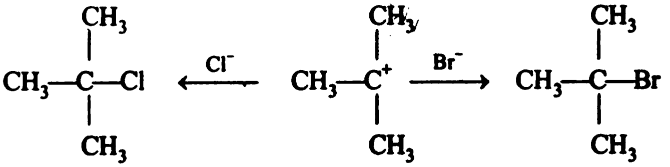
**Q. 129. If *tert*-butyl alcohol is treated with an equimolar mixture of HCl and HBr, *tert*-butyl bromide is the major product, not *tert*-butyl chloride. Explain.**

**Ans.** *tert*-Butyl alcohol first forms *tert*-butyl cation. As bromide ion, Br⁻, is a better nucleophile than chloride ion, Cl⁻, *tert*-butyl bromide is the major product.



$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-OH \underset{}{\overset{H^+}{\rightleftharpoons}} CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C^+}}}}$$

tert-Butyl alcohol tert-Butyl cation



$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-Cl \xleftarrow{Cl^-} CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C^+}}}} \xrightarrow{Br^-} CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-Br$$

*tert*-Butyl chloride.
(minor)

*tert*-Butyl bromide
(major)

**Q. 130. Many nucleophiles are anions, but some anions are not nucleophiles. Explain.**

**Ans.** A nucleophile must have a non-bonding electron pair to provide for bond making. Tetrafluoborate anion, $BF_4^-$ is an anion but not a nucleophile, as it does not have a lone pair of electrons on the boron atom.

**Q. 131. Hydrolysis of an alkyl halide by an aqueous hydroxide is essentially an irreversible process. Explain.**

**Ans.** Basic hydrolysis of an alkyl halide produces an alcohol and the halide ion.

$$\text{R—X} \xrightarrow{\bar{O}H} \underset{\text{Alcohol}}{\text{R—OH}} + \underset{\text{Halide ion}}{X^-}$$

Alcohol reacts with the halide ion only when the acid ($H^+$) is present in the medium. As there is no acid in the basic medium, backward reaction does not occur.

**Q. 132. Explain why silver chloride is soluble in aqueous solution of methylamine.**

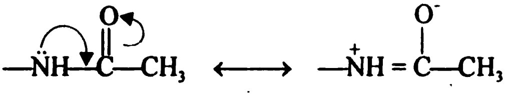
**Ans.** Silver chloride reacts with aqueous solution of methylamine to form water soluble complex salt.

$$AgCl + 2CH_3NH_2 \longrightarrow [Ag(CH_3NH_2)_2]^+Cl^-$$

bis-(Methylamine) silver (I)
Chloride
(Water soluble complex salt)

**Q. 133. —$NH_2$ is a more powerful benzene activating group than —$NHCOCH_3$. Explain.**

**Ans.** An amino group, —$NH_2$, is more basic than amide; the electron pair on nitrogen can be delocalised more into the ring in the amine thereby producing activating effect.

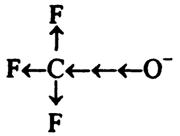


$$\text{—}\ddot{N}H\text{—}\overset{\overset{O}{\|}}{C}\text{—}CH_3 \longleftrightarrow \text{—}\overset{+}{N}H=\overset{\overset{O^-}{|}}{C}\text{—}CH_3$$

Since electron pair on nitrogen is delocalized towards carbonyl group, it is not available for a activating the benzene ring.

**Q. 134. 2, 2, 2— Trifluoroethanol is about 1000 times greater in acid strength than ethanol. Explain.**

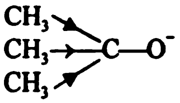
**Ans.** Trifluoroethoxy ion produced as a result of dissociation gets stabilized due to inductive effect of three fluorines thereby making 2, 2, 2 trifluoroethanol a very strong acid.



$$F \leftarrow \underset{\underset{F}{\downarrow}}{\overset{\overset{F}{\uparrow}}{C}} \leftarrow \leftarrow \leftarrow O^-$$

**Q. 135. Of primary, secondary and tertiary alcohols, primary alcohol is the strongest acid. Explain.**

**Ans.** As an acid, alcohol dissociates into an alkoxides ion and hydrogen ion; $R—OH \rightleftharpoons R—O^- + H^+$. The acid strength is determined by the stability of an alkoxide ion. Tertiary alkoxides ion is the least stable and primary alkoxides ion is the most stable.



Methyl groups exert electron repelling effect. Instead of dissipation of negative charge on the tert. alkoxide ion, it is being increased. Hence it is highly unstable and will combine back with $H^+$ to give undissociated alcohol.

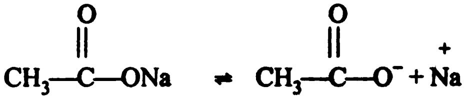
Even in primary alkoxides, the electron-repelling effect of methyl group destabilizes the alkoxide. But this effect is minimum in the case of primary alkoxides. Hence primary alcohols are the strongest acids.

$$CH_3 \rightarrow O^-$$

**Q. 136. Acetic acid is less acidic in sodium acetate solution than in sodium chloride solution. Explain.**

**Ans.** Ionisation of acetic acid is supressed by the addition of acetate ion (from sodium acetate) due to the common ion effect.

$$CH_3COOH \rightleftharpoons \underset{\textbf{Acetate ion}}{CH_3COO^- + H^+}$$



$$CH_3—\overset{\overset{\displaystyle O}{\|}}{C}—ONa \rightleftharpoons CH_3—\overset{\overset{\displaystyle O}{\|}}{C}—O^- + \overset{+}{Na}$$

**Acetate ion**

It behaves as a strong acid in the presence of sodium chloride.

$$CH_3COOH \longrightarrow CH_3COO^- + H^+$$

$$NaCl \longrightarrow Na^+ + Cl^-$$

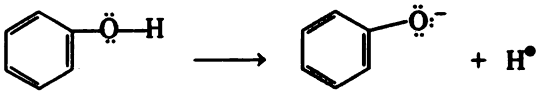
$$H^+ + Cl^- \longrightarrow HCl$$

**(weak electrolyte)**

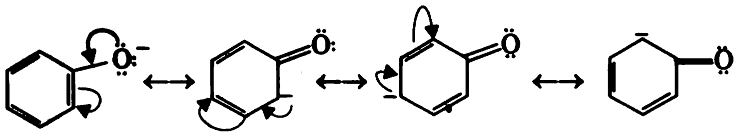
Protons released by acetic acid combine with chloride ions produced by sodium chloride to give weakly ionised HCl. This shifts the equilibrium of dissociation of acetic acid towards the right. Thus acetic acid in sodium chloride solution is more acidic.

**Q. 137. Phenol is acidic while ethanol is neutral. Explain.**

**Ans.** Due to delocalisation of negative charge through interaction with $\pi$-orbitals of benzene, phenoxide ion is resonance stabilised. The proton and the phenoxide ion will exist independently. Thus phenol is acidic.



**Phenoxide ion**



In alcohols there is no such resonance stabilization of the alkoxide ion.

**Q. 138. Explain why phenol fails to react with sodium bicarbonate.**

**Ans.** This is because sodium phenoxide is a stronger base than $NaHCO_3$ and carbonic acid is a stronger acid than phenol. The equilibria lies towards L.H.S., and thus phenol fails to react with $NaHCO_3$.

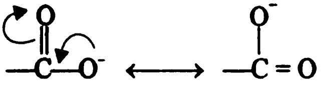
$$C_6H_5OH + NaHCO_3 \leftrightarrow C_6H_5ONa + H_2CO_3$$

| Phenol<br>(Weaker acid)<br>$Ka = 10^{-10}$ | (weaker base) | (Stronger base) | (Stronger acid)<br>$Ka = 10^{-7}$ |
|---|---|---|---|

**Q. 139. A carboxylic acid is a stronger acid than phenol. Explain.**

*(I.I.T.)*

**Ans.** The negative charge in the carboxylate ion resides on the more electronegative oxygen in two resonating structures of equal energy, hence these structures are of greater stability.

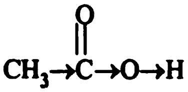


Carboxylic ion

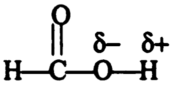
The negative charge in phenoxide ion resides on the less electronegative carbon in resonating structures of unequal energy of phenoxide ion, hence they are of higher energy and less stable.

**Q. 140. Formic acid is stronger than acetic acid. Explain.**

**Ans.** Methyl group is electron-donating group. It hinders in the ionisation of acetic acid into proton and acetate ions. This situation does not exist in formic acid.



$$CH_3 \rightarrow \overset{\overset{\displaystyle O}{\|}}{C} \rightarrow O \rightarrow H$$



$$H—\overset{\overset{\displaystyle O}{\|}}{C}—\overset{\delta-}{O}—\overset{\delta+}{H}$$

**Q. 141. Benzoic acid is slightly stronger than acetic acid. Explain.**

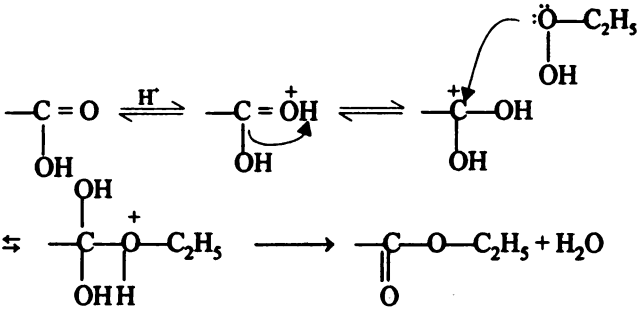
**Ans.** Stronger the eletron-donating group attached to the carboxy group, the weaker is the acid. Phenyl group is less electron-donating than methyl group towards the carboxyl group due to the $sp^2$ hybridised carbon atom to which the carboxyl group is attached.

**Q. 142. Fluoroacetic acid is stronger than chloroacetic acid. Explain.**

**Ans.** Due to greater electron-attracting (–I) effect of fluorine atom than chlorine atom fluoroacetate ion is more stable than chloroacetate ion. The negative charge on fluoroacetate ion can be more easily dissipated.

**Q. 143. Catalytic amount of conc. $H_2SO_4$ is used for the preparation of an ester from carboxylic acid and alcohol. Explain.**

**Ans.** As per the mechanism, proton from conc. $H_2SO_4$ gets attached to the carbonyl oxygen of the carboxyl group, thus increasing the electrophilic character of the carbonyl carbon of the carboxyl group, hence the attack by the nucleophile alcohol is much easier, leading to the formation of the ester.



Moreover, conc. $H_2SO_4$ also absorbs water formed in the reaction, this helps shifting the equilibrium to the right and the greater amount of the ester is produced.

**Q. 144. α-Chloropropionic acid is stronger than β-chloropropionic acid. Explain.**

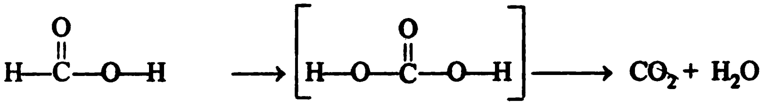
**Ans.** Inductive effect due to an atom or group decays fast along the carbon-chain away from the point of origin. The iductive effect on the α-carbon is greater than that of β-carbon. Hence α-chloropropionic acid is stronger than β-chloropropionic acid.

**Q. 145. Trichloroacetic acid is stronger than acetic acid. Explain.**

**Ans.** Due to highly electronegative (hence electron-attracting) chlorine atoms joined to carboxyl group the trichloroacetate ion is much more stable than acetate ion. This can also be explained by saying that due to electron attracting effect of three chlorines, the proton is easily removed.

**Q. 146. Formic acid shows reducing properties, acetic acid does not. Explain.**

**Ans.** The carbon-hydrogen bond in the formic acid is easier to be oxidised to carbon-hydroxy bond, C—OH, and unstable carbonic acid is formed, which at once decomposes to $CO_2$ and $H_2O$.



$$\underset{\text{Formic acid}}{H-\overset{\overset{O}{\|}}{C}-O-H} \longrightarrow \underset{\text{(Carbonic acid)}}{\left[H-O-\overset{\overset{O}{\|}}{C}-O-H\right]} \longrightarrow CO_2 + H_2O$$

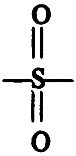
As formic acid is easily oxidised, it acts as a reducing agent. There is no such characteristic in acetic acid.

**Q. 147. Formic acid reacts with $KMnO_4$, acetic acid does not. Explain.**

**Ans.** The violet colour of acidified $KMnO_4$ solution disappears when boiled with formic acid due to its reducing properties. Formic acid is easily oxidised to $CO_2$ and $H_2O$ due to rapid conversion of C—H bond to C—OH.

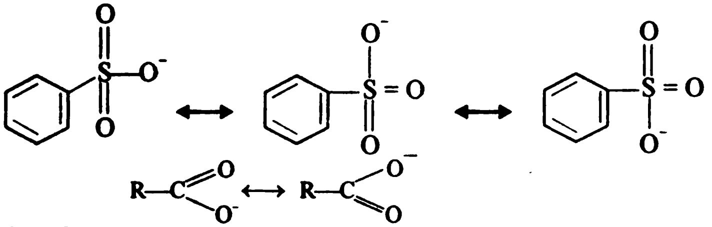
**Q. 148. Benzenesulphonic acid is much stronger than carboxylic acid. Explain.**

**Ans.** Because of the strong electron-withdrawing (−*I*) effect of the sulphone group,



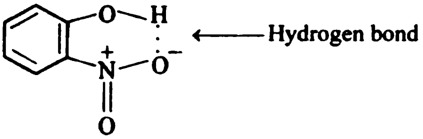
$-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-$

and the greater delocalisation of charge in the sulphonate ion, benzensulphonic acid is stronger than carboxylic acid. There are three resonating structures of sulphonate ion compared to two for carboxylate ion.



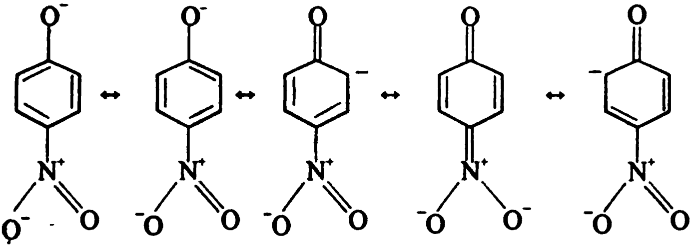
**Q. 149. *o*-Nitrophenol is steam-volatile but not *m*-and *p*-nitrophenols, Explain.**

**Ans.** The intramolecular hydrogen bond in *o*-nitrophenol decreases the size of the molecule. As a result it boils at lower temperature. It is thus steam volatile. No such intramolecular hydrogen bonding takes places in *m*-and *p*-isomers because the groups are at a distance.



**Q. 150. *p*-Nitrophenol is stronger acid than phenol itself. Explain.**

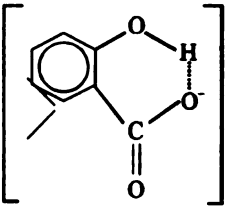
**Ans.** Nitro group is an electron-withdrawing group. *p*-Nitrophenoxide ion produced by the dissociation of *p*-nitrophenol is more resonance stabilised than the phenoxide ion, hence *p*-nitrophenol is a stronger acid than phenol.



Resonance structures of p-nitrophenoxide ion

**Q. 151. *o*-Hydroxybenzoic acid (salicylic acid) is stronger than *p*-hydroxybenzoic acid. Explain.**

**Ans.** The anion from salicyclic acid is stabilised by intramolecular hydrogen bonding which does not happen in *p*-isomer.



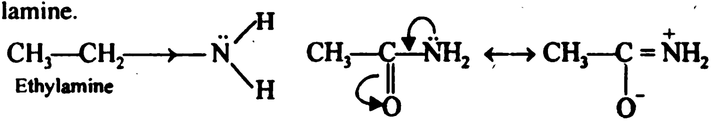
Salicylate ion

**Q. 152. Phenol does not react with $Na_2CO_3$, but 2, 4. dinitrophenol does react with evolution of $CO_2$. Explain.**

**Ans.** 2, 4-Dinitrophenol is a stronger acid than carbonic acid beause the negative charge on the oxygen of 2, 4-dinitrophenoxide ion is still further delocalised due to two strong electron-withdrawing nitro-groups. This gives rise to a number of resonance structures making 2, 4-dinitrophenol a much stronger acid.

**Q. 153. Ethylamine is more basic than acetamide.**

**Ans.** In ethylamine, +I effect of ethyl group increases the electron density on nitrogen. As a result the tendancy to accept proton increases. In acetamide the acetyl group pulls the electrons from nitrogen towards itself so that the electron density on nitrogen is markedly reduced and it is less basic than ethylamine.



**Q. 154. Oxalic acid is stronger than acetic or formic acid. Explain.**

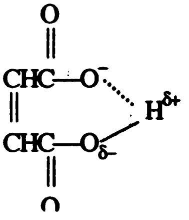
**Ans.** The electron-withdrawing carboxyl group in oxalic acid facilitates the removal of proton from the second carboxyl group. That is why oxalic acid is stronger than acetic or formic acid.

**Q. 155. *o*-Nitrobenzoic acid is stronger than *p*-nitrobenzoic acid. Explain.**

**Ans.** The inductive effect and resonance effect fall off quite rapidly as the distance from the point of origin of the effect increases. *o*-Nitro group is quite closer to the carboxyl group campared to the situation when it is in para position. Nitro is an electron withdrawing group. It pulls the electrons towards itself, thus increasing the acid strength of *o*-nitrobenzoic acid.

**Q. 156. Maleic acid is stronger than fumaric acid. Explain.**

**Ans.** This is due to the fact that the anion obtained from first ionisation of maleic acid is stabilised by intramolecular hydrogen bonding which does not happen in fumaric acid, a trans isomer of maleic acid.

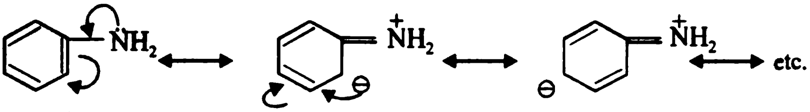


**Q. 157. Ammonia is a stronger base than water, though oxygen in water molecule contains two lone pair of electrons. Explain.**

**Ans.** Basic strength depends on the availability of electron, and also on the electron-donating ability of the atom containing lone pair of electrons. Nitrogen atom is less electronegative and hence more electron-donating than oxygen atom. As a result, ammonia is a stronger base than water.

**Q. 158. Aniline is a weaker base than ammonia. Explain.**

**Ans.** This is due to electron-attracting phenyl group and resonance effect of the $\pi$-orbitals of the benzene ring with the lone pair of electrons on the nitrogen atom compared with that of ammonia.



This reduces the availability of electron pair on amino group making it a poorer base.

**Q. 159. Cyclohexylamine is a stronger base than aniline. Why ?**

**Ans.** Like aliphatic amine, cyclohexylamine is a stronger base as a lone pair of electrons is completely available on N for sharing with a proton.

$$\underset{\text{Cychlohexylamine}}{C_6H_{11}\ddot{N}H_2 + \overset{+}{H}} \longrightarrow \underset{\text{Protonated cyclohexylamine}}{C_6H_{11}\overset{+}{N}H_3}$$

However, aniline exhibits resonance effect. As a result, the electron density on N is appreciably reduced for sharing with a proton. Moreover, the presence of partial positive charge on N hinders the proton attack.

**Q. 160. Dimethylamine is a stronger base than methylamine. Explain.**

**Ans.** Basic strength of an amine depends on the availability of electron pair on nitrogen. The greater the electron density, the greater is the basic strength. Due to two electron-donating methyl groups in dimethylamine there is greater electron density on nitrogen than on methylamine.

**Q. 161. Methylamine is a stronger base than ammonia. Explain.**

**Ans.** Methyl group, an electron-releasing group increases the electron density on the nitrogen atom. As a result, methylamine is a stronger base than ammonia.

**Q. 162. Ethylamine is more basic than ethanol. Explain.**

**Ans.** Nitrogn atom is less electronegative than oxygen atom, hence nitrogen has greater tendency to donates its lone pair than the oxygen atom in ethanol. Hence ethylamine is more basic than ethanol.

**Q. 163. Trimethylamine is less basic than dimethylamine in water. Explain.**

**Ans.** Though there is maximum electron density on nitrogen due to three electron-donating methyl groups in trimethylamine, it is slightly difficult for the proton to approach the electron due to crowding by three methyl groups, and also there is difficulty in solvation of the protonated trimethylamine. Hence trimethylamine is less basic than dimethylamine much against expectation.

**Q. 164. Explain why aniline is soluble in aqueous HCl.**

**Ans.** Aniline is soluble in aqueous HCl because of the formation of water soluble salt anilinium chloride.

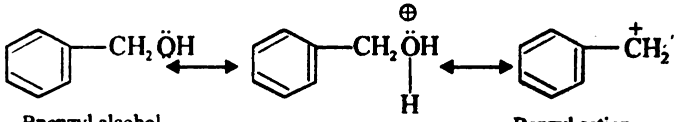
$$\underset{\text{Aniline}}{C_6H_5NH_2 + HCl} \longrightarrow \underset{\substack{\text{Anilinium chloride}\\\text{(water soluble salt)}}}{C_6H_5\overset{+}{N}H_3\overset{-}{Cl}}$$

**Q. 164. Nitrobenzene does not undergo Friedel-Crafts reaction. Explain.**

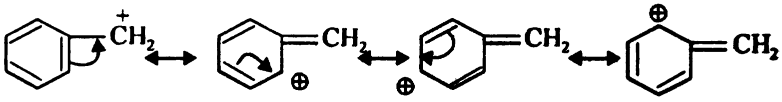
**Ans.** Nitro group —$NO_2$, being a strong deactivating group decreases electron density in benzene ring to a greater extent, thus it renders the benzene ring incapable of accepting an electrophile.

**Q. 166. Benzyl alcohol forms benzyl chloride with conc. HCl in cold in contrast with aliphatic alcohol. Explain.**

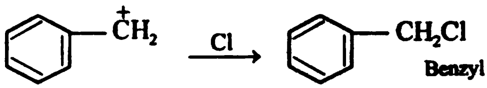
**Ans.** A proton from HCl combines with OH group of benzyl alcohol to generated resonance stabilised benzyl cation. There is no similar situation with aliphatic alcohols.



**Bnenzyl alcohol** **Benzyl cation**



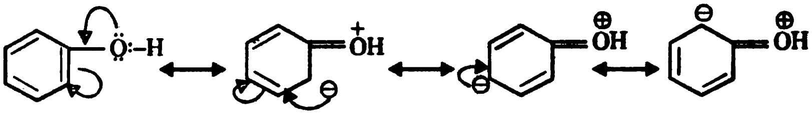
**Resonance of stabilization Benzyl cation**



**Benzyl chloride**

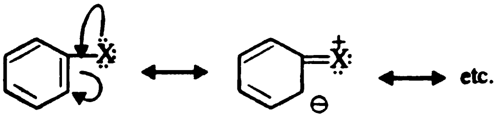
**Q. 167. The hydroxy group,—OH is ortho and para directing group. Explain.**

**Ans.** There is greater electron density on the ortho and para positions than the meta position due to resonance.



**Q. 168. Aryl halides are not used as the reagent in Friedal-Crafts reaction. Explain.**

**Ans.** Carbon-halogen bond in the aryl halide is slightly strong due to its double bond character arising out of resonance, and also due to shorter bond length formed by the overlap between $sp^2$ carbon of the aromatic ring and *p*-orbital of the halogen, Hence it is not easy to form a carbonium ion as required in Friedal-Crafts reaction mechanism.



**Q. 169. Explain why glycine exists as a zwitter ion but anthranilic acid does not.**

**Ans.** The —COOH group of glycine releases $H^+$ ion which is accepted by —$NH_2$ group. Thus glycine exists as a zwitter ion.

$$H_3\overset{+}{N}—CH_2—CO\overset{-}{O}$$

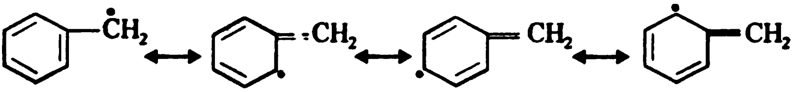
Zwitter ion of glycine

However, the electron withdrawing nature of —COOH group reduces electron density on N in anthranilic acid. This nitrogen atom of amino group fails to accept the proton released by the —COOH group. That is why anthranilic acids does not exist as Zwitter ion.

**Anthranilic acid**
**(*o*-Aminobenzoic acid)**

**Q. 170. Benzyl radical, $C_6H_5\dot{C}H_2$ is more stable and less reactive than simple alkyl radicals. Explain.**

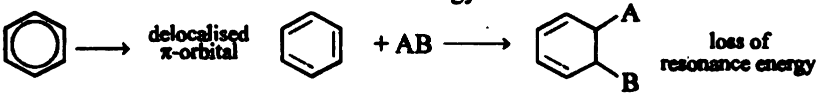
**Ans.** There is delocalisation of the unpaired electron over the π-orbital system in benzylic radical, hence the result. Higher the stability, less is the reactivity of a species.



**Benzylic radical**

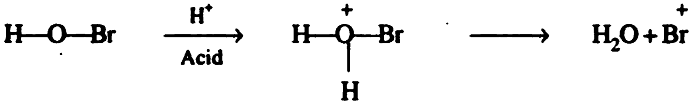
**Q. 171. Aromatic compounds undergo reaction through substitution rather than addition. Explain.**

**Ans.** The addition reaction destroys the cyclic π-elctronic system of benzene (or in general, aromatic compounds), thereby the benzene ring is destabilised due to loss of resonance energy.



**Q. 172. Explain why benzene does not react with HOBr (the hypobromous acid) but in the presence of mineral acid the same reaction yields bromobenzene.**

**Ans.** HOBr gets protonated in the presence of a strong acid to yield bromonium ion, $\overset{+}{Br}$, which is an electrophile.

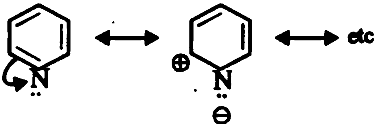


$$H—O—Br \xrightarrow[\text{Acid}]{H^+} H—\overset{+}{\underset{\displaystyle H}{\underset{|}{O}}}—Br \longrightarrow H_2O + \overset{+}{Br}$$

Benzene reacts with electrophiles to yield electrophilic substitution products. In this case bromobenzene, is formed.

**Q. 173. Pyridine is less reactive than benzene towards electrophiles. Explain.**

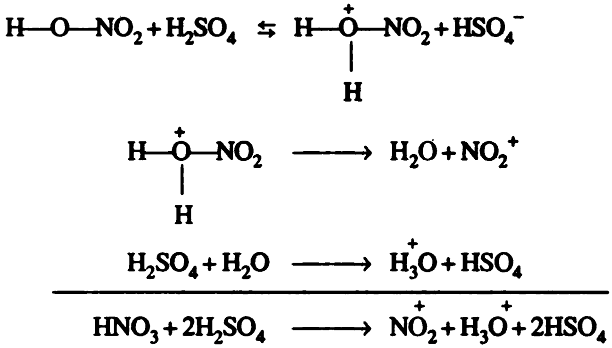
**Ans.** Availability of electron on benzene ring decreases due to resonance as shown below.



It creates positive charge on the ring which repels the electophiles. Also, pyridine is a base because of a lone pair of electrons on the nitrogen. Hence nitrogen is protonated in the presence of mineral acids. As a result, pyridine is resistant to electophilic substitution.

**Q. 174. A mixture of conc. $HNO_3$ and conc. $H_2SO_4$ is used for nitration rather than conc. $HNO_3$ alone. Explain.**

**Ans.** Nitration of an aromatic compound proceeds through the electrophiles, $NO_2^+$, nitronium ion. The electrophile is produced in greater concentration in the acid mixture as conc. $H_2SO_4$ functions as an acid and $HNO_3$ as a base.



$$H{-}O{-}NO_2 + H_2SO_4 \rightleftharpoons H{-}\underset{\displaystyle H}{\underset{|}{\overset{+}{O}}}{-}NO_2 + HSO_4^-$$

$$H{-}\underset{\displaystyle H}{\underset{|}{\overset{+}{O}}}{-}NO_2 \longrightarrow H_2O + NO_2^+$$

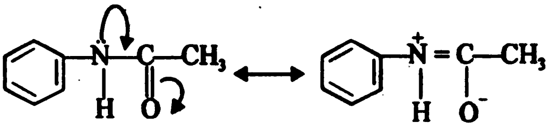
$$H_2SO_4 + H_2O \longrightarrow H_3\overset{+}{O} + HSO_4$$

$$HNO_3 + 2H_2SO_4 \longrightarrow \overset{+}{NO_2} + H_3\overset{+}{O} + 2HSO_4$$

[Conc. $HNO_3$ alone possesses too low concentration of nitronium ion to produce the nitration product in good yield.]

**Q. 175. On bromination aniline gives 2, 4, 6-tribromoaniline but acetanilide forms *p*-bromoacetanilide. Explain.**

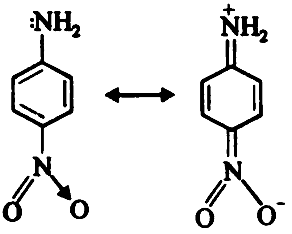
**Ans.** The group $-\underset{\displaystyle H}{\underset{|}{\ddot{N}}}-\underset{\displaystyle O}{\underset{\|}{C}}-CH_3$ is much less activating than $-\ddot{N}H_2$ group because electron availability on nitrogen in acetanilide is reduced by delocalisation over the adjacent electron-withdrawing carbonyl group.



But this situation does not exist in aniline. Moreover 2 and 6 positions in the ring in acetanilide are sterically hindered. Substitution does not take place in these positions.

**Q. 175. *p*-Nitroaniline is a weaker base than aniline. Explain.**

**Ans.** Electron-availability on the nitrogen atom in *p*-nitroaniline is decreased by the presence of nitro group due to resonance as shown below.



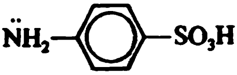
For this reason, *p*-nitroaniline is a weaker base than aniline.

**Q. 176. Benzene homologue are more readily nitrated than benzene. Explain.**

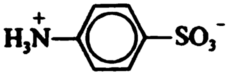
**Ans.** An alkyl group in the alkylbenzene is electron-donating and the electron density ring in alkylbenzenes is increased compared with benzene alone, hence alkylbenzenes are more reactive towards electrophiles like nitronium ion, $\overset{+}{N}O_2$.

**Q. 178. The sodium salt of sulphanilic acid can readily be acetylated with acetic anhydride, but not the free acid. Explain.**

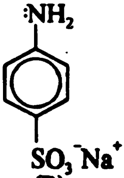
**Ans.** Sulphanilic acid exists as the dipolar ion (A)



**Sulphanilic acid**



**(A)**

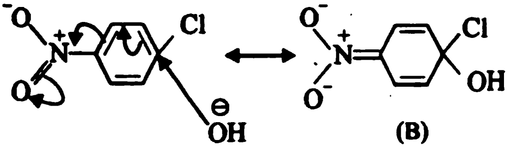


**(B)**

There is no availability of a lone pair of electrons on the nitrogen atom, hence it is not possible to acetylate (A). In the sodium salt of the sulphanilic acid (B) the lone pair is available and is readily acetylated.

**Q. 179. Chlorobenzene undergoes hydrolysis to phenol with great difficulty, but *p*-nitrochlorobenzene is hydrolysed conveniently. Explain.**

**Ans.** When the hydroxide ion, $OH^-$ attacks the *p*-nitrochlorobenzene, the nitro group can accommodate the negative charge as in the structure (B).



This stabilisation of the transition state lowers the activation energy which facilitates reaction.

**Q. 180. A higher fatty acid is insoluble in water, but is soluble in aqueous sodium carbonate solution. Explain.**

**Ans.** The organic acid is soluble in aqueous sodium carbonate because a reaction takes place and the acid forms a water-soluble sodium salt.

$$2RCOOH + Na_2CO_3 \longrightarrow RCOONa + CO_2 + H_2O$$

**Q. 181. Cyclohexanone readily forms a sodium bisulphite addition compound, whereas diethyl ketone does not. Explain.**

**Ans.** Steric hindrance by the ethyl groups of diethyl ketone prevents the bisulphite ion from approaching the carbonyl carbon atom, whereas in cyclohexanone the carbon chains are held back. Also, the $sp^2$ hybrid carbon of cyclohexanone produces some ring strain, which is relieved by the addition of the bisulphite to form a tetrahedral $sp^3$ carbon atom.

**Q. 182. Acetyl chloride is more reactive than ethyl chloride towards nucleophilic reagents. Explain.**

**Ans.** The polar character of the carbonyl bond $CH_3{-}\overset{+}{C}{-}O^-$ facilitates reaction with a nucleophilic reagent. Hence the result.

**Q. 183. Aldoses reduce Tollens' and Fehling's reagents, but do not restore the colour of Schiff's reagent. Explain.**

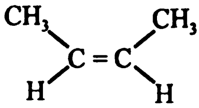
**Ans.** The open-chain structure of an aldose is in equilbrium with its ring structure. As a result, the aldehyde content is so small that Schiff's reagent cannot react. The small quantity of the aldehydic form of an aldose however reacts with Tollens and Fehling's reagents to given positive tests.

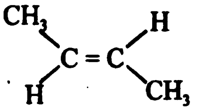
**Q. 184. Nitromethane, an organic compound, does not have a high solubility in hydrocarbons, *e.g.*, *n*-hexane as a solvent. Explain.**

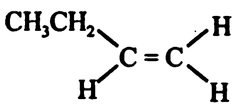
**Ans.** Nitromethane is a very polar molecule, and therefore, is insoluble in non-polar liquids such as *n*-hexane.

**Q. 185. 2-butene shows *cis*-trans isomerism whereas 1-butene does not. Explain.**

**Ans.** Alkenes in which doubly bonded carbons are attached to different atoms or groups exhibit geometrical isomerism. 2-Butene has such characteristics , *i.e.*, each doubly bonded carbon is linked to methyl and hydrogen, hence shows *cis*-trans isomerism. In 1-Butene, one of the doubly bonded carbon atoms contains two similar groups (—H groups). Hence geometrical isomerism is not possible.


*cis* 2-Butene


*trans* 2-Butene

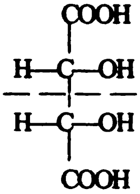

1-Butene

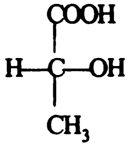
**Q. 186. Physical propeties of geometrical isomers differ while those of enanticmers are the same. Explain.**

**Ans.** Physical properties in general depend on intra and intermolecular forces. The intermolecular forces are certainly not the same in geometrical isomes. Geometrical isomers pack differently in the solid state; hence geometrical isomers have different physical properties, like density m.p, b.p, etc. On the other hand, optical isomers have identical interatomic distance within the molecules. They have identical intermolecular as well as intramolecular forces. Hence, they have identical physical properties.

**Q. 187. There is no optical isomer such as meso form of lactic acid, but one optical isomer of tartaric acid is meso-tartaric acid. Explain.**

**Ans.** Meso optical isomerism occurs in those compounds which possess an element of symmetry. Meso-Tartaric acid has a plane of symmetry, so it has a meso form. Lactic acid has no plane of symmetry, hence no meso form.

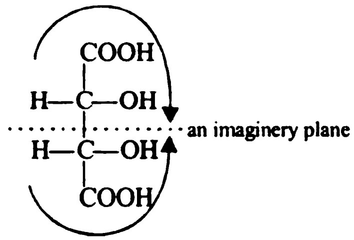




meso-Tartaric acid opticallly active lactic acid

**Q. 188. Meso-Tartaric acid has two asymmetric carbon-atoms, yet it is optically inactive. Explain.**

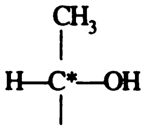
**Ans.** A compound possessing an element of symmetry is optically inactive. Meso-Tartaric acid does have a plane of symmetry— an imaginary plane which bisects the molecule into two equal halves. Optical activity of the two parts are working in opposite direction and they cancel each other with the result that net optical activity is zero.



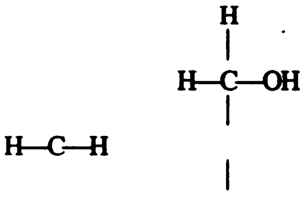
Meso-Tartaric acid

**Q. 189. 2-Butanol (or 2-chlorobutane) is optically active but 1-butnol is not. Explain.**

**Ans.** There is an asymmetric carbon atom (marked with *) in 2-butanol — one of the requirements for compounds to exhibit optical activity. 1-Butanol does not have such asymmetric carbon. Thus it does not show optical activity.



2-Butanol



1-Butanol (no asymmetric carbon)

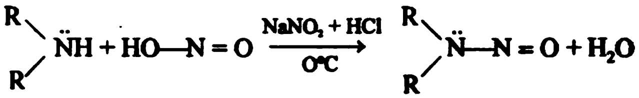
**Q. 190. $SO_3$ is an electrophile. Explain.**

**Ans.** There are two positive charges on central sulphur in $SO_3$. Two negative charges one each on two oxygens are scattered.

Since the positive charge is concentrated on sulphur, $SO_3$ behaves as an electrophile.

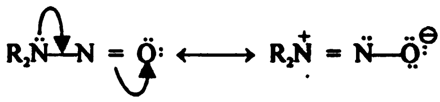
**Q. 191. The N-nitrosamines are least basic. Explain.**

**Ans.** The N-nitrosamines are the products obtained when a secondary amine reacts with nitrous acid.



N-nitrosamines

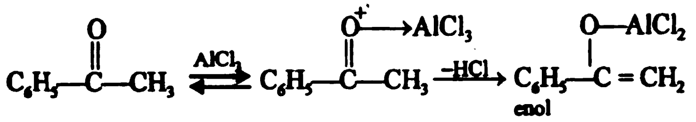
Electron pair in nitrosamine is delocalised as shown below.



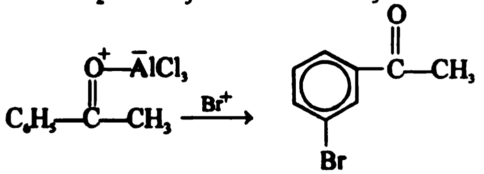
This reduces the basicity of the compound.

**Q. 192. An ether solution of acetophenone reacts with bromine in the presence of a trace of $AlCl_3$ to give $C_6H_5-\underset{\underset{O}{\|}}{C}-CH_2Br$ in good yield. If 2.5 molar equivalents of $AlCl_3$ are mixed, this mixture slowly reacts to give m-bromoacetophenone. Explain.**

**Ans.** A trace of $AlCl_3$ in the acetophenone bromine reaction serves as a catalyst for enolization. If a large excess of this Lewis acid is used, it complexes with the ketone transforming into a meta-directing cationic substituent.



$Br_2 + AlCl_3 \rightleftharpoons Br^-AlCl_3Br^+$

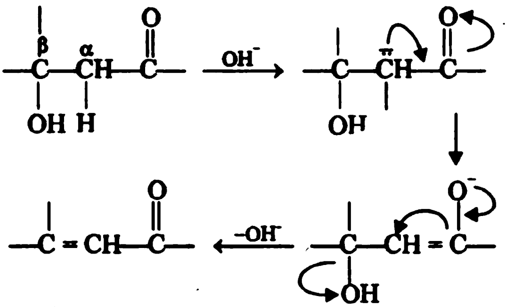


**Q. 193. Nitration reactions of aromatic systems usually give only one mononitro substitution product even when an excess of nitrating reagent is used. Explain.**

**Ans.** A nitro group deactivates the aromatic ring with respect to electrophilic substitution reactions. When one nitro group has been introduced, further nitration is difficult because of deactivating nitro group.

**Q. 194. Simple alcohols do not undergo dehydration by treatment with base, whereas β-hydroxycarbonyl compounds lose water by base catalyst, Explain.**

**Ans.** The presence of the carbonyl group enhances the acidity of the α-hydrogen atom that must be removed in dehydration. In some cases, an enolate anion will be an intermediate in these elimination reactions.



**Q. 195. Which will add bromine more readily, 1-butene or 2-butene. Give reasons for your answer.**

**Ans.** Addition of bromine to an alkene is electrophilic. Greater the electron density between doubly bonded carbons, greater is the rate of reation with an electrophile. Two methyl groups in 2-butene increase electron density more than one alkyl group viz., ethyl in 1-butene.

Therefore, 2-butene will react with bromine more readily than 1-butene.

**Q. 196. Isopropyl cation is more stable than *n*-propyl cation. Explain.**

**Ans.** The stability of an alkyl cation depends on the dispersal of the positive charge. The alkyl group exerts + I effect. The increase in the number of alkyl groups attached to the positively charged carbon helps in dispersing the positive charge due to + I effect and thus increasing the stability of a particular alkyl cation. Positvely charged carbon in the isopropyl cation, $CH_3—\overset{+}{C}H—CH_3$, is attached to two methyl groups and that in $CH_3—CH_2\,CH_2^+$ to only one alkyl group viz., ethyl. This explains greater stability of isopropyl cation.

**Q. 197. Picric acid is a much stronger acid. Explain.**

**Ans.** Picric acid is 2, 4, 6-trinitrophenol. In this structure nitro groups are attached in ortho and para positions to the hydroxyl group. Nitro group is a strong electron-attracting group (negative inductive effect). Also, these nitro groups delocalise the negative charge on oxygen in 2, 4, 6-trinitrophenoxide ion through resonance thus making it more stable. In fact, the picric acid is as strong as hydrochloric acid.

**Q. 198. Hydrocarbons are not soluble in water. Explain.**

**Ans.** Water-solubility of a compound depends on (*i*) its polar nature, (*ii*) forming hydrogen bond with water and (*iii*) solvation energy. Hydrocarbons are nonpolar and are unable to form hydrogen bond with water, hence they are insoluble in water.

**Q. 199. Although propene adds chlorine at room temperature, at high temperature substitution of chlorine for hydrogen takes place. Explain.**

**Ans.**

$$CH_3CH=CH_2 \xrightarrow{Cl_2} \underset{\text{1, 2-Dichloropropane}}{CH_3—CHCl—CH_2Cl}$$

$$CH_2=CH—CH_3 \xrightarrow[600°C]{Cl_2} CH_2=CH—CH_2Cl$$

High temperature produces chlorine radicals. Chlorine radical does add to propene to give a stable radical. At this temperature this step is reversible and condition favours the formation of an allyl radical with the removal of allylic hydrogen to form HCl. Hence allyl chloride is formed. Note that allyl radical is resonance stabilised.

$$CH_3—CH=CH_2+Cl_2 \overset{600°}{\rightleftharpoons} CH_2=CH—CH_2Cl+HCl$$

$$CH_3—CH=CH_2+\dot{C}l \longrightarrow \underset{\text{Allyl radical}}{\dot{C}H_2—CH=CH_2}+HCl$$

**Q. 200. Account for the fact that acetic acid is stronger acid in water than in methanol.**

**Ans.** Water can take up protons from acetic acid with greater efficiency than methanol can take up protons from acetic acid to form protonated methanol.

$$CH_3—COOH+H_2O \rightleftharpoons CH_3COO^-+H_3O^+$$

$$CH_3—COOH+CH_3OH \rightleftharpoons CH_3COO^-+CH_3OH_2^+$$

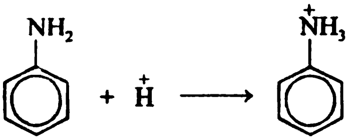
This is because water solvates ions better than does methanol;

**Q. 201. 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 electrophilic substitution. Explain.** [*I.I.T., 1992*]

**Ans.** The intermediate complex formed when an electrophile attacks a benzene molecules has only three resonance structures, but the intermediate formed from diphenyl has six resonance structures, three derived from each phenyl group in diphenyl. Greater the number of resonance structures, more stable is the species. Diphenyl produces more stable intermediate and is thus more reactive.

**Q. 202. Explain why aniline undergoes bromination at ortho-para position while in concentrated acid it yields *m*-bromoaniline.**

**Ans.** In aniline —$NH_2$ is electron-donating, therefore, it gives ortho-para substitution products. Concentrated acid converts —$NH_2$ group to anilinium ion, $NH_3^+$ (attracts electron) which is meta directing and hence *m*-bromoaniline, is obtained.



**Q. 203. Chloroacetic acid is a stronger acid than bromoacetic acid while *o*-chlorobenzoic acid is a weaker acid than *o*-bromobenzoic acid. Why ?**

**Ans.** In substituted acetic acids it is inductive effect that operates. Since chlorine is more electronegative than bromine, chloroacetic acid is a stronger acid than bromoacetic acid. Coming to substituted benzoic acids, H-bonding between Cl and H of the carboxylic group is strong compared to that between Br and H of the COOH group. Thus the loss of a proton is comparatively difficult in *o*-chlorobenzoic acid, hence it is a weaker acid than *o*-bromobenzoic acid.

**Q. 204. Give reasons for the following in one or two sentences.**

**(*a*) Acid catalysed dehydration of *t*-butanol is faster than that of *n*-butanol.**

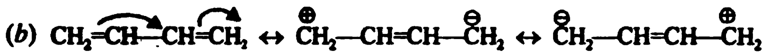
**(*b*) The central carbon-carbon bond in 1,3-butadiene is shorter than that of *n*-butane.**

**(*c*) Dimethylamine is a stronger base than trimethylamine.**

**(*d*) Nitrobenzene does not undergo Friedal-Crafts alkylation.**

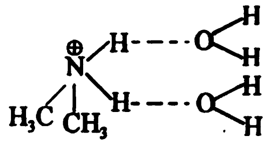
*(I.I.T 1998)*

**Ans.** (*a*) Due to the formation of 3° carbocation. Reaction proceeds through $S_N{}^1$ mechanism, Stability order of carbocation is $3° > 2° > 1°$.

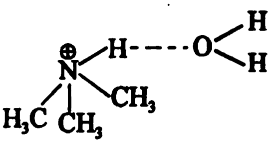
(*b*) 
$CH_2{=}CH{-}CH{=}CH_2 \leftrightarrow \overset{\oplus}{C}H_2{-}CH{=}CH{-}\overset{\ominus}{C}H_2 \leftrightarrow \overset{\ominus}{C}H_2{-}CH{=}CH{-}\overset{\oplus}{C}H_2$

[Due to resonance in conjugated diene, central C—C bond in 1, 3-butadiene is shorter than that in *n*-butane.

(*c*) Dimethylamine is a stronger base than trimethylamine due to (*i*) Less steric hindrance of $H^+$ ion to nitrogen site in dimethyl amine. (*ii*) More stabilization of resulting positively charged species due to greater extent of hydrogen bonding with $H_2O$.



(2H-bonds in dimethyl amine)



(1H-bonds in trimethyl amine)

(*d*) Nitro group is deactivating towards electrophilic substitution.

**Q. 205. (*a*) Acetophenone on reaction with hydroxylamine-hydrochloride can products two isomeric oximes. Write structures of the oximes.**

**(*b*) Which of the following is the correct method for synthesising methyl-*t*-butyl ether and why ?**

**(*i*) $(CH_3)_3CBr + NaOMe \longrightarrow$**

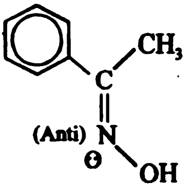
**(*ii*) $CH_3Br + NaO—t—Bu \longrightarrow$**

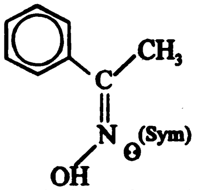
**(c) Although phenoxide ion has more number of resonating structures than benzoate ion, benzoic acid is stronger acid than phenol. Why ?**

(*IIT 1997*)

**Ans.**

(*a*)



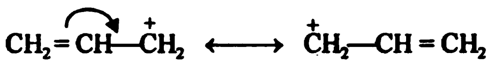


(*b*) The preparation of an ether from an alkyl halide and an alkoxide ion proceeds through nucleophilic substitution. In (*i*) the alkyl halide is 3°. The mechanism possible is $S_N{}^1$. But since it is 3°, elimination would compete with substitution. Therefore, It is 1° alkyl halide which is preferrable and the mechanism is $S_N{}^2$.

(*c*) In phenoxide ion, all the resonating structures (except one) have the –ve charge on the less electronegative carbon atom. In benzoate ion, there are two resonance structures and in both of them the –ve charge is on the more electronegative O atom. Resonance, structures in which the negative charge is on the more electronegative atom are more stabilising than the ones in which it is on the lesser electronegative atom.

**Q. 206. Allyl cation is more stable than *n*-propyl cation. Explain.**

**Ans.** Allyl cation $CH_2{=}CH—\overset{+}{C}H_2$, stabilizes itself through two resonance structures of identical energy.

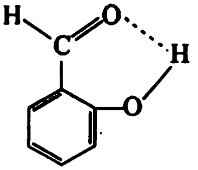


$$CH_2{=}CH—\overset{+}{C}H_2 \longleftrightarrow \overset{+}{C}H_2—CH{=}CH_2$$

The propyl cation, $CH_3CH_2CH_2$, does not show resonance. The stability is explained on the basis of +I effect of alkyl group and hyperconjugation structure, Note that the inductive effect and hyperconjugation is much less dominating than reasonance. For this reason, allyl cation is more stable than *n*-propyl cation.

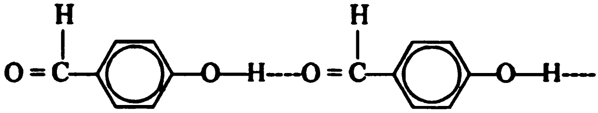
**Q. 207. Explain why *o*-hydroxybenzaldehyde is a liquid at room temperature. Why *p*-hydroxybenzaldehyde is a high melting solid.** (*I.I.T. 1999*)

**Ans.** Intramolecular hydrogen bonding takes place in *o*-hydroxybenzaldehyde, leading to decrease in size of the molecule. Hence it melts at a low temperature.



*o*-hydroxybenzaldehyde

Intermolecular hydrogen bonding takes place in *p*-hydroxybenzaldehyde, leading to association of molecules and consequent rise in melting point.



*p*-hydroxybenzaldehyde

**Q. 208. Account for the following :**

**(i) Ammonolysis of an alkyl halide does not yield a pure amine.**

**(ii) Substitution of a —$NO_2$ or a —COOH group on the benzene ring makes electrophilic substitution reactions difficult.**

**(iii) Haloalkanes undergo nucleophilic substitution reactions.**

**(iv) Alcohols act as weak bases.**

**(v) Phenols exhibit an acidic character**

**(vi) Phenol has a smaller dipole moment than methanol**

**(vii) Phenols do not give protonation reactions readily**

**(viii) Haloarenes undergo electrophilic substitution reactions**

**(ix) The boiling points of ethers are lower than those of isomeric alcohols**

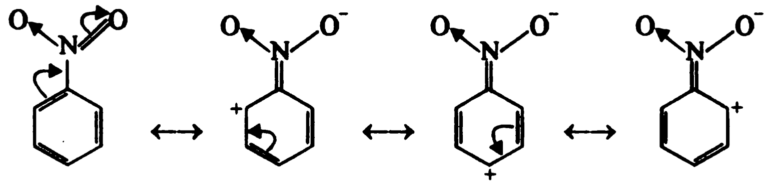
**(x) Acetic acid is a weaker acid than chloroacetic acid**

**(xi) During the preparation of ammonia derivatives from aldehydes and ketones, pH of the reaction is fully controlled.** (*A.I.S.B. 2000*)

**Ans.** (*i*) This is because the amine obtained reacts further with more of alkyl halide to form secondary and tertiary amines and quarternary salts.

$$R{-}X + NH_3 \longrightarrow RNH_2 + HX$$
$$R{-}NH_2 + RX \longrightarrow RNHR + HX$$
$$RNHR + RX \longrightarrow R_3N + HX$$
$$R_3N + RX \longrightarrow R_4N^+X^-$$

(*ii*) —$NO_2$ and —COOH groups are electron withdrawing. They reduce the electron density on the ring, making electrophilic substitution difficult.



Thus we find that there is a positive charge on the benzene ring. Similarly carboxylic acid will also reduce electron density on the ring.

(*iii*) Haloalkanes undergo nucleophilic substitution reaction either by $SN^2$ and $SN^1$ mechanism as explained below.

**$SN^2$ Mechanism**

$$R—X + Z^- \longrightarrow [Z.....R......X]^- \quad \text{(slow step)}$$

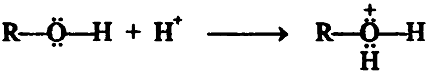
$$[Z......R.....X]^- \longrightarrow RZ + X^- \quad \text{(fast step)}$$

**$SN^1$ Mechanism**

$$R_3CX \longrightarrow R_3C^+ + X^- \quad \text{(slow step)}$$

$$R_3C^+ + Z^- \longrightarrow R_3CZ$$

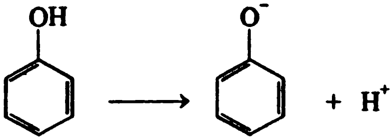
(*iv*) Alcohols act as weak bases because they have two lone pairs of electrons which they can donate to a proton



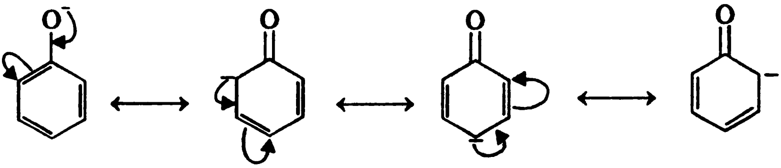
$$R—\ddot{\underset{..}{O}}—H + H^+ \longrightarrow R—\overset{+}{\underset{H}{\ddot{O}}}—H$$

However, due to electronegative nature of oxygen, the electron pair is not readily available. Therefore alcohols are weak bases.

(*v*) Phenols exhibit acidic character because they can liberate protons. Phenoxide ion left after liberating proton can stabilize itself by resonance and the possibility of the combination of proton and phenoxide to give undissociated phenol molecule is minimised.

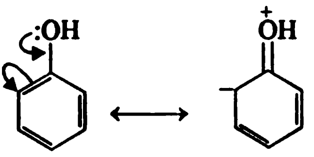


Phenoxide ion



(*vi*) Dipole moment depends upon the length between the two poles. Greater the length, greater the dipole moment. The distance between the two poles is smaller in phenol, because of shorter carbon-oxygen double bond (in phenoxide ion).

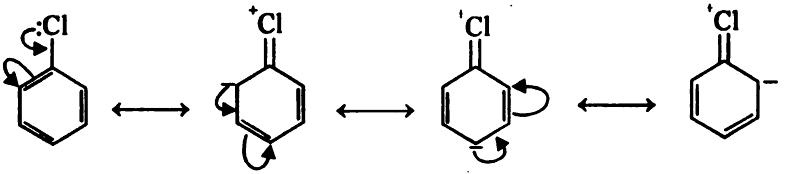
(*vii*) The electrons on oxygen in phenol are involved in resonance with the benzene ring and hence they are not available for protonation



and so on

(*viii*) The bond between the halogen and ring carbon acquires a double bond character because of resonance. Hence it is difficult to break this bond. Therefore it does not easily give nucleophilic substitution reactions.

However electrophilic reactions are easily given because resonance creates negative centres on the rings.



(*ix*) There is hydrogen bonding in alcohols which raises the boiling points. There is no such hydrogen bonding in ethers. Hence the boiling points remain low.

(*x*) Chlorine exerts —I inductive effect in chloroacetic acid. This helps in the release of protons. Hence it is a stronger acid than acetic acid or acetic acid is a weaker acid than chloroacetic acid.

(*xi*) Formation of ammonia derivatives from aldehydes and ketones is a nucleophilic reaction. Carbonyl carbon has to have a positive charge which can be achieved in an acidic medium. Hence pH of the reaction is controlled.

**Q. 209. Give reasons for the following :**

**(i) *ter*-Butylbenzene does not give benzoic acid on treatment with acidic $KMnO_4$.**

**(ii) $CH_2 = CH^-$ is more basic than $HC \equiv C^-$.**

**(iii) Normally, benzene gives electrophilic substitution reactions rather than electrophilic addition reaction although it contains double bonds.**

(*I.I.T. 2000*)

**Ans.** (*i*) It is necessary to have a benzylic hydrogen for a group attached to the benzene ring for oxidation to —COOH. *Tert*-butylbenzene does not contain such hydrogen. Hence no oxidation to —COOH group.

(*ii*) Conjugate base of a strong acid is a weak base. Out of $CH \equiv CH$ and $CH_2 = CH_2$, the former is a stronger acid because of greater percentage of *s*-character (50%). Hence the conjugate base of $CH \equiv CH$ *viz.* $CH \equiv C^-$ is weaker than the conjugate base of $CH_2 = CH_2$ *viz.* $CH_2 = CH^-$.

(*iii*) An aromatic structure is a stable structure. Hence that course will be followed in which the aromatic structure is retained. This is possible when electrophilic substitution takes place. In electrophilic addition, the aromatic character (alternate single and double bonds in a hexagon) will be destroyed.

**Q. 210. Account for the following :**

**(i) It is difficult to prepare pure amines by ammonolysis of alkyl halides**

**(ii) Aniline is a weaker base than cyclohexyl amine**

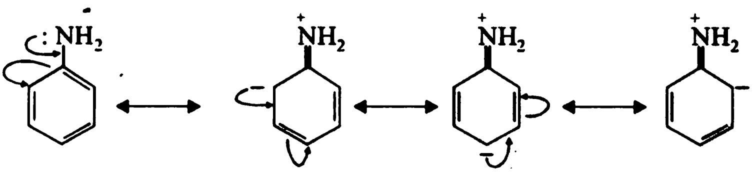
**(iii) Aldehydes are more reactive than ketones in nucleophilic reactions.**

*(A.I.S.B. 2002)*

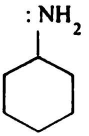
**Sol** (i) We obtain a mixture of primary, secondary and tertiary amines.

$$R{-}X \xrightarrow{NH_3} \underset{\text{Primary amine}}{R{-}NH} \xrightarrow[-HX]{R-X} \underset{\text{Sec. amine}}{R_2NH} \xrightarrow[-HX]{RX} \underset{\text{Tert. amine}}{R_3N}$$

(ii) The electron pair on nitrogen in aniline takes part in resonance with the benzene ring. It is thus not available on nitrogen. Aniline is thus a weak base.



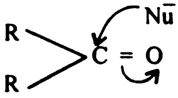
No such delocalization of electrons takes place on cyclohexylamine. Electron pair remains on nitrogen atom and the compound behaves as basic.



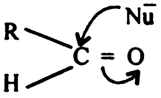
Cyclohexylamine

(iii) Aldehydes are more reactive than ketones in nucleophilic reactions.

In a nucleophilic reaction, the nucleophile first attaches to carbonyl carbon (aldehyde or ketone). Due to two alkyl groups present in ketone, the nucleophile experiences steric hindrance. Smaller hindrance is experienced with aldehyde which contains only one alkyl group.



(Greater steric hindrance)



(Smaller steric hindrance)

Moreover, due to electron repelling inductive effect of two alkyl groups in the ketone, carbonyl carbon becomes negative which hinders the attachment of the nucleophile on carbonyl carbon.

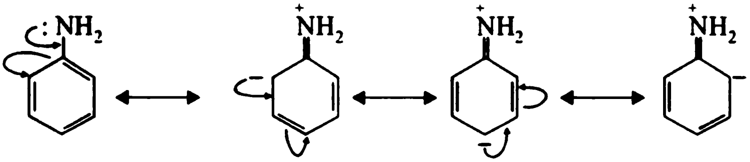
**Q. 211. Give appropriate reasons for the following observations.**

**(i) The aromatic amines are weaker bases than aliphatic amines.**

**(ii) Even under mild conditions, aniline on bromination gives 2,4,6 tribromoaniline instantaneously.**

**(iii) The diazonium ion acts as an electrophile.** ***(A.I.S.B. 2004)***

**Ans.** (*i*) Lone pair of electrons on nitrogen in aromatic amines takes part in resonance with benzene as under :

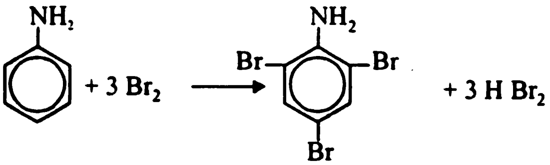


As electrons are not available on nitrogen, the aromatic amine is a weaker base.

No such resonance takes place in aliphatic amine. The electron remains on nitrogen in aliphatic amine and therefore aliphatic amines are comparatively stronger bases.

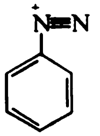
(*ii*) Amino group is an activating group. It increases electron density on 2,4 and 6 positions as given under (*i*) above.

Therefore further electrophilic substitution takes place readily and we get 2,4,6-tribromoaniline instantaneously.

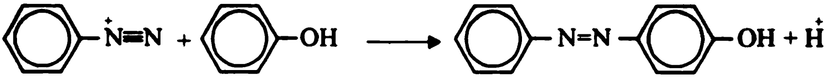


2, 4, 6-tribromo
aniline

(*iii*) Diazonium ion has the following structure :



As there is a net positive charge on the ion, it acts as an electrophile like nitronium ion ($\overset{+}{N}O_2$) and chloronium ion ($Cl^+$). It combines with phenol to form p-hydroxyazobenzene (orange dye)



Phenol p-hydroxyazobenzene

# SUMMARY OF IMPORTANT NAME REACTIONS

## 1. Aldol Condensation

$$CH_3CHO + HCH_2.CHO \xrightarrow[NaOH]{dil.} CH_3.CHOH.CH_2CHO \xrightarrow{\Delta} \text{Crotonaldehyde}$$

$$\underset{\text{Acetone(2moles)}}{(CH_3)_2\,CO+HCH_2.COCH_3} \xrightarrow{Ba(OH)_2} \underset{\text{Diacetone alc. (Keto)}}{(CH_3)_2\,COH.CH_2O.CH_3} \xrightarrow{\Delta} \text{Mesityl oxide}$$

## 2. Benzoin Condensation

$$\underset{\substack{\text{Benzaldehyde}\\ \text{(2 moles)}}}{2C_6H_5CHO} \xrightarrow[H_2O, C_2H_5OH]{KCN, heat} \underset{\text{Benzoin}}{C_6H_5CHOH.CO.C_6H_5}$$

## 3. Carbylamine Reaction

$$\underset{\text{Chloroform}}{CHCl_3} + \underset{\text{Ethylamine}}{C_2H_5NH_2} + 3KOH \longrightarrow \underset{\text{Ethyl isocyanide}}{C_2H_5NC} + 3KCl + 3H_2O$$

$$CHCl_3 + \underset{\text{Aniline}}{C_6H_5NH_2} + 3KOH \longrightarrow \underset{\text{Phenyl isocyanide}}{C_6H_5NC} + 3KCl + 3H_2O$$

## 4. Cannizzaro's Reaction

$$\underset{\text{Formaldehyde}}{2HCHO} + NaOH \longrightarrow \underset{\text{Sod. formate}}{HCOONa} + \underset{\text{Methanol}}{CH_3OH}$$

$$\underset{\text{Benzaldehyde}}{2C_6H_5CHO} + NaOH \longrightarrow \underset{\text{Sod. benzoate}}{C_6H_5COONa} + \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH}$$

## 5. Clemmensen Reduction

$$\underset{\substack{\text{Carbonyl group}\\ \text{Ald. or Ketone}}}{>C=O} \xrightarrow[NH_2-NH_2, NaOH]{Zn-Hg, HCl} \underset{\substack{\text{Methylene}\\ \text{group}}}{>CH_2}$$

## 6. Claisen Condensation

$$C_6H_5CHO + \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{OH^-} C_6H_5CHOHCH_2CHO \xrightarrow[-H_2O]{} \underset{\text{Cinnamaldehyde}}{C_6H_5CH=CHCHO}$$

## 7. Coupling Reaction

$$\underset{\text{Benz. diazonium chloride}}{C_6H_5-N=NCl} + \underset{\text{Aniline}}{C_6H_5NH_2} \xrightarrow[40^\circ C]{H^+} \underset{p\text{-Amino azobenzene(Azo dye)}}{C_6H_5-N=N-C_6H_5-NH_2}$$

## 8. Crossed Cannizzaro's Reaction

$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} + HCHO \xrightarrow[heat]{NaOH} \underset{\text{Benzyl alc.}}{C_6H_5CH_2\,OH} + \underset{\text{Sod. formate}}{HCOONa}$$

## 9. Diazotisation

$$\underset{\text{Aniline}}{C_6H_5NH_2} \xrightarrow[HCl]{NaNO_2+} \underset{\text{Benz. diazonium chloride}}{C_6H_5-N^+ \equiv NCl^-}$$

## 10. Friedel-Crafts' Alkylation

$$\underset{\text{Benzene}}{C_6H_6} + ClCH_3 \xrightarrow[AlCl_3]{Anhy} \underset{\text{Toluene}}{C_6H_5CH_3} + HCl$$

## 11. Friedel-Crafts' Acylation

$$C_6H_6 + \underset{\text{Acetyl chloride}}{ClCOCH_3} \xrightarrow[AlCl_3]{Anhy} \underset{\text{Acetophenone}}{C_6H_5COCH_3} + HCl$$

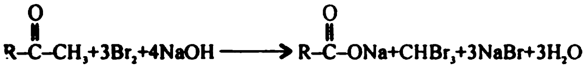
## 12. Gattermann's Reaction

$$\underset{\substack{\text{Benz. diazonium}\\ \text{chloride}}}{C_6H_5N_2Cl} \xrightarrow{Cu+HCl} \underset{\text{Chlorobenzene}}{C_6H_5Cl + N_2}$$

## 13. Gatterman Aldehyde Synthesis

$$C_6H_6 + \underset{\text{or (HCl + HC}\equiv\text{N)}}{ClCH=NH} \xrightarrow{AlCl_3} C_6H_5-CH=NH \xrightarrow{H_2O} \underset{\text{Benzaldehyde}}{C_6H_5CHO} + NH_3$$

### 14. Haloform Reaction



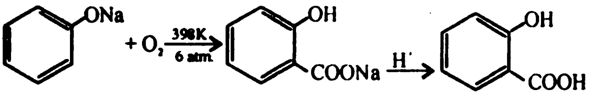
$$R-\overset{O}{\overset{\|}{C}}-CH_3+3Br_2+4NaOH \longrightarrow R-\overset{O}{\overset{\|}{C}}-ONa+CHBr_3+3NaBr+3H_2O$$

Methyl ketone Bromoform

### 15. Hofmann Bromamide Reaction

$$\underset{\text{Benzamide}}{C_6H_5CONH_2} + Br_2 + 4KOH \longrightarrow \underset{\text{Anline}}{C_6H_5NH_2} + 2KBr + K_2CO_3 + 2H_2O$$

### 16. Kolbe-Schmidt Reaction

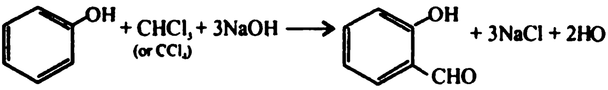


Sod. phenoxide Sod. salicylate Salicylic acid

### 17. Kolbe Electrolysis

$$\underset{\text{Sod. acetate}}{2CH_3COONa} + 2H_2O \xrightarrow{\text{Electrolysis}} \underset{\text{At Anode}}{CH_3-CH_3 + 2CO_2} + \underset{\text{At Cathode}}{NaOH+H_2}$$

### 18. Reimer–Tiemann's Reaction



Phenol Salicyldehyde (or Salicylic acid)

### 19. Rosenmund Reduction

$$\underset{\text{Acid chloride}}{RCOCl} \xrightarrow[Pd/BaSO_4]{H_2} \underset{\text{Aldehyde}}{RCHO}$$

### 20. Sandmeyer's Reaction

$$\underset{\text{Benz. diazonium chloride}}{C_6H_5N_2Cl} + CuCN \longrightarrow \underset{\text{Phenyl benzoate}}{C_6H_5CN} + N_2 + CuCl$$

### 21. Schotten Baumann Reaction

$$\underset{\text{Phenol}}{C_6H_5OH} + \underset{\text{Benoyl chloride}}{C_6H_5COCl} \xrightarrow{NaOH} \underset{\text{Phenyl benzoate}}{C_6H_5OCOC_6H_5} + HCl$$

### 22. Stephen Reduction

$$\underset{\text{Methyl cyanide}}{CH_3C\equiv N} + 2H \xrightarrow[HCl]{SnCl_2} \underset{\text{Aldimine}}{CH_3CH=NH} \xrightarrow{H_2O} CH_3CHO + NH_3$$

### 23. Tischenko Reaction

$$\underset{\text{Benzaldehyde}}{2C_6H_5CHO} \xrightarrow{Al(OC_2H_5)_3} \underset{\text{Benzyl benzoate}}{C_6H_5CH_2OOC.C_6H_5}$$

### 24. Ulmann Reaction

$$\underset{\text{Iodobenzene}}{C_6H_5I} + 2Cu + IC_6H_5 \xrightarrow{\text{Heat}} \underset{\text{Diphenyl}}{C_6H_5 - C_6H_5} + 2CuI$$

### 25. Williamson Synthesis

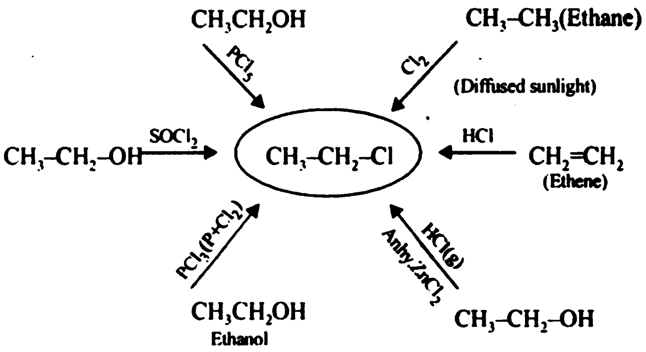
$$\underset{\text{Sod. alkoxide}}{RONa} + \underset{\text{Alkyl halide}}{XR} \xrightarrow{\text{Heat}} \underset{\text{Ether}}{R-O-R} + NaX$$

### 26. Wurtz-Fitting Reaction

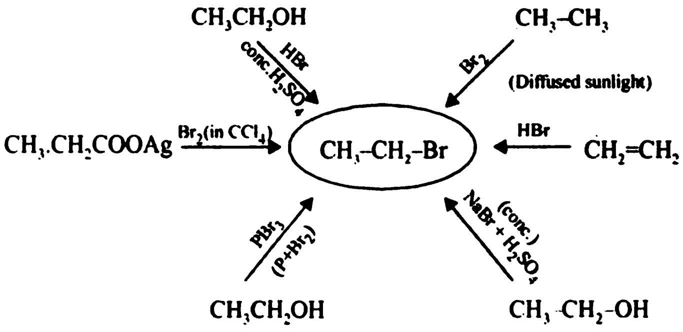
$$\underset{\text{Bromobenzene}}{C_6H_5Br} + 2Na + \underset{\text{Methyl bromide}}{BrCH_3} \xrightarrow[\text{ether}]{\text{Dry}} \underset{\text{Toluene}}{C_6H_5CH_3} + 2NaBr$$

# Flow Charts of Organic Reactions

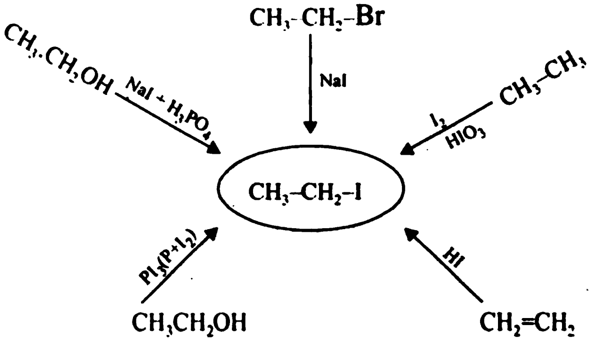
## Preparation of ethyl Chloride



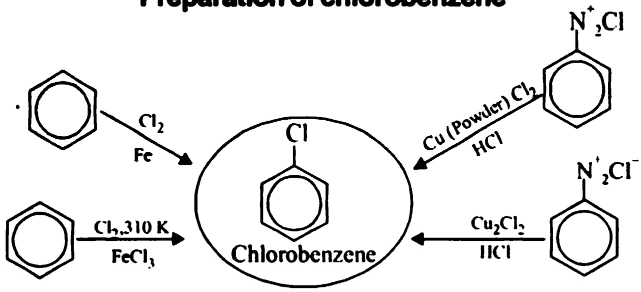
## Preparation of ethyl bromide



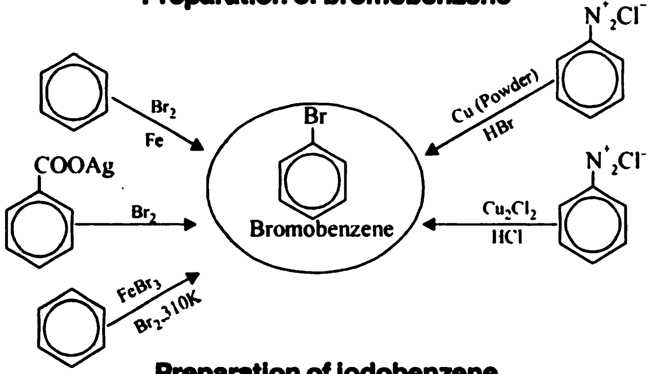
## Preparation of ethyl iodide



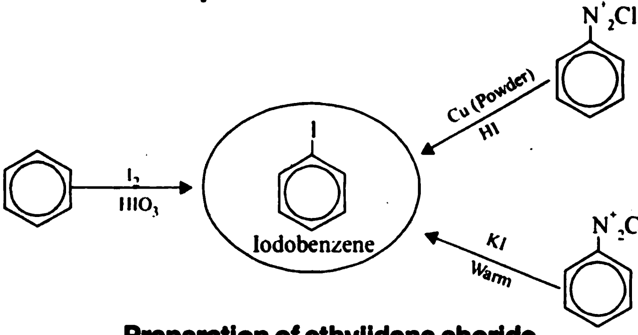
## Preparation of chlorobenzene



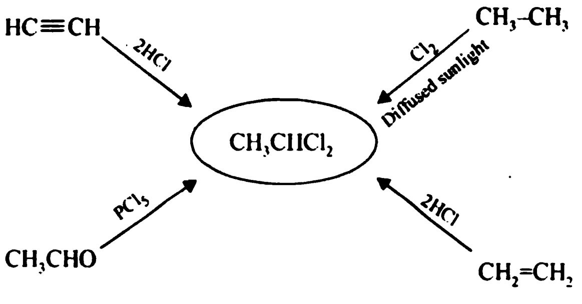
## Preparation of bromobenzene



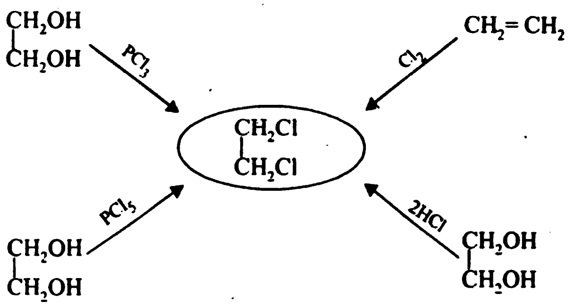
## Preparation of iodobenzene



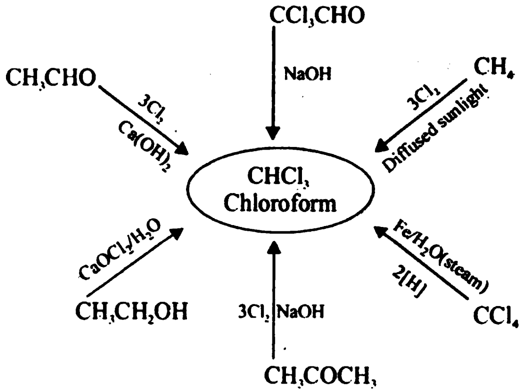
## Preparation of ethylidene choride



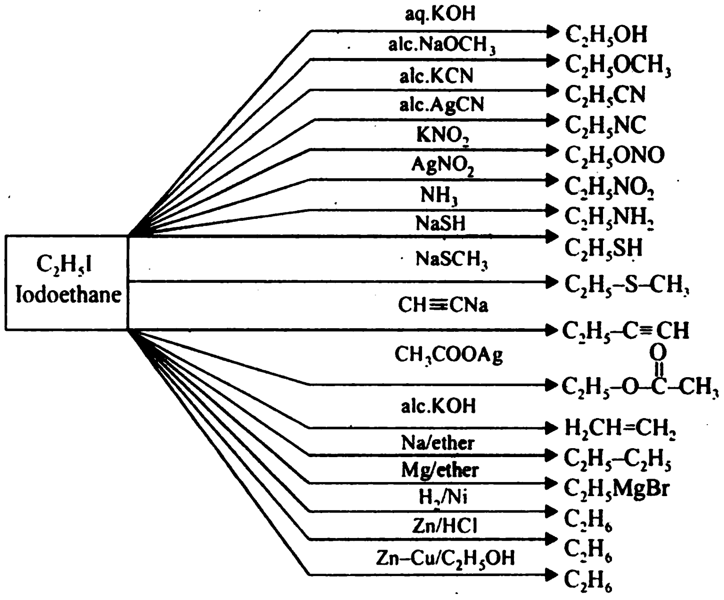
## Preparation of ethylene dichloride



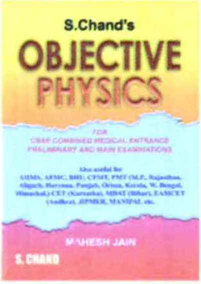
## Preparation of iodoform



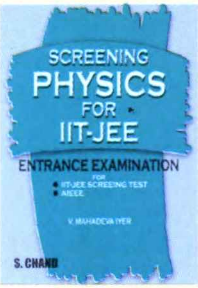
## Reactions of iodoethane



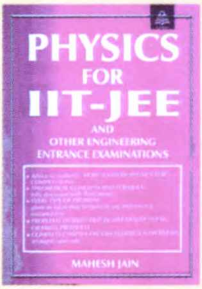
# BOOKS FOR COMPETITIVE EXAMINATIONS



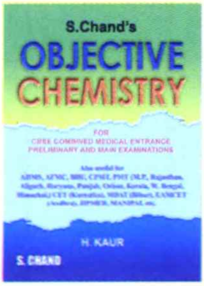
MAHESH JAIN



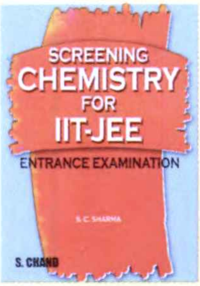
V. MAHADEVA IYER



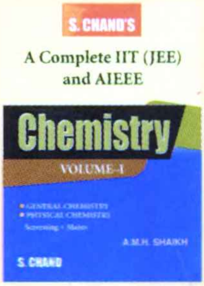
MAHESH JAIN



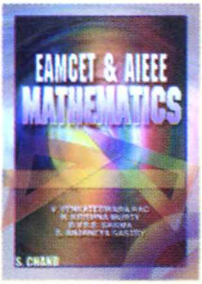
H. KAUR

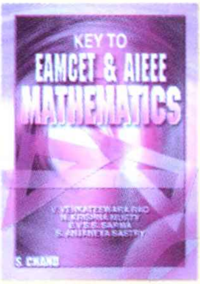


S.C. SHARMA



A.M.H. SHAIKH





V. VENKATESWARA RAO
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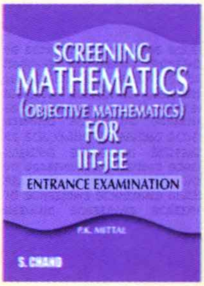

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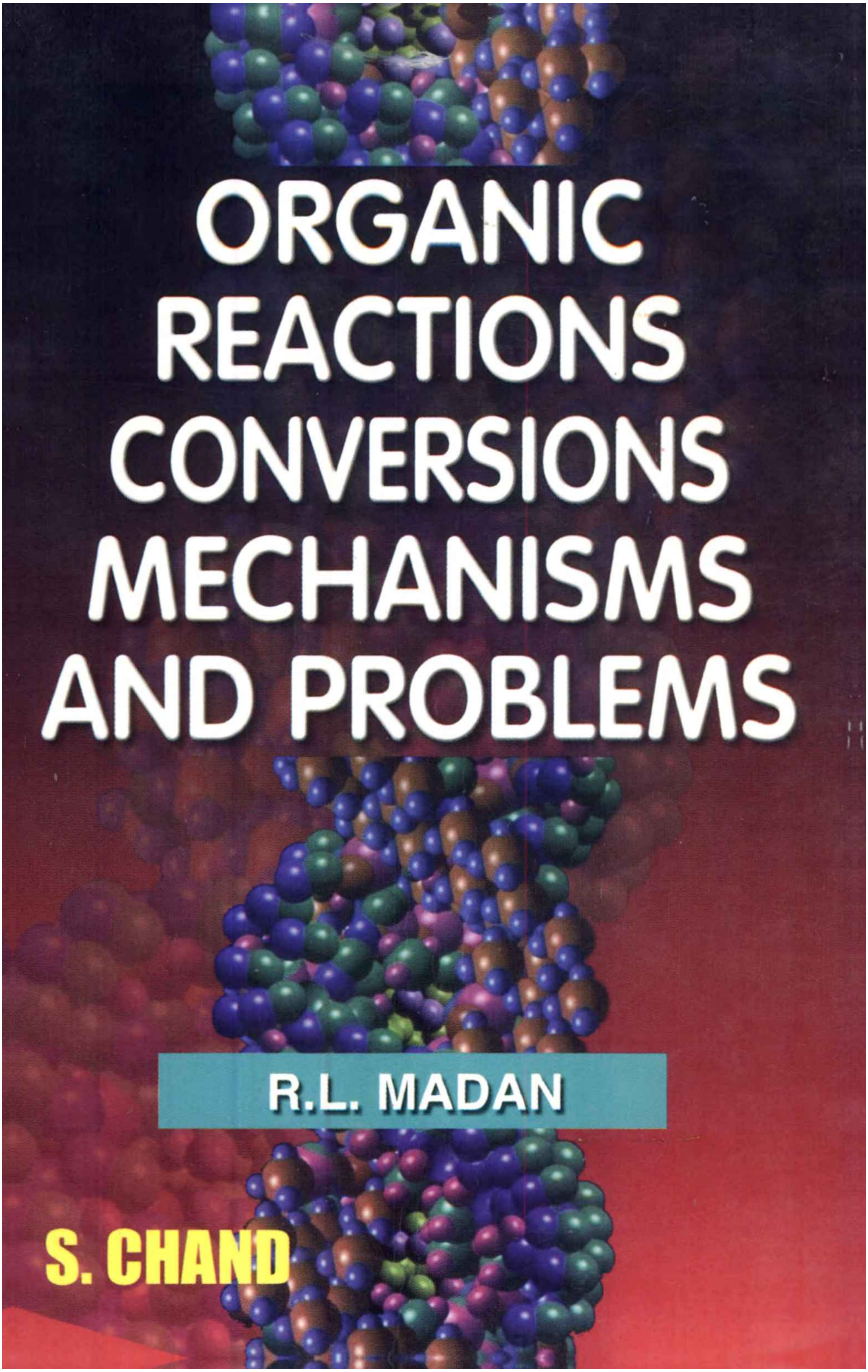

# ORGANIC REACTIONS CONVERSIONS MECHANISMS AND PROBLEMS

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S. CHAND