UNIT

17

Organic Compounds with Functional Groups Containing Halogens

(Haloalkanes and Haloarenes)

SYLLABUS

Nature of C—X bond in haloalkanes and Haloarenes

Nomenclature

Physical properties, Chemical properties with emphasis on mechanism of substitution reactions

Difference in reactivity of C—X bond in haloalkanes and haloarenes.

Some commercially important compounds—names and structures of some compounds and their uses.

17.1. General Introduction

In unit 15, we have learnt that saturated hydrocarbons (*i.e.* alkanes) react with halogens and unsaturated hydrocarbons (*i.e.* alkenes and alkynes) react with halogen halides to give compounds containing one or more halogen atoms.

Since these compounds are derived from hydrocarbons they are collectively called the halogen derivatives of hydrocarbons. In all these compounds, the halogen atom acts as the functional group and is attached to the carbon atom by a covalent bond.

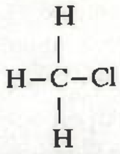
Many halogen containing organic compounds occur in nature and some of these are medicinally useful. For example, the chlorine containing antibiotic chloromycetin or chloramphenicol, produced by soil microorganism, is very effective for the treatment of typhoid fever. Our body produces an iodine containing hormone called thyroxine, the deficiency of which causes the disease goitre. Some synthetic halogen containing compounds are very useful in health-care and medicine. For example, chloroquine is used for the treatment of malaria fever and halothane ($CF_3-CHClBr$) is an anaesthetic agent used during surgery. Certain perfluorinated (*i.e.* fully fluorinated compounds are thought to be potential blood substitutes in surgery. Many synthetic organic halogen compounds are extensively used in agriculture and industry and hence are being manufactured in large quantities every year. Organic halogen compounds serve as valuable intermediates for the synthesis of a variety of other classes of organic compounds. Therefore, in this unit, we shall briefly discuss the preparation, properties and uses of simple organic halogen compounds.

17.2. Classification of Halogen Compounds

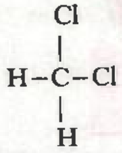
The halogen derivatives of hydrocarbons are broadly classified into the following two types :

1. Aliphatic halogen compounds. These are obtained by replacement of one or more hydrogen atoms of an aliphatic hydrocarbon by an equal number of halogen atoms. Depending upon the nature of the aliphatic hydrocarbon, whether alkane, alkene or alkyne, aliphatic halogen compounds are of the following three types :

(*a*) **Haloalkanes.** *The halogen derivatives of alkanes are called* **haloalkanes.** These are classified as fluoro, chloro, bromo or iodo compounds according to the type of halogen present and as *mono-, di-, tri-, tetrahaloalkanes etc.* according as they contain *one, two, three, four etc.* halogen atoms respectively in their molecules. For example,

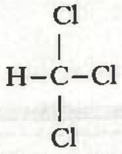


$H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-Cl$

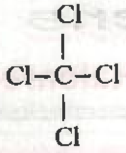


$H-\overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-Cl$

IUPAC Name :	Chloromethane	Dichloromethane
Common Name :	Methyl chloride (*Monohalogen derivative*)	Methylene chloride (*Dihalogen derivative*)



$H-\overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle Cl}{|}}{C}}-Cl$



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

IUPAC Name :	Trichloromethane	Tetrachloromethane
Common Name :	Chloroform (*Trihalogen derivative*)	Carbon tetrachloride (*Tetrahalogen derivative*)

The monohalogen derivatives of alkanes are called **alkyl halides** *or monohaloalkanes or simply* **haloalkanes.** Their general formula is R – X where R is any alkyl group and X is any halogen atom *i.e.*, F, Cl, Br, or I. They are also represented as $C_nH_{2n+1}X$ where $n = 1, 2, 3, ...$ etc. These are obtained by replacement of one hydrogen atom of an alkane with a suitable halogen atom. Thus,

$$\underset{\text{Alkane}}{R-H} \xrightarrow[+X]{-H} \underset{\substack{\text{Haloalkane}\\ (\textit{Alkyl halide})}}{R-X}$$

Some important examples of haloalkanes are :

CH_3-Cl
Chloromethane
(*Methyl chloride*)

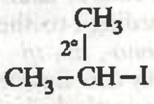
CH_3CH_2-Br
Bromoethane
(*Ethyl bromide*)

$CH_3CH_2CH_2-I$
1–Iodopropane
(*n–Propyl* iodide)

Note. Wherever two names are given under the formulae, the one outside the brackets refers to the IUPAC name while that given within the brackets denotes the common or the trivial name.

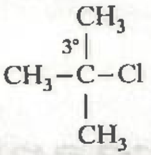
Classification of alkyl halides. *Alkyl halides are further classified as primary (1°), secondary (2°) and tertiary (3°) according as the halogen atom is attached to primary, secondary and tertiary carbon atoms respectively.* For example,

$CH_3CH_2\overset{1°}{CH_2}-Br$
1–Bromopropane
(*Primary*)



$CH_3-\overset{\overset{\displaystyle CH_3}{2°\,|}}{CH}-I$

2–Iodopropane
(*Secondary*)



$CH_3-\overset{\overset{\displaystyle CH_3}{3°\,|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-Cl$

2–Chloro–2–methylpropane
(*Tertiary*)

(*b*) **Haloalkenes or Alkenyl halides** *are the halogen derivatives of alkenes.* Their general formula is $C_nH_{2n-1}X$ where X = F, Cl, Br or I and $n = 2, 3, 4$ .... etc. For example,

$CH_2=CH-Cl$
Chloroethene
(*Vinyl chloride*)

$Br-\overset{3}{C}H_2-\overset{2}{C}H=\overset{1}{C}H_2$
3–Bromoprop–1–ene
(*Allyl bromide*)

$\overset{4}{C}H_3-\overset{3}{C}H=\overset{2}{C}H-\overset{1}{C}H_2Cl$
1–Chlorobut–2–ene
(*Crotyl chloride*)

$C_6H_5-\overset{1}{C}H=\overset{2}{C}H-\overset{3}{C}H_2Cl$
3–Chloro–1–phenylprop–1–ene
(*Cinnamyl chloride*)

(*c*) **Haloalkynes or Alkynyl halides** *are the halogen derivatives of alkynes.* Their general formula is $C_nH_{2n-3}X$ where X = F, Cl, Br or I and $n = 2, 3, 4$ .... etc. For example,

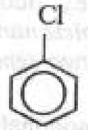
$H-C\equiv C-Cl$
Chloroethyne
(*Chloroacetylene*)

$\overset{3}{C}H_3-\overset{2}{C}\equiv\overset{1}{C}-Br$
1–Bromoprop–1–yne

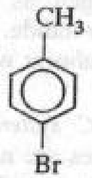
$Br-\overset{3}{C}H_2-\overset{2}{C}\equiv\overset{1}{C}H$
3–Bromoprop–1–yne
(*Propargyl bromide*)

2. Aromatic halogen compounds. These are obtained by replacement of one or more hydrogen atoms of an aromatic hydrocarbon by an equal number of halogen atoms. These have been further classified into the following two major categories :

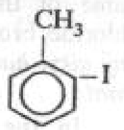
(*i*) **Nuclear halogen derivatives.** *Halogen derivatives of aromatic hydrocarbons in which the halogen atom (F, Cl, Br or I) is directly attached to an aromatic ring are called* **aryl halides.** **Their general formula is Ar – X where Ar (short name for aryl) represents a phenyl, a substituted phenyl or any other aryl group such as naphthyl etc.** Some examples of aryl halides are :



Chlorobenzene

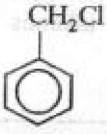


1−Bromo−4−methylbenzene
or 4−Bromotoluene
(*p-Bromotoluene*)

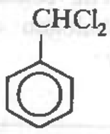


2−Iodo−4−methylbenzene
or 2−Iodotoluene
(*o-Iodotoluene*)

(*ii*) **Side chain halogen derivatives.** *Halogen derivativies of aromatic hydrocarbons in which the halogen atom is linked to one of the carbon atoms of the side chain carrying the aryl group are called* **aralkyl halides.** *For example,*

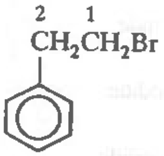


1−Chloro−1−phenylmethane
(*Benzyl chloride*)



1, 1−Dichloro−1−phenylmethane
(*Benzal dichloride*)

1, 1, 1−Trichloro−1−phenylmethane
(*Benzotrichloride*)



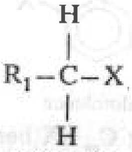
1-Bromo-2-phenylethane
(*β-Phenylethyl bromide*)

Like alkyl halides, aralkyl halides are very reactive and thus undergo a number of substitution reactions. On the other hand, aryl halides are far less reactive and thus undergo only a few substitution reactions and that too under drastic conditions.

3. Classification on the basis of type of hybridization of carbon bonded to the halogen atom. On the basis of type of hybridization of carbon to which the halogen is attached, halogen derivatives of hydrocarbons are of the following three types :

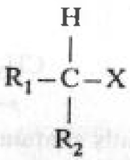
(*a*) **Compounds containing $C_{sp^3}-X$ bond** (**X = F, Cl, Br or I**). This class is further divided into the following three types :

(*i*) **Haloalkanes or alkyl halides (R–X).** In alkyl halides, the halogen atom (X) is bonded to an alkyl group (R). They form a homologous series with the general formula, $C_n H_{2n+1} X$. They are further classified as primary, secondary or tiartiary according as the halogen is linked to primary, secondary or tertiary carbon atom. For example,



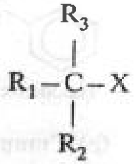
$$R_1-\overset{\overset{\large H}{|}}{\underset{\underset{\large H}{|}}{C}}-X$$

Primary (1°)



$$R_1-\overset{\overset{\large H}{|}}{\underset{\underset{\large R_2}{|}}{C}}-X$$

Secondary (2°)



$$R_1-\overset{\overset{\large R_3}{|}}{\underset{\underset{\large R_2}{|}}{C}}-X$$

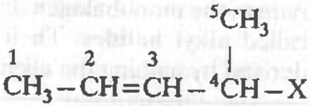
Tertiary (3°)

If R in R–X is alicyclic, then R–X is called either halocycloalkane or cycloalkyl halide which, in turn, may be secondary or tertiary.

(*b*) **Allylic halides.** In these halides, the halogen is linked to an sp^3-hybridised carbon atom which is next to a carbon-carbon double bond, *i.e.*, to an allylic carbon. For example,

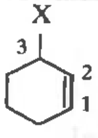
$$\overset{1}{C}H_2=\overset{2}{C}H-\overset{3}{C}H_2-X$$

3−Haloprop−1−ene
(*Allyl halide*)



$$\overset{1}{C}H_3-\overset{2}{C}H=\overset{3}{C}H-{}^4\overset{\overset{{}^5CH_3}{|}}{C}H-X$$

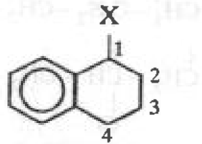
4−Halopent−2−ene



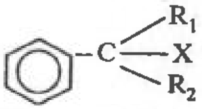
3−Halocyclohex−1−ene

(*iii*) **Benzylic halides.** In these halides, the halogen is attached to an sp^3-hybridized carbon atom next to an aromatic ring, *i.e.*, to a benzylic carbon. For example,

Phenylhalomethane
(*Benzyl halide*)



1−Halo−1, 2, 3, 4−tetrahydronaphthalene



(*b*) **Compounds containing $C_{sp^2}-X$ bond** (**X = F, Cl, Br, I**). This includes the following two types :

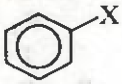
(*i*) **Vinylic halides.** In these halides, the halogen is attached to one of the carbon atoms of the carbon-carbon double bond. For example,

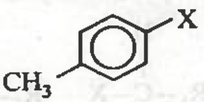
$CH_2=CH_2-X$

Haloethene
(*Vinyl halide*)

1−Halocyclohex−1−ene

(*ii*) **Aryl halides.** In these halides, halogen is directly attached to the aromatic ring


Halobenzene


p−Halotoluene

(*c*) **Compounds containing $C_{sp}-X$ bond (X = F, Cl, Br or I).** In these halides, halogen is directly attached to one of the carbon atoms of the triple bond. For example,

$H-C\equiv C-Cl$ Chloroethyne

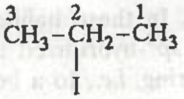
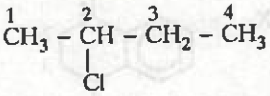
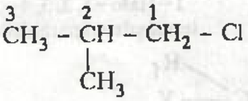
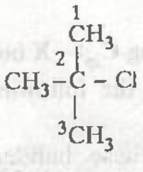
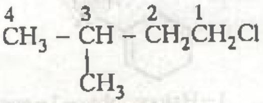
$CH_3-C\equiv C-Cl$ Chloropropyne

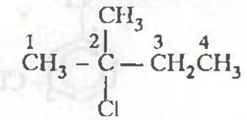
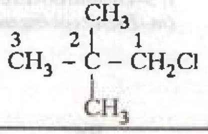
17.3. Nomenclature of Haloalkanes

(*a*) **Alkyl halides.** In the *common or trivial system*, the monohalogen derivatives of alkanes are called **alkyl halides**. Their individual names are derived by naming the alkyl group followed by the name of the halogen as halide *i.e.*, fluoride, chloride, bromide or iodide. *The complete name of any alkyl halide is always written as two separate words.*

In the *IUPAC system,* the monohalogen derivatives of alkanes are named as **haloalkanes.** Their individual names are derived by prefixing the word *'halo'* to the name of the longest straight chain alkane. The numbering of the parent straight chain alkane is always done in such a way that the carbon atom carrying the halogen atom gets the lowest possible number. *The IUPAC name of any monohalogen derivative of alkane is always written as one word.*

The common and IUPAC names of some monohalogen derivatives of alkanes are given below :

STRUCTURAL FORMULA	COMMON OR TRIVIAL NAME	IUPAC NAME
CH_3-Cl	Methyl chloride	Chloromethane
CH_3-CH_2-Br	Ethyl bromide	Bromoethane
$\overset{3}{CH_3}-\overset{2}{CH_2}-\overset{1}{CH_2}-I$	*n*-Propyl iodide	1-Iodopropane
 $\overset{3}{CH_3}-\underset{\underset{I}{\mid}}{\overset{2}{CH_2}}-\overset{1}{CH_3}$	Isopropyl iodide	2-Iodopropane
$\overset{4}{CH_3}-\overset{3}{CH_2}-\overset{2}{CH_2}-\overset{1}{CH_2}-Cl$	*n*-Butyl chloride	1-Chlorobutane
 $\overset{1}{CH_3}-\underset{\underset{Cl}{\mid}}{\overset{2}{CH}}-\overset{3}{CH_2}-\overset{4}{CH_3}$	*sec*-Butyl chloride	2-Chlorobutane
 $\overset{3}{CH_3}-\underset{\underset{CH_3}{\mid}}{\overset{2}{CH}}-\overset{1}{CH_2}-Cl$	Isobutyl chloride	1-Chloro-2-methylpropane
 $CH_3-\underset{\underset{^{3}CH_3}{\mid}}{\overset{\overset{1}{CH_3}}{\overset{2\mid}{C}}}-Cl$	*tert*-Butyl chloride	2-Chloro-2-methylpropane
$\overset{5}{CH_3}\overset{4}{CH_2}\overset{3}{CH_2}\overset{2}{CH_2}\overset{1}{CH_2}Cl$	*n*-Pentyl chloride or *n*-Amyl chloride	1-Chloropentane
 $\overset{4}{CH_3}-\underset{\underset{CH_3}{\mid}}{\overset{3}{CH}}-\overset{2}{CH_2}\overset{1}{CH_2}Cl$	Isopentyl chloride or Isoamyl chloride	1-Chloro-3-methylbutane

 $\overset{1}{CH_3}-\overset{2}{C}(CH_3)(Cl)-\overset{3}{CH_2}\overset{4}{CH_3}$	*tert*-Pentyl chloride or *tert*-Amyl chloride	2-Chloro-2-methylbutane
 $\overset{3}{CH_3}-\overset{2}{C}(CH_3)_2-\overset{1}{CH_2}Cl$	Neopentyl chloride or Neoamyl chloride	1-Chloro-2, 2-dimethylpropane

(*b*) **Dihalogen derivatives.** These are of the following three types :

(*i*) **Alkylidene dihalides.** In the common system, dihaloalkanes in which two halogen atoms of the same type are present on the same carbon atom are called **alkylidene dihalides. Further** since the positions on the same carbon atom are called **geminal positions,** therefore, alkylidene dihalides are also called **germinal dihalides or gem-halides.**

In the IUPAC system, they are named as dihaloalkanes in which the position of the locant for the halogen after being repeated twice is prefixed to the name of the dihaloalkane. For example,

CH_3CHBr_2
1, 1–Dibromoethane
(*Ethylidene dibromide*)

$CH_3-CCl_2-CH_3$
2, 2–Dichloropropane
(*Isopropylidene dichloride*)

$CH_3CH_2CHCl_2$
1, 1–Dichloropropane
(*Propylidene dichloride*)

(*ii*) **Alkylene dihalides.** *In the common system* dihalogen derivatives of alkanes in which the two halogen atoms of the same type are present on the adjacent carbon atoms of the carbon chain are called **alkylene dihalides.** Further since positions on the adjacent carbon atoms are vicinal positions, therefore, alkylene dihalides are also called **vicinal dihalides** or simply **vic-dihalides.**

In the IUPAC system, the locants for the two halogen atoms are prefixed to the name of dihaloalkane. For example,

CH_2Cl_2
Dichloromethane
(*Methylene* dichloride)

$BrCH_2CH_2Br$
1, 2–Dibromoethane
(*Ethylene dibromide*)

$CH_3-CHCl-CH_2Cl$
1, 2–Dichloropropane
(*Propylene dichloride*)

(*iii*) **Polymethylene dihalides.** *In the common system*, dihalogen derivatives of alkanes in which the same two halogen atoms are present on the terminal carbon atoms, *i.e.*, α, ω-positions of the carbon chain are called **polymethylene dichlorides.**

In the IUPAC system, the locants for the same or different halogen atoms are prefixed to the name of the dihaloalkane. For example,

$ClCH_2CH_2CH_2CH_2Cl$
1, 4–Dichlorobutane
(*Tetramethylene dichloride*)

$BrCH_2CH_2CH_2Cl$
1–Bromo–3–chloropropane

(*c*) **Polyhaloalkanes.** *In the common system*, trihalomethanes and tetrahalomethanes are called haloforms and carbon tetrahalides respectively. For example,

$CHCl_3$
Chloroform

CHI_3
Iodoform

$CHBr_3$
Bromoform

CCl_4
Carbon tetrachloride

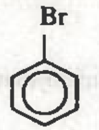
CBr_4
Carbon tetrabromide

Fully halogenated hydrocarbons are called perhalohydrocarbons (per = thoroughly). For example,

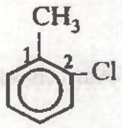
$CF_3-CF_2-CF_3$
Octafluoropropane
or Perfluoropropane

17.4. Nomenclature of Haloarenes (Aryl Halides)

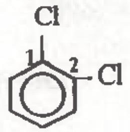
Systematic names of aryl halides are obtained by prefixing "halo" (*fluoro, chloro, bromo* or *iodo*) to the name of the parent aromatic hydrocarbon. In case the parent aromatic hydrocarbon carries a side chain or a substituent, the position of the halogen atom with respect to this substituent is indicated either by an arabic numerical or by prefixes *ortho* (*o*-), *meta* (*m*-) and *para* (*p*-) according as the relative position of the halogen atom with respect to the substituent is 1, 2- ; 1, 3- and 1, 4-respectively. If, however, parent aromatic hydrocarbon chosen is benzene, then the numbering begins with the halogen. For example,



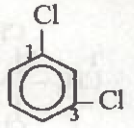
Bromobenzene
(*Phenyl bromide*)



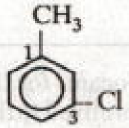
1−Chloro−2−methylbenzene
or 2–Chlorotoluene
(*o–Chlorotoluene*)



1,2–Dichlorobenzene
(*o–Dichlorobenzene*)

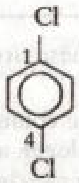


1, 3–Dichlorobenzene
(*m–Dichlorobenzene*)

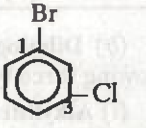


1−Chloro−3−methylbenzene
or 3–Chlorotoluene
(*m–Chlorotoluene*)

1−Chloro−
4−methylbenzene
or 4–Chlorotoluene
(*p–Chlorotoluene*)



1,4–Dichlorobenzene
(*p–Dichlorobenzene*)



1–Bromo–3–chlorobenzene

PROBLEMS FOR PRACTICE

1. Draw the structures of all eight structural isomers that have the molecular formula $C_5H_{11}Br$. Name each isomer according to IUPAC system and classify them as primary, secondary or tertiary bromide. Point out if any one is optically active.
(D.S.B. 1980 S ; A.I.S.B. 1983 S ; H.P.S.B. 1992 ; N.C.E.R.T.)

2. Amongst the aromatic compounds, having molecular formula, C_7H_7Cl, how many isomers are possible ? Write their structures and the IUPAC names.
(A.I.S.B. 1985 ; P.S.B. 1990 S)

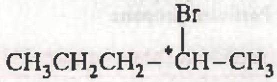
HINTS FOR DIFFICULT PROBLEMS

1. Eight isomers are possible. Their structures and IUPAC names are given below :

(*i*) $CH_3CH_2CH_2CH_2CH_2Br$

1–Bromopentane (1°)

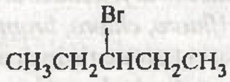
(*ii*)



$CH_3CH_2CH_2-\overset{\overset{Br}{|}}{\overset{*}{C}H}-CH_3$

2–Bromopentane (2°)

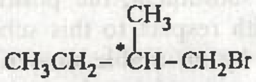
(*iii*)



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

3–Bromopentane (2°)

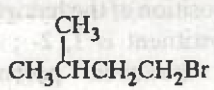
(*iv*)



$CH_3CH_2-\overset{\overset{CH_3}{|}}{\overset{*}{C}H}-CH_2Br$

1–Bromo–2–methylbutane (1°)

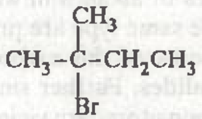
(*v*)



$CH_3\overset{\overset{CH_3}{|}}{C}HCH_2CH_2Br$

1–Bromo–3–methylbutane (1°)

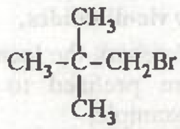
(*vi*)



$CH_3-\underset{\underset{Br}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2CH_3$

2–Bromo–2–methylbutane (3°)

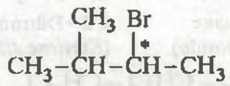
(*vii*)



$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2Br$

1–Bromo–2, 2–dimethylpropane (1°)

(*viii*)



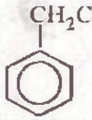
$CH_3-\overset{\overset{CH_3}{|}}{C}H-\overset{\overset{Br}{|}}{\overset{*}{C}H}-CH_3$

2–Bromo–3–methylbutane (2°)

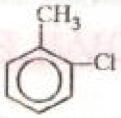
Only three isomers, *i.e.*, (*ii*), (*iv*) and (*viii*) are optically active

2. Four isomers are possible. Their structures and IUPAC names are given below :

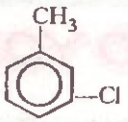
HINTS CONTD.

(i) 

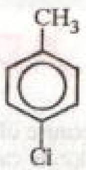
Phenylchloromethane

(ii) 

2–Chlorotoluene

(iii) 

3–Chlorotoluene

(iv) 

4–Chlorotoluene

17.5. Methods of Preparation of Haloalkanes

Haloalkanes or alkyl halides are usually prepared in the laboratory by the following general methods :

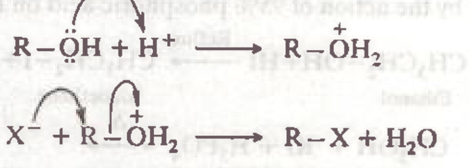
1. From alcohols : The most convenient method for the preparation of haloalkanes involves the substitution of the –OH group of an alcohol by the halogen atom. This can be done by the following methods :

(i) By the action of halogen acids. Alcohols are converted into haloalkanes by the action of halogen acids.

$$\underset{\text{Alcohol}}{R-OH} + HX \longrightarrow \underset{\text{Haloalkane}}{R-X} + H_2O$$

For a given alcohol, the reactivity of the halogen acids in the above reaction follows the sequence : HI > HBr > HCl and that of alcohols for a given halogen acid follows the order : *tertiary > secondary > primary, i.e.*, 3° > 2° > 1°.

Reason. This reaction is an example of a nucleophilic substitution reaction in which the nucleophile, *i.e.*, halide ion attacks the protonated alcohol molecule with the expulsion of water—*a good leaving group.*



$$R-\ddot{O}H + H^+ \longrightarrow R-\overset{+}{O}H_2$$

$$X^- + R-\overset{+}{O}H_2 \longrightarrow R-X + H_2O$$

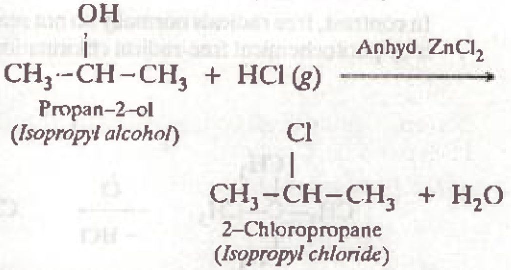
Since the *nucleophilicity* (*i.e.* tendency to donate an electron pair to the carbon atom) of the halide ions decreases in the order, $I^- > Br^- > Cl^-$, the order of reactivity of the halogen acids decreases in the same order, *i.e.*, HI > HBr > HCl.

Further since the order of stability of the carbocations (or the incipient carbocations in the transition state of these reactions) follows the sequence : 3° > 2° > 1°, the order of reactivity of the alcohols follows the same sequence, *i.e.*, 3° alcohol > 2° alcohol > 1° alcohol.

Chloroalkanes or alkyl chlorides.

(*a*) Primary and secondary chloroalkanes or alkyl chlorides are prepared by passing hydrochloric acid gas through a suitable alcohol in the presence of anhydrous zinc chloride (*Grove's Process*).

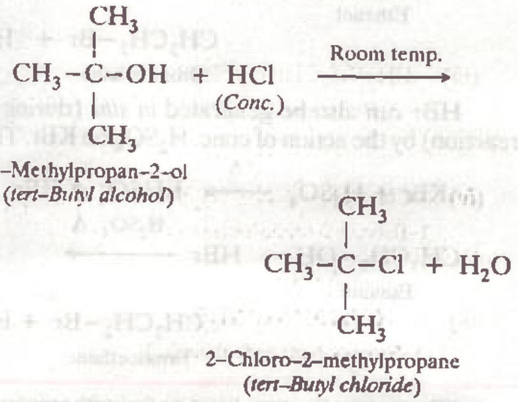
$$\underset{\substack{\text{Ethanol}\\(\textit{Ethyl alcohol})}}{CH_3CH_2-OH} + HCl\,(g) \xrightarrow{\text{Anhyd. }ZnCl_2} \underset{\substack{\text{Chloroethane}\\(\textit{Ethyl chloride})}}{CH_3CH_2-Cl} + H_2O$$



$$\underset{\substack{\text{Propan–2–ol}\\(\textit{Isopropyl alcohol})}}{CH_3-\overset{\overset{\displaystyle OH}{|}}{C}H-CH_3} + HCl\,(g) \xrightarrow{\text{Anhyd. }ZnCl_2} \underset{\substack{\text{2–Chloropropane}\\(\textit{Isopropyl chloride})}}{CH_3-\overset{\overset{\displaystyle Cl}{|}}{C}H-CH_3} + H_2O$$

The purpose of anhydrous $ZnCl_2$ is to help in the cleavage of the C–O bond. Being a *Lewis acid*, it co-ordinates with the oxygen atom of the alcohols. As a result, C–O bond weakens and ultimately breaks to form **carbocations**. These carbocations then readily react with chloride ion to form chloroalkanes.

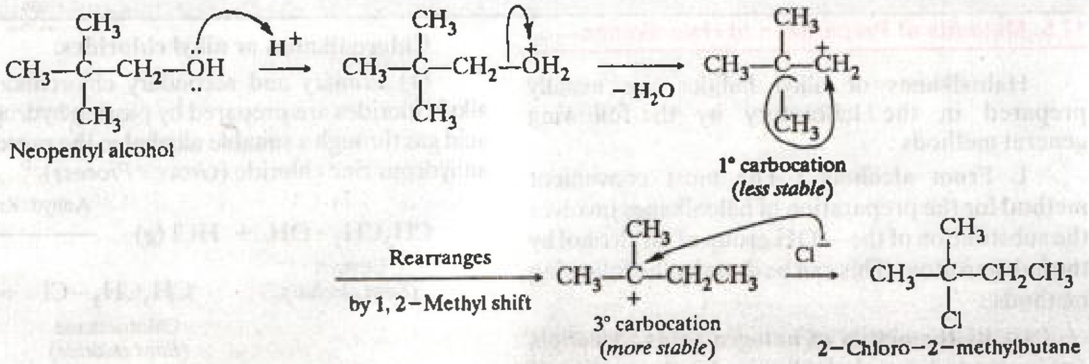
(*b*) Tertiary alcohols, however, react readily with conc. HCl even in the absence of zinc chloride.



$$\underset{\substack{\text{2–Methylpropan–2–ol}\\(\textit{tert–Butyl alcohol})}}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-OH} + \underset{(\textit{Conc.})}{HCl} \xrightarrow{\text{Room temp.}} \underset{\substack{\text{2–Chloro–2–methylpropane}\\(\textit{tert–Butyl chloride})}}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-Cl} + H_2O$$

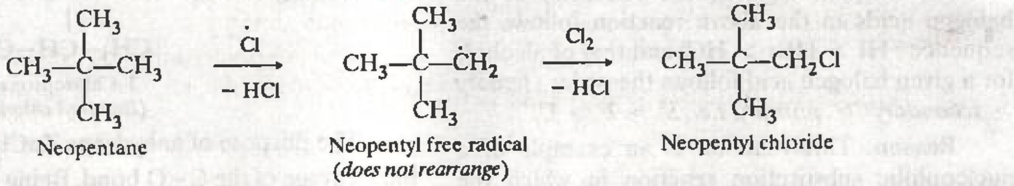
ADD TO YOUR KNOWLEDGE

Because of the strong tendency of neopentyl cation to rearrange to the more stable 3° carbocation, neopentyl chloride cannot be prepared by the action of HCl on neopentyl alcohol. Instead 2-chloro-2-methylbutane is formed as shown below :



In contrast, free radicals normally do not rearrange. Therefore, the best method to prepare neopentyl chloride is by photochemical free-radical chlorination of neopentane.

$$Cl_2 \xrightarrow{h\nu} 2\,\dot{C}l$$



Bromoalkanes or alkyl bromides are obtained by refluxing* a suitable alcohol with constant boiling hydrobromic acid (48%) in presence of a little conc. H_2SO_4 as catalyst.

$$\underset{\text{Ethanol}}{CH_3CH_2-OH} + HBr \xrightarrow{H_2SO_4,\ \text{Reflux}} \underset{\text{Bromoethane}}{CH_3CH_2-Br} + H_2O$$

HBr can also be generated *in situ* (during the reaction) by the action of conc. H_2SO_4 on KBr. Thus,

$$KBr + H_2SO_4 \xrightarrow{\Delta} KHSO_4 + HBr$$

$$\underset{\text{Ethanol}}{CH_3CH_2-OH} + HBr \xrightarrow{H_2SO_4,\ \Delta} \underset{\text{Bromoethane}}{CH_3CH_2-Br} + H_2O$$

Iodoalkanes or alkyl iodides are prepared by refluxing a suitable alcohol with constant boiling hydriodic acid (57%). HI may also be generated *in situ* by the action of 95% phosphoric acid on KI.

$$\underset{\text{Ethanol}}{CH_3CH_2-OH} + HI \xrightarrow{\text{Reflux}} \underset{\text{Iodoethane}}{CH_3CH_2-I} + H_2O$$

$$\underset{\text{Methanol}}{CH_3OH} + KI + H_3PO_4 \xrightarrow{\Delta} \underset{\text{Iodomethane}}{CH_3-I} + KH_2PO_4 + H_2O$$

***(ii)* By the action of phosphorus halides.** Phosphorus halides react with alcohols to form haloalkanes or alkyl halides in excellent yields (80% or above).

Chloroalkanes or alkyl chlorides are prepared by the action of either phosphorus pen-

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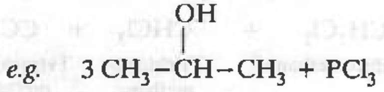
*The process of heating a liquid in a flask with a condenser so that the vapours are condensed back into the flask is called refluxing.

tachloride (PCl_5) or phosphorus trichloride (PCl_3) on suitable alcohols.

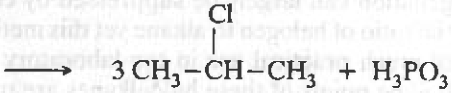
$$\underset{\text{Alcohol}}{R-OH} + \underset{\text{Phosphorus pentachloride}}{PCl_5} \longrightarrow \underset{\substack{\text{Chloroalkane}\\ \textit{(Alkyl chloride)}}}{R-Cl} + \underset{\text{Phosphorus oxychloride}}{POCl_3} + HCl$$

e.g. $$\underset{\substack{\text{Ethanol}\\ \textit{(Ethyl alcohol)}}}{CH_3CH_2-OH} + PCl_5 \longrightarrow \underset{\substack{\text{Chloroethane}\\ \textit{(Ethyl chloride)}}}{CH_3CH_2-Cl} + POCl_3 + HCl$$

Also, $$\underset{\text{Alcohol}}{3R-OH} + \underset{\text{Phosphorus trichloride}}{PCl_3} \longrightarrow \underset{\text{Alkyl chloride}}{3R-Cl} + \underset{\text{Phosphorus acid}}{H_3PO_3}$$

e.g. 

$$3\,\underset{\substack{\text{Propan-2-ol}\\ \textit{(Isopropyl alcohol)}}}{CH_3-\overset{\displaystyle OH}{\overset{|}{C}H}-CH_3} + PCl_3$$



$$\longrightarrow 3\,\underset{\substack{\text{2-Chloropropane}\\ \textit{(Isopropyl chloride)}}}{CH_3-\overset{\displaystyle Cl}{\overset{|}{C}H}-CH_3} + H_3PO_3$$

Similarly, **bromoalkanes (or alkyl bromides) and iodoalkanes (or alkyl iodides)** are prepared by the action of phosphorus tribromide (PBr_3) and phosphorus tri-iodide (PI_3) respectively on suitable alcohols.

Since PBr_3 and PI_3 are not very stable compounds, these are generally prepared *in situ* by the action of red phosphorus on bromine and iodine respectively. Thus,

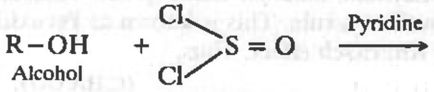
$$P_4 + 6\,Br_2 \longrightarrow 4\,PBr_3$$

$$P_4 + 6\,I_2 \longrightarrow 4\,PI_3$$

$$3\,\underset{\substack{\text{Propan-1-ol}\\ \textit{(n-Propyl alcohol)}}}{CH_3CH_2CH_2-OH} + PBr_3 \longrightarrow 3\,\underset{\substack{\text{1-Bromopropane}\\ \textit{(n-Propyl bromide)}}}{CH_3CH_2CH_2-Br} + H_3PO_3$$

$$3\,\underset{\substack{\text{Methanol}\\ \textit{(Methyl alcohol)}}}{CH_3-OH} + PI_3 \longrightarrow 3\,\underset{\substack{\text{Iodomethane}\\ \textit{(Methyl iodide)}}}{CH_3-I} + H_3PO_3$$

(*iii*) By the action of thionyl chloride. Chloroalkanes or alkyl chlorides are conveniently prepared by refluxing alcohols with thionyl chloride in presence of pyridine (C_5H_5N).



$$\underset{\text{Alcohol}}{R-OH} + \underset{\text{Thionyl chloride}}{\overset{Cl}{\underset{Cl}{>}}S=O} \xrightarrow{\text{Pyridine}} \underset{\text{Chloroalkane}}{R-Cl} + SO_2\uparrow + HCl\uparrow$$

e.g. $$\underset{\substack{\text{Ethanol}\\ \textit{(Ethyl alcohol)}}}{CH_3CH_2-OH} + \underset{\text{Thionyl chloride}}{SOCl_2} \xrightarrow{\text{Pyridine}} \underset{\substack{\text{Chloroethane}\\ \textit{(Ethyl chloride)}}}{CH_3CH_2-Cl} + SO_2\uparrow + HCl\uparrow$$

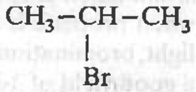
Thionyl chloride method is preferred over hydrogen chloride or phosphorus pentachloride method for the preparation of chloroalkanes since both the by-products (SO_2 and HCl) in this reaction being gases escape leaving behind the chloroalkanes in almost pure state.

2. From hydrocarbons. Haloalkanes can be prepared from alkenes, alkynes and alkanes as discussed below :

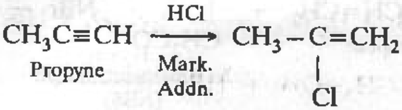
(*a*) From alkenes and alkynes. Alkenes react with halogen acids to form haloalkanes. The order of reactivity being : HI > HBr > HCl > HF.

$$\underset{\substack{\text{Ethene}\\ \textit{(Ethylene)}}}{CH_2=CH_2} + HI \longrightarrow \underset{\substack{\text{Iodoethane}\\ \textit{(Ethyl iodide)}}}{CH_3-CH_2-I}$$

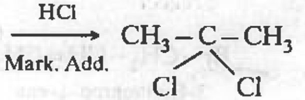
$$\underset{\substack{\text{Propene}\\ \textit{(Propylene)}}}{CH_3CH=CH_2} + HBr \xrightarrow[\text{Mark. addn.}]{\text{Absence of peroxide}}$$



$$\underset{\substack{\text{2-Bromopropane}\\ \textit{(Isopropyl bromide)}}}{CH_3-\underset{\displaystyle Br}{\underset{|}{C}H}-CH_3}$$



$$\underset{\text{Propyne}}{CH_3C\equiv CH} \xrightarrow[\text{Mark. Addn.}]{HCl} CH_3-\underset{\displaystyle Cl}{\underset{|}{C}}=CH_2$$



$$\xrightarrow[\text{Mark. Add.}]{HCl} \underset{\text{2, 2-Dichloropropane}}{CH_3-C(Cl)_2-CH_3}$$

The addition of hydrogen halides to an unsymmetrical alkene takes place according to **Markovnikov's rule**.

However, in presence of peroxides such as benzoyl peroxide ($C_6H_5CO-O-O-COC_6H_5$), the addition of HBr (but not of HCl or HI) to unsymmetrical alkenes takes place contrary to Markovnikov's rule. This is known as **Peroxide effect** or **Kharasch effect**. Thus,

$$\underset{\substack{\text{Propene}\\ \textit{(Propylene)}}}{CH_3CH{=}CH_2} + HBr \xrightarrow[\text{Anti-Mark. addn.}]{(C_6H_5COO)_2} \underset{\substack{\text{1-Bromopropane}\\ \textit{(n-Propyl bromide)}}}{CH_3CH_2-CH_2Br}$$

eP

Allylic halogenation. When alkenes (except ethylene) are heated with Cl_2 or Br_2 at a high temperature of about 773 K, the hydrogen atom at the allylic carbon (*i.e.* carbon atom next to the double bond) is substituted by a halogen atom forming allyl halides. For example,

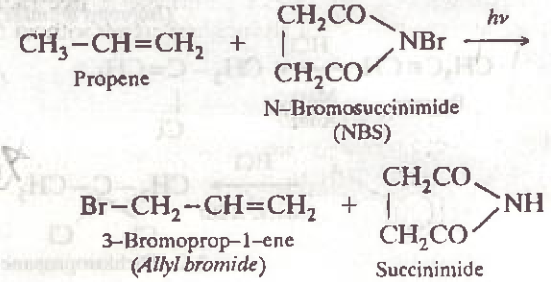
$$\underset{\text{Propene}}{CH_3-CH{=}CH_2} + Cl_2 \xrightarrow{773\text{ K}} \underset{\substack{\text{3-Chloroprop-1-ene}\\ \textit{(Allyl chloride)}}}{Cl-CH_2-CH=CH_2} + HCl$$

eP

$$\underset{\text{Propene}}{CH_3-CH{=}CH_2} + Br_2 \xrightarrow{773\text{ K}} \underset{\text{3-Bromoprop-1-ene}}{Br-CH_2-CH{=}CH_2} + HBr$$

Such reactions in which halogenation occurs at the allylic position of an alkene are called **allylic halogenation** *reactions*.

However, *a more specific reagent for allylic bromination is* **N-bromosuccinimide** (**NBS**). Thus, when propene is treated with NBS in presence of light, bromination occurs at the methyl group giving a good yield of 3-bromo-prop-1-ene.



$$\underset{\text{Propene}}{CH_3-CH{=}CH_2} + \underset{\substack{\text{N-Bromosuccinimide}\\ \text{(NBS)}}}{\begin{matrix}CH_2CO\\ |\\ CH_2CO\end{matrix}\!\!>\!NBr} \xrightarrow{h\nu} \underset{\substack{\text{3-Bromoprop-1-ene}\\ \textit{(Allyl bromide)}}}{Br-CH_2-CH{=}CH_2} + \underset{\text{Succinimide}}{\begin{matrix}CH_2CO\\ |\\ CH_2CO\end{matrix}\!\!>\!NH}$$

eP

Allylic chlorination can also be carried out by treating an alkene with sulphuryl chloride (SO_2Cl_2) at 475 K in presence of light and traces of organic peroxides. Thus

$$\underset{\text{Propene}}{CH_3-CH=CH_2} + SO_2Cl_2 \xrightarrow[\text{traces of peroxides}]{475\text{ K}, h\nu} \underset{\text{3-Chloroprop-1-ene}}{Cl-CH_2-CH=CH_2} + SO_2 + HCl$$

(b) From alkanes. Halogenation of alkanes with Cl_2 or Br_2 in presence of heat or light usually gives a complex mixture of mono-, di- and polyhaloalkanes. For example, chlorination of methane gives four products, *i.e.*,

$$\underset{\text{Methane}}{CH_4} \xrightarrow[h\nu \text{ or } 520-670\text{ K}]{Cl_2} \underset{\text{Chloromethane}}{CH_3Cl} + \underset{\text{Dichloromethane}}{CH_2Cl_2} + \underset{\substack{\text{Trichloro-}\\ \text{methane}}}{CHCl_3} + \underset{\substack{\text{Tetrachloro-}\\ \text{methane}}}{CCl_4}$$

Although substitution beyond monohalogenation can largely be suppressed by controlling the ratio of halogen to alkane yet this method is not of much practical use in the laboratory since the boiling points of these haloalkanes are quite close and hence cannot be easily separated. However, in industry, such complex mixtures can be easily separated using long fractionating columns.

In case of higher alkanes, even monohalogenation gives a mixture of all the possible isomeric haloalkanes indicating thereby that all types of hydrogens whether 1°, 2° or 3° are substituted by the halogen atom. For example,

$$\underset{\text{Propane}}{CH_3-CH_2-CH_3} \xrightarrow[298\text{ K}]{Cl_2,\, h\nu} \underset{\text{1-Chloropropane (45\%)}}{CH_3-CH_2-CH_2-Cl} + \underset{\text{2-Chloropropane (55\%)}}{CH_3-CHCl-CH_3}$$

$$\underset{\text{Butane}}{CH_3CH_2CH_2CH_3} \xrightarrow[298\text{ K}]{Cl_2,\, h\nu} \underset{\text{1-Chlorobutane (28\%)}}{CH_3CH_2CH_2CH_2Cl} + \underset{\text{2-Chlorobutane (72\%)}}{CH_3CH_2-CHCl-CH_3}$$

The relative amounts of these isomeric haloalkanes, however, depend upon the nature of the halogen (Cl_2 or Br_2) and the number and type of hydrogen (1°, 2° or 3°) being substituted. In general, the ease of substitution of various hydrogens follows the sequence : *3° > 2° > 1°* but their relative rates vary with the nature of halogen. For example, with Cl_2, the relative rate of substitution of 3°, 2° and 1° hydrogens at 298 K is 5 : 3·8 : 1 while with Br_2, it is 1600 : 82 : 1 at 400 K.

Iodination is reversible, but it may be carried out in the presence of an oxidising agent, such as HIO_3, HNO_3, HgO, etc. which destroys the HI as it is formed and thus drives the reaction in the forward direction, *e.g.*,

$$CH_4 + I_2 \rightleftharpoons CH_3I + HI$$

OA

$$5\,HI + HIO_3 \longrightarrow 3\,I_2 + 3\,H_2O$$

Flourination of hydrocarbons with pure F_2 gas occurs explosively. This is partly due to low bond dissociation energy of F_2 molecule (150·6 kJ mol^{-1}) and partly due to strongly exothermic nature of one of the termination steps (*i.e.*, $R\cdot + F\cdot \longrightarrow RF$). This step is so exothermic (447·7 kJ mol^{-1}) that the energy released is larger than that required to break a C – C bond (347·3 kJ mol^{-1}), thereby resulting in fission of the molecule. However direct fluorination of hydrocarbons may be carried out successfully by diluting F_2 with an inert gas such as N_2 or Ar. Alternatively, alkyl fluorides are more conveniently prepared indirectly by heating suitable chloro or bromo alkanes with inorganic fluorides, such as AsF_3, SbF_3, CoF_3, AgF, Hg_2F_2 etc. For example,

$$CH_3Br + AgF \longrightarrow CH_3F + AgBr$$

Bromomethane Fluromethane

$$2\,CH_3CH_2-Cl + Hg_2F_2 \longrightarrow 2\,CH_3CH_2-F + Hg_2Cl_2$$

Chloroethane Fluoroethane

This reaction is called Swarts reaction.

When the organic halide contains two or three halogen atoms at the same carbon, CoF_3 or the more easily available SbF_3 is used. For example,

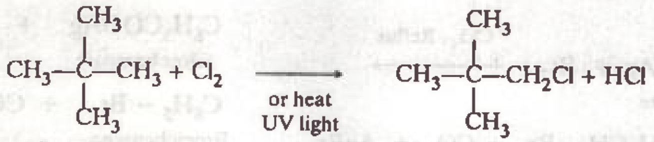
$$3CH_3-CCl_2-CH_3 + 2SbF_3 \longrightarrow 3CH_3-CF_2-CH_3 + 2SbCl_3$$

2, 2–Dichloropropane 2, 2–Difluoropropane

ADD TO YOUR KNOWLEDGE

Although free radical halogenation of alkanes is not suitable for the laboratory preparation of pure haloalkanes, it is still useful in certain cases :

1. **When the structure of the alkane is such that formation of isomeric products is not possible. For example,**



$$(CH_3)_3C-CH_3 + Cl_2 \xrightarrow[\text{UV light}]{\text{or heat}} (CH_3)_3C-CH_2Cl + HCl$$

Neopentane Neopentyl chloride

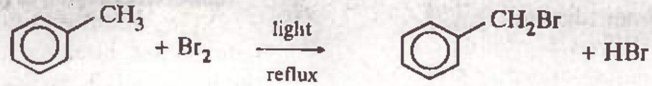
2. **When the difference in reactivity of hydrogens attached to different types of carbon atoms is so large that only one product is formed under given conditions. The reactivity of different types of hydrogens follows the order :**

benzylic ≈ allylic > tertiary > secondary > primary > vinylic ≈ aryl

Actually vinylic and aryl hydrogens are so much unreactive that they do not participate in free radical halogenations. However, allylic and benzylic halides can be prepared from alkenes and arenes without any complication,

$$CH_2=CH-CH_3 + Cl_2 \xrightarrow[\text{gas phase}]{773-873\text{ K}} CH_2=CH-CH_2Cl$$

Propene 3–Chloroprop–1–ene



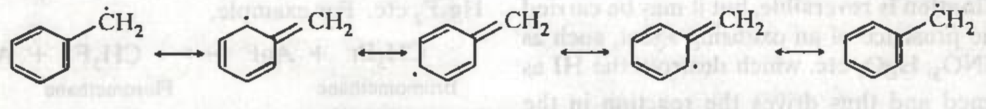
Toluene Benzyl bromide

ADD TO YOUR KNOWLEDGE CONTD.

The high reactivity of allylic and benzylic hydrogen atoms is due to resonance stabilization of allylic and benzylic free radical intermediates formed during the reaction.

$$CH_2 = CH—\dot{C}H_2 \longleftrightarrow \dot{C}H_2—CH = CH_2$$

Resonance stabilization of allyl radical



Resonance stabilization of benzyl radical.

3. By halide exchange. Iodoalkanes can be easily prepared from the corresponding chloroalkanes or bromoalkanes by heating with sodium iodide in acetone or methanol.

$$\underset{\text{Bromoethane}}{CH_3CH_2-Br} + NaI \xrightarrow{\text{Acetone, }\Delta} \underset{\text{Iodoethane}}{CH_3CH_2-I} + NaBr$$

This reaction is called **Finkelstein reaction** and is based upon the fact that NaBr being less soluble than NaI in acetone or methanol gets deposited during the course of the reaction. As a result, the equilibrium shifts in the forward direction.

4. From silver salt of fatty acids. Bromoalkanes can be easily prepared by refluxing the silver salt of a fatty acid with bromine in carbon tetrachloride.

$$\underset{\text{Silver propanoate}}{CH_3CH_2COOAg} + Br_2 \xrightarrow{CCl_4\text{, Reflux}} \underset{\text{Bromoethane}}{CH_3CH_2-Br} + CO_2 + AgBr$$

This reaction is called **Borodine Hundsdiecker reaction** or simply **Hunsdiecker reaction** and is believed to occur by a **free radical mechanism.**

The yield of the alkyl halide is *primary* > *secondary* > *tertiary*. Chloroalkanes can also be prepared by this method by using Cl_2 instead of Br_2 but the yields are poor. With I_2, silver salts give esters instead of iodoalkanes.

$$2\,RCOOAg + I_2 \xrightarrow{CCl_4\text{, Reflux}} RCOOR + CO_2 + 2\,AgI$$

This is known as **Birnbaum-Simonini reaction.**

Besides alkyl bromides, aryl bromides can also be prepared by this reaction.

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

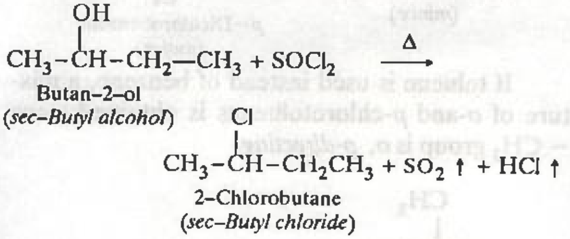
PROBLEMS FOR PRACTICE

1. Write IUPAC names of all isomers and one method of preparation of sec-butyl chloride. *(A.I.S.B. 1989)*
2. Suggest one convenient method for the synthesis of the following
   (*i*) 1-Iodobutane from 1-butene
   (*ii*) *sec*-Propyl bromide from isobutyric acid
   (*iii*) Fluoroethane from ethanol.
3. Identify all the possible monochloro structural isomers that would be expected to form on free radical chlorination of $(CH_3)_2CHCH_2CH_3$.

ANSWERS

1. Four isomers are possible. Their structures and IUPAC names are given on page 17/4.

sec-Butyl chloride may be prepared by the action of $SOCl_2$ or PCl_5 or PCl_3 on sec-butyl alcohol.

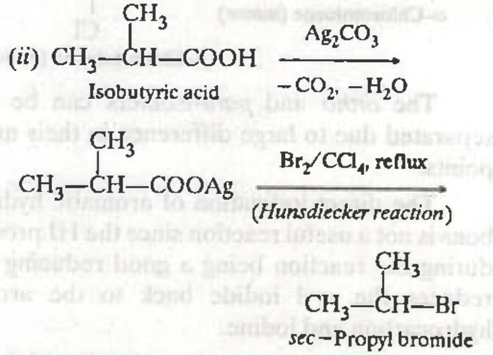


$$CH_3-\overset{\overset{OH}{|}}{C}H-CH_2-CH_3 + SOCl_2 \xrightarrow{\Delta} CH_3-\overset{\overset{Cl}{|}}{C}H-CH_2CH_3 + SO_2\uparrow + HCl\uparrow$$

Butan-2-ol (*sec-Butyl alcohol*) → 2-Chlorobutane (*sec-Butyl chloride*)

2. (*i*) $CH_3CH_2CH=CH_2 \xrightarrow[\text{(Ant. mark. addn.)}]{\text{HBr, peroxide}}$
1-Butene

$CH_3CH_2CH_2CH_2-Br \xrightarrow[\text{(Finkelstein reaction)}]{\text{NaI/acetone, }\Delta} CH_3CH_2CH_2CH_2-I$
1-Bromobutane → 1-Iodobutane



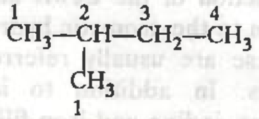
$$\text{(ii) } CH_3-\overset{\overset{CH_3}{|}}{C}H-COOH \xrightarrow[-CO_2,\ -H_2O]{Ag_2CO_3} CH_3-\overset{\overset{CH_3}{|}}{C}H-COOAg \xrightarrow[\text{(Hunsdiecker reaction)}]{Br_2/CCl_4,\ \text{reflux}} CH_3-\overset{\overset{CH_3}{|}}{C}H-Br$$

Isobutyric acid → *sec*-Propyl bromide

(*iii*) $CH_3CH_2OH \xrightarrow[-SO_2,\ -HCl]{SOCl_2} CH_3CH_2Cl$
Ethanol → Chloroethane

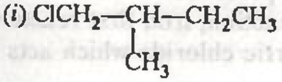
$\xrightarrow[-Hg_2Cl_2]{Hg_2F_2,\ \Delta} CH_3CH_2F$
Fluoroethane

3. In the given compound, there are four different types of hydrogen atoms as shown below :

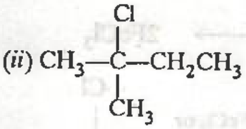


$$\overset{1}{CH_3}-\underset{\underset{\underset{1}{CH_3}}{|}}{\overset{2}{CH}}-\overset{3}{CH_2}-\overset{4}{CH_3}$$

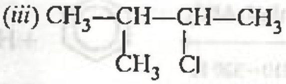
The replacement of each of these hydrogen atoms will give the following four monochloro derivatives.



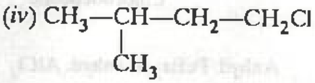
(*i*) $ClCH_2-\underset{\underset{CH_3}{|}}{CH}-CH_2CH_3$



(*ii*) $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{Cl}{|}}{C}}-CH_2CH_3$



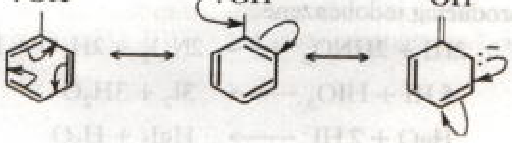
(*iii*) $CH_3-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{Cl}{|}}{CH}-CH_3$

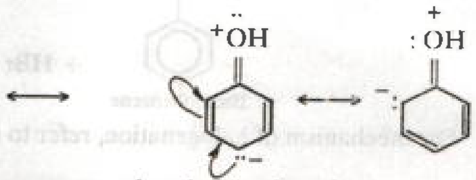


(*iv*) $CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_2Cl$

17.6. Preparation of Haloarenes

We have discussed above that haloalkanes can be easily prepared from alcohols by replacement of the OH group by the halogen atom. In contrast, haloarenes or aryl halides cannot be prepared from phenols because it is difficult to replace the hydroxyl group of phenols by a halogen atom. This is due to the reason that because of resonance, the carbon-oxygen bond in phenols has partial double bond character, and is, therefore, stronger than carbon-oxygen single bond in alcohols. Consequently, cleavage of carbon-oxygen bond in phenols is difficult under ordinary conditions. Therefore, these are usually prepared by the following methods :

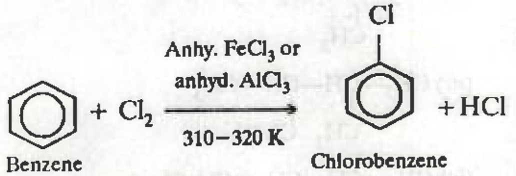


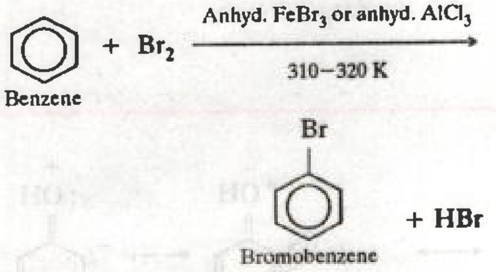


1. From aromatic hydrocarbons – by direct halogenation.

(*a*) **Nuclear halogenation.** Chloroarenes (aryl chlorides) and bromoarenes (aryl bromides) can be easily prepared by direct chlorination or bromination of aromatic hydrocarbons. *The reaction is usually carried out at a low temperature (310-320 K), in the absence of sunlight and in the presence of a Lewis acid such as anhydrous ferric or aluminium halide as catalyst*. The function of the Lewis acids is to carry the halogen to the aromatic hydrocarbon. That is why these are usually referred to as **halogen carriers**. In addition to iron and aluminium halides, iodine and iron filings have also been used as halogen carriers. Thus, chlorobenzene is formed when benzene is treated with chlorine in the presence of iron. Under the conditions of the reaction, iron first reacts with chlorine to form ferric chloride which acts as a catalyst.

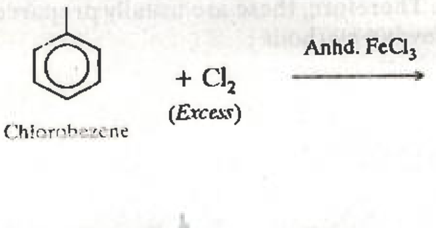
$$2Fe + 3Cl_2 \longrightarrow 2FeCl_3$$

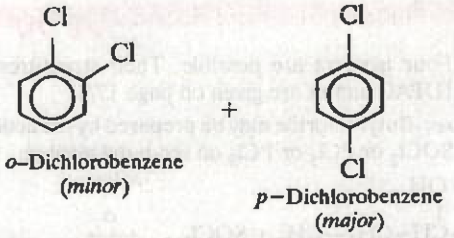




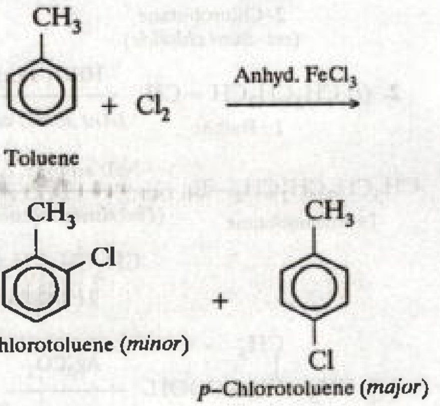
For mechanism of halogenation, refer to unit 15.

If excess of halogen is used – a second halogen is introduced in the ring mainly at *o*- and *p*-positions *w.r.t.* to the first since halogens are *o, p- directing*.



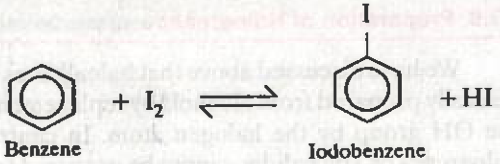


If toluene is used instead of benzene, a mixture of *o*-and *p*-chlorotoluenes is obtained since – CH_3 group is *o, p-directing.*



The *ortho* and *para*-isomers can be easily separated due to large difference in their melting points.

The direct iodination of aromatic hydrocarbons is not a useful reaction since the HI produced during the reaction being a good reducing agent reduces the aryl iodide back to the aromatic hydrocarbon and iodine.



However, in the presence of oxidising agents such as nitric acid, iodic acid (HIO_3), mercuric oxide etc. the HI produced is either oxidised to iodine or is eliminated as mercuric iodide and thus the reaction proceeds in the forward direction producing iodobenzene.

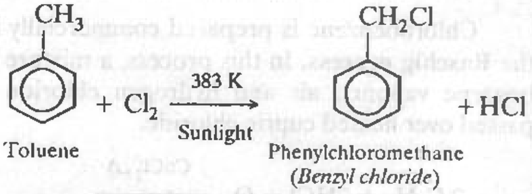
$$2HI + 2HNO_3 \longrightarrow 2NO_2 + 2H_2O + I_2$$

$$5\,HI + HIO_3 \longrightarrow 3I_2 + 3H_2O$$

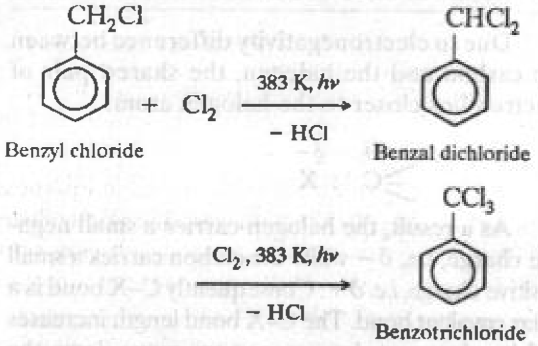
$$HgO + 2\,HI \longrightarrow HgI_2 + H_2O$$

Fluoroarenes (aryl fluorides), however, cannot be prepared by direct fluorination of aromatic hydrocarbons since the reaction is very violent and cannot be easily controlled.

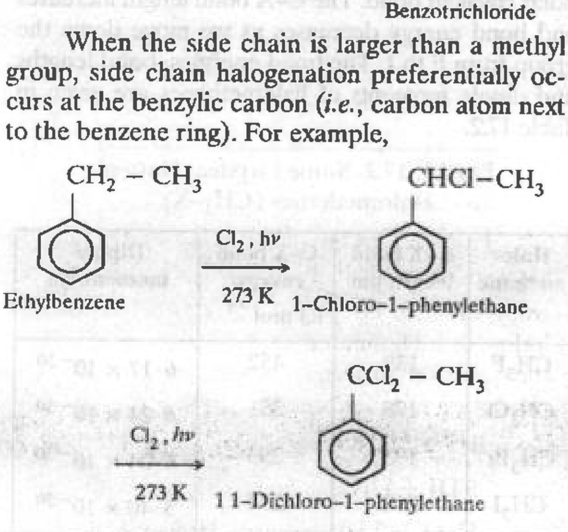
(*b*) **Side chain halogenation.** The most convenient method for the preparation of side chain substituted aryl halides or aralkyl halides is by the direct halogenation of a suitable hydrocarbon. For example, when Cl_2 is passed through boiling toluene in the presence of sunlight and absence of halogen carrier, phenylchloromethane (benzyl chloride) is formed.



If Cl_2 is passed for a longer time, the initially formed benzyl chloride reacts further to form first benzal dichloride and then benzotrichloride.



When the side chain is larger than a methyl group, side chain halogenation preferentially occurs at the benzylic carbon (*i.e.*, carbon atom next to the benzene ring). For example,



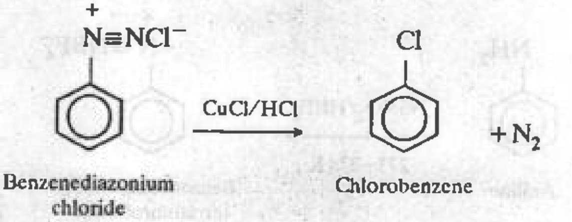
Instead of Cl_2, sulphuryl chloride (SO_2Cl_2) at 475 K in presence of light and traces of peroxide can also be used for side chain halogenation of arenes. For example,

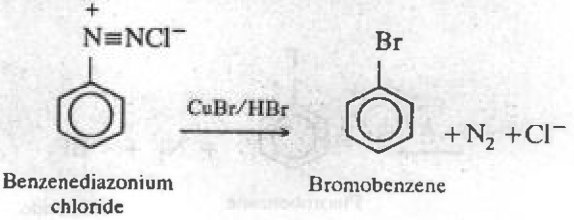
$$\underset{\text{Toluene}}{C_6H_5CH_3} + SO_2Cl_2 \xrightarrow[\text{traces of peroxide}]{475\text{ K}, h\nu} \underset{\text{Benzyl chloride}}{C_6H_5-CH_2Cl} + SO_2\uparrow + HCl\uparrow$$

Unlike nuclear halogenation which occurs through the intermediate formation of carbocations, side chain halogenation occurs through the intermediate formation of free radicals. *Thus side chain halogenation like halogenation of alkanes is a free-radical substitution reaction.*

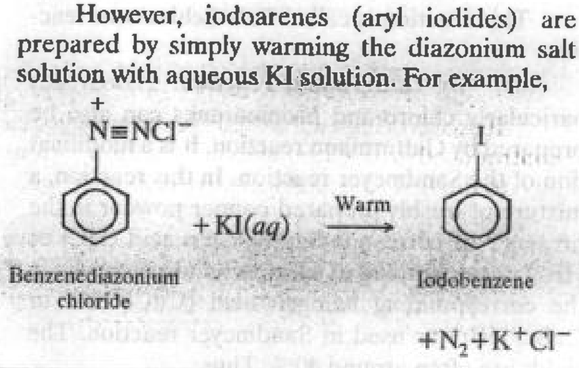
2. From diazonium salts.

(*i*) **By Sandmeyer reaction.** Chloroarenes (aryl chlorides) and bromoarenes (aryl bromides) are easily prepared when the diazonium salts are treated with CuCl dissolved in HCl or CuBr dissolved in HBr. This reaction is called **Sandmeyer reaction.***





However, iodoarenes (aryl iodides) are prepared by simply warming the diazonium salt solution with aqueous KI solution. For example,



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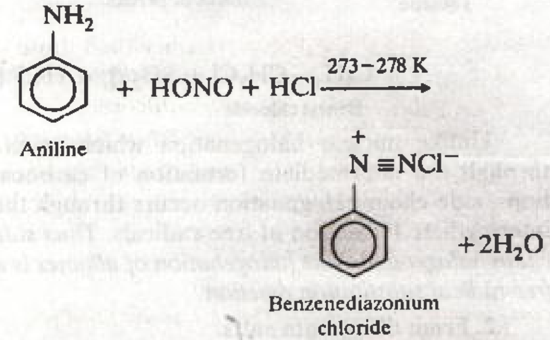
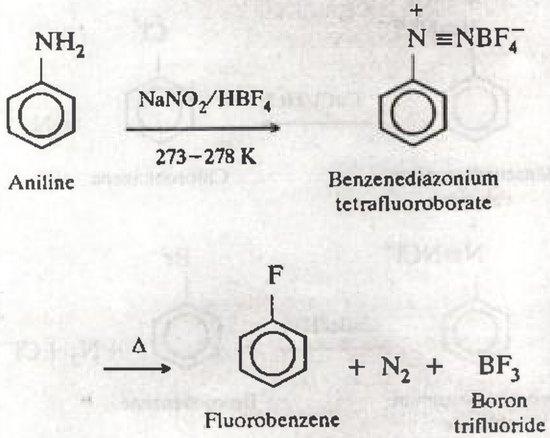
*In Sandmeyer reaction, it is the halogen attached to copper which enters the benzene ring.

Benzenediazonium chloride needed for this purpose is obtained by treating aniline dissolved in dil. HCl with an aqueous solution of sodium nitrite at 273-278 K. (0°– 5°C).

$$\underset{\text{Sod. nitrite}}{NaNO_2} + HCl\,(dil.) \longrightarrow \underset{\text{Nitrous acid}}{HONO} + NaCl$$

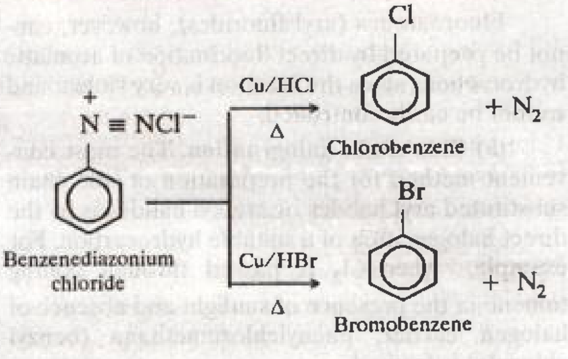


Fluoroarenes (aryl fluorides) are prepared by heating the corresponding diazonium tetrafluoroborates which, in turn, are obtained by the diazotisation of a suitable aromtic primary amine with aq. $NaNO_2$ in presence of fluoroboric acid (HBF_4) at 273 – 278 K.



This reaction is called **Balz-Schiemann** reaction.

(*ii*) **By Gattermann reaction.** Haloarenes paricularly chloro-and bromoarenes can also be prepared by Gattermann reaction. It is a modification of the Sandmeyer reaction. In this reaction, a mixture of freshly prepared copper powder in the presence of corresponding halogen acid (HCl or HBr) is used instead of cuprous halide dissolved in the corresponding halogen acid (CuCl/HCl or CuBr/HBr) as used in Sandmeyer reaction. The yields are often around 40%. Thus,



Commercial preparation of chlorobenzene.

Chlorobenzene is prepared commercially by the **Raschig process.** In this process, a mixture of benzene vapours, air and hydrogen chloride is passed over heated cupric chloride.

$$2\,C_6H_6 + 2HCl + O_2 \xrightarrow{CuCl_2,\,\Delta} 2\,C_6H_5Cl + 2H_2O$$

17.7. Nature of the C–X Bond

Due to electronegativity difference between the carbon and the halogen, the shared pair of electron lies closer to the halogen atom.

$$\overset{\delta+}{>C} : \overset{\delta-}{X}$$

As a result, the halogen carries a small negative charge, *i.e.*, $\delta-$ while the carbon carries a small positive charge, *i.e.* $\delta+$. Consequently C–X bond is a polar covalent bond. The C–X bond length increases and bond energy decreases as we move down the group from F to I. The bond energies, bond lengths and dipole moments of halomethanes are given in Table 17.2.

TABLE 17.2. Some Physical Data of Halomethanes (CH_3–X)

Halo-methane	C–X bond length/pm	C–X bond energy/ kJ mol^{-1}	Dipole moment/cm
CH_3F	139	452	$6{\cdot}17 \times 10^{-30}$
CH_3Cl	178	351	$6{\cdot}24 \times 10^{-30}$
CH_3Br	193	293	$6{\cdot}04 \times 10^{-30}$
CH_3I	214	234	$5{\cdot}40 \times 10^{-30}$

17.8. Physical Properties of Haloalkanes and Haloarenes

Some important physical properties of haloalkanes and haloarenes are discussed below :

1. Physical state, colour, odour etc. Alkyl halides are colourless when pure, but bromides particularly iodides develop colour when exposed to light. Methyl chloride, methyl bromide, ethyl chloride and some chlorofluoromethanes and chlorofluoroethanes are gases at room temperatures. Other chloro, bromo, iodo compounds are either liquids or solids. Many volatile halogen compounds have sweet smell.

2. Melting points and boiling points

(*a*) Haloalkanes. (*i*) The molecular masses of haloalkanes (alkyl halides) are higher than those of parent alkanes. As a result, the *melting points and boiling points of haloalkanes are several degrees higher than those of parent alkanes mainly due to greater magnitude of van der Waals forces of attraction.*

(*ii*) *For the same alkyl group, the boiling points of haloalkanes decrease in the order : RI > RBr > RCl > RF.* This is because with the increase in the size and mass of the halogen, the magnitude of the *van der Waals forces of attraction increases*. Thus,

Compound :	CH_3I	CH_3Br	CH_3Cl	CH_3F	CH_4
b.p. (K) :	315	277	249	195	111

(*iii*) *For the same halogen atom, the boiling points increase with increase in the size of the alkyl group.* Thus,

Haloalkane :	CH_3Cl	CH_3CH_2Cl	$CH_3(CH_2)_2Cl$	$CH_3(CH_2)_3Cl$
b.p. (K) :	249	285·5	320	351·5

(*iv*) *For isomeric alkyl halides, the boiling points decrease with branching.* This is due to the reason that with branching the surface area of the alkyl halide decreases and hence the magnitude of the van der Waals' forces of attraction decreases. Thus,

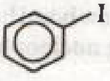
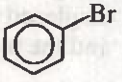
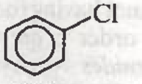
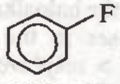
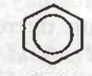
Haloalkane :	$CH_3(CH_2)_3Cl$	$(CH_3)_2CHCH_2Cl$	$CH_3CH_2CHClCH_3$	$(CH_3)_3C-Cl$
b.p. (K) :	351·5	342	341	324

(*v*) *Generally, the boiling points of chloro, bromo and iodo compounds increase as the number of halogen atoms increases.* For example,

Haloalkane :	CH_3Cl	CH_2Cl_2	$CHCl_3$	CCl_4
b.p. (K) :	249	313	334	350

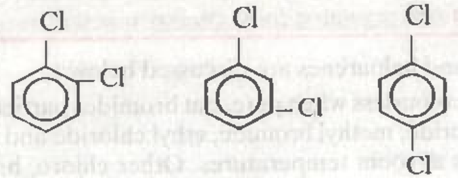
(*b*) Haloarenes. (*i*) *The melting and boiling points of haloarenes are nearly the same as those of haloalkanes with the same number of carbon atoms.*

(*ii*) *For the same aryl group, the melting and boiling points increase as the size of the halogen atom increases, i.e., iodoarenes > bromoarenes > chloroarenes > fluoroarenes > arene*. Thus,

Haloalkane :					
b.p. (K) :	462	429	405	358	353

(*iii*) *For the same halogen atom, the melting and boiling points increase as the size of the aryl group increases.*

(*iv*) *The boiling points of isomeric dihalobenzenes are nearly the same but their melting points are quite different.* Generally, the melting point of the *p*-isomer is always higher than that of the *o*- or the *m*-isomer. *This is due to the reason that the p-isomer is more symmetrical and hence its molecules pack closely in the crystal lattice.* As a result, intermolecular forces of attraction are stronger and hence the *p*-isomer melts at a higher temperature than the corresponding *o*-and *m*-isomers. For example,



b.p.	453 K	446 K	448 K
m.p.	256 K	249 K	325 K

2. Solubility. Even though haloalkanes (dipole moment, 2.05 – 2.15 D) and haloarenes (dipole moment, 1.6 – 1.8 D) are polar molecules still they are insoluble in water. This is due to the reason that *haloalkanes and haloarenes can neither form hydrogen bonds with water nor can they break the hydrogen bonds already existing between water molecules.* However, they are quite soluble in organic solvents of low polarity such as petroleum ether, benzene, ether, chloroform, carbon tetra-chloride etc. since the intermolecular forces in these halo compounds are similar to those in the above solvents.

3. Density. Alkyl fluorides and chlorides are generally lighter than water whereas alkyl bromides and iodides are heavier. Their relative densities follow the order : RI > RBr > RCl.

Among the alkyl halides, methyl iodide has the highest density. However, as the size of the alkyl group increases, the densities of alkyl halides go on decreasing.

Further the density increases with increasing number and atomic mass of the halogen.

	CH_2Cl_2	$CHCl_3$	CCl_4
Density (g/ml)	1·336	1·489	1·595

All aryl halides are, however, heavier than water.

4. Stability. Since the strength of the C – X bond decreases in the order : C – F > C – Cl > C – Br > C – I, therefore, stability of the haloalkanes having the same alkyl group decreases in the order : *alkyl fluorides > alkyl chlorides > alkyl bromides > alkyl iodides*. That is why alkyl iodides, on standing become violet or brown because of their decomposition in presence of light to give iodine.

$$2\,R-I \xrightarrow{\text{Light}} R-R+I_2$$

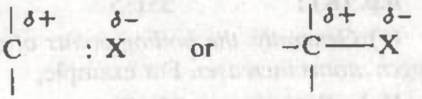
Same stability trends are observed for haloarenes. Further, because of higher stability and easy availability, the most commonly used solvents in industry are *organic chlorides rather than bromides and iodides.*

5. Inflammability. Organic halogen compounds are less inflammable than the corresponding hydrocarbons. The inflammability, however, decreases with increasing halogen content. Since organic halogen compounds are good solvents for fats and oils and also do not catch fire easily, polychloro compounds such as tri and tetrachloroethylenes are widely used as solvents for dry cleaning. Carbon tetrachloride is used as a fire extinguisher under the name *'pyrene'*.

17.9. Chemical Properties of Haloalkanes

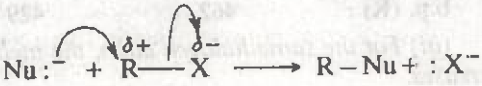
Haloalkanes or alkyl halides are highly reactive compounds due to the presence of a polar carbon-halogen bond in their molecules. They undergo a number of important reactions such as nucleophilic substitution, elimination, halogenation, formation of organometallic reagents such as Grignard reagents etc. It is because of this reason that haloalkanes are considered to be one of the most valuable synthetic reagents in organic chemistry. Some of the important reactions of haloalkanes are discussed below :

1. Nucleophilic substitution reactions. The halogen atom in haloalkanes (alkyl halides) is more electronegative than the carbon atom attached to it. As a result, carbon atom acquires a partial positive charge and the halogen atom a partial negative charge.



$$-\overset{|}{\underset{|}{C}}{}^{\delta+}\;:\overset{\delta-}{X} \quad \text{or} \quad -\overset{|}{\underset{|}{C}}{}^{\delta+}\!-\!\overset{\delta-}{X}$$

The presence of this small positive charge on the carbon atom makes it susceptible to attack by nucleophilic reagents (*i.e.* reagents possessing a lone pair of electrons). Thus, when a nucleophile stronger than the halide ion approaches the positively charged carbon atom of an alkyl halide, the halogen atom with its bonding pair of electrons is displaced and a new bond between the carbon atom and the incoming nucleophile is formed :



$$Nu:^- + \overset{\delta+}{R}-\overset{\delta-}{X} \longrightarrow R-Nu + :X^-$$

Such reactions in which a stronger nucleophile displaces a weaker nucleophile are called **nucleophilic substitution reactions** *and the atom or group (halide ion in the present case) which departs with its bonding pair of electrons is called the* **leaving group.** *Better the leaving group, more facile is the nucleophilic substitution reaction.* Amongst the halide ions, the order in which the leaving groups depart follows the sequence :

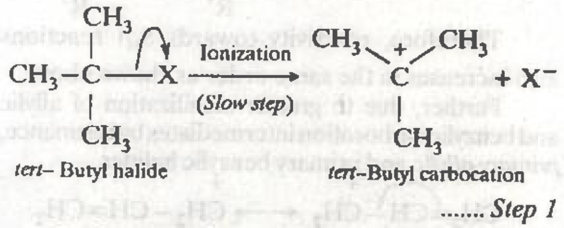
$I^- > Br^- > Cl^- > F^-$. It is because of this reason that the order of reactivity of haloalkanes follows the sequence : *iodoalkanes > bromoalkanes > chloroalkanes > fluoroalkanes*.

Types of Nucleophilic Substitution reactions. There are two types of nucleophilic substitution reactions. These are :

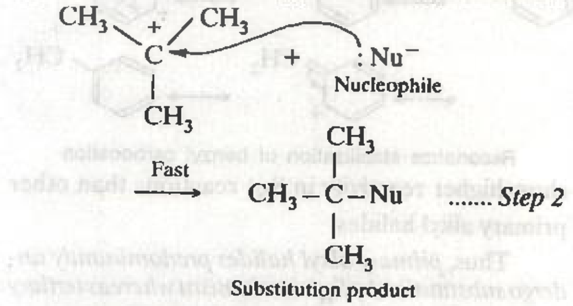
(*i*) S_N1 (*Substitution, nucleophilic, unimolecular*)

(*ii*) S_N2 (*Substitution, nucleophilic, bimolecular*)

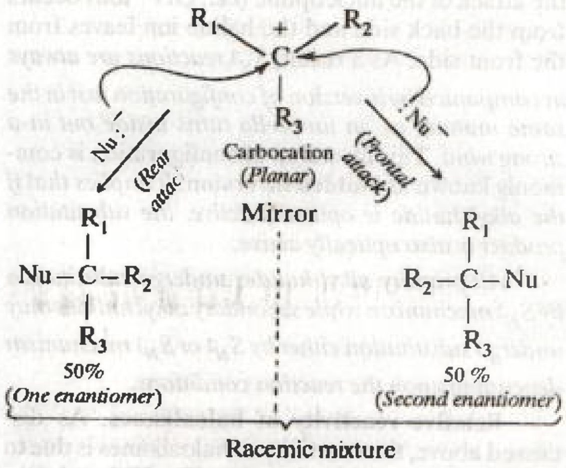
(*i*) S_N1 reactions. The rate of S_N1 reactions depends only upon the concentration of the alkyl halide and is independent of the concentration of the nucleophile *i.e.*, Rate = k [RX]. This rate law suggests that the reaction occurs in *two-steps*. In the first step, the alkyl halide undergoes ionization to produce a carbocation. *This step is slow and hence is the rate-determining step of the reaction.*



In the second step, the carbocation being a reactive chemical species, immedialety reacts with the nucleophile to give the substitution product. *This step is fast and hence does not affect the rate of the reaction.*



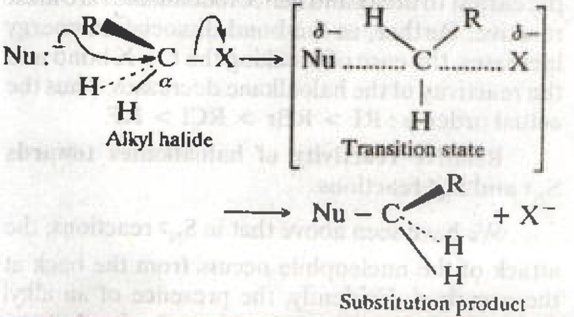
If the alkyl halide is optically active, then the product is a racemic mixture.* This is due to the reason that carbocations are planar species. Therefore, the attack of the nucleophile on it can occur from both the faces (front and rear) with almost equal ease giving a 50 : 50 mixture of the two enantiomers.



All tertiary alkyl halides undergo substitution by S_N1 mechanism.

S_N1 reactions are facilitated by polar protic (hydroxylic) solvents such as water, alcohols, formic acid, acetic acid, aqueous organic solvents etc. since these solvents promote ionization by stabilizating the ions by solvation.

(*ii*) S_N2 reactions. The rate of S_N2 reactions depends upon the concentration of both the alkyl halide as well as the nucleophile *i.e.* Rate = k [RX] [$Nu:^-$]. This implies that both the alkyl halide and the nucleophile are taking part simultaneously in the rate-determining step of the reaction. In other words, *S_N2 reactions are concerted reactions, i.e., they occur in one-step.* Such reactions occur through a *transition state* in which both the reactant molecules are partially bonded to each other as shown below :



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*Ordinary light has vibrations in all the planes. When it is passed through **Nicol prism** (made from a particular crystalline form of $CaCO_3$ known as calcite), the emergent light has vibrations only in one plane. This is called **plane-polarized light**. Substances which rotate the plane polarized light either towards right or left are called **optically active**. Those which rotate the plane-polarized light towards right are called **dextrorotatory** and are represented by the algebraic sign (+) and those which rotate the plane polarized light towards left are called **laevorotatory** and are represented by the algebraic sign (–). The optical isomers which are non-superimposable mirror images of each other are called **enantiomers**. Enantiomers have identical physical and chemical properties but rotate the plane of polarized light in opposite directions but to the same extent. A 50 : 50 mixture of two enantiomers is optically inactive and is called a **racemic mixture**. It is represented by the sign (±).

It is interesting to note that in S_N2 reactions, the attack of the nucleophile (*i.e.*, OH^- ion) occurs from the back side and the halide ion leaves from the front side. As a result, *S_N2 reactions are always accompanied by inversion of configuration just in the same manner as an umbrella turns inside out in a strong wind*. This inversion of configuration is commonly known as **Walden inversion.** *It implies that if the alkyl halide is optically active, the substitution product is also optically active.*

All primary alkyl halides undergo substitution by S_N2 mechanism while secondary alkyl halides may undergo substitution either by S_N2 or S_N1 mechanism depending upon the reaction conditions.

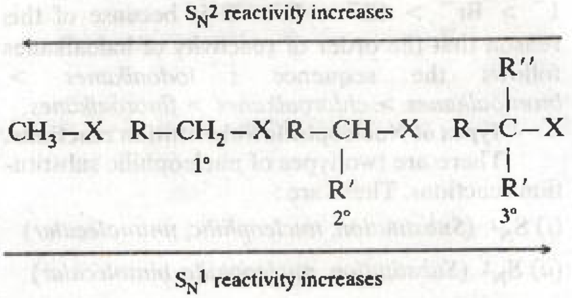
Relative reactivity of haloalkanes. As discussed above, the reactivity of haloalkanes is due to polarity of the carbon- halogen (C–X) bond. Obviously at the first sight, it appears that *greater the polarity of the C–X bond, more reactive should be the haloalkane.* Now polarity of the C–X bond in methyl halides decreases in the order.

$$\underset{1.94\text{ D}}{CH_3-Cl} > \underset{1.82\text{ D}}{CH_3-F} > \underset{1.79\text{ D}}{CH_3-Br} > \underset{1.64\text{ D}}{CH_3-I}$$

therefore, the reactivity of the haloalkanes should also decrease in the same order, *i.e.*, RCl > RF > RBr > RI. However the actual order is : RI > RBr > RCl > RF. This can be explained in terms of the bond dissociation energies of the C–X bond : 452 (CH_3-F), 351 (CH_3-Cl), 293 (CH_3-Br) and 234 (CH_3-I) kJ mol^{-1}. Thus, C–I has the minimum bond dissociation energy while C–F has the maximum. Therefore, C–I bond is the easiest to break and hence iodoalkanes are most reactive. Further, as the bond dissociation energy increases, the ease of breaking the C–X bond and the reactivity of the haloalkane decreases. Thus the actual order is : RI > RBr > RCl > RF.

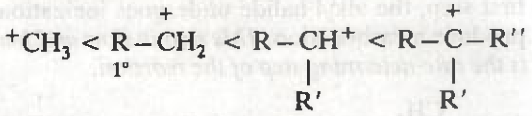
Relative reactivity of haloalkanes towards S_N1 and S_N2 reactions.

We have seen above that in S_N2 reactions, the attack of the nucleophile occurs from the back at the α-carbon. Evidently, the presence of an alkyl group at the α-carbon, being bigger in size than the hydrogen atom, tends to hinder or block the approach of nucleophile to this carbon due to **steric hindrance** and thus makes the reaction difficult to occur. As a result, as the number of alkyl groups increases at the α-carbon, the S_N2 reaction becomes more and more difficult. Thus



$$CH_3-X \quad \underset{1^\circ}{R-CH_2-X} \quad \underset{2^\circ}{R-\underset{R'}{\underset{|}{CH}}-X} \quad \underset{3^\circ}{R-\underset{R'}{\underset{|}{\overset{R''}{\overset{|}{C}}}}-X}$$

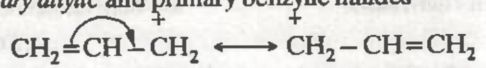
In contrast, in S_N1 reactions, carbocations are the intermediates. Thus, the more stable the carbocation, the more easily it is formed, more facile is the reaction. Since the order of stability of the carbocations follows the order :



$$^+CH_3 < \underset{1^\circ}{R-\overset{+}{C}H_2} < R-\underset{R'}{\underset{|}{CH^+}} < R-\underset{R'}{\underset{|}{\overset{+}{C}}}-R''$$

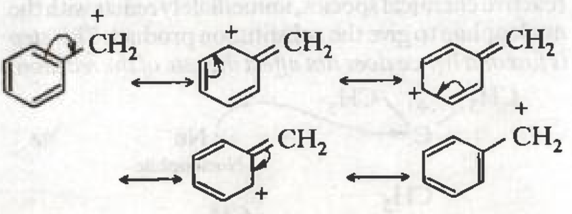
Therefore, reactivity towards S_N1 reactions also increases in the same order as shown above.

Further, due to greater stabilization of allylic and benzylic carbocation intermediates by resonance, *primary allylic* and primary benzylic halides show higher reactivity in S_N1 reactions than other primary alkyl halides.



$$CH_2=CH-\overset{+}{C}H_2 \longleftrightarrow \overset{+}{C}H_2-CH=CH_2$$

Resonance stabilization of allyl carbocation



Resonance stabilization of benzyl carbocation

Thus, *primary alkyl halides predominantly undergo substitution by S_N2 mechanism whereas tertiary alkyl halides react predominantly by S_N1 mechanism. Secondary alkyl, primary allylic and primary benzylic halides may react predominantly either by S_N1 or S_N2 mechanism or by both the mechanisms without much preference, depending upon the nature of the nucleophile and the solvent.*

A few typical nucleophilic substitution reactions of haloalkanes are given below :

(a) Substitution of halogen by hydroxyl group. *(Formation of alcohols).* **Haloalkanes on treatment with boiling aqueous alkalies or silver oxide in boiling water (AgOH) undergo hydrolysis to** ***form alcohols.***

$$R-X + K^+\ {}^-OH\ (aq) \xrightarrow{\Delta} R-OH + K^+X^-$$

Haloalkane (*Alkyl halide*) — Alcohol

$$e.g.,\ CH_3CH_2-Br + K^+\ {}^-OH\ (aq) \xrightarrow{\Delta} CH_3CH_2-OH + K^+Br^-$$

Bromoethane (*Ethyl bromide*) — Ethanol (*Ethyl alcohol*)

$$CH_3-I + Ag^+\ {}^-OH \xrightarrow{\Delta} CH_3-OH + AgI$$

Iodomethane (*Methyl iodide*) — Moist silver oxide — Methanol (*Methyl alcohol*)

(ii) Subsitution of halogen by alkoxy group. (*Formation of ethers*). Haloalkanes when treated with sodium or potassium alkoxides form *ethers or alkoxyalkanes*.

$$R-X + Na^+\ {}^-OR' \xrightarrow{\Delta} R-O-R' + Na^+X^-$$

Alkyl halide — Sod. alkoxide — Ether

$$i.e.\ CH_3CH_2-Br + Na^+\ {}^-OCH_2CH_3 \xrightarrow{\Delta} CH_3CH_2-O-CH_2CH_3 + Na^+Br^-$$

Bromoethane (*Ethyl bromide*) — Sod. ethoxide — Ethoxyethane (*Diethyl ether*)

$$CH_3-I + Na^+\ {}^-OCH_3 \xrightarrow{\Delta} CH_3-O-CH_3 + Na^+I^-$$

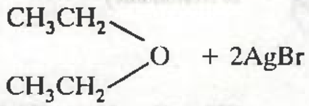
Iodomethane (*Methyl iodide*) — Sod. methoxide — Methoxymethane (*Dimethyl ether*)

This reaction is called **Williamson's Synthesis.**

Ethers can also be formed by heating alkyl halides with dry silver oxide, *e.g.*,

$$\begin{matrix} CH_3CH_2-Br \\ CH_3CH_2-Br \end{matrix} + Ag_2O \xrightarrow{\Delta}$$

Bromoethane (*Ethyl bromide*)



$+ 2AgBr$

Ethoxyethane (*Diethyl ether*)

(iii) Substitution of halogen by cyano group. (*Formation of alkyl cyanides or alkanenitriles*). Haloalkanes or alkyl halides react with alcoholic solution of potassium cyanide to form alkyl cyanides or alkanenitriles as the major product along with a small amount of alkyl isocyanides.

$$R-X + K^+\ {}^-CN\ (alc.) \xrightarrow{\Delta} R-C\equiv N + K^+X^-$$

Haloalkane (*Alkyl halide*) — Alkanenitrile (*Alkyl cyanide*)

$$e.g.,\ CH_3-I + K^+\ {}^-CN\ (alc.) \xrightarrow{\Delta} CH_3-C\equiv N + K^+I^-$$

Iodomethane (*Methyl iodide*) — Ethanenitrile (*Methyl cyanide or Acetonitrile*)

$$CH_3CH_2-Br + K^+\ {}^-CN\ (alc.) \xrightarrow{\Delta} CH_3CH_2-C\equiv N + K^+Br^-$$

Bromoethane (*Ethyl bromide*) — Propanenitrile (*Ethyl cyanide or Propionitrile*)

Alkyl cyanides are very useful compounds since they can be converted into (*i*) **amides** on partial hydrolysis with conc. HCl or alkaline hydrogen peroxide. (*ii*) **carboxylic acids** on complete hydrolysis with dilute mineral acids or alkalies and (*iii*) **primary amines** by reduction with nascent hydrogen obtained by the action of sodium on alcohol (**Mendius reduction**) or catalytically with H_2/Ni or with lithium aluminium hydride ($LiAlH_4$). Thus :

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$$\underset{\substack{\text{Ethanenitrile}\\ \textit{(Methyl cyanide}\\ \textit{or Acetonitrile)}}}{CH_3-C\equiv N} + H_2O \xrightarrow[\text{or } H_2O_2-NaOH]{\text{Conc. HCl}} \underset{\substack{\text{Ethanamide}\\ \textit{(Acetamide)}}}{CH_3-CONH_2}$$

$$\underset{\substack{\text{Ethanenitrile}\\ \textit{(Methyl cyanide)}}}{CH_3-C\equiv N} + 2H_2O \xrightarrow[\text{or Dil. alkali}]{\text{Dil. acid}} \underset{\substack{\text{Ethanoic acid}\\ \textit{(Acetic acid)}}}{CH_3-COOH} + NH_3$$

$$\underset{\substack{\text{Ethanenitrile}\\ \textit{(Acetonitrile)}}}{CH_3-C\equiv N} + 4[H] \xrightarrow[\textit{(Mendius reduction)}]{Na/C_2H_5OH} \underset{\substack{\text{Ethanamine}\\ \textit{(Ethylamine)}}}{CH_3CH_2-NH_2}$$

The reaction of alkyl halides with potassium cyanide gives us a convenient method for increasing the length of the carbon chain by one carbon atom at a time, *i.e.*, for **ascending the homologous series.**

(*iv*) Substitution of halogen by isocyanide group (*Formation of alkyl isocyanides*). When the aqueous ethanolic solution of a haloalkane (particularly iodoalkane) is heated with siliver cyanide, **alkyl isocyanide or alkyl isonitrile** or **alkyl carbylamine** is produced as the chief product alongwith a small amount of the corresponding alkyl cyanide.

$$\underset{\text{Haloalkane}}{R-\boxed{X + Ag}-CN} \xrightarrow[\Delta]{C_2H_5OH/H_2O} \underset{\text{Alkyl isocyanide}}{R-N \stackrel{\rightarrow}{=} C} \text{ or } \underset{\text{or Alkyl carbylamine}}{R-\overset{+}{N}\equiv \overset{-}{C}:} + AgX$$

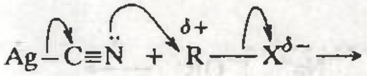
e.g., $$\underset{\text{Iodomethane}}{CH_3-\boxed{I + Ag}-CN} \xrightarrow[\Delta]{C_2H_5OH/H_2O} \underset{\text{Methyl isocyanide}}{CH_3-N \stackrel{\rightarrow}{=} C} \text{ or } \underset{\text{or Methyl carbylamine}}{CH_3-\overset{+}{N}\equiv \overset{-}{C}:} + AgI$$

Alkyl isocyanides on reduction give **secondary amines.**

$$\underset{\text{Methyl isocyanide}}{CH_3-N \stackrel{\rightarrow}{=} C} + 4[H] \xrightarrow{Na/C_2H_5OH} \underset{\text{Dimethylamine}}{CH_3-NH-CH_3}$$

Explanation. In the cyanide ion, $^-:C\equiv N:$, both the carbon and nitrogen atoms have a pair of electrons. Therefore, either the carbon or the nitrogen atom can act as the electron donor to the alkyl halide. *Such nucleophiles which have more than one site through which the reaction can occur are called* **ambident nucleophiles.** Thus, cyanide ion is an ambident nucleophile. Alkali metal cyanides like NaCN, KCN are predominantly *ionic*. In principle, the reaction can occur either through carbon or nitrogen. But in practice, the reaction occurs through carbon since *C–C bonds are stronger than C–N bonds* and hence alkyl cyanides are the chief products. On the other hand, silver cyanide is predominantly *covalent*. Therefore, only nitrogen electron pair is available for bond formation. As a result, alkyl isocyanides are the chief products.

$$\longrightarrow \underset{\text{Alkyl cyanide}}{R-C\equiv N} + K^+X^-$$



$$\longrightarrow \underset{\text{Alkyl isocyanide}}{R-\overset{+}{N}\equiv C:^-} + AgX$$

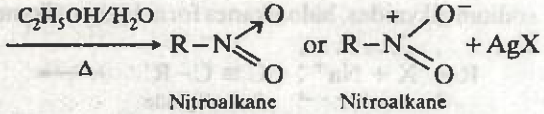
(*v*) Substitution of halogen by nitrite group (*Formation of alkyl nitrites*). Haloalkanes react with sodium or potassium nitrite to form **alkyl nitrites.**

$$\underset{\text{Haloalkane}}{R-\boxed{X + K^+}} \underset{\text{Pot. nitrite}}{^-O-N=O} \xrightarrow{\Delta} \underset{\text{Alkyl nitrite}}{R-O-N=O} + K^+X^-$$

e.g., $$\underset{\text{Ethyl bromide}}{CH_3CH_2-\boxed{Br + K^+}}\ ^-O-N=O \xrightarrow{\Delta} \underset{\text{Ethyl nitrite}}{CH_3CH_2-O-N=O} + K^+Br^-$$

(*vi*) Substitution of halogen by nitro group (*Formation of nitroalkanes*). When an aqueous ethanolic solution of a haloalkane is heated with silver nitrite, a **nitroalkane** is formed.

$$\underset{\text{Haloalkane}}{R-X} + \underset{\text{Silver nitrite}}{Ag-O-N=O}$$



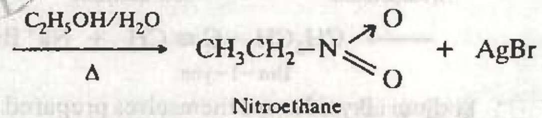
$$\xrightarrow[\Delta]{C_2H_5OH/H_2O} R-N^{\nearrow O}_{\searrow O} \text{ or } R-\overset{+}{N}{}^{O^-}_{=O} + AgX$$

Nitroalkane Nitroalkane

e.g., $CH_3CH_2-Br + Ag-O-N=O$

Bromoethane

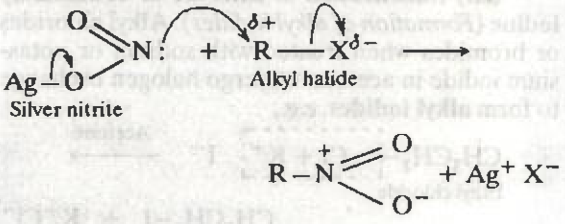
AB



$$\xrightarrow[\Delta]{C_2H_5OH/H_2O} CH_3CH_2-N^{\nearrow O}_{\searrow O} + AgBr$$

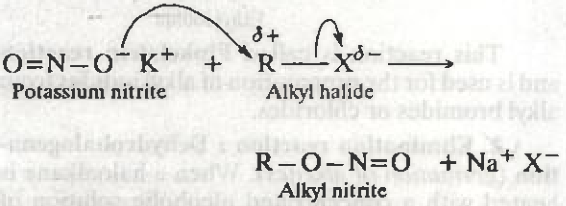
Nitroethane

Explanation. Nitrite ion ($^-O-N=O$) like cyanide ion is an *ambident nucleophile* since it has two sites (oxygen and nitrogen) through which it can attack an alkyl halide. *Whereas attack through nitrogen gives nitro compounds, attack through oxygen gives nitrites*



$$O=\ddot{N}-\ddot{O}-Ag + \overset{\delta+}{R}-X^{\delta-} \longrightarrow R-\overset{+}{N}{}^{=O}_{-O^-} + Ag^+X^-$$

Silver nitrite Alkyl halide

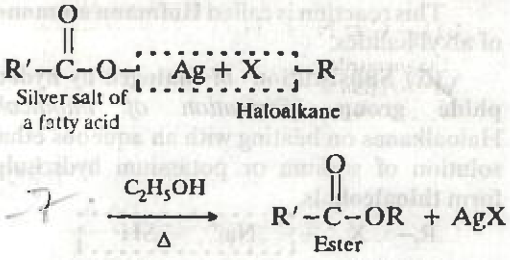


$$O=N-O^-K^+ + \overset{\delta+}{R}-X^{\delta-} \longrightarrow R-O-N=O + Na^+X^-$$

Potassium nitrite Alkyl halide Alkyl nitrite

Alkali metal nitrites are *ionic* compounds and hence have a negative charge on one of the oxygen atoms. Nucleophilic attack through this negatively charged oxygen atom on the alkyl halides mainly gives alkyl nitrites. In contrast, silver nitrite is a *covalent* compound and hence does not have a negative charge on the oxygen atom. Instead both the oxygen atoms and the nitrogen atom carry lone pair of electrons. Since nitrogen is less electronegative, therefore, lone pair of electrons on the nitrogen atom are more easily available for bond formation. In other words, nucleophilic attack occurs through nitrogen and hence silver nitrite predominantly gives nitro compounds.

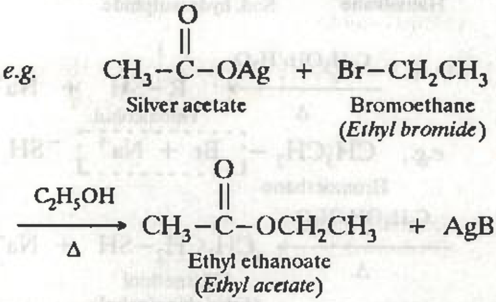
(vii) Substitution of halogen by carboxylate group (*Formation of esters*). Haloalkanes form esters when heated with an ethanolic solution of silver salt of a fatty acid.



$$R'-\overset{O}{\overset{\|}{C}}-O-Ag + X-R \xrightarrow[\Delta]{C_2H_5OH} R'-\overset{O}{\overset{\|}{C}}-OR + AgX$$

Silver salt of a fatty acid Haloalkane Ester

A-7



$$CH_3-\overset{O}{\overset{\|}{C}}-OAg + Br-CH_2CH_3 \xrightarrow[\Delta]{C_2H_5OH} CH_3-\overset{O}{\overset{\|}{C}}-OCH_2CH_3 + AgBr$$

e.g. Silver acetate Bromoethane (*Ethyl bromide*)

Ethyl ethanoate (*Ethyl acetate*)

(viii) Substitution of halogen by amino group (*Formation of amines*). Haloalkanes when heated with an ethanolic solution of ammonia in a sealed tube at 373 K, **form a mixture of primary, secondary and tertiary amines** alongwith **quaternary ammonium salts.**

$CH_3CH_2-Br + H-NH_2$

Bromoethane (*Ethyl bromide*) Ammonia

AC

$\xrightarrow[\Delta]{C_2H_5OH} CH_3CH_2-NH_2 + HBr$

Ethanamine (1°) (*Ethylamine*)

$CH_3CH_2NH-H + Br-CH_2CH_3$

Ethanamine Bromoethane

$\xrightarrow[\Delta]{C_2H_5OH} (CH_3CH_2)_2NH + HBr$

N–Ethylethanamine (2°) (*Diethylamine*)

$(CH_3CH_2)_2N-H + Br-CH_2CH_3$

N–Ethylethanamine Bromoethane

$\xrightarrow[\Delta]{C_2H_5OH} (CH_3CH_2)_3N + HBr$

N, N–Diethylethanamine (3°) (*Triethylamine*)

$(CH_3CH_2)_3N + Br-CH_2CH_3$

N,N–Diethylethanamine Bromoethane

$\xrightarrow[\Delta]{C_2H_5OH} (CH_3CH_2)_4N^+Br^-$

Tetraethylammonium bromide (*Quaternary salt*)

This reaction is called **Hofmann ammonolysis** of alkyl halides.

(x) Substitution of halogen by hydro sulphide group (*Formation of thioalcohols*). Haloalkanes on heating with an aqueous ethanolic solution of sodium or potassium hydrosulphide form **thioalcohols**.

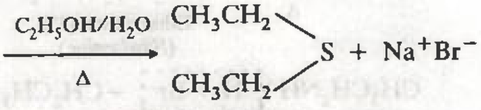
$$\underset{\text{Haloalkane}}{R-\boxed{X} +} \underset{\text{Sod. hydrosulphide}}{\boxed{Na^+}\ {}^-SH} \xrightarrow[\Delta]{C_2H_5OH/H_2O} \underset{\text{Thioalcohol}}{R-SH} + Na^+X^-$$

e.g.,
$$\underset{\text{Bromoethane}}{CH_3CH_2-\boxed{Br + Na^+}}\ {}^-SH \xrightarrow[\Delta]{C_2H_5OH/H_2O} \underset{\substack{\text{Ethanethiol}\\ \textit{(Ethyl thioalcohol)}}}{CH_3CH_2-SH} + Na^+Br^-$$

(xi) Substitution of halogen by mercaptide group (*Formation of thioethers*). (*a*) *By heating an alkyl halide with sodium or potassium mercaptide*

$$\underset{\text{Haloalkane}}{R-\boxed{X + Na^+}}\ \underset{\substack{\text{Sod.}\\ \text{mercaptide}}}{{}^-SR'} \xrightarrow[\Delta]{C_2H_5OH/H_2O} \underset{\text{Thioether}}{R-S-R'} + Na^+X^-$$

$$\underset{\text{Ethyl bromide}}{CH_3CH_2-Br} + \underset{\text{Sod. ethyl mercaptide}}{Na^+\ {}^-SCH_2CH_3}$$



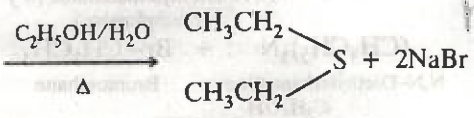
$$\xrightarrow[\Delta]{C_2H_5OH/H_2O} (CH_3CH_2)_2S + Na^+Br^-$$

Diethyl thioether

(*b*) *By heating an alkyl halide with sodium or potassium sulphide*

$$\underset{\text{Haloalkane}}{2R-X} + \underset{\text{Sod. sulphide}}{Na_2S} \xrightarrow[\Delta]{C_2H_5OH/H_2O} \underset{\text{Thioether}}{R-S-R} + 2NaX$$

e.g.,
$$\underset{\text{Bromoethane}}{2CH_3CH_2-Br} + \underset{\text{Sod. sulphide}}{Na_2S}$$



$$\xrightarrow[\Delta]{C_2H_5OH/H_2O} (CH_3CH_2)_2S + 2NaBr$$

Diethyl thioether

(xii) Substitution of halogen by alkynyl group (*Formation of higher alkynes*). When treated with sodium alkynides, haloalkanes form higher alkynes, *e.g.*,

$$R-\boxed{X + Na^+}\ \underset{\text{Sod. alkynide}}{{}^-C\equiv C-R'} \longrightarrow \underset{\text{Higher alkyne}}{R-C\equiv C-R'} + Na^+X^-$$

$$\underset{\text{Bromoethane}}{CH_3CH_2-\boxed{Br + Na^+}}\ \underset{\text{Sod. acetylide}}{{}^-C\equiv CH} \longrightarrow \underset{\text{But}-1-\text{yne}}{CH_3CH_2-C\equiv CH} + Na^+Br^-$$

Sodium alkynides are themselves prepared by the action of sodamide (or Na in liquid NH_3 at 196 K) on terminal alkynes.

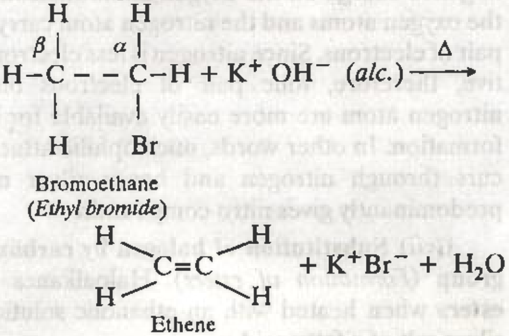
$$R-C\equiv CH + NaNH_2 \xrightarrow{\text{Liq. } NH_3\text{, 196 K}} R-C\equiv C^-Na^+ + NH_3$$

(xiii) Substitution of chlorine or bromine by iodine (*Formation of alkyl iodides*). Alkyl chlorides or bromides when treated with sodium or potassium iodide in acetone undergo halogen exchange to form **alkyl iodides**. *e.g.*,

$$\underset{\text{Ethyl chloride}}{CH_3CH_2-\boxed{Cl + K^+}}\ I^- \xrightarrow{\text{Acetone}} \underset{\text{Ethyl iodide}}{CH_3CH_2-I} + K^+Cl^-$$

This reaction is called **Finkelstein reaction** and is used for the preparation of alkyl iodides from alkyl bromides or chlorides.

2. Elimination reaction : Dehydrohalogenation (*Formation of alkenes*). **When a haloalkane is heated with a concentrated alcoholic solution of potassium hydroxide, a molecule of hydrogen halide is eliminated and an alkene is formed.** The hydrogen of the alkyl halide which is eliminated comes from a β-carbon (*i.e.*, the carbon atom next to that which carries the halogen) and the halogen from the α-carbon (*i.e.*, the carbon atom which carries the halogen).



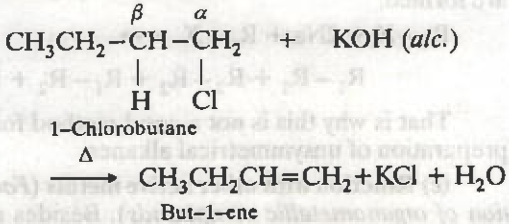
$$\underset{\substack{\text{Bromoethane}\\ \textit{(Ethyl bromide)}}}{H-\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}-\overset{H}{\underset{Br}{\overset{|}{\underset{|}{C}}}}-H} + K^+OH^-\ (alc.) \xrightarrow{\Delta} \underset{\substack{\text{Ethene}\\ \textit{(Ethylene)}}}{H_2C=CH_2} + K^+Br^- + H_2O$$

Bromoethane
(Ethyl bromide)

Ethene
(Ethylene)

Since in this reaction, the hydrogen atom is lost from the β-carbon, therefore, this reaction is classified as **β-elimination reaction.**

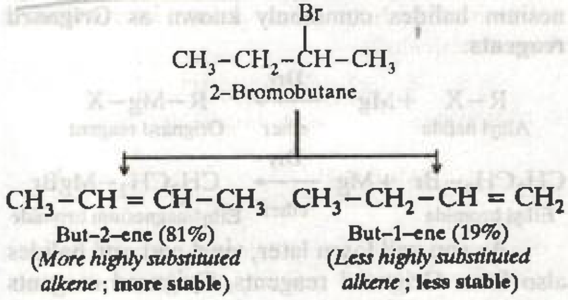
Similarly, 1-chlorobutane on dehydrohalogenation gives but-1-ene.



$$\underset{\text{1-Chlorobutane}}{CH_3CH_2-\overset{\beta}{\underset{H}{CH}}-\overset{\alpha}{\underset{Cl}{CH_2}}} + KOH\ (alc.) \xrightarrow{\Delta} \underset{\text{But-1-ene}}{CH_3CH_2CH=CH_2} + KCl + H_2O$$

AC

However, if the structure of the alkyl halide is such that it can undergo elimination in two different ways, due to the availability of different types of β-hydrogens, then the more highly substituted alkene (i.e. having lesser number of hydrogen atoms on the doubly bonded carbon atoms) is the major product of dehydrohalogenation. This generalization is known as **Saytzeff's rule.** For example,



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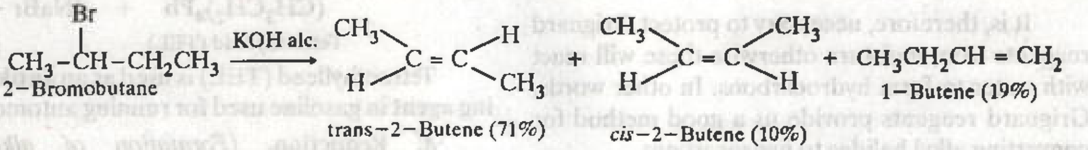
If the substituted alkene formed during dehydrohalogenation, is capable of showing *cis-trans* isomerism, *the trans-alkene being more stable is always formed as the major product.* For example,



Ease of dehydrohalogenation. In the light of Saytzeff rule, any alkyl halide that gives a more stable (*i.e.*, more highly substituted) alkene must undergo dehydrohalogenation faster than the one which gives a less stable (*i.e.*, less highly substituted) alkene. Consider, for example, the dehydro- halogenation of chloroethane (1°), 2-chloro- propane (2°) and 2-chloro-2-methylpropane (3°).

$$\underset{\text{Chloroethane (1°)}}{CH_3-CH_2Cl} \xrightarrow[-HCl]{KOH\ (alc.),\ \Delta} \underset{\text{Ethene (Unsubstituted alkene, least stable, least easily formed)}}{CH_2=CH_2}$$

17/23

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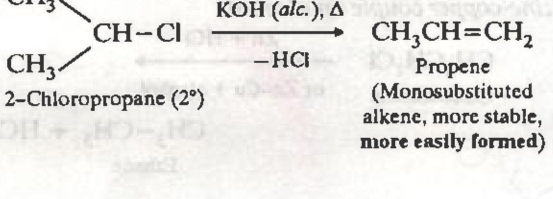
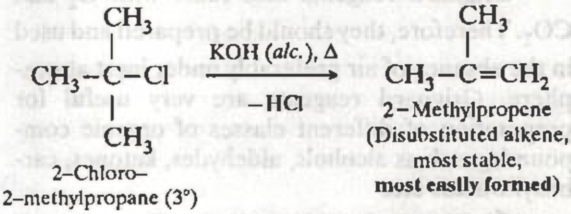


2-Chloropropane (2°)

Propene (Monosubstituted alkene, more stable, more easily formed)



$$\underset{\text{2-Chloro-2-methylpropane (3°)}}{CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Cl} \xrightarrow[-HCl]{KOH\ (alc.),\ \Delta} \underset{\text{2-Methylpropene}}{CH_3-\overset{CH_3}{C}=CH_2}$$

(Disubstituted alkene, most stable, most easily formed)

Thus, the ease of dehydrohalogenation of these three alkyl halides increases as the number of β- hydrogens increases, *i.e.*

In general, the ease of dehydrogenation for a given alkyl group decreases in the order :

tertiary (3°) > secondary (2°) > primary (1°)

and for a given halogen, it decreases in the order : $R-I > R-Br > R-Cl$.

3. Reaction with metals. Most of the organic chlorides, bromides and iodides react with certain metals to form compounds containing carbon-metal bond. Such compounds are called **organometallic compounds.** Some important reactions of alkyl halides with metals are discussed below :

(a) Reaction with magnesium (*Formation of Grignard reagents*). Haloalkanes react with magnesium turnings in dry ether to form alkylmagnesium halides commonly known as **Grignard reagents.**

$$\underset{\text{Alkyl halide}}{R-X} + Mg \xrightarrow[\text{ether}]{\text{Dry}} \underset{\text{Grignard reagent}}{R-Mg-X}$$

$$\underset{\text{Ethyl bromide}}{CH_3CH_2-Br} + Mg \xrightarrow[\text{ether}]{\text{Dry}} \underset{\text{Ethylmagnesium bromide}}{CH_3CH_2-MgBr}$$

As you will learn later, vinyl and aryl halides also form Grignard reagents. Grignard reagents are highly reactive compounds. They react with all compounds which can donate a proton to form hydrocarbons. Even water, alcohols, amines, terminal alkynes etc. are sufficiently acidic to react with Grignard reagents to form the corresponding hydrocarbons.

$$RMgX + ZH \longrightarrow R + ZMgX$$

(where Z = OH, RO, NH_2, RNH, RC ≡ C etc.)

It is, therefore, necessary to protect Grignard reagents from moisture otherwise these will react with water to form hydrocarbons. In other words, Grignard reagents provide us a good method for converting alkyl halides to hydrocarbons.

Grignard reagents also react with O_2 and CO_2. Therefore, they should be prepared and used in the absence of air preferably under inert atmosphere. Grignard reagents are very useful for preparation of different classes of organic compounds, such as alcohols, aldehydes, ketones, carboxylic acids etc.

(b) Reaction with sodium (*Formation of higher alkanes*). Alkyl halides 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.

$$R-\boxed{X + 2Na + X}-R \xrightarrow[\text{ether}]{\text{Dry}} \underset{\text{Alkane}}{R-R} + 2Na^+X^-$$

$$e.g.,\quad \underset{\text{Methyl bromide}}{CH_3-\boxed{Br + 2Na + Br}-CH_3} \xrightarrow[\text{ether}]{\text{Dry}} \underset{\text{Ethane}}{CH_3-CH_3} + 2Na^+Br^-$$

This reaction is called **Wurtz reaction.**

This reaction generally fails with tertiary alkyl halides since under the basic conditions of the reaction, they prefer to undergo dehydrohalogenation to form alkenes. When a mixture of two different alkyl halides is used, all the three possible alkanes are formed.

$$R_1-X + 2Na + R_2-X \longrightarrow R_1-R_1 + R_2-R_2 + R_1-R_2 + NaX$$

That is why this is not a good method for the preparation of unsymmetrical alkanes.

(c) Reaction with other active metals (*Formation of organometallic compounds*). Besides magnesium and sodium, alkyl halides also react with other active metals such as lithium, zinc, mercury, lead etc. in presence of dry ether to form the corresponding organometallic compounds. For example,

$$\underset{\text{Ethyl bromide}}{CH_3CH_2Br} + 2\,Li \xrightarrow[\text{ether}]{\text{Dry}} \underset{\text{Ethyllithium}}{CH_3CH_2Li} + LiBr$$

$$\underset{\text{Ethyl bromide}}{4CH_3CH_2Br} + \underset{\text{Sod. lead alloy}}{4\,Pb/Na} \xrightarrow[\text{ether}]{\text{Dry}} \underset{\text{Tetraethyllead (TEL)}}{(CH_3CH_2)_4Pb} + 4NaBr + 3Pb$$

Tetraethyllead (TEL) is used as an **antiknocking agent** in gasoline used for running automobiles.

Reduction. (*Formation of alkanes*). Haloalkanes are reduced to the corresponding *alkanes*. This reduction can be done by any of the following reagents :

(i) *Hydrogen in the presence of a metal catalyst such as nickel or palladium or platinum.*

$$\underset{\text{Bromoethane}}{CH_3CH_2Br} + H_2 \xrightarrow{Ni} \underset{\text{Ethane}}{CH_3-CH_3} + HBr$$

(ii) *Hydriodic acid in the presence of red phosphorus.* Alkyl iodides can be reduced to the corresponding alkanes on reducton with HI in presence of red phosphorus at 420 K.

$$\underset{\text{Iodoethane}}{CH_3CH_2-I} + HI \xrightarrow[\text{420 K}]{\text{Red P}} \underset{\text{Ethane}}{CH_3-CH_3} + I_2$$

(iii) *Nascent hydrogen produced by the action of zinc or tin on hydrochloric acid or by the action of zinc-copper couple on alcohol.*

$$\underset{\text{Chloroethane}}{CH_3CH_2Cl} \xrightarrow[\text{or Zn–Cu + alcohol}]{\text{Zn + HCl}} \underset{\text{Ethane}}{CH_3-CH_3} + HCl$$

(iv) Substitution by hydride ion or reduction. Primary and secondary alkyl halides are readily reduced to alkanes by lithium aluminium hydride ($LiAlH_4$).

$$\underset{\text{(from } LiAlH_4)}{H^-} + \overset{\delta+}{R} - \overset{\delta-}{X} \longrightarrow R-H + HX$$

$$\text{or} \quad LiAlH_4 + 4RX \longrightarrow 4R-H + AlX_3 + LiX$$

Tertiary alkyl halides, however, undergo dehydrohalogenation to give alkenes. On the other hand sodium borohydride ($NaBH_4$) reduces secondary and tertiary alkyl halides but not primary whereas triphenyltin hydride (Ph_3SnH) reduces all the three types of alkyl halides.

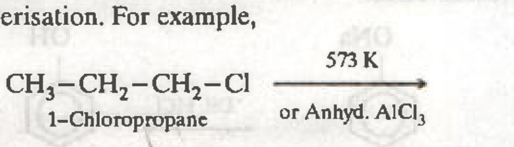
5. Halogenation. Alkyl halides on treatment with halogens in presence of light, heat or a catalyst, give *di, tri, tetra* or polysubstituted alkanes. For example,

$$\underset{\text{Chloromethane}}{CH_3Cl} + Cl_2 \xrightarrow[\text{or } 520-670\text{ K}]{h\nu} \underset{\text{Dichloromethane}}{CH_2Cl_2} + HCl$$

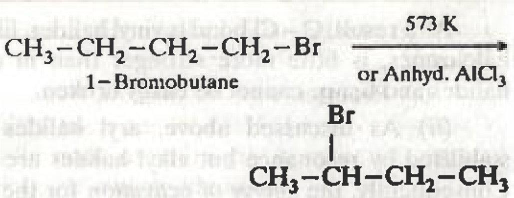
$$\underset{\text{Dichloromethane}}{CH_2Cl_2} + Cl_2 \xrightarrow[\text{or } 520-670\text{ K}]{h\nu} \underset{\substack{\text{Trichloromethane}\\(\textit{Chloroform})}}{CHCl_3} + HCl$$

$$\underset{\text{Trichloromethane}}{CHCl_3} + Cl_2 \xrightarrow[\text{or } 520-670\text{ K}]{h\nu} \underset{\substack{\text{Tetrachloromethane}\\(\textit{Carbon tetrachloride})}}{CCl_4} + HCl$$

6. Isomerisation. When a haloalkane is heated to 573K or at a lower temperature in presence of a *Lewis acid* such as anhydrous aluminium chloride as catalyst, it undergoes isomerisation. For example,



$$\underset{\text{1-Chloropropane}}{CH_3-CH_2-CH_2-Cl} \xrightarrow[\text{or Anhyd. } AlCl_3]{573\text{ K}} \underset{\text{2-Chloropropane}}{CH_3-\overset{\overset{\displaystyle Cl}{|}}{C}H-CH_3}$$

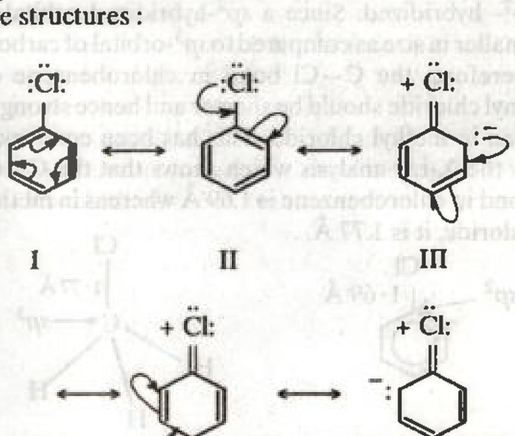


$$\underset{\text{1-Bromobutane}}{CH_3-CH_2-CH_2-CH_2-Br} \xrightarrow[\text{or Anhyd. } AlCl_3]{573\text{ K}} \underset{\text{2-Bromobutane}}{CH_3-\overset{\overset{\displaystyle Br}{|}}{C}H-CH_2-CH_3}$$

17.10. Reasons for Low Reactivity of Haloarenes (Aryl Halides)

Both haloalkanes (alkyl halides) and haloarenes (aryl halides) or vinyl halides contain a C – X bond but haloarenes and vinyl halides are far less reactive than haloalkanes towards nucleophilic substitution reactions. The following reasons can be given to account for the low reactivity of aryl halides taking chlorobenzene as an example.

1. Resonance effect. Chlorobenzene can be represented as a resonance hybrid of the following five structures :



(*i*) As a result, C – Cl bond acquires some double bond character, *i.e.*, X is attached to C by little more than a single pair of electrons. On the other hand, in case of alkyl halides (say methyl chloride) carbon is attached to chlorine by a pure single bond. Consequently, C – X bond in chlorobenzene is little stronger than in alkyl halides, and hence cannot be easily broken.

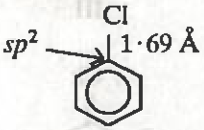
Like chlorobenzene, vinyl halides such as vinyl chloride can be represented as a resonance hybrid of the following structures :

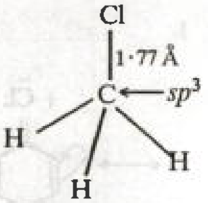
$$CH_2=CH-\ddot{\underset{\cdot\cdot}{Cl}}: \longleftrightarrow {}^{-}:CH_2-CH=\overset{+}{\underset{\cdot\cdot}{Cl}}:$$

As a result, C – Cl bond is vinyl halides, like in haloarenes, is little more stronger than in alkyl halides and hence cannot be easily broken.

(*ii*) As discussed above, aryl halides are stabilised by resonance but alkyl halides are not. Consequently, the *energy of activation* for the displacement of halogen from aryl halides is much greater than that of alkyl halides. Thus, *aryl halides are much less reactive than alkyl halides towards nucleophilic substitution reactions*.

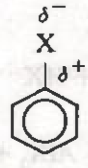
2. Hybridization of carbon bearing the halogen atom. An alternative explanation for the stronger C – Cl bond in chlorobenzene or vinyl chloride as compared to methyl chloride can be offered on the basis of the type of hybridization of the carbon atom holding the chlorine atom. In methyl chloride, this carbon is sp^3-hybridized whereas in chlorobenzene or vinyl chloride it is sp^2- hybridized. Since a sp^2-hybridized orbital is smaller in size as compared to sp^3-orbital of carbon, therefore, the C – Cl bond in chlorobenzene or vinyl chloride should be 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 whereas in methyl chloride, it is 1.77 Å.



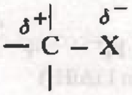


3. Polarity (or Nature) of the carbon-halogen bond. Another reason for the low reactivity of aryl halides over alkyl halides is their lesser polar character.

We know that a sp^2-hybrid carbon is more electronegative than a sp^3-hybrid carbon. Therefore, the sp^2-hybrid carbon of C – Cl bond in aryl halides or vinyl halides have less tendency to release electrons to the halogen than a sp^3-hybrid carbon in alkyl halides. As a result, the C – Cl bond in aryl halides or vinyl halides is less polar than in alkyl halides. This is supported by the observation that the dipole moment of chlorobenzene is just 1.7 D as compared to the dipole moment of methyl chloride, *i.e.*, 1.94 D. Consequently, the halogen atom present in aryl halides cannot be easily displaced by nucleophiles.



Haloarene or aryl (*C—X bond is less polar and hence X cannot be displaced easily by nucleophiles.*)



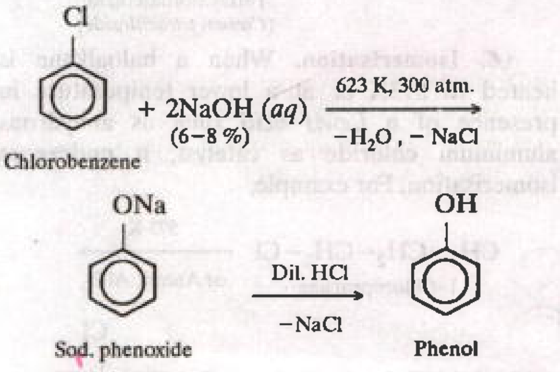
Haloalkane or alkyl (*C—X bond is more polar than in aryl halides and hence X can be easily displaced by nucleophiles.*)

17.11. Chemical Properties of Haloarenes (Aryl Halides)

Some important reactions of haloarenes are given below :

1. Nucleophilic substitution reactions. We have discussed above that the halogen atom attached to the benzene ring is firmly held and hence cannot be easily displaced by nucleophiles such as OH^-, CN^- etc. In other words, *haloarenes are much less reactive than haloalkanes towards nucleophilic substitution reactions*. However, under drastic conditions, they do undergo nucleophilic substitution reactions as shown below :

(*i*) **Reaction with sodium hydroxide.** When heated with an aqueous solution of NaOH at 623 K and under a pressure of 300 atmospheres, haloarenes form sodium phenoxides, which upon acidification give phenols.



This reaction forms the basis of **Dow process** *for the manufacture of phenol.*

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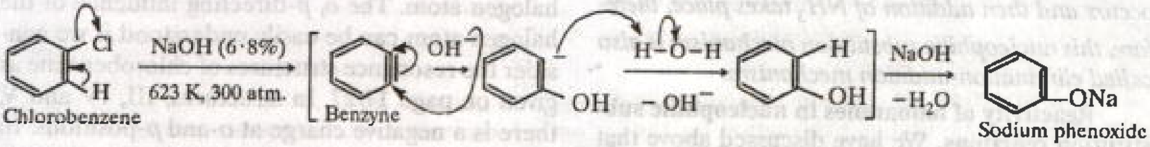
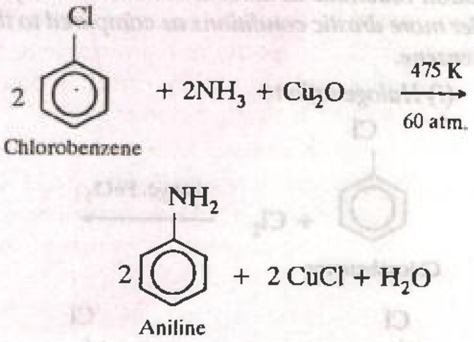
Dow process occurs through benzyne intermediate as shown below :

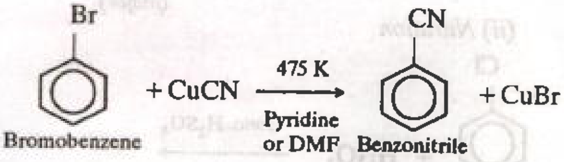


This mechanism is supported by the observation that diphenyl ether and *p*-phenylphenol are the by products of this reaction.

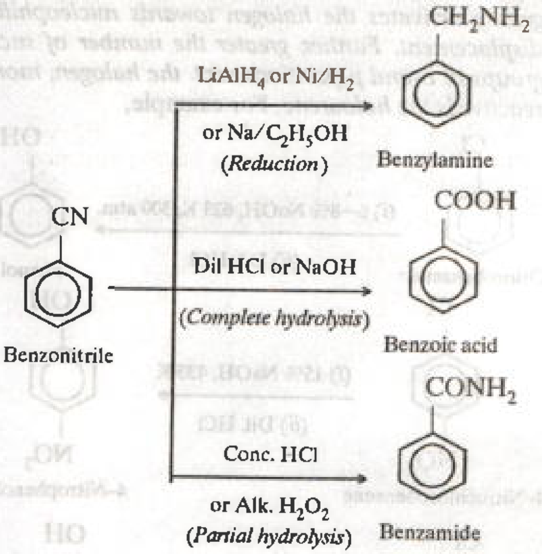
(*ii*) Reaction with ammonia. When haloarenes are heated with aqueous NH_3 solution in presence of cuprous oxide as catalyst at 475 K and under a pressure of 60 atmospheres, the halogen is replaced by the amino group. For example,



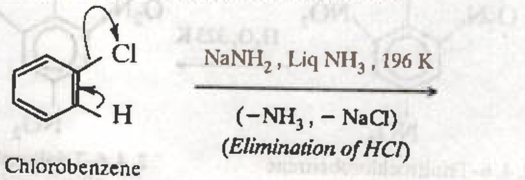
(*iii*) Reaction with cuprous cyanide. When heated with cuprous cyanide at 475 K in presence of pyridine or dimethylformamide (DMF), the bromine atom of the aryl bromides is replaced by the –CN group. For example,

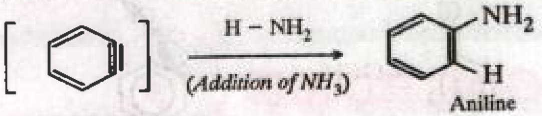


Benzonitrile can be converted into other useful compounds. For example,



(*iv*) Reaction with sodamide in liquid ammonia. All the three reactions mentioned above occur by an aromatic S_N2 *mechanism*. However, if chlorobenzene is treated with sodamide in liquid ammonia at 196 K, the reaction occurs through the intermediate formation of 1,2-didehydrobenzene (formerly called benzyne) to give aniline.



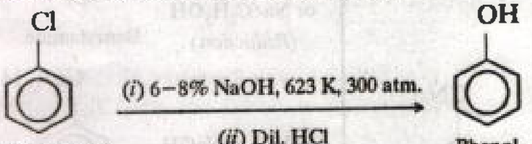


1, 2-Didehydrobenzene
(formerly also benzyne)

Aniline

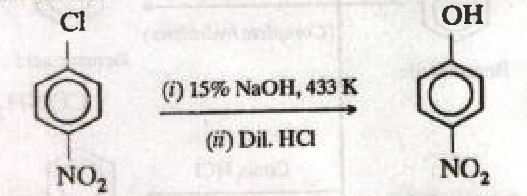
Since in this reaction, first elimination of HCl occurs and then addition of NH_3 takes place, therefore, this nucleophilic substituion mechanism is also called elimination-addition mechanism.

Reactivity of haloarenes in nucleophilic substitution reactions. We have discussed above that displacement of the halogen in haloarenes takes place under drastic conditions. However, it has been observed that *the presence of electron-withdrawing groups such as $-NO_2$, CN etc. at o-and p-positions (but not at m-positions) w.r.t. the halogen greatly activates the halogen towards nucleophilic displacement. Further, greater the number of such groups at o-and p-positions w.r.t. the halogen, more reactive is the haloarene.* For example,



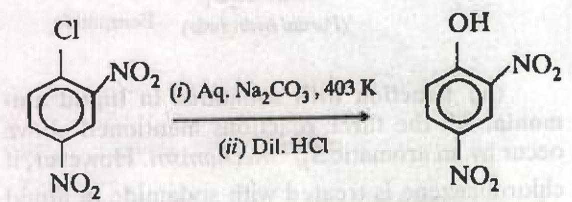
Chlorobenzene

Phenol



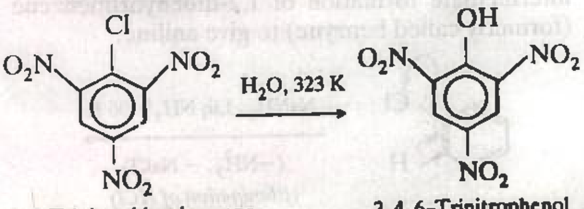
4-Nitrochlorobenzene

4-Nitrophenol



2, 4-Dinitro-chlorobenzene

2, 4-Dinitrophenol

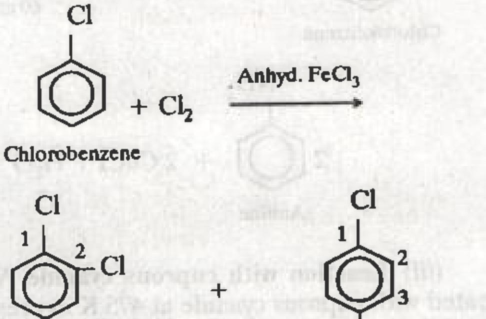


2, 4, 6-Trinitrochlorobenzene
(Picryl chloride)

2, 4, 6-Trinitrophenol
(Picric acid)

2. Electrophilic substitution reactions. Haloarenes undergo the usual electrophilic substitution reactions of the benzene ring such as halogenation, nitration, sulphonation and Friedel-Crafts reactions. *Halogen atom is slightly deactivating and o, p- directing,* therefore, further substitution occurs at *o-* and *p*-positions *w.r.t.* the halogen atom. The *o, p*-directing influence of the halogen atom can be easily understood if we consider the resonance structures of chlorobenzene as given on page 17/27. In structures, III, IV and V, there is a negative charge at *o*-and *p*-positions. In other words, because of resonance, the electron density increases more at *o*-and *p*-positions than at *m*-positions. Therefore, further electrophilic substitution in haloarenes occurs at *o*-and *p*-positions. However, because of steric hindrance at the *o*-position, the *p*-product usually predominates over the *o*-product. Further, the halogen atom because of its − I-effect has some tendency to withdraw electrons from the benzene ring. As a result, the ring gets somewhat deactivated as compared to benzene and hence the further electrophilic substitution reactions in haloarenes occur *slowly and under more drastic conditions as compared to those in benzene.*

(i) Halogenation

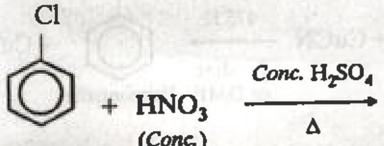


Chlorobenzene

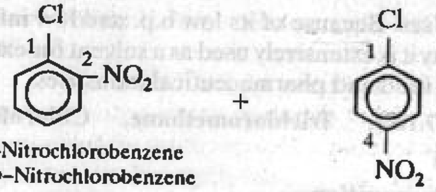
1, 2-Dichlorobenzene
(o-Dichlorobenzene)
(minor)

1, 4-Dichlorobenzene
(p-Dichlorobenzene)
(major)

(ii) Nitration



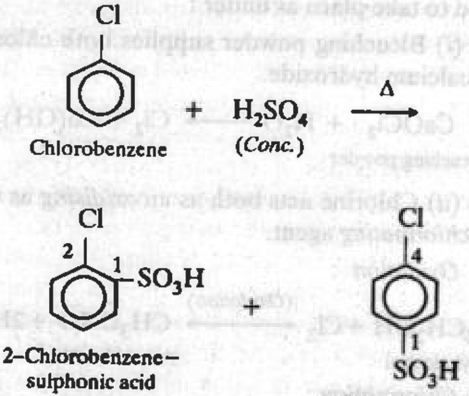
Chlorobenzene



2-Nitrochlorobenzene or *o*-Nitrochlorobenzene (*minor*)

4-Nitrochlorobenzene or *p*-Nitrochlorobenzene (*major*)

(iii) Sulphonation

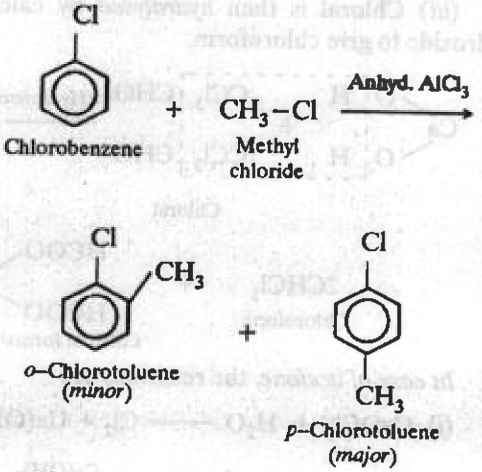


Chlorobenzene

2–Chlorobenzene-sulphonic acid (*minor*)

4–Chlorobenzene-sulphonic acid (*major*)

(iv) Friedel-Crafts reaction

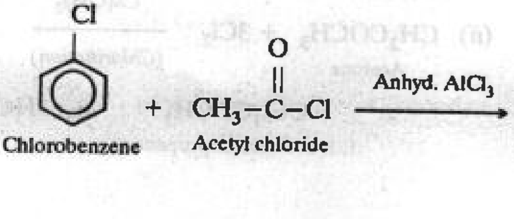


Chlorobenzene

Methyl chloride

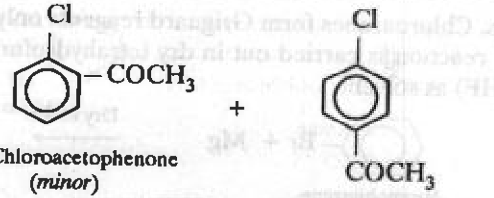
o–Chlorotoluene (*minor*)

p–Chlorotoluene (*major*)



Chlorobenzene

Acetyl chloride

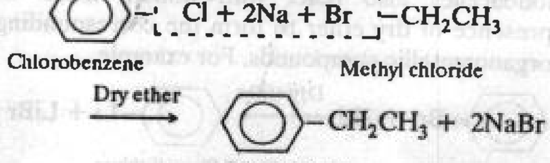


o–Chloroacetophenone (*minor*)

p–Chloroacetophenone (*major*)

3. Miscellaneous reactions. Besides these nucleophilic and electrophilic substitution reactions, haloarenes undergo a number of other reactions as described below :

(i) **Reaction with sodium (*a*) Wurtz-Fittig reaction.** Haloarenes when treated with an ethereal solution of an alkyl halide in presence of sodium, form alkyl derivatives of benzene. This reaction is called *Wurtz-Fittig reaction*.

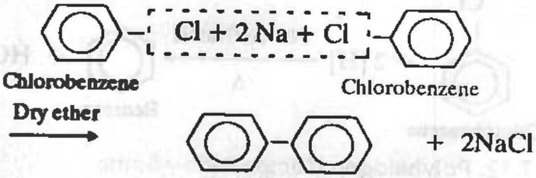


Chlorobenzene

Methyl chloride

Ethylbenzene

(*b*) Fittig reaction. When only haloarenes are treated with sodium, diaryls are produced. This reaction is called *Fittig reaction*.

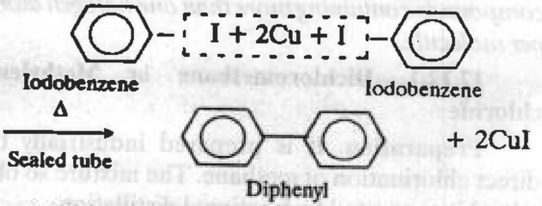


Chlorobenzene

Chlorobenzene

Diphenyl

(ii) **Reaction with copper powder—Ullmann biaryl synthesis.** When an iodoarene is heated with copper powder in a sealed tube, diaryl is formed. This is called *Ullmann biaryl synthesis*.



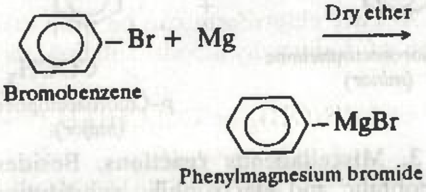
Iodobenzene

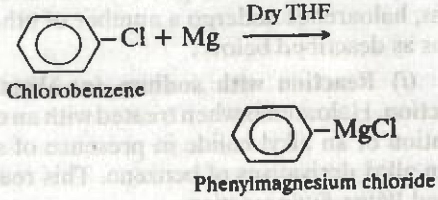
Iodobenzene

Diphenyl

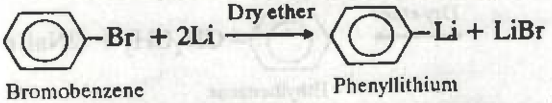
(iii) **Reaction with magnesium.** Bromo-and iodoarenes form Grignard reagents when their ethereal solution is treated with magnesium turn-

ings. Chloroarenes form Grignard reagents only if the reaction is carried out in dry tetrahydrofuran (THF) as solvent.

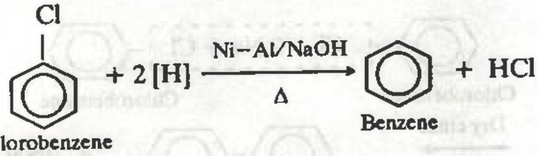




(*iv*) **Reaction with lithium.** Bromo- and iodoarenes also react with lithium metal in presence of dry ether to form the corresponding organometallic compounds. For example,



(*v*) **Reduction.** Haloarenes can be converted into the corresponding arenes by reduction with nickel-aluminium alloy in presence of alkali.



17.12. Polyhalogen Compounds—Some Commercially Important Compounds

We have so far studied the general methods of preparation and properties of haloalkanes and haloarenes. Let us now study, in detail, certain compounds which are of commercial importance. These are generally polyhalogen compounds, *i.e. compounds containing more than one halogen atom per molecule.*

17.12.1. Dichloromethane or Methylene chloride

Preparation. It is prepared industrially by direct chlorination of methane. The mixture so obtained is separated by fractional distillation.

Properties. It is a colourless, sweet-smelling volatile liquid, b.p. 313 K.

Uses. Because of its low b.p. and low inflammability it is extensively used as a solvent for extraction in food and pharmaceutical industries.

17.12.2. Trichloromethane, Chloroform, $CHCl_3$

Preparation.

1. By distilling ethanol (ethyl alcohol) or propanone (acetone) with a suspension of bleaching powder in water (*Laboratory method*) :

The reaction *in case of ethyl alcohol* is supposed to take place as under :

(*i*) Bleaching powder supplies both chlorine and calcium hydroxide.

$$\underset{\text{Bleaching powder}}{CaOCl_2} + H_2O \longrightarrow Cl_2 + Ca(OH)_2$$

(*ii*) Chlorine acts both as an *oxidising* as well as a *chlorinating* agent.

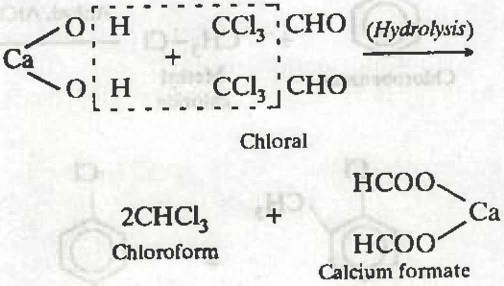
Oxidation :

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} + Cl_2 \xrightarrow{(Oxidation)} \underset{\text{Acetaldehyde}}{CH_3CHO} + 2HCl$$

Chlorination :

$$CH_3CHO + 3Cl_2 \xrightarrow[(Chlorination)]{Ca(OH)_2} \underset{\substack{\text{Trichloroacetaldehyde}\\ \text{or Chloral}}}{CCl_3CHO} + 3HCl$$

(*iii*) Chloral is then *hydrolysed* by calcium hydroxide to give chloroform.

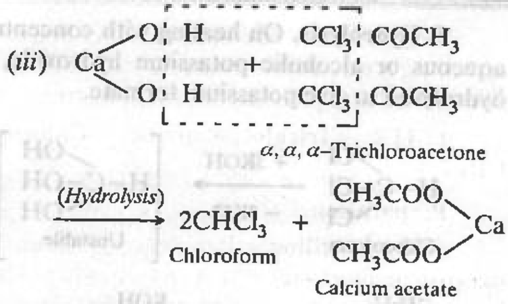


$$Ca(OH)_2 + \underset{\text{Chloral}}{2CCl_3CHO} \xrightarrow{(Hydrolysis)} \underset{\text{Chloroform}}{2CHCl_3} + \underset{\text{Calcium formate}}{(HCOO)_2Ca}$$

In case of acetone, the reactions are :

$$(i)\ CaOCl_2 + H_2O \longrightarrow Cl_2 + Ca(OH)_2$$

$$(ii)\ \underset{\text{Acetone}}{CH_3COCH_3} + 3Cl_2 \xrightarrow[(Chlorination)]{Ca(OH)_2} \underset{\text{1, 1, 1–Trichloropropanone}}{CCl_3COCH_3} + 3HCl$$



$$(iii)\ \mathrm{Ca}(\mathrm{O}\,\mathrm{H})_2 + 2\,\mathrm{CCl_3COCH_3} \xrightarrow{(Hydrolysis)} \underset{\text{Chloroform}}{2\mathrm{CHCl_3}} + \underset{\text{Calcium acetate}}{(\mathrm{CH_3COO})_2\mathrm{Ca}}$$

α, α, α–Trichloroacetone

Acetone is preferred to ethyl alcohol, as the yield is better.

In place of bleaching powder, we may use in the laboratory, an alkaline solution of sodium hypochlorite, NaOCl obtained by the action of chlorine on cold sodium hydroxide solution.

The various reactions taking place are as follows :

$$2\mathrm{NaOH} + \mathrm{Cl_2} \longrightarrow \underset{\text{Sod. hypochlorite}}{\mathrm{NaOCl}} + \mathrm{NaCl} + \mathrm{H_2O}$$

(i) Chlorination :

$$\underset{\substack{\text{Propanone}\\(Acetone)}}{\mathrm{CH_3COCH_3}} + 3\mathrm{NaOCl} \longrightarrow \underset{\text{1, 1, 1, –Trichloropropanone}}{\mathrm{CH_3COCCl_3}} + 3\mathrm{NaOH}$$

(ii) Hydrolysis :

$$\mathrm{CH_3CO}\,\boxed{\mathrm{CCl_3} + \mathrm{H}}\,\mathrm{ONa} \longrightarrow \underset{\text{Trichloromethane}}{\mathrm{CHCl_3}} + \underset{\text{Sod. acetate}}{\mathrm{CH_3COONa}}$$

2. Chlorination of methane. *(Industrial method)*. It is manufactured by chlorination of methane.

$$\underset{\text{Methane}}{\mathrm{CH_4}} \xrightarrow[-\mathrm{HCl}]{\mathrm{Cl_2}/h\nu} \underset{\substack{\text{Methyl}\\\text{chloride}}}{\mathrm{CH_3Cl}} \xrightarrow[-\mathrm{HCl}]{\mathrm{Cl_2}/h\nu} \underset{\substack{\text{Methylene}\\\text{chloride}}}{\mathrm{CH_2Cl_2}} \xrightarrow[-\mathrm{HCl}]{\mathrm{Cl_2}/h\nu} \underset{\text{Chloroform}}{\mathrm{CHCl_3}}$$

The mixture so formed is separated by fractional distillation.

3. Reduction of carbon tetrachloride. *(Industrial method)*. Reduction is brought about with iron filings and steam.

$$\underset{\substack{\text{Carbon}\\\text{tetrachloride}}}{\mathrm{CCl_4}} + 2[\mathrm{H}] \xrightarrow{\text{Fe + Steam}} \underset{\text{Chloroform}}{\mathrm{CHCl_3}} + \mathrm{HCl}$$

4. Pure chloroform can be prepared by the action of sodium hydroxide solution on chloral hydrate.

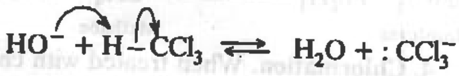
$$\underset{\text{Chloral hydrate}}{\mathrm{CCl_3CH(OH)_2}\ \text{or}\ \mathrm{CCl_3CHO.H_2O}} + \mathrm{NaOH} \longrightarrow \underset{\text{Chloroform}}{\mathrm{CHCl_3}} + \underset{\text{Sod. formate}}{\mathrm{HCOONa}} + \mathrm{H_2O}$$

Physical Properties. Chloroform is a heavy colourless mobile liquid, boiling point 334 K, freezing point 210 K. It has a sickly sweet smell and burning taste. It is sparingly soluble in water but readily dissolves in alcohol and ether. It is a very good solvent for organic compounds. Inhalation of its vapours produces loss of consciousness and is, therefore, used as a general anaesthetic agent in surgery.

Chemical Properties.

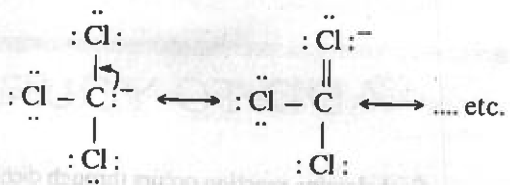
1. Acidic nature. The H-atom in $\mathrm{CHCl_3}$ is slightly acidic because of the following two reasons:

(i) Due to – **I-effect** of the three Cl-atoms, the electron density in the C – H bond is low. As a result, C – H bond is weak and hence can be easily abstracted by a base.



$$\mathrm{HO^-} + \mathrm{H{-}CCl_3} \rightleftharpoons \mathrm{H_2O} + :\mathrm{CCl_3^-}$$

(ii) The $:\mathrm{CCl_3^-}$ ion left after the removal of a proton from $\mathrm{CHCl_3}$ is stabilized by resonance in which Cl-atom can expand its valence shell to a decet (*i.e.* ten) because of the presence of *d*-orbitals,



This type of resonance is also called *$p\pi - d\pi$-electron delocalization or* **d-orbital resonance.**

2. Oxidation : On exposure to air and sunlight, chloroform undergoes slow oxidation to form highly poisonous phosgene gas, $\mathrm{COCl_2}$.

$$\underset{\text{Chloroform}}{CHCl_3} \xrightarrow{O_2,\ \text{light}} \underset{\substack{\text{Carbonyl chloride}\\ (\textit{Phosgene})}}{COCl_2} + HCl$$

So to keep chloroform pure, to be used as an anaesthetic agent,

(*i*) it is stored in brown bottles to cut off light.

(*ii*) the bottles are filled to the brim to exclude any air.

(*iii*) 0.6 – 1% alcohol is added which destroys traces of phosgene that may be formed on storage. Phosgene thus formed combines with ethyl alcohol to form non-toxic diethyl carbonate.

$$\underset{\text{Ethyl alcohol}}{2C_2H_5OH} + \underset{\text{Phosgene}}{COCl_2} \longrightarrow \underset{\text{Diethyl carbonate}}{(C_2H_5)_2CO_3} + 2HCl$$

3. Reduction. Reduction of chloroform with zinc and HCl gives methylene chloride.

$$\underset{\text{Chloroform}}{CHCl_3} + 2[H] \xrightarrow{Zn\,+\,HCl} \underset{\substack{\text{Methylene}\\ \text{chloride}}}{CH_2Cl_2} + HCl$$

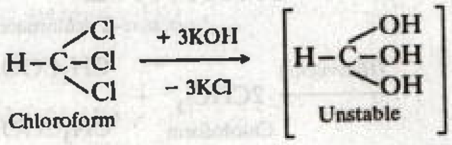
Reduction with zinc dust and water yields methane.

$$\underset{\text{Chloroform}}{CHCl_3} + 6[H] \xrightarrow{Zn\,+\,H_2O} \underset{\text{Methane}}{CH_4} + 3HCl$$

4. Chlorination. When treated with chlorine in presence of sunlight, it is converted into carbon tetrachloride.

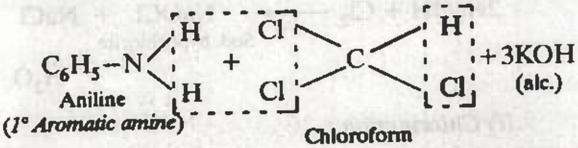
$$\underset{\text{Chloroform}}{CHCl_3} + Cl_2 \xrightarrow{\text{Sunlight}} \underset{\substack{\text{Carbon}\\ \text{tetrachloride}}}{CCl_4} + HCl$$

5. Hydrolysis. On heating with concentrated aqueous or alcoholic potassium hydroxide, it is hydrolysed to give potassium formate.



$$\xrightarrow{-H_2O} \left[\underset{\text{Formic acid}}{HCOOH}\right] \xrightarrow[-\,H_2O]{KOH} \underset{\text{Pot. formate}}{HCOOK}$$

6. Carbylamine reaction. Chloroform on warming with a suitable aromatic or aliphatic primary amine and alcoholic potash gives the corresponding isocyanide or the carbylamine which has extremely unpleasant smell.



$$\xrightarrow{\Delta} \underset{\substack{\text{Phenyl isocyanide}\\ (\textit{Phenyl carbylamine})}}{C_6H_5N \overrightarrow{=} C} + 3KCl + 3H_2O$$

$$\underset{\substack{\text{Ethylamine}\\ (1^\circ\ \textit{Aliphatic amine})}}{CH_3CH_2NH_2} + CHCl_3 + 3\,\underset{(\textit{alc.})}{KOH} \xrightarrow{\Delta}$$

$$\underset{\substack{\text{Ethyl isocyanide}\\ (\textit{Ethyl carbylamine})}}{CH_3CH_2N \overrightarrow{=} C} + 3\,KCl + 3\,H_2O$$

This reaction is used as a test (under the name **carbylamine test** or **isocyanide test**) for both aliphatic and aromatic primary amines.

ADD TO YOUR KNOWLEDGE

Carbylamine reaction occurs through dichlorocarbene intermediate.

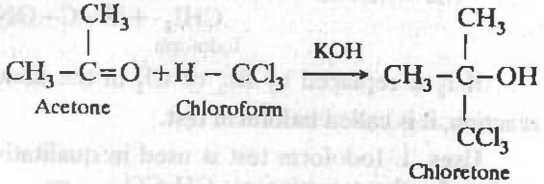
$$CHCl_3 + OH^- \rightleftharpoons H_2O + :CCl_3^- \quad ; \quad :CCl_3^- \xrightarrow{\text{slow}} \underset{\text{Dichlorocarbene}}{:CCl_2} + Cl^-$$

$$\underset{1^\circ\text{Amine}}{RNH_2} + :CCl_2 \longrightarrow R\text{–}\overset{+}{N}H_2\text{–}\bar{C}Cl_2 \xrightarrow{-\,H^+} RNH\text{–}\bar{C}Cl_2 \xrightarrow{-\,HCl} RN = \bar{C}Cl \xrightarrow{-\,Cl^-} \underset{\text{Alkyl isocyanide}}{R\text{–}\overset{+}{N} \equiv C:^-}$$

7. Dehalogenation. Chloroform on warming with silver powder undergoes dehalogenation to give acetylene.

$$\underset{\text{Chloroform}}{HC}\boxed{Cl_3 + 6Ag + Cl_3}\underset{\text{Chloroform}}{CH} \xrightarrow{\Delta} \underset{\text{Acetylene}}{HC\equiv CH} + 6AgCl$$

8. Condensation with ketones. Chloroform adds to ketones in the presence of potassium hydroxide. For example, with acetone it gives chloretone.



$$\underset{\text{Acetone}}{CH_3-\overset{\overset{CH_3}{|}}{C}=O} + \underset{\text{Chloroform}}{H-CCl_3} \xrightarrow{KOH} \underset{\text{Chloretone}}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CCl_3}{|}}{C}}-OH}$$

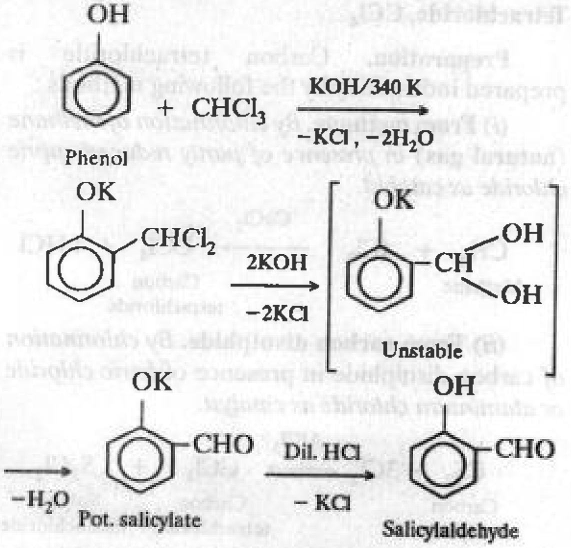
Chloretone is used as an hypnotic (*sleep inducing drug*).

9. Nitration. Chloroform may be nitrated on heating with concentrated nitric acid to give *chloropicrin* or *nitrochloroform*.

$$\underset{\text{Chloroform}}{CHCl_3} + \underset{\substack{\text{Nitric acid}\\ (conc.)}}{HONO_2} \longrightarrow \underset{\text{Chloropicrin}}{CCl_3NO_2} + H_2O$$

It is used as an insecticide. It has also been used as a war gas.

10. Reimer-Tiemann reaction. Chloroform reacts with phenol and alcoholic KOH at 340 K to form salicylaldehyde as the major product.



A small amount of *p*-hydroxybenzaldehyde is also obtained in this reaction.

This reaction is called **Reimer-Tiemann reaction.**

Uses. Chloroform is used as :

1. a solvent for resins, rubbers, oils and fats.
2. a preservative for anatomical specimens.
3. a laboratory reagent (*e.g.* for testing primary amines).
4. In medicines.
5. It was once used as an anaesthetic agent in surgery and as a flavouring agent in cough syrups. But because of its toxicity, it is no longer used for such purposes.

17.12.3. Triiodomethane, Iodoform, CHI_3

Preparation. Iodoform can be prepared by heating ethyl alcohol or acetone with sodium hydroxide and iodine or sodium carbonate and iodine.

(*a*) With ethyl alcohol. The reactions taking place are :

$$2\,NaOH + I_2 \longrightarrow \underset{\text{Sod. hypoiodite}}{NaOI} + NaI + H_2O$$

(*i*) *Oxidation* : $\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} + NaOI \longrightarrow \underset{\text{Acetaldehyde}}{CH_3CHO} + NaI + H_2O$

(*ii*) *Iodination* : $\underset{\text{Acetaldehyde}}{CH_3CHO} + 3\,NaOI \longrightarrow \underset{\text{Triiodoacetaldehyde}}{CI_3CHO} + 3\,NaOH$

(*iii*) *Hydrolysis* : $NaO\boxed{H + CI_3}-CHO \longrightarrow \underset{\text{Iodoform}}{CHI_3} + \underset{\text{Sod. formate}}{HCOONa}$

The complete reaction may be written as :

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} + 4I_2 + 6NaOH \longrightarrow \underset{\text{Iodoform}}{CHI_3} + \underset{\text{Sod. formate}}{HCOONa} + 5NaI + 5H_2O$$

If Na_2CO_3 is used in place of NaOH, the reaction is :

$$CH_3CH_2OH + 4I_2 + 3Na_2CO_3 \longrightarrow CHI_3 + 5NaI + HCOONa + 3CO_2 + 2H_2O$$

(*b*) **With acetone.** The reactions taking place are :

$$2NaOH + I_2 \longrightarrow \underset{\text{Sod. hypoiodite}}{NaOI} + NaI + H_2O$$

(*i*) *Iodination* :

$$\underset{\text{Acetone}}{CH_3COCH_3} + 3NaOI \longrightarrow \underset{\alpha,\alpha,\alpha\text{-Triiodoacetone}}{CH_3COCI_3} + 3\,NaOH$$

(*ii*) *Hydrolysis* :

$$CH_3CO\,[\,CI_3 + H\,]\,ONa \longrightarrow \underset{\text{Iodoform}}{CHI_3} + \underset{\text{Sod. acetate}}{CH_3COONa}$$

The complete reaction may be written as :

$$\underset{\text{Acetone}}{CH_3COCH_3} + 3I_2 + 4NaOH \longrightarrow \underset{\text{Iodoform}}{CHI_3} + 3NaI + \underset{\text{Sod. acetate}}{CH_3COONa} + 3H_2O$$

Physical properties. It is a pale yellow solid, m.p. 392 K, having a characteristic odour. It is insoluble in water but dissolves readily in ethyl alcohol and ether.

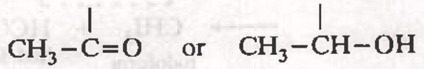
Chemical properties. Its chemical properties are similar to that of chloroform.

Uses 1. Iodoform is used as an antiseptic for dressing wounds. When it comes in contact with skin, *i.e.*, organic matter, iodine is set free and this explains its antiseptic action. Because of its unpleasant smell, it has now been replaced by other formulations containing iodine.

2. It is used in the manufacture of certain pharmaceuticals.

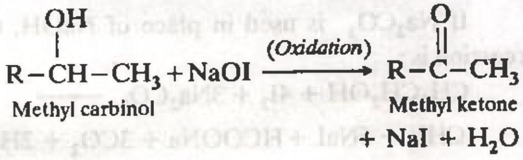
17.12.3.1. Iodoform Test

When ethanol, ethanal, propan-2-ol, propanone etc. or any compound containing the

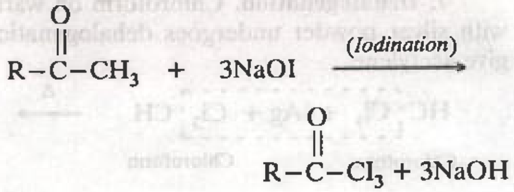


$$CH_3-\overset{|}{C}=O \quad \text{or} \quad CH_3-\overset{|}{C}H-OH$$

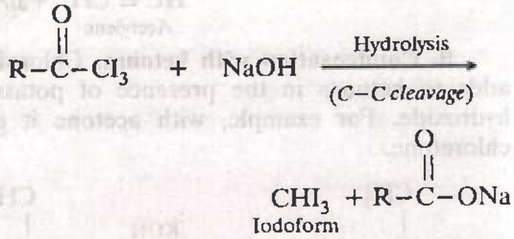
grouping (linked either to carbon or hydrogen) is heated with iodine and an aqueous solution of sodium carbonate or sodium hydroxide, yellow ppt. of iodoform are produced. This reaction which involves oxidation, iodination and cleavage of C – C bond is called **iodoform test.**



$$\underset{\text{Methyl carbinol}}{R-\overset{\overset{\displaystyle OH}{|}}{C}H-CH_3} + NaOI \xrightarrow{(Oxidation)} \underset{\text{Methyl ketone}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3} + NaI + H_2O$$



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + 3NaOI \xrightarrow{(Iodination)} R-\overset{\overset{\displaystyle O}{\|}}{C}-CI_3 + 3NaOH$$



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-CI_3 + NaOH \xrightarrow[(C-C\ cleavage)]{Hydrolysis} \underset{\text{Iodoform}}{CHI_3} + R-\overset{\overset{\displaystyle O}{\|}}{C}-ONa$$

If I_2 is replaced by Br_2 or Cl_2 in the above reaction, it is called **haloform test.**

Uses. 1. Iodoform test is used in qualitative analysis for the detection of CH_3CO- or CH_3CHOH- grouping in any organic compound.

2. This test can be used to distinguish between some of the following pairs of compounds :

(*i*) Ethyl alcohol and methyl alcohol.

(*ii*) *n*-Propyl alcohol and isopropyl alcohol.

(*iii*) *sec*-Butyl alcohol and *n*-butyl alcohol (or isobutyl alcohol or *tert*-butyl alcohol).

(*iv*) Acetaldehyde and propionaldehyde (or any other aldehyde).

(*v*) Pentan-2-one and pentan-3-one etc.

17.12.4. Tetrachloromethane, Carbon Tetrachloride, CCl_4

Preparation. Carbon tetrachloride is prepared industrially by the following methods :

(*i*) **From methane.** *By chlorination of methane* **(natural gas)** *in presence of partly reduced cupric chloride as catalyst.*

$$\underset{\text{Methane}}{CH_4} + 4Cl_2 \xrightarrow{CuCl_2} \underset{\text{Carbon tetrachloride}}{CCl_4} + 4\,HCl$$

(*ii*) **From carbon disulphide.** *By chlorination of* carbon disulphide in presence of *ferric chloride or aluminium chloride as catalyst.*

$$\underset{\text{Carbon disulphide}}{CS_2} + 3Cl_2 \xrightarrow{AlCl_3} \underset{\text{Carbon tetrachloride}}{CCl_4} + \underset{\text{Sulphur monochloride}}{S_2Cl_2}$$

Sulphur monochloride thus formed is separated by fractional distillation and then treated with fresh carbon disulphide to yield more carbon tetrachloride.

$$2S_2Cl_2 + CS_2 \longrightarrow CCl_4 + 6S$$

Physical properties. It is a colourless, volatile, non- inflammable liquid, *b.p.* 350 K. It has sickly smell. It is insoluble in water but dissolves readily in organic solvents such as alcohol, ether etc.

Chemical properties. Some important properties of carbon tetrachloride are given below :

1. Stability. CCl_4 is stable to red heat (about 773 K). Its vapours are highly non-inflammable *i.e.* do not catch fire. It is because of this property that CCl_4 is used as a fire extinguisher under the name *Pyrene.* At this high temperature, it is hydrolysed by water vapours to some extent to form highly poisonous gas, *i.e.*, phosgene.

$$CCl_4 + \underset{(steam)}{H_2O} \longrightarrow \underset{\text{Phosgene}}{COCl_2} + 2HCl$$

2. Reduction. On reduction with moist iron filings, carbon tetrachloride gives chloroform.

$$\underset{\text{Carbon tetrachloride}}{CCl_4} + 2[H] \xrightarrow{Fe/H_2O} \underset{\text{Chloroform}}{CHCl_3} + HCl$$

Therefore, after using CCl_4 to extinguish fire, the room should be well ventilated.

3. Hydrolysis. On boiling with alcoholic KOH solution, it undergoes hydrolysis to produce potassium carbonate.

$$CCl_4 + 4KOH \xrightarrow[-4KCl]{\Delta} \underset{\text{Unstable}}{[C(OH)_4]} \longrightarrow CO_2 + 2H_2O$$

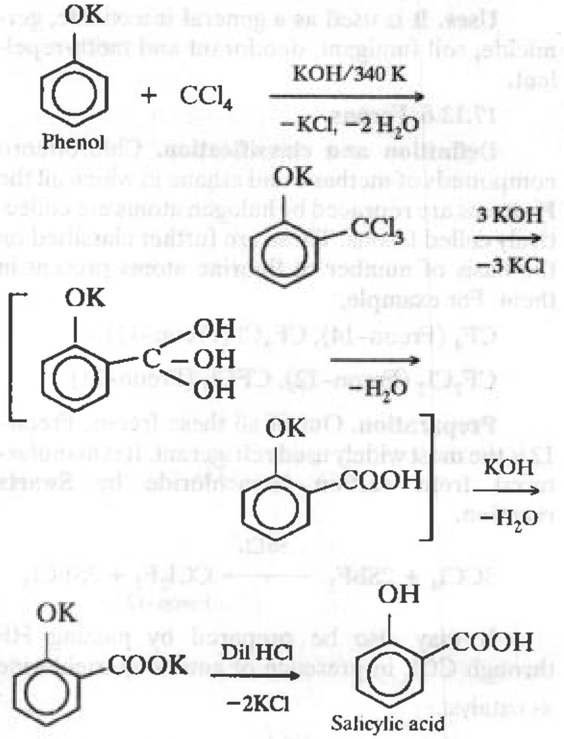
$$CO_2 + 2KOH \longrightarrow K_2CO_3 + H_2O$$

4. Reaction with antimony triflouride. It reacts with antimony trifluoride in presence of antimony pentachloride as catalyst to form dichlorodifluoromethane or *Freon.*

$$3CCl_4 + 2SbF_3 \xrightarrow{SbCl_5} \underset{\text{Freon}}{3CCl_2F_2} + 2SbCl_3$$

Freon is widely used as a refregerant (cooling agent) in refrigerators and air conditioners.

5. Riemer-Tiemann reaction. Carbon tetrachloride reacts with phenol and alcoholic KOH at 340 K to form salicylic acid as the major product.



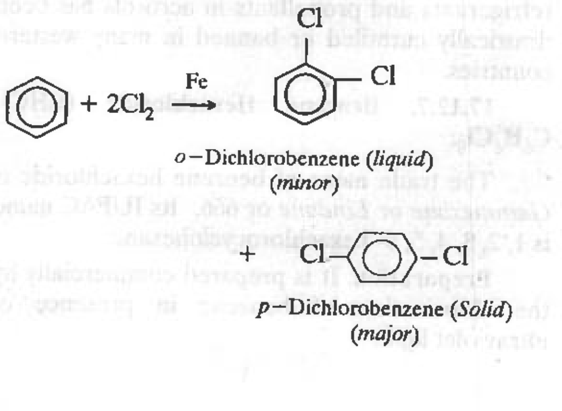
A small amount of *p*-hydroxybenzoic acid is also obtained in this reaction.

Uses. Carbon tetrachloride is used :

1. As an industrial solvent for oils, fats, resins, lacquers etc., and also in dry cleaning.
2. As a fire extinguisher under the name '*Pyrene*'.
3. For the industrial preparation of chloroform.
4. As a medicine for hook-worms.

17.12.5. p-Dichlorobenzene

Preparation. It is prepared by chlorination of benzene followed by filtration.



o−Dichlorobenzene (*liquid*) (*minor*)

p−Dichlorobenzene (*Solid*) (*major*)

Properties. It is a white, volatile solid, m.p. 323 K, which readily sublimes.

Uses. It is used as a general insecticide, germicide, soil fumigant, deodorant and moth-repellent.

17.12.6. Freons

Definition and classification. Chlorofluoro compounds of methane and ethane in which all the H-atoms are repraced by halogen atoms are collectively called freons. These are further classified on the basis of number of fluorine atoms present in them. For example,

CF_4 (Freon–14), CF_3Cl (Freon–13),

CF_2Cl_2 (Freon–12), $CFCl_3$ (Freon–11)

Preparation. Out of all these freons, Freon-12 is the most widely used refrigerant. It is manufactured from carbon tetrachloride by **Swarts reaction.**

$$3CCl_4 + 2SbF_3 \xrightarrow{SbCl_5} \underset{\text{Freon–12}}{CCl_2F_2} + 2SbCl_3$$

It may also be prepared by passing HF through CCl_4 in presence of antimony trichloride as catalyst.

$$CCl_4 + 2HF \xrightarrow{SbCl_3} CCl_2F_2 + 2HCl$$

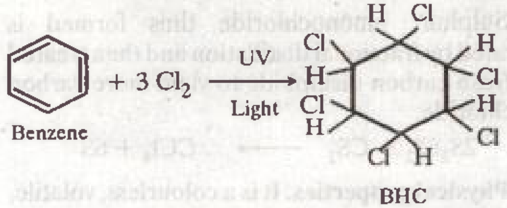
Uses. Freon is an odourless, non-corrosive, non-toxic gas which is stable even at high temperatures and pressures. It has low *b.p.*, low specific heat and can be easily liquefied by applying pressure at room temperature. It is, therefore, *widely used as a refrigerant (cooling agent) in refrigerators and air conditioners. It is also used as a propellant in aerosols and foams (i.e., hair sprays, deodorants, shaving creams, cleansers, insecticides etc).*

Recently, it has been shown that freon is **responsible for destruction of the ozone layer in the upper atmosphere. Therefore, the use of freons as refrigerants and propellants in aerosols has been drastically curtailed or banned in many western countries.**

17.12.7. Benzene Hexachloride (BHC), $C_6H_6Cl_6$.

The trade name of benzene hexachloride is *Gammexane* or *Lindane* or 666. Its IUPAC name is 1, 2, 3, 4, 5, 6- hexachlorocyclohexane.

Preparation. It is prepared commercially by the chlorination of benzene in presence of ultraviolet light.



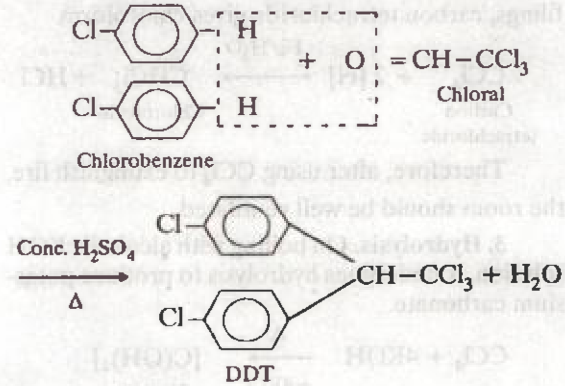
It occurs in a number of stereoisomeric forms but the γ-isomer is the most effective.

Uses. It is extensively used as a pesticide in agriculture for exterminating (killing) termite (white ants) from soil.

17.12.8. DDT [2, 2-Bis(4-chlorophenyl)-1, 1, 1-trichloroethane]

General. DDT stands for *p,p'*-dichlorodiphenyltrichloroethane. In fact, this name is a misnomer. Its actual name is 2, 2-bis (4-chlorophenyl)-1, 1, 1-trichloroethane.

Preparation. It is prepared by heating chlorobenzene with chloral (trichloroacetaldehyde) in presence of conc. H_2SO_4



Uses. DDT is a cheap but powerful insecticide. It is widely used for sugarcane and fodder crops and to kill mosquitoes and other insects. It is particularly very effective against *Anopheles mosquitoes* which spread malaria. Through its use, malaria has virtually been eliminated from India and large part of the world.

Tragic side effects. DDT is not *biodegradable.* Its residues accumulate in environment which are toxic to mammals and human beings. Therefore, its use has been abandoned in many western countries. However, in India, in spite of these tragic side effects, DDT is still being widely used due to the non-availability of any other cheaper insecticide.

17.12.9. Perfluorocarbons (PFC's)

Their general formula is $C_n F_{2n+2}$.

Preparation. These are obtained by controlled fluorination of alkanes diluted with N_2 gas in the vapour phase in the presence of a catalyst.

$$\underset{\text{Heptane}}{C_7H_{16}} + 16F_2 \xrightarrow[\text{CoF}_2\text{ (catalyst)}]{\text{vapour phase, }N_2\text{, 573 K}} \underset{\text{Perfluoroheptane}}{C_7F_{16}} + 16HF$$

Properties. (*i*) Perfluorocarbons are colourless, odourless, non-toxic, non-flammable, non-corrosive, non-polar, extremely stable, unreactive gases, liquids or solids.

(*ii*) They are stable to UV light and other ionising radiations and, therefore, do not deplete the ozone layer.

Uses. (*i*) They are good electrical insulators. They are also used as lubricants, surface coatings, dielectrics, heat transfer media in high voltage electrical equipment etc.

(*ii*) In electronic industry, they are used for vapour phase soldering, gross leak detection of sealed microchips etc.

(*iii*) They find several applications in health care and medicine. For example, in skin-care cosmetics, wound healing, liquid ventilation, retina reattachment, carbon monoxide poisoning and medical diagnosis.

17.12.10. Westron or 1,1,2,2-Tetrachloroethane

Preparation. Westron or acetylene tetrachloride is prepared by passing acetylene and chlorine over iron filings.

$$HC \equiv CH + Cl_2 \xrightarrow{\text{Fe}}$$

$$\underset{\text{Acetylene dichloride}}{ClCH = CHCl} \xrightarrow{Cl_2/Fe} \underset{\text{Acetylene tetrachloride}}{Cl_2HC - CHCl_2}$$

Uses. It is a colourless, non-inflammable heavy liquid with b.p. 419 K. It is widely used as a solvent for oils, fats, paints varnishes, rubber etc.

17.12.11. Westrosol or 1,1,2–Trichloroethene

Preparation. Westrosol or trichloroethylene is prepared by passing Westron over heated $BaCl_2$ as catalyst.

$$\underset{\text{Westron}}{Cl_2CH - CHCl_2} \xrightarrow{BaCl_2\text{, }\Delta} \underset{\text{Westrosol}}{ClCH = CCl_2} + HCl$$

Uses. Westrosol is a colourless, non-inflammable heavy liquid with b.p. 363. It is a better solvent than Westron. It is used in dry cleaning and also as a solvent for rubber.

Conceptual Questions

Q. 1. **Arrange each of the following sets of compounds in order of increasing boiling points :**

(*a*) Bromoethane, bromoform, chloromethane, dibromomethane.

(*b*) Propane, 1-chloropropane, isopropyl chloride, 1- chlorobutane. *(N.C.E.R.T.)*

Ans. (*a*) Since boiling points increase with increasing molecular mass due to greater magnitude of van der Waals' forces of attraction, the boiling points of these compounds increase in the order :

Chloromethane, bromomethane, dibromomethane, bromoform.

(*b*) The boiling points increase with increasing molecular mass but decrease with branching. Isopropyl chloride being branched has lower boiling point than 1-chloropropane. The actual order of increasing boiling points is : Propane, isopropyl chloride, 1-chloropropane, 1-chlorobutane.

Q. 2. **Arrange the following in order of increasing boiling points**

(*i*) *n*-amyl chloride, neoamyl chloride, *tert*-amyl chloride, isoamyl chloride.

(*ii*) *n*-hexyl chloride, *n*-pentyl chloride, *tert*-butyl chloride, *n*-propyl chloride, *sec*-butyl chloride.

Ans. (*i*) Amongst isomeric alkyl halides, boiling points decrease as the branching increases. Since branching increases in the order : *n*-amyl chloride, isoamyl chloride, *tert*-amyl chloride, neoamyl chloride, therefore, the boiling points decrease in the same order : *n-amyl chloride > isoamyl chloride > tert-amyl chloride > neoamyl chloride.*

(*ii*) As the length of the carbon chain increases, the boiling point increases and amongst isomeric alkyl halides, boiling point decreases as the branching increases. Thus, *n*- hexyl chloride with *six* carbon atoms has the highest b.p. followed by *n*-pentyl chloride with *five* carbon atoms followed by *sec*- butyl chloride and *tert*-butyl chloride with *four* carbon atoms each followed by *n*-propyl chloride with *three* carbon atoms. Amongst *sec*-butyl chloride and *tert*-butyl chloride, *tert*-butyl chloride has lower boiling point because of *two* branches than *sec*-butyl chloride with no branching. Thus, the overall order is :

n-hexyl chloride > n-pentyl chloride > sec-butyl chloride > tert-butyl chloride > n-propyl chloride.

Q. 3. Haloarenes are insoluble in water but are soluble in benzene. *(D.S.B. 1998)*

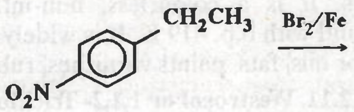
Ans. Haloarenes are insoluble in water because neither can they form H-bonds with water nor can they break the H-bonds already existing in water. However, in accordance with the general principle of solubility, *i.e., like dissolves like*, haloarenes due to the presence of a large hydrocarbon part (benzene ring) are soluble in hydrocarbon solvents such as benzene, petroleum ether etc.

Q. 4. *p*-Dichlorobenzene has higher melting point and lower solubility than those of *o*- and *m*-isomers.

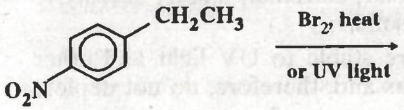
Ans. The *p*-isomer being more symmetrical fits closely in the crystal lattice and thus has stronger inter molecular forces of attraction than *o*- and *m*-isomers. Since during melting or dissolution, the crystal lattice breaks, therefore, a larger amount of energy is needed to melt or dissolve the *p*-isomer than the corresponding *o*-and *m*- isomers. In other words, the *melting point of the p-isomer is higher and its solubility lower than the corresponding o- and m- isomers.*

Q. 5. Draw the structures of the major monohalo product in each of the following reactions :

(*a*)

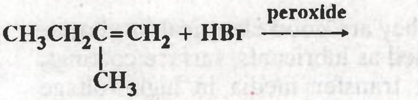


(*b*)



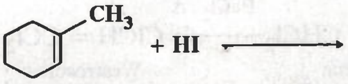
(*c*) $CH_3CH_2C\equiv CH + HCl$ (1 equiv) $\longrightarrow$

(*d*)

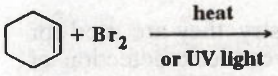


$CH_3CH_2\underset{CH_3}{\underset{|}{C}}=CH_2 + HBr \xrightarrow{\text{peroxide}}$

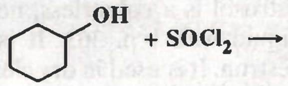
(*e*)



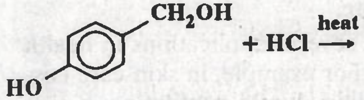
(*f*)



(*g*)

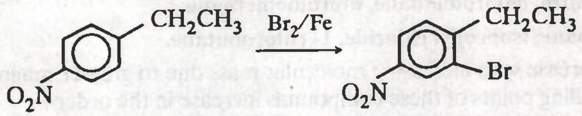


(*h*)

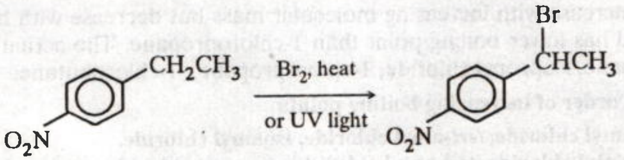


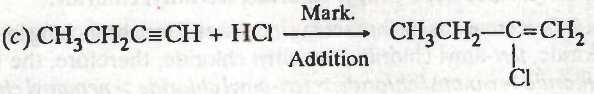
(*i*) $CH_3CH_2Br + NaI \xrightarrow[\text{reflux}]{\text{acetone}}$ (*j*) $CH_3CH_2Br + Hg_2F_2 \longrightarrow$ *(N.C.E.R.T.)*

Ans. (*a*) In presence of halogen carrier and absence of light, electrophilic substitution occurs at position *ortho* (since the *p*-position is already occupied) to the electron-donating CH_2CH_3 group.

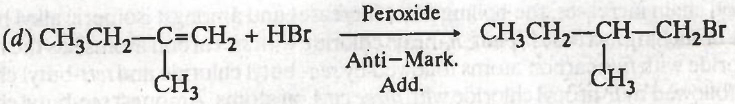


(*b*) In presence of light, side chain (free radical)- halogenation occurs at the benzylic hydrogen.



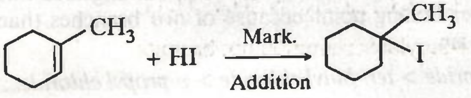


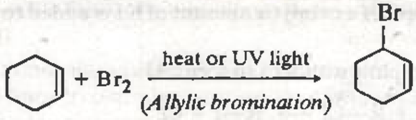
(*c*) $CH_3CH_2C\equiv CH + HCl \xrightarrow[\text{Addition}]{\text{Mark.}} CH_3CH_2-\underset{Cl}{\underset{|}{C}}=CH_2$

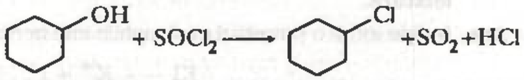


(*d*) $CH_3CH_2-\underset{CH_3}{\underset{|}{C}}=CH_2 + HBr \xrightarrow[\text{Anti-Mark. Add.}]{\text{Peroxide}} CH_3CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_2Br$

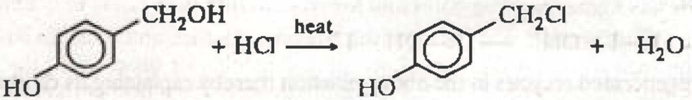
(*e*)



(*f*)


(*g*)


(*h*) Due to resonance, C–O bond in phenols is much stronger than C–O bond in alcohols and hence substitution occurs only at the alcoholic group.



(*i*) $CH_3CH_2Br + NaI \xrightarrow[\text{(Finkelstein reaction)}]{\text{acetone, reflux}} CH_3CH_2I + NaBr$

(*j*) $2CH_3CH_2Br + Hg_2F_2 \xrightarrow[\text{(Swarts reaction)}]{\text{Halogen exchange}} 2CH_3CH_2F + Hg_2Cl_2$

Q. 6. Give the structures of the main organic substitution product expected from the reaction of 1-bromobutane with (*a*) $(CH_3)_3N$ (*b*) $(CH_3)_2S$ (*c*) CH_3COOAg (*d*) $LiAlH_4$ (*e*) C_6H_5ONa. (*N.C.E.R.T.*)

Ans. (*a*) $(CH_3)_3\ddot{N} + \underset{\text{1−Bromobutane}}{CH_3CH_2CH_2CH_2{-}Br} \longrightarrow \underset{\textbf{Butyltrimethylammonium bromide}}{[(CH_3)_3\overset{+}{N}{-}CH_2CH_2CH_2CH_3]\,Br^-}$

(*b*) $(CH_3)_2\ddot{S}: + CH_3CH_2CH_2CH_2{-}Br \longrightarrow \underset{\textbf{Butyldimethylsulphonium bromide}}{[(CH_3)_2\overset{+}{S}{-}CH_2CH_2CH_2CH_3]\,Br^-}$

(*c*) $CH_3COOAg + CH_3CH_2CH_2CH_2{-}Br \longrightarrow \underset{\textbf{Butyl ethanoate}}{CH_3COOCH_2CH_2CH_2CH_3} + AgBr$

(*d*) $LiAlH_4 + 4CH_3CH_2CH_2CH_2Br \longrightarrow 4\,CH_3CH_2CH_2CH_3 + LiBr + AlBr_3$

(*e*) $C_2H_5O^-Na^+ + CH_3CH_2CH_2{-}Br \xrightarrow[\text{synthesis}]{\text{Williamson's}} \underset{\textbf{Butyl ethyl ether}}{CH_3CH_2CH_2CH_2{-}O{-}C_2H_5} + NaBr$

Q. 7. Give reagents inorganic or organic, needed to convert benzyl bromide into (*a*) benzyl iodide (*b*) benzyl ethyl ether (*c*) benzyl alcohol (*d*) benzyl cyanide (*e*) benzyl acetate (*f*) (nitromethyl)benzene (*g*) tri-*n*-butylbenzylammonium bromide. (*N.C.E.R.T.*)

Ans.

$C_6H_5CH_2{-}Br$ **Benzyl bromide**

(*a*) NaI/acetone → $C_6H_5CH_2I$ (benzyl iodide)

(*b*) $NaOC_2H_5$ → $C_6H_5{-}O{-}CH_2CH_3$ (benzyl ethyl ether)

(*c*) NaOH (*aq*) → $C_6H_5CH_2OH$ (benzyl alcohol)

(*d*) KCN (alc.) → $C_6H_5CH_2CN$ (benzyl cyanide)

(*e*) CH_3COOAg → $CH_3COOCH_2C_6H_5$ (benzyl acetate)

(*f*) $AgNO_2$ → $C_6H_5CH_2NO_2$ (phenylnitromethane)

(*g*) $(CH_3CH_2CH_2CH_2)_3N$ → $[(CH_3CH_2CH_2CH_2)_3\overset{+}{N}CH_2C_6H_5]\,Br^-$ (tri-*n*-butylbenzylammonium bromide)

Q. 8. RCl is hydrolysed to ROH slowly but the reaction is rapid if a catalytic amount of KI is added to the reaction mixture.

Ans. Iodide ion is a powerful nucleophile and hence reacts rapidly with RCl to form RI.

$$KI \longrightarrow K^+ + I^- \quad ; \qquad I^- + R\text{—}Cl \longrightarrow R\text{—}I + Cl^-$$

Further because I^- ion is a better leaving group than Cl^- ion, therefore, RI is more rapidly hydrolysed than RCl to form ROH,

$$R\text{—}I + OH^- \longrightarrow R\text{—}OH + I^-$$

The I^- ion thus regenerated recycles in the above reaction thereby explaining its catalytic effect.

Q. 9. The treatment of alkyl chloride with aqueous KOH leads to the formation of alcohols but in presence of alcoholic KOH, alkenes are the major products. Explain why ? *(H.S.B. 1990 S ; H.P.S.B. 1991)*

Ans. In aqueous solution, KOH is almost completely ionized to give OH^- ions which being a strong nucleophile brings about a substitution reaction on alkyl halides to form alcohols. Further in the aqueous solution, OH^- ions are highly solvated (hydrated). This solvation reduces the basic character of OH^- ions which, therefore, fail to abstract a hydrogen from the β-carbon of the alkyl chloride to form an alkene.

In contrast, an alcoholic solution of KOH contains alkoxide (RO^-) ions which being a much stronger base than OH^- ions preferentially eliminates a molecule of HCl from an alkyl chloride to form alkenes.

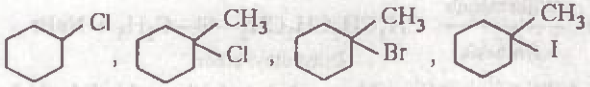
Q. 10. Arrange the following halides in order of increasing S_N2 reactivity :

CH_3Cl, CH_3Br, CH_3CH_2Cl, $(CH_3)_2CHCl$. *(N.C.E.R.T.)*

Ans. As the size of the alkyl group increases, S_N2 reactivity decreases. Further C—Br being weaker is easier to break than C—Cl bond. Therefore, the overall increasing S_N2 reactivity follows the order :

$(CH_3)_2CHCl < CH_3CH_2Cl < CH_3Cl < CH_3Br$.

Q. 11. Predict the order of reactivity of the following compounds in S_N1 reactions. *(N.C.E.R.T.)*



Ans. The first compound is a 2° alkyl halide while all others are 3° alkyl halides. Since 3° alkyl halides are more reactive than 2° alkyl halides in S_N1 reactions, therefore, first compound is the least reactive. Further reactivity increases in the order : chloride < bromide < iodide. Thus, the increasing order of reactivity in S_N1 reactions is the same in which they are listed above.

Q. 12. Predict the order of reactivity of the following compounds in S_N1 and S_N2 reactions.

(a) The four isomeric bromobutanes.

(b) $C_6H_5CH_2Br$, $(C_6H_5)_2CH\text{—}Br$, $C_6H_5CH(CH_3)Br$, $(C_6H_5)_2C(CH_3)Br$. *(N.C.E.R.T.)*

Ans. (*a*) In S_N1 reactions, the order of reactivity depends upon the stability of the intermediate carbocations, therefore, $(CH_3)_3CBr$ which gives a 3° carbocation, *i.e.* $(CH_3)_3C^+$ is the most reactive. $CH_3CH_2CH(Cl)CH_3$ which gives a 2° carbocation, *i.e.* $CH_3CH_2\overset{+}{C}HCH_3$ and hence is less reactive that $(CH_3)_3CBr$. Out of the remaining two 1° alkyl halides, the carbocation $(CH_3)_2CHCH_2^+$ is more stable than the carbocation $CH_3CH_2CH_2CH_2^+$ due to greater +I-effect of $(CH_3)_2CHCH_2$-group *w.r.t.* $CH_3CH_2CH_2CH_2$-group and hence the alkyl halide, $(CH_3)_2CHCH_2Br$ is more reactive than $CH_3CH_2CH_2CH_2Br$. Thus the overall increasing reactivity of the four isomeric bromobutanes towards S_N1 reaction follows the order :

$CH_3CH_2CH_2CH_2Br < (CH_3)_2CHCH_2Br < CH_3CH_2CH(Br)CH_3 < (CH_3)_3CBr$

The reactivity in S_N2 reactions, however, follows the reverse order, *i.e.*,

$CH_3CH_2CH_2CH_2Br > (CH_3)_2CHCH_2Br > CH_3CH_2CH(Br)CH_3 > (CH_3)_3CBr$

since the steric hindrance around the electrophilic carbon (*i.e.* α-carbon) increases in that order

(*b*) Since the reactivity in S_N1 reactions increases as the stability of the intermediate carbocation increases, therefore, $(C_6H_5)_2C(CH_3)Br$ which gives 3° carbocation, *i.e.*, $(C_6H_5)_2\overset{+}{C}(CH_3)$ is the most reactive. Of the two 2° bromides, the carbocation intermediate derived from $(C_6H_5)_2CHBr$ *i.e.* $(C_6H_5)_2CH^+$ is more stable as compared to the carbocation $C_6H_5\overset{+}{C}HCH_3$ obtained from $C_6H_5CH(CH_3)Br$ because it is stabilized by two phenyl groups due to resonance. The fourth alkyl bromide, *i.e.*, $C_6H_5CH_2Br$ which gives the 1° carbocation, *i.e.*, $C_6H_5CH_2^+$ is, however, the least reactive. Thus, the overall reactivity of these alkyl bromides towards S_N1 reactions follows the order :

$(C_6H_5)_2C(CH_3)Br > (C_6H_5)_2CHBr > C_6H_5CH(CH_3)Br > C_6H_5CH_2Br$

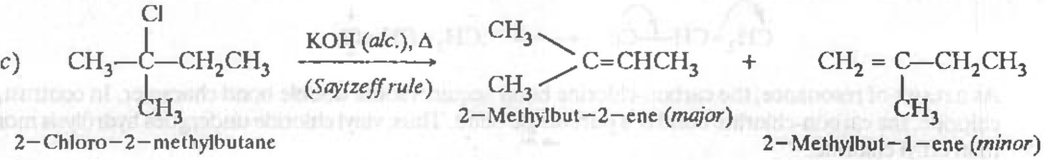
In S_N2 reactions, it is the steric hindrance which determines the reactivity. Since a phenyl group is much bulkier than a methyl group, therefore, $(C_6H_5)_2C(CH_3)Br$ is the least reactive followed by $(C_6H_5)_2CHBr$ and $C_6H_5CH(CH_3)Br$ while $C_6H_5CH_2Br$ is the most reactive. Thus the overall reactivity of these alkyl bromides towards S_N2 reactions follows the order :

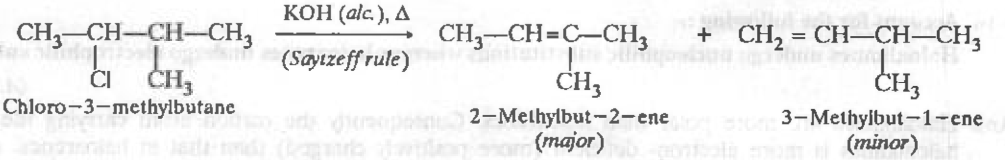
$C_6H_5CH_2Br > C_6H_5CH(CH_3)Br > (C_6H_5)_2CHBr > (C_6H_5)_2C(CH_3)Br$

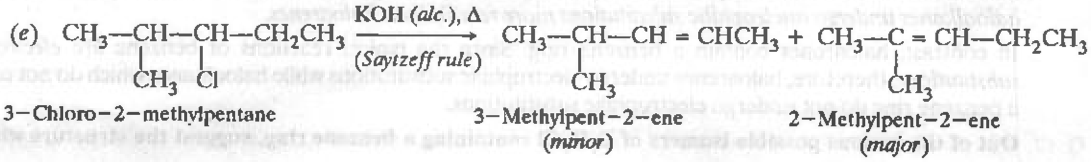
Q. 13. **Identify the possible alkenes that would be formed on dehydrohalogenation of the following organic halides with alcoholic KOH. Also identify the major alkene.**
(*a*) 1-Chloropentane (*b*) 2-Chloropentane (*c*) 2-Chloro-2-methylbutane (*d*) 2-Chloro-3-methylbutane (*e*) 3-Chloro-2-methylpentane. (*N.C.E.R.T.*)

Ans. (*a*) $\underset{\text{1-Chloropentane}}{CH_3CH_2CH_2CH_2CH_2Cl} \xrightarrow[\Delta]{\text{KOH } (alc.)} \underset{\text{Pent-1-ene}}{CH_3CH_2CH_2CH{=}CH_2}$

(*b*) $\underset{\text{2-Chloropentane}}{CH_3—CHCl—CH_2CH_2CH_3} \xrightarrow[(Saytzeff\ rule)]{\text{KOH } (alc.)\ \Delta} \underset{\text{Pent-2-ene } (major)}{CH_3CH{=}CHCH_2CH_3} + \underset{\text{Pent-1-ene } (minor)}{CH_3CH_2CH_2CH{=}CH_2}$

(*c*)

$$\underset{\text{2-Chloro-2-methylbutane}}{CH_3—\underset{CH_3}{\overset{Cl}{C}}—CH_2CH_3} \xrightarrow[(Saytzeff\ rule)]{\text{KOH } (alc.),\ \Delta} \underset{\text{2-Methylbut-2-ene } (major)}{\begin{matrix}CH_3\\ \\ CH_3\end{matrix}\!\!>\!C{=}CHCH_3} + \underset{\text{2-Methylbut-1-ene } (minor)}{CH_2 = \underset{CH_3}{C}—CH_2CH_3}$$

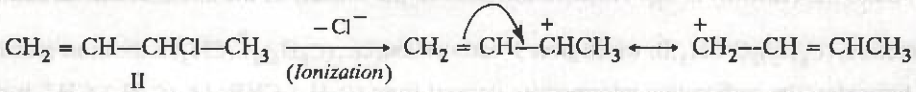
(*d*)

$$\underset{\text{2-Chloro-3-methylbutane}}{CH_3—\underset{Cl}{CH}—\underset{CH_3}{CH}—CH_3} \xrightarrow[(Saytzeff\ rule)]{\text{KOH } (alc.),\ \Delta} \underset{\text{2-Methylbut-2-ene } (major)}{CH_3—CH{=}\underset{CH_3}{C}—CH_3} + \underset{\text{3-Methylbut-1-ene } (minor)}{CH_2 = CH—\underset{CH_3}{CH}—CH_3}$$

(*e*)

$$\underset{\text{3-Chloro-2-methylpentane}}{CH_3—\underset{CH_3}{CH}—\underset{Cl}{CH}—CH_2CH_3} \xrightarrow[(Saytzeff\ rule)]{\text{KOH } (alc.),\ \Delta} \underset{\text{3-Methylpent-2-ene } (minor)}{CH_3—\underset{CH_3}{CH}—CH = CHCH_3} + \underset{\text{2-Methylpent-2-ene } (major)}{CH_3—\underset{CH_3}{C} = CH—CH_2CH_3}$$

Q. 14. **Arrange the following halides in the decreasing order of S_N1 reactivity.**

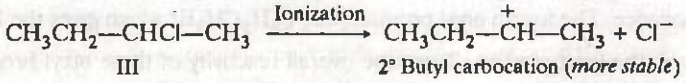
$CH_3CH_2CH_2Cl$ (I), $CH_2 = CHCHClCH_3$ (II) and $CH_3CH_2CHClCH_3$ (III)

Ans. (*i*) In S_N1 reactions, carbocations are the intermediates. Obviously more stable the carbocation, more reactive is the alkyl halide. Since alkyl halide (II) gives an allylic carbocation which is stabilized by resonance, therefore, *alkyl halide* (II) *is the most reactive.*

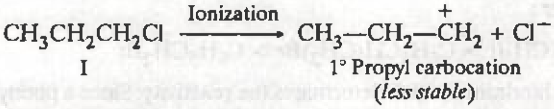


$$\underset{\text{II}}{CH_2 = CH-CHCl-CH_3} \xrightarrow[\text{(Ionization)}]{-Cl^-} CH_2 = CH-\overset{+}{C}HCH_3 \longleftrightarrow \overset{+}{C}H_2-CH = CHCH_3$$

(*ii*) Out of alkyl halides (I) and (III), III gives a more stable 2° carbocation while I gives a less stable 1° carbocation, therefore, alkyl halide (III) is more reactive than alkyl halide (I).



$$\underset{\text{III}}{CH_3CH_2-CHCl-CH_3} \xrightarrow{\text{Ionization}} \underset{\text{2° Butyl carbocation (more stable)}}{CH_3CH_2-\overset{+}{C}H-CH_3} + Cl^-$$



$$\underset{\text{I}}{CH_3CH_2CH_2Cl} \xrightarrow{\text{Ionization}} \underset{\substack{\text{1° Propyl carbocation}\\ \text{(less stable)}}}{CH_3-CH_2-\overset{+}{C}H_2} + Cl^-$$

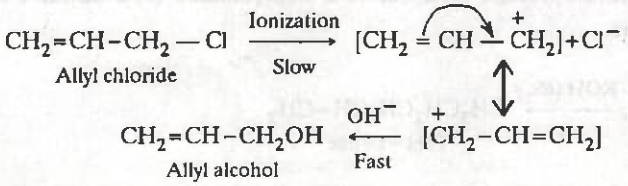
Thus from the above discussion, it follows that the overall reactivity in S_N1 reaction follows the sequence : II > III > I.

Q. 15. **Explain the following in one or two sentences.**

(*i*) Allyl chloride is hydrolysed more readily than *n*-propyl chloride

(*ii*) Vinyl chloride is hydrolysed more slowly than ethyl chloride.

Ans. (*i*) Allyl chloride readily undergoes ionization to produce resonance stabilized allyl carbocation. Since carbocations are reactive species, therefore, allyl cation readily combines with OH^- ions to form allyl alcohol.



$$\begin{tikzcd} \underset{\text{Allyl chloride}}{CH_2=CH-CH_2-Cl} \arrow[r, "\text{Ionization}", "\text{Slow}"'] & {[CH_2=CH-\overset{+}{C}H_2]+Cl^-} \arrow[d, leftrightarrow] \\ \underset{\text{Allyl alcohol}}{CH_2=CH-CH_2OH} & {[\overset{+}{C}H_2-CH=CH_2]} \arrow[l, "OH^-"', "\text{Fast}"] \end{tikzcd}$$

In contrast, *n*-propyl chloride does not undergo ionization to produce *n*-propyl carbocation and hence allyl chloride is hydrolysed more readily than *n*-propyl chloride.

(*ii*) Vinyl chloride may be represented as a resonance hybrid of the following two structures :

$$CH_2=CH-\underset{..}{\ddot{Cl}}: \longleftrightarrow :\overset{-}{C}H_2-CH=\overset{+}{\underset{..}{Cl}}:$$

As a result of resonance, the carbon-chlorine bond acquires some double bond character. In contrast, in ethyl chloride, the carbon-chlorine bond is a pure single bond. Thus, vinyl chloride undergoes hydrolysis more slowly than ethyl chloride.

Q. 16. **Account for the following :**

Haloalkanes undergo nucleophilic substitutions whereas haloarenes undergo electrophilic substitutions.

(A.I.S.B. 1997)

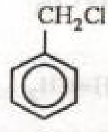
Ans. Haloalkanes are more polar than haloarenes. Consequently the carbon atom carrying the halogen in haloalkanes is more electron- deficient (more positively charged) than that in haloarenes. As a result, *haloalkanes undergo nucleophilic substitutions more readily than haloarenes.*

In contrast, haloarenes contain a benzene ring. Since the typical reactions of benzene are *electrophilic substitutions,* therefore, haloarenes undergo electrophilic substitutions while haloalkanes which do not contain a benzene ring do not undergo electrophilic substitutions.

Q. 17. **Out of the various possible isomers of C_7H_7Cl containing a benzene ring, suggest the structure with the weakest C—Cl bond.**

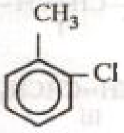
Ans. Four isomers are possible, their structures are :

(*i*)



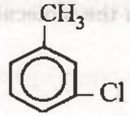
Benzyl chloride

(*ii*)



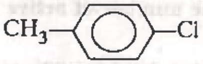
o-Chlorotoluene

(*iii*)



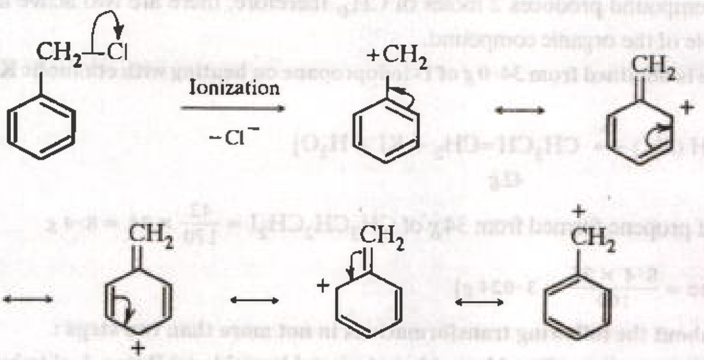
m-Chlorotoluene

(*iv*)



p-Chlorotoluene

Just as in chlorobenzene, the C—Cl bond in *o, m-* and *p*-chlorotoluenes, has some double bond character due to resonance. In contrast, in benzyl chloride, the C—Cl bond is a *pure single bond.* Hence, out of the four isomers, the C—Cl bond is the weakest in benzyl chloride. *Alternatively*, the cleavage of C—Cl bond in benzyl chloride gives benzyl cation which is stabilized by resonance.

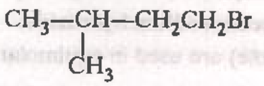


Resonance structures of benzyl cation

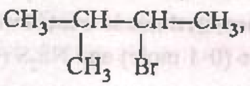
On the other hand, cleavage of C—Cl bond in *o-*, *m-* or *p*-chlorotoluene gives tolyl cation which is highly unstable. As a result, the energy of activation for the cleavage of C—Cl bond in benzyl chloride is much smaller than that of C—Cl bond in *o-*, *m-* or *p*-chlorotoluenes. Consequently, the C—Cl bond is the weakest in benzyl chloride.

Q. 18. An alkyl halide (A), on reaction with magnesium in dry ether followed by treatment with ethanol gave 2-methylbutane. Write all the possible structures of A. *(N.C.E.R.T.)*

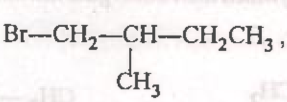
Ans. The structures of all the possible alkyl halides that can be obtained by monohalogenation of 2-methylbutane are :



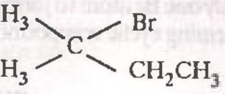
$CH_3—\underset{CH_3}{\underset{|}{C}H}—CH_2CH_2Br$,



$CH_3—\underset{CH_3}{\underset{|}{C}H}—\underset{Br}{\underset{|}{C}H}—CH_3$,



$Br—CH_2—\underset{CH_3}{\underset{|}{C}H}—CH_2CH_3$,



The Grignard reagents of all these four alkyl halides will give 2-methylbutane on treatment with ethanol.

Q. 19. Explain the formation of two products in the following reaction.

$$CH_3CH{=}CHCH_2Cl + H_2O \longrightarrow CH_3CH{=}CHCH_2OH + CH_3CH(OH)CH{=}CH_2$$ *(N.C.E.R.T.)*

Ans. Ionization of the given alkylic chloride gives a carbocation which is a resonance hybrid of structures (I and II). Nucleophilic attack by H_2O followed by loss of a proton on either of these two carbocations gives the corresponding alcohols (III and IV)

$$CH_3CH{=}CHCH_2{-}Cl \xrightarrow{\text{Ionization}} [\underset{I}{CH_3{-}CH{=}CH{-}\overset{+}{C}H_2} \longleftrightarrow \underset{II}{CH_3{-}\overset{+}{C}H{-}CH{=}CH_2}$$

$$\xrightarrow[-H^+]{(i)\ +\ H_2O} \underset{III}{CH_3CH{=}CHCH_2OH} + \underset{IV}{CH_3{-}CH(OH){-}CH{=}CH_2}$$

Q. 20. An excess of methylmagnesium iodide reacts with 0·6 *g* of organic compound $C_3H_6O_3$ to evolve 295·7 ml of methane gas at S.T.P. Calculate the number of active hydrogen atoms in the molecule of the organic compound. *(N.C.E.R.T.)*

Ans. Mol. mass of $C_3H_6O_3 = 3 \times 12 + 6 \times 1 + 3 \times 16 = 90$ g mol^{-1}

0·6 *g* of the compound evolve CH_4 = 295·7 ml at S.T.P.

$\therefore$ 90 *g* of the compound will evolve $CH_4 = \frac{295 \cdot 7}{0 \cdot 6} \times 90 = 44355$ ml at S.T.P.

No. of moles of CH_4 produced $= \frac{44355}{22400} = 1 \cdot 980 = 2$ (approx)

Thus 1 mole of the compound produces 2 moles of CH_4, therefore, there are two active hydrogen atoms present in one molecule of the organic compound.

Q. 21. What mass of propene is obtained from 34·0 *g* of 1-iodopropane on heating with ethanolic KOH, if the yield is 36%. *(N.C.E.R.T.)*

Ans. $$\underset{170\,g}{CH_3CH_2CH_2I} + KOH\,(alc.) \xrightarrow{\Delta} \underset{42\,g}{CH_3CH{=}CH_2} + KI + H_2O]$$

Theoretical amount of propene formed from 34 *g* of $CH_3CH_2CH_2I = \frac{42}{170} \times 34 = 8 \cdot 4\ g$

Actual yield of propene $= \frac{8 \cdot 4 \times 36}{100} = 3 \cdot 024\ g]$

Q. 22. Write steps to bring about the following transformations in not more than two steps :

(*a*) Acetylene to pent-2-yne (*b*) *tert*-Butyl bromide to isobutyl bromide (*c*) Butan-1-ol to but-1-ene *(N.C.E.R.T.)*

Ans. For answers refer to Appendix 3.

Q. 23. How will you affect the following two step conversions ?

(*a*) chlorobenzene to *p*-nitrophenol (*b*) benzene to monodeuteratedbenzene. *(N.C.E.R.T.)*

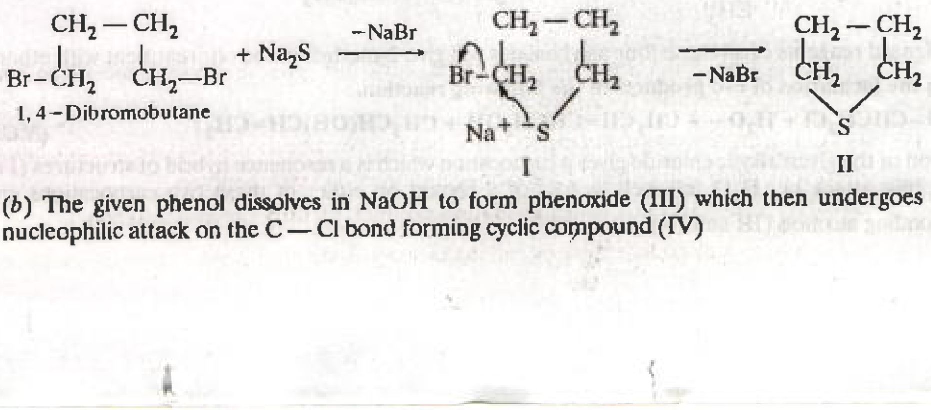
Ans. For answers refer to Appendix 3.

Q. 24. In each of the following reactions, a new ring is formed. Use curved arrow notations to explain the formation of new ring.

(*a*) 1, 4-Dibromobutane (0·1 mole) is treated with sodium sulphide (0·1 mole) is aqueous ethanol.

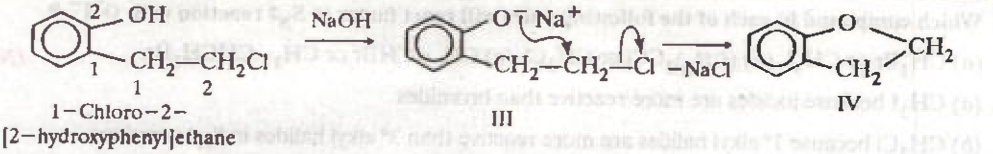
(*b*) 1-Chloro-2-(2-hydroxyphenyl)ethane is treated with aqueous sodium hydroxide. *(N.C.E.R.T.)*

Ans. (*a*) Since 1, 4-dibromobutane (0·1 mole) and Na_2S (0·1 mole) are used in equimolar amounts, therefore, sulphide ion (S^{2-}) displaces only one Br atom to form ion (I) which then undergoes intramolecular nucleophilic attack on the C — Br bond forming cyclic compound (II)



(N.C.E.R.T.)

(*b*) The given phenol dissolves in NaOH to form phenoxide (III) which then undergoes intramolecular nucleophilic attack on the C — Cl bond forming cyclic compound (IV)



Q. 25. **How will you bring about the following conversions in not more than two steps ?**
(*a*) Ethanol to but-1-yne (*b*) Ethene to bromoethene (*c*) Propene to 1-nitropropane
(*d*) Toluene to benzyl alcohol (*e*) Propene to propyne (*f*) Ethanol to ethyl fluoride
(*g*) Bromomethane to propanone (*h*) But-1-ene to but-2-ene (*i*) 1-Chlorobutane to *n*-octane
(*j*) Bromoethane to *cis*-hex-3-ene (*k*) Benzyl alcohol to phenylethanenitrile
(*l*) Benzene to diphenyl (*m*) Cyclopentene to cyclopenta-1, 3-diene (*n*) Aniline to phenyl isocyanide
(N.C.E.R.T.)

Ans. For answers refer to Appendix 3.

Very Short Answer Questions CARRYING 1 MARK

Q. 1. Give the common and the IUPAC name for $C_6H_5CH_2CH_2Cl$.

Ans. Common : β-chloroethylbenzene ; IUPAC : 1-chloro-2- phenylethane.

Q. 2. Give the IUPAC and the trivial name of $C_6H_6Cl_6$.

Ans. Trivial name : benzene hexachloride; IUPAC : 1, 2, 3, 4, 5, 6- hexachlorocyclohexane.

Q. 3. What type of isomerism is shown by 1, 2-dichloroethene ?

Ans. *cis-trans* or geometrical isomerism.

Q. 4. Out of chlorobenzene and chloromethane which is more reactive towards nucleophilic substitution reactions :

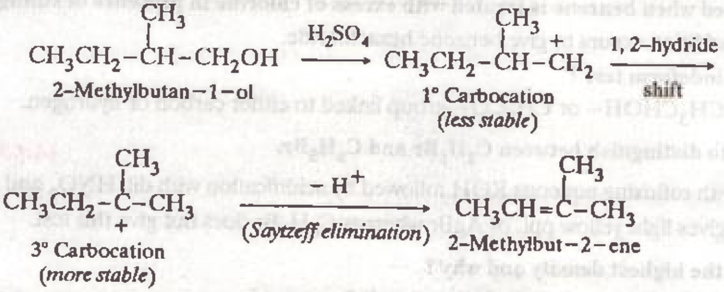
Ans. Chloromethane since it is an alkyl halide.

Q. 5. Which is a better nucleophile, a bromide ion or an iodide ion ?

Ans. Iodide ion because of its bigger size and lower electronegativity.

Q. 6. Write the structure of the main product obtained by the action of conc. H_2SO_4 on 2-methylbutan-1-ol.

Ans. 2-Methylbut-2-ene ; the initially formed 1° carbocation rearranges to the more stable 3° carbocation by a 1, 2-hydride shift which then eliminates a proton to give 2-methylbut- 2-ene as the main product in accordance with the **Saytzeff rule.**



$$\underset{\text{2-Methylbutan-1-ol}}{CH_3CH_2-\overset{CH_3}{\overset{|}{C}}H-CH_2OH} \xrightarrow{H_2SO_4} \underset{\text{1° Carbocation (less stable)}}{CH_3CH_2-\overset{CH_3}{\overset{|}{C}}H-\overset{+}{C}H_2} \xrightarrow[\text{shift}]{\text{1, 2-hydride}}$$

$$\underset{\text{3° Carbocation (more stable)}}{CH_3CH_2-\underset{+}{\overset{CH_3}{\overset{|}{C}}}-CH_3} \xrightarrow[\text{(Saytzeff elimination)}]{-H^+} \underset{\text{2-Methylbut-2-ene}}{CH_3CH=\overset{CH_3}{\overset{|}{C}}-CH_3}$$

Q. 7. A hydrocarbon C_5H_{10} does not react with chlorine in dark but gives a single monochloro compound C_5H_9Cl in bright sunlight. Identify the hydrocarbon.
(N.C.E.R.T.)

Ans. The compound C_5H_{10} contains one site of unsaturation but behaves like a saturated compound. Since it gives a single monochloro derivative, therefore, it must be symmetrical, *i.e.* cyclopentane.

Q. 8. A hydrocarbon C_5H_{12} gives only one monochlorination product. Identify the hydrocarbon. *(N.C.E.R.T.)*

Ans. C_5H_{12} gives only one monochloroderivative, *i.e.*, all the hydrogens are equivalent. It must be neopentane.

Q. 9. Which compound in each of the following pairs will react faster in S_N2 reaction with OH^- ?

(*a*) CH_3Br or CH_3I (*b*) $(CH_3)_3CCl$ or CH_3Cl (*c*) $CH_2=CHBr$ or $CH_2=CHCH_2Br$. *(N.C.E.R.T.)*

Ans. (*a*) CH_3I because iodides are more reactive than bromides

(*b*) CH_3Cl because 1° alkyl halides are more reactive than 3° alkyl halides in S_N2 reactions

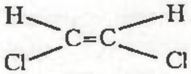
(*c*) $CH_2=CHCH_2Br$ because allyl bromides are more reactive than vinyl bromides.

Q. 10. What happens when chlorine is passed through boiling toluene in the presence of sunlight ? *(I.I.T. 1987)*

Ans. Free radical substitution occurs at the methyl group giving first benzyl chloride, then benzal dichloride and finally benzotrichloride.

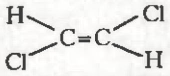
Q. 11. Write the structures of the possible isomers of dichloroethene. Which of them will have zero dipole moment ? *(I.I.T. 1985)*

Ans. (*i*)

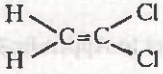


cis–1, 2–Dichloroethene
($\mu > 0$)

(*ii*)



trans–1, 2–Dichloroethene
($\mu = 0$)



1, 1–Dichloroethene
($\mu > 0$)

Q. 12. Describe a method for the preparation of haloarenes from diazonium salts. *(D.S.B. 1993)*

Ans. By treatment with CuCl / HCl or CuBr / HBr (*Sandmeyer reaction*) or treatment of diazonium salts with KI in presence of copper powder.

$$C_6H_5N_2Cl \xrightarrow[\text{or KI + Cu powder}]{CuCl/HCl \text{ or } CuBr/HBr} C_6H_5X\ (X = Cl\text{, Br or I})$$

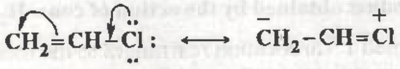
Fluorobenzene is, however, prepared by *Balz-Schiemann reaction* as follows :

$$C_6H_5N_2Cl \xrightarrow[-HCl]{HBF_4} C_6H_5N_2BF_4 \xrightarrow{\Delta} C_6H_5F + N_2 + BF_3$$

Q. 13. Give one example (with equation) of Wurtz-Fittig reaction. *(P.S.B. 1990 S)*

Ans. $C_6H_5Cl + 2Na + ClCH_3 \xrightarrow{\text{Dry ether, }\Delta} C_6H_5CH_3 + 2\ NaCl.$

Q. 14. What effect should the following resonance of vinyl chloride have on its dipole moment ?



$$CH_2{=}CH{-}\ddot{\underset{..}{Cl}}: \longleftrightarrow \overset{-}{C}H_2{-}CH{=}\overset{+}{Cl}$$

(I.I.T. 1987)

Ans. This resonance effect decreases the dipole moment of vinyl chloride relative to ethyl chloride.

Q. 15. Name the product formed when benzene is treated with excess of chlorine in presence of sunlight.

Ans. In presence of sunlight addition occurs to give benzene hexachloride.

Q. 16. Which compounds give iodoform test ?

Ans. Compounds containing CH_3CHOH- or CH_3CO- group linked to either carbon or hydrogen.

Q. 17. Give one chemical test to distinguish between C_2H_5Br and C_6H_5Br. *(A.I.S.B. 1991 S)*

Ans. Hydrolysis of C_2H_5Br with refluxing aqueous KOH followed by acidification with dil. HNO_3 and subsequent treatment with $AgNO_3$ gives light yellow ppt. of AgBr whereas C_6H_5Br does not give this test.

Q. 18. Which alkyl halide has the highest density and why ?

Ans. CH_3I ; because of its smallest carbon content and heaviest halogen *i.e.* I.

Q. 19. Explain why thionyl chloride method is preferred for preparing alkyl chlorides from alcohols ?

Ans. Because the by products of the reaction, *i.e.*, SO_2 and HCl being gases escape into the atmosphere leaving behind alkyl chlorides in almost pure state.

Q. 20. Draw the structure and give the chemical name of DDT.

Ans. For structure, refer to the text. Its chemical name is 2, 2-bis (4-chlorophenyl)-1, 1, 1-trichloroethane.

Q. 21. Iodoform gives precipitate with silver nitrate on heating but chloroform does not. Explain.

Ans. C—I bond is much weaker (bond energy 234 kJ mol^{-1}) than C—Cl bond (bond energy 351 kJ mol^{-1}). Therefore, when CHI_3 is heated, C—I bond breaks easily to give I^- ions which react with $AgNO_3$ solution to give yellow ppt of AgI. On the other hand when $CHCl_3$ is heated C—Cl bond does not break to give Cl^- ions and hence ppt. of AgCl is not formed.

Q. 22. Under what conditions, 2-methylpropene can be converted into isobutyl bromide by hydrogen bromide ? *(I.I.T. 1984)*

Ans. In presence of peroxides anti-Markovnikov's addition of HBr to 2-methylpropene gives isobutyl bromide.

Q. 23. Write the structural formula of 4-chloro-2-pentene. *(I.I.T. 1988)*

Ans. $CH_3CH = CHCHClCH_3$.

Q. 24. Arrange the following in order of increasing ease towards nucleophilic substitution.
4-nitrochlorobenzene, chlorobenzene, 2, 4, 6- trinitrochlorobenzene, 2, 4-dinitrochlorobenzene.

Ans. Chlorobenzene < 4- Nitrochlorobenzene < 2, 4- Dinitrochlorobenzene < 2, 4, 6- Trinitrochlorobenzene.

Q. 25. Arrange the following in order of increasing boiling point :
(*i*) $CH_3CH_2CH_2CH_2Br$ (*ii*) $(CH_3)_3CBr$ (*iii*) $(CH_3)_2CHCH_2Br$.

Ans. The b.p. increases as the branching decreases, *i.e.*, $(CH_3)_3CBr < (CH_3)_2CHCH_2Br < CH_3CH_2CH_2CH_2Br$.

Q. 26. Arrange the following in increasing order of reactivity towards sulphonation with fuming sulphuric acid : benzene, toluene, methoxybenzene, chlorobenzene. *(I.I.T. 1988)*

Ans. Reactivity increases as the electron density in the benzene ring increases, *i.e.*, Chlorobenzene < Benzene < Toluene < Methoxybenzene.

Q. 27. How will you obtain 1-bromopropane from propene ?

Ans. With HBr in presence of peroxides ($CH_3CH = CH_2 \xrightarrow{\text{HBr, peroxides}} CH_3CH_2CH_2Br$)

Q. 28. Arrange the following in order of their increasing reactivity in nucleophilic substitution reactions :
CH_3F, CH_3I, CH_3Br, CH_3Cl. *(I.I.T. 1992)*

Ans. Reactivity increases as the carbon-halogen bond dissociation energy decreases, *i.e.*,
$CH_3F < CH_3Cl < CH_3Br < CH_3I$.

Q. 29. Write a chemical reaction to illustrate Saytzeff's rule. *(H.P.S.B. 1994)*

Ans.
$$CH_3CHBrCH_2CH_3 \xrightarrow[\Delta]{\text{Alc. KOH}} \underset{80\%}{CH_3CH{=}CHCH_3} + \underset{20\%}{CH_3CH_2CH{=}CH_2}$$

Q. 30. Name the alkyl halide which can be used to prepare methane and ethane in single steps.

Ans. Methyl iodide (CH_3I). $CH_3I + HI \xrightarrow{\text{red P, }\Delta} CH_4 + I_2$

$$2\,CH_3I + 2Na \xrightarrow[\text{Wurtz reaction}]{\text{dry ether}} CH_3{-}CH_3 + 2NaI$$

Q. 31. How is DDT prepared ? *(P.S.B. 2001)*

Ans. DDT is prepared by condensation of chlorobenzene with chloral, *i.e.*, trichloroacetaldehyde in presence of conc. H_2SO_4. For equation, refer to the text.

Q. 32. What happens when chlorobenzene is treated with sodamide in liquid ammonia ? *(West Bengal J.E.E. 2001)*

Ans. Aniline is formed *via* intermediate formation of benzyne. For equation, refer to the text on page 7/29—7/30.

Short Answer Questions CARRYING 2 or 3 MARKS

Sec. 17.1. to 17.4.

1. Name the following halides according to IUPAC system and classify them as alkyl, allylic, benzylic (prmary, secondary, tertiary), vinylic or aryl halides.

(*a*) $(CH_3)_2CHCH(Cl)CH_3$ (*b*) $CH_3CH_2CH(CH_3)CH(C_2H_5)Cl$

(*c*) $CH_3CH_2C(CH_3)_2CH_2I$ (*d*) $(CH_3)_3CCH_2CH(Br)C_6H_5$

(*e*) $CH_3CH(CH_3)CH(Br)CH_3$ (*f*) $CH_3C(Cl)(C_2H_5)CH_2CH_3$

(*g*) $CH_3C(C_2H_5)_2CH_2Br$ (*h*) $CH_3CH{=}C(Cl)CH_2CH(CH_3)_2$

(*i*) $CH_3CH{=}CHC(Br)(CH_3)_2$ (*j*) $p-ClC_6H_4CH_2CH(CH_3)_2$

(*k*) $m-ClCH_2C_6H_4CH_2C(CH_3)_3$ (*l*) $o-Br-C_6H_4CH(CH_3)CH_2CH_3$. (*N.C.E.R.T.*)

[Ans. (*a*) 2-Chloro-3-methylbutane, 2° alkyl halide, (*b*) 3-Chloro-4-methylhexane, 2° alkyl halide (*c*) 1-Iodo-2, 2-dimethylbutane, 1° alkyl halide (*d*) 1-Bromo-2, 2-dimethyl-1-phenylbutane, 2° benzylic halide (*e*) 2-Bromo-3-methylbutane, 2° alkyl halide

(*f*) 3-Chloro-3- methylpentane, *3° alkyl halide* (*g*) 1-Bromo-2-ethyl-2-methylpentane, *1° alkyl halide* (*h*) 3-Chloro-5-methylhex-2-ene, *vinylic halide*

= (*i*) 4-Bromo-4-methylpent-2-ene, *allylic halide*

(*j*) 1-(4-Chlorophenyl)-2-methylpropane, *aryl halide*

(*k*) 1-Chloromethyl-3-(2, 2-dimethylpropyl) benzene, *1° benzylic halide*

(*l*) 1-Bromo-2-(1-methylpropyl)benzene, *aryl halide*]

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

(*a*) $CH_3CH(Cl)CH(Br)CH_3$ (*b*) $CHF_2CBrClF$ (*c*) $ClCH_2C \equiv CCH_2Br$

(*d*) $(CCl_3)_3CCl$ (*e*) $CH_3C(p-ClC_6H_4)_2CH(Br)CH_3$ (*f*) $(CH_3)_3CCH{=}C(Cl)C_6H_4I-p$

(*g*) $CH_3CHCl(CH_2)_2CCl_2C_2H_5$ (*N.C.E.R.T.*)

[Ans. (*a*) 2-Bromo-3-chlorobutane (*b*) 1-Bromo-1-chloro- 1, 2, 2-trifluoroethane (*c*) 1-Bromo-4-chlorobut-2-yne (*d*) 2-Trichloromethyl-1, 1, 1, 2, 3, 3, 3-heptachloropropane (*e*) 2, 2-Bis (4-chlorophenyl)butane (*f*) 1-Chloro-1-(4-iodophenyl)-3, 3-dimethylbut-1-ene (*g*) 2, 5, 5-Trichloroheptane]

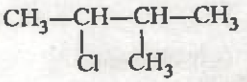
3. Write the structures of the following organic halogen compounds :

(*a*) 2-Chloro-3-methylpentane (*b*) *p*-Bromochlorobenzene

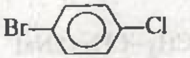
(*c*) 1-Chloro-4-ethylcyclohexane (*d*) 2-(2-Chlorophenyl)-1-iodooctane

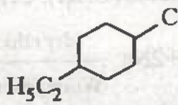
(*e*) Perfluorobenzene (*f*) 4-*tert*-Butyl-3-iodoheptane

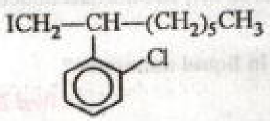
(*g*) 1-Bromo-4-*sec*-butyl-2-methylbenzene (*h*) 1, 4-Dibromobut-2-ene. (*N.C.E.R.T.*)

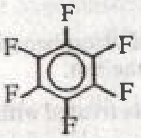
[Ans. (*a*) 

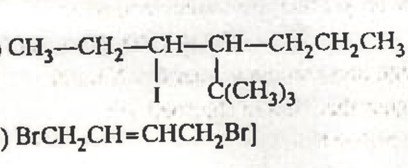
$$CH_3-\underset{Cl}{\underset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-CH_3$$

(*b*) 

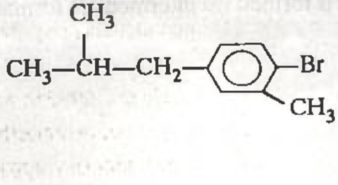
(*c*) 

(*d*) 

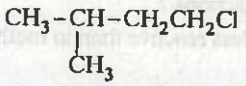
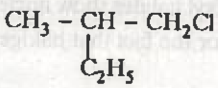
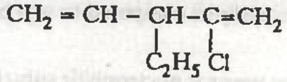
(*e*) 

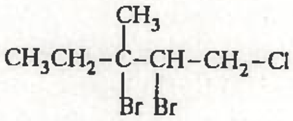
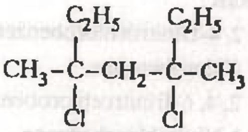
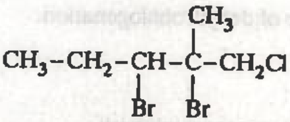
(*f*) 

$$CH_3-CH_2-\underset{I}{\underset{|}{CH}}-\underset{C(CH_3)_3}{\underset{|}{CH}}-CH_2CH_2CH_3$$

(*g*) 

(*h*) $BrCH_2CH{=}CHCH_2Br$]

4. Give the IUPAC names of the following :
(*i*) $CH_3CHClCH_2CH_3$ ***(H.S.B. 1989)*** (*ii*) $(CH_3)_3CCl$ ***(A.I.S.B. 1987, 90 S ; D.S.B. 1992)***
(*iii*) $ClCH_2CH_2Cl$ ***(D.S.B. 1988)*** (*iv*) $BrCH_2CH_2Br$ ***(D.S.B. 1988 S)***
(*v*)

$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2CH_2Cl$ ***(A.I.S.B. 1985 S)*** (*vi*)

$CH_3-\underset{C_2H_5}{\underset{|}{CH}}-CH_2Cl$ ***(D.S.B. 1993)***
(*vii*)

$CH_2=CH-\underset{C_2H_5}{\underset{|}{CH}}-\underset{Cl}{\underset{|}{C}}=CH_2$ ***(A.I.S.B. 1993)***
(*viii*) $CH_3-CHBr-CH_2-CH_2Br$ (*ix*) $BrCH_2-CH_2-CH_2-CH_2Cl.$ ***(A.I.S.B. 1994 ; H.S.B. 1994)***
(*x*) $(CH_3)_3CCH_2CH_2Cl$ ***(D.S.B. 1997)***

5. Give the IUPAC names of the following :
(*i*)

$CH_3CH_2-\overset{CH_3}{\overset{|}{\underset{Br}{\underset{|}{C}}}}-\underset{Br}{\underset{|}{CH}}-CH_2-Cl$
(*ii*)

$CH_3-\overset{C_2H_5}{\overset{|}{\underset{Cl}{\underset{|}{C}}}}-CH_2-\overset{C_2H_5}{\overset{|}{\underset{Cl}{\underset{|}{C}}}}-CH_3$
(*iii*) $C_6H_5CH_2CH_2Cl$ ***(D.S.B. 1982)*** (*iv*) $CH_3CHClCHBrCH_2CH_3$ ***(A.I.S.B. 1982)***
(*v*)

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

6. Write structural formulae and give their IUPAC names :
(*i*) Isopropyl bromide ***(D.S.B. 1989)*** (*ii*) *tert*-Butyl chloride ***(A.I.S.B. 1989)***
(*iii*) Allyl chloride (*iv*) Vinyl chloride (*v*) Isobutyl iodide (*vi*) Crotyl chloride
(*vii*) Propargyl bromide (*viii*) Cinnamyl chloride (*ix*) o-Bromotoluene ***(A.I.S.B. 1989)***
(*x*) Benzyl chloride ***(D.S.B. 1987)***

7. Write names and possible structures for the compounds having the molecular formula, C_3H_7Cl. ***(H.S.B. 1990)***

8. Write the possible structural isomers of C_4H_9Br. Point out optically active isomer, if any. ***(H.P.S.B. 1991)***

9. Write the structural formulae and IUPAC names of two optically active halides containing five carbon atoms each in their molecules. ***(P.S.B. 1988)*** **[Ans.** 2-Bromopentane and 1-bromo-2-methylbutane]

10. How many primary halides are possible for the molecular formula, $C_5H_{11}Br$. Give their structures and IUPAC names. **[Ans.** Four. For structures and IUPAC names refer to Q. 1. on page 17/6]

Sec. 17.5. to 17.11.

11. Write the equations for the preparation of 1-iodobutane from (*a*) 1-Butanol (*b*) 1-Chlorobutane (*c*) But-1-ene. ***(N.C.E.R.T.)***

12. How is chlorobenzene prepared from :
(*i*) Benzene and (*ii*) Aniline or Benzenediazonium chloride ? ***(A.I.S.B. 1989)***

13. Explain why free radical bromination of *n*-butane yields 2- bromobutane as the major product.

14. Explain the following :
(*i*) Although haloalkanes are polar in character yet they are insoluble in water. ***(P.S.B. 1993, 2000, 2001 ; H.P.S.B. 2000)***
or Alkyl halides are insoluble in water though they contain a polar C—X bond. ***(H.P.S.B. 1997)***
(*ii*) The boiling point of bromoethane is higher than that of chloroethane. ***(P.S.B. 2000)***
(*iii*) The dipole moment of chloroethane is higher than that of chlorobenzene ***(P.S.B. 2001)***

15. What do you understand by :

(*i*) nucleophilic substitution and (*ii*) electrophilic substitution reactions ?

Illustrate by taking one example in each case.

16. Why do alkyl halides show nucleophilic substitution reactions ? ***(P.S.B. 1991 S)***

17. Account for the fact that halogen in chlorobenzene is less reactive than in methyl chloride. ***(P.S.B. 1990 S)***

18. Explain why alkyl halides undergo hydrolysis more easily as compared to aryl halides ? ***(D.S.B. 1992 S)***

19. Why are aryl halides less reactive than alkyl halides towards nucleophilic substitution reactions ? ***(P.S.B. 1990)***

20. Why are haloarenes more stable than haloalkanes and undergo electrophilic substitution at ortho- and para-positions ? ***(A.I.S.B. 1991)***

21. Arrange the following compounds in order of increasing reactivity towards nucleophilic substitution reactions :

(*i*) 2, 4-Dinitrochlorobenzene

(*ii*) Chlorobenzene

(*iii*) 2, 4, 6-Trinitrochlorobenzene

(*iv*) 4-Nitrochlorobenzene

Give reasons.

22. Rearrange the following in order of increasing ease of dehydrohalogenation.

CH_3CH_2Cl, $CH_3CHClCH_3$ and $CH_3CCl(CH_3)_2$

Give reasons. ***(A.I.S.B. 1991 S)***

23. How do the products differ when ethyl bromide reacts separately with :

(*i*) Aqueous KOH and alcoholic KOH ***(H.S.B. 2000)***

(*ii*) KCN and AgCN (*iii*) KNO_2 and $AgNO_2$? ***(H.S.B. 2000)***

24. How will you convert ethyl bromide into :

(*i*) ethane (*ii*) butane (*iii*) propanoic acid and (*iv*) ethoxyethane ? ***(P.S.B. 1990)***

25. How will you convert *n*-propyl bromide into isopropyl bromide ? ***(H.P.S.B. 1992)***

26. How is ethyl iodide converted into (*i*) diethyl ether (*ii*) ethylene ? ***(A.I.S.B. 1992 S)***

27. What are ambident nucleophiles ? Explain with an example. ***(N.C.E.R.T.)***

28. Outline the preparation of following compounds using a nucleophilic substitution reaction.

(*a*) $CH_3OC(CH_3)_3$ (*b*) $CH_3C\equiv CCH_2CH_3$ (*c*) $CH_3CH_2CH_2N(CH_3)_2$ (*d*) $C_6H_5CH_2OCOCH_3$

(*e*) $CH_3CH_2CH_2CH_2NO_2$ (*f*) $CH_3CH_2CH_2CN$ (*g*) $C_6H_5CH_2\overset{+}{N}\equiv C:^-$ (*h*) $CH_3CH_2—O—N=O$ ***(N.C.E.R.T.)***

[**Hint.** (*a*) $(CH_3)_3CONa + CH_3I$ and not the reverse $CH_3ONa + (CH_3)_3CI$]

29. Arrange the following compounds in increasing order of S_N1 reactivity.

(*a*) $ClCH_2CH=CHCH_2CH_3$, $CH_3C(Cl)=CHCH_2CH_3$, $CH_3CH=CHCH_2CH_2Cl$

(*b*) CH_3CH_2Br, $CH_2=CHCH(Br)CH_3$, $CH_2=CHBr$, $CH_3CH(Br)CH_3$

(*c*) $(CH_3)_3CCl$, $C_6H_5C(CH_3)_2Cl$, $(CH_3)_2CHCl$, $CH_3CH_2CH_2Cl$ ***(N.C.E.R.T.)***

[**Ans.** (*a*) $CH_3C(Cl)=CHCH_2CH_3$, $CH_3CH=CHCH_2CH_2Cl$, $ClCH_2CH=CHCH_2CH_3$

(*b*) $CH_2=CHBr$, CH_3CH_2Br, $CH_3CH(Br)CH_3$, $CH_2=CHCH(Br)CH_3$

(*c*) $CH_3CH_2CH_2Cl$, $(CH_3)_2CHCl$, $(CH_3)_3CCl$, $C_6H_5C(CH_3)_2Cl$]

30. Predict all the alkenes that would be formed by dehydrohalogenation of the following halides with sodium ethoxide in ethanol and identify the major alkene.

(*a*) 1-Bromo-1-methylcyclohexane (*b*) Cyclohexylmethyl bromide (*c*) 2-Chloro-2-methylbutane (*d*) 3-Bromopent-1-ene (*e*) 2, 2, 3-Trimethyl-3-bromopentane *(N.C.E.R.T.)*

[**Ans.** (*a*) 1-Methylcyclohexene (*major*) + methylenecyclohexane (*minor*) (*b*) same as in (*a*) (*c*) 2-Methylbut-2-ene (major) + 2-methylbut-1-ene (minor) (*d*) Penta-1, 3-diene (*e*) 3, 4, 4-Trimethylpent-2-ene (major) 2, 3, 3- trimethylbut-1-ene (minor)]

31. Predict the order of reactivity of the following compounds in dehydrohalogenation.

(*a*) $CH_3CH_2CH_2CH_2Cl$, $(CH_3)_2CHCH_2Cl$, $(CH_3)_2CH—CH_2Br$, $CH_3CH(Br)CH_2CH_3$, $(CH_3)_3C—Br$

(*b*) $CH_3CH(Br)CH_3$, $CH_3CH_2CH_2Br$, $(CH_3)_2CH—CH_2Br$, $(CH_3)_3C—CH_2Br$ *(N.C.E.R.T.)*

[**Ans.** (*a*) $(CH_3)_3CBr > CH_3CH(Br)CH_2CH_3 > (CH_3)_2CHCH_2Br > (CH_3)_2CHCH_2Cl > CH_3CH_2CH_2CH_2Cl$]

(*b*) $(CH_3)_3CCH_2Br > (CH_3)_2CH—CH_2Br > CH_3CH(Br)CH_3 > CH_3CH_2CH_2Br$]

32. Whcih of the following compounds wil give positive iodoform test ?

Butan-1-ol, butan-2-ol, *tert*-butyl alcohol, ethanal, propanal, propanone, buta-2-one, pentan-3-one, cyclohexanone, 1-methylcyclohexanol, 1-phenylethanol, 2-phenylethanol. *(N.C.E.R.T.)*

[**Ans.** Butan-2-ol, ethanal, propanone, butan-2-one, 2- phenylethanol]

33. How will you distinguish between :

(*a*) Methanol and ethanol (*b*) Propan-1-ol and propan- 2-ol (*c*) Benzyl chloride and chlorobenzene (*d*) *n*-Butylamine and diethylamine. *(N.C.E.R.T.)*

34. Explain why

(*a*) the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride.

(*b*) alkyl halides, though polar, are immiscible with water

(*c*) Vinyl chloride is unreactive in nucleophilic substitution reactions.

(*d*) Neopentyl bromide undergoes nuclephilic substitution reaction very slowly.

(*e*) 3-bromocyclohexene is more reactive than 4- bromocyclohexene in hydrolysis with aqueous NaOH.

(*f*) *tert*-butyl chloride reacts with aqueous sodium hydroxide by S_N1 mechanism while *n*-butyl chloride reacts by S_N2 mechanism.

(*g*) Grignard reagents should be prepared under anhydrous conditions. *(N.C.E.R.T.)*

35. Explain. Why ?

(*a*) The nucleophilic substitution of primary alkyl chlorides with sodium acetate is catalysed by sodium iodide. *(N.C.E.R.T.)*

[**Hint.** In presence of NaI, alkyl chlorides form alkyl iodides which being more reactive catalyse the nucleophilic substitution reaction]

(*b*) *p*-Methoxybenzyl bromide reacts faster than *p*-nitrobenzyl bromide with ethanol to form an ether product. *(N.C.E.R.T.)*

[**Hint.** *p*-Methoxybenzyl cation is stabilized by the +R- effect of the methoxy group while *p*-nitrobenzyl cation is destabilized by the –R-effect of the NO_2 group]

36. With the help of chemical equations, show how will you convert :

(*i*) 1-propanol to 2-bromopropane. ***(D.S.B. 1996)***

(*ii*) 2-bromopropane to 1-bromopropane ? ***(A.I.S.B. 1996, D.S.B. 1998, 2001)***

(*iii*) 1-Bromopropane to 2-bromopropane ***(D.S.B. 1998 ; P.S.B. 2000,2001)***

(*iv*) Propanone to iodoform. ***(D.S.B. 1998)***

(*v*) Isopropyl chloride to n-propyl chloride. ***(P.S.B. 2000)***

37. Explain why chlorobenzene does not react with aqueous potassium hydroxide and ammonia under the conditions in which alkyl chlorides react ?

38. Haloalkanes react with potassium cyanide to give alkyl cyanides but give alkyl isocyanides with silver cyanide. Explain.

39. Discuss briefly the mechanism of $S_N{}^1$ and $S_N{}^2$ reactions.

40. Account for the following :

(*i*) Haloalkanes are more reactive than haloarenes. ***(H.S.B. 1998 ; A.I.S.B. 1999 ; P.S.B. 2000)***

(*ii*) Methyl chloride is hydrolysed more readily than chlorobenzene. ***(H.S.B. 1992, 99 ; P.S.B. 2001)***

(*iii*) Haloalkanes undergo nucleophilic substitution reactions. ***(A.I.S.B. 2000)***

(*iv*) Haloarenes undergo electrophilic substitution reactions. ***(A.I.S.B. 2000)***

(*v*) Vinyl chloride is hydrolysed more slowly than ethyl chloride. ***(P.S.B. 2000)***

41. How will you prepare chloroform from

(*a*) acetone ***(H.P.S.B. 1992, P.S.B. 2000, 2001)***

(*b*) ethanol ? ***(H.P.S.B. 1992, P.S.B. 2000, 2001)***

42. How will you convert acetone into chloroform ? ***(H.S.B. 1992 ; H.P.S.B. 1993 S)***

43. Write equations for the reactions involved in the manufacture of chloroform from ethanol. ***(D.S.B. 1992 S)***

44. What products are formed when chloroform is :

(*i*) boiled with aqueous KOH ***(D.S.B. 1992 S ; H.P.S.B. 1998)***

(*ii*) exposed to air and sunlight ***(D.S.B. 1992 S ; 95)***

(*iii*) heated with silver powder ***(D.S.B. 1992 S)***

(*iv*) aniline in presence of alcoholic KOH ***(A.I.S.B. 1990)***

(*v*) phenol in presence of alcoholic KOH at 340 K ?

45. How is iodoform prepared from

(*a*) acetone ***(C.B.S.E. Sample Paper 1990, H.S.B. 2001 ; P.S.B. 2001)***

(*b*) ethanol ? ***(P.S.B. 2001)***

46. Describe the preparation of iodoform. How does it react with : (*i*) silver powder (*ii*) caustic potash ? ***(H.P.S.B. 1992 S)***

47. Write the reaction involved in the preparation of iodoform from 2-propanol. ***(A.I.S.B. 1999)***

48. What happens when :

(*i*) Iodoform is heated with silver powder ? (Give equations). ***(H.P.S.B. 1991)***

(*ii*) Iodoform is warmed with a primary amine and alcoholic KOH ? (Give equations). ***(H.P.S.B. 1992)***

49. Explain, giving equations, what happens when :

(*a*) Ethyl alcohol is treated with iodine in presence of alkali ***(H.P.S.B. 1999)***

(*b*) Chloroform is heated with a solution of phenol and sodium hydroxide ? ***(H.S.B. 1994)***

50. Give reasons :

(*i*) Chloroform is a chlorine compound but it does not give white precipitate with silver nitrate solution. ***(A.I.S.B. 1990 S ; H.P.S.B. 1993 ; P.S.B. 2000)***

(*ii*) A small amount of alcohol is usually added to chloroform bottles.

51. Describe carbylamine reaction and illustrate with a balanced chemical equation.

52. What is an iodoform test ? Briefly describe its utility in organic chemistry.

53. How is carbon tetrachloride prepared on a commercial scale ? How does it react with (*i*) Fe / H_2O (*ii*) boiling alcoholic KOH and (*iii*) antimony trifluoride in presence of antimony pentachloride as catalyst ?

54. How will you prepare chloroform from ethanol ? Give reactions of chloroform with (*i*) Nitric acid (*ii*) Silver powder. ***(H.P.S.B. 1997)***

55. Write the complete reactions involved in (*a*) the isocyanide test, and in (*b*) the iodoform test. ***(D.S.B. 1999)***

56. What does DDT stand for ? What is its chemical name ?

57. How is DDT prepared from chlorobenzene ? Give the chemical equation only. *(H.P.S.B. 1998)*

58. How is DDT prepared commercially ? Discuss briefly its uses and tragic side effects.

59. What does BHC stand for ? How is it prepared and what are its uses ?

60. What are perfluorocarbons. Write their uses.

MISCELLANEOUS QUESTIONS

1. Write the structures of the major organic product formed in each of the following reactions :

(*a*) $CH_3CH_2CH_2Cl + NaI \xrightarrow[\text{heat}]{\text{acetone}}$

(*b*) $(CH_3)_3CBr + KOH \xrightarrow[\text{heat}]{\text{ethanol}}$

(*c*) $CH_3CH(Br)CH_2CH_3 + NaOH \xrightarrow{\text{warm}}$

(*d*) $CH_3CH_2Br + KCN \xrightarrow{\text{aq. ethanol}}$

(*e*) $(CH_3)_3CBr + H_2O \xrightarrow{\text{heat}}$

(*f*) $(CH_3)_2CH{-}CH(Br)CH_2CH_3 \xrightarrow[\text{ethanol/heat}]{C_2H_5ONa}$

(*g*) $CH_3CH_2Cl + SbF_3 \xrightarrow{\text{heat}}$

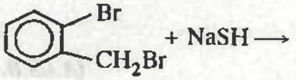
(*h*) $CH_2{=}CHCH_2Br + CH_3C{\equiv}CNa \xrightarrow{\text{Liq. } NH_3}$

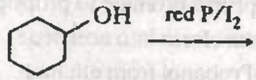
(*i*) $C_6H_5CH_2Cl + C_2H_5ONa \longrightarrow$

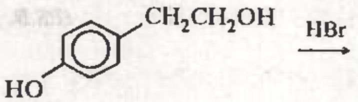
(*j*) $CH_3CH_2CH_2OH + SOCl_2 \longrightarrow$

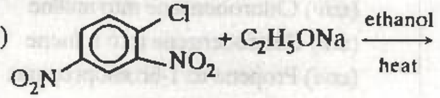
(*k*) $CH_3CH_2CH{=}CH_2 + HBr \xrightarrow{\text{peroxide}}$

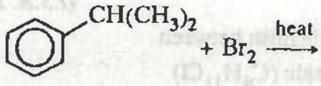
(*l*) $CH_3CH{=}C(CH_3)_2 + HBr \longrightarrow$

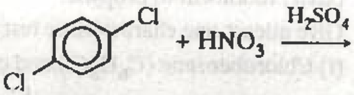
(*m*) 

(*n*) 

(*o*) 

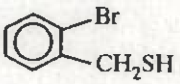
(*p*) 

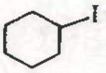
(*q*) 

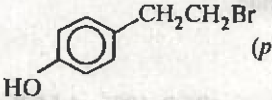
(*r*) 

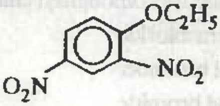
(N.C.E.R.T.)

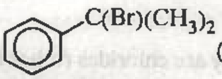
[**Ans.** (*a*) $CH_3CH_2CH_2I$ (*b*) $(CH_3)_2C{=}CH_2$ (*c*) $CH_3CH(OH)CH_2CH_3$ (*d*) CH_3CH_2CN (*e*) $(CH_3)_3COH$ (*f*) $(CH_3)_2C{=}CHCH_2CH_3$ (*g*) CH_3CH_2F (*h*) $CH_2{=}CHCH_2C{\equiv}CCH_3$ (*i*) $C_6H_5CH_2OC_2H_5$ (*j*) $CH_3CH_2CH_2Cl$ (*k*) $CH_3CH_2CH_2CH_2Br$ (*l*) $CH_3CH_2C(Br)(CH_3)_2$

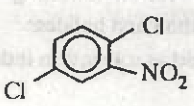
(*m*) 

(*n*) 

(*o*) 

(*p*) 

(*q*) 

(*r*) 

2. How are the following conversions carried out ?

(*i*) 2-Propanol into 1-bromopropane *(C.B.S.E. Sample Paper, 1997)*
(*ii*) Toluene into benzyl chloride *(D.S.B. 1981, S)*
(*iii*) Ethyl bromide to ethylamine *(D.S.B. 1984 ; P.S.B. 2001)*
(*iv*) *n*-Propyl chloride to *n*-propylamine *(D.S.B. 1989)*
(*v*) Ethyl alcohol to chloroform *(D.S.B. 1984 S ; P.S.B. 2001)*
(*vi*) 2-Chlorobutane to 2-butanol *(P.S.B. 1989)*
(*vii*) Methyl bromide to ethyl bromide *(P.S.B. 2001)*
(*viii*) Acetone to iodoform *(D.S.B. 1994)*
(*ix*) Carbon tetrachloride to freon *(H.P.S.B. 1990)*
(*x*) Benzene into benzene hexachloride *(H.P.S.B. 1990)*
(*xi*) Chloroform into chloropicrin *(H.P.S.B. 1990)*
(*xii*) Aniline into fluorobenzene *(D.S.B. 1992)*
(*xiii*) Aniline into bromobenzene *(A.I.S.B. 1992)*
(*xiv*) Aniline into chlorobenzene *(H.P.S.B. 1998 ; D.S.B. 1998)*
(*xv*) Acetone into chloretone *(H.S.B. 1992 ; P.S.B. 2001)*
(*xvi*) Propene into 1-bromopropane *(D.S.B. 1992)*
(*xvii*) Chloroform into diethyl carbonate *(D.S.B. 1992)*
(*xviii*) Acetone into chloroform *(H.P.S.B. 1993 S)*
(*xix*) Ethyl alcohol into tri-iodomethane *(A.I.S.B. 1986)*
(*xx*) Methyl bromide to acetic acid *(P.S.B. 1988 ; H.S.B. 2001)*
(*xxi*) Isopropyl bromide to propylene *(P.S.B. 1988)*
(*xxii*) Chloroform into acetylene *(P.S.B. 1994, 1996)*
(*xxiii*) 2-Propanol from ethanol *(A.I.S.B. 1994 ; P.S.B. 1998)*
(*xxiv*) Chlorobenzene into aniline *(P.S.B. 1994 ; H.S.B. 2001)*
(*xxv*) Chlorobenzene into toluene
(*xxvi*) Propene to 1-bromopropane. *(D.S.B. 2000)*
(*xxvii*) Iodoform to propyne. *(P.S.B. 2000 ; H.S.B. 2001)*

3. Give atleast one characteristic test which can distinguish between

(*i*) Chlorobenzene (C_6H_5Cl) and cyclohexyl chloride ($C_6H_{11}Cl$) *(D.S.B. 1979 S)*
(*ii*) Chlorobenzene and benzyl chloride *(D.S.B. 1995 ; C.B.S.E. Sample Paper, 1997)*
(*iii*) *n*-Propyl bromide and isopropyl bromide
(*iv*) 1, 1-Dibromoethane and 1, 2-dibromo- ethane *(D.S.B. 1980, Kerala 1996)*
(*v*) Chlorobenzene and *n*-hexyl chloride. *(A.I.S.B. 1988)*
(*vi*) $CH_2{=}CH{-}CH_2Br$ and $CH_3CH_2CH_2Br$ *(D.S.B. 1985)*
(*vii*) Ethyl bromide and bromobenzene *(A.I.S.B. 1991 S)*
(*viii*) *o*-Chlorotoluene and benzyl chloride
(*ix*) *o*-Chlorobenzyl bromide and *o*-bromobenzyl chloride
(*x*) Chloroform and carbon tetrachloride
(*xi*) Benzyl chloride and benzyl bromide.
(*xii*) Bromobenzene and benzyl bromide *(P.S.B. 1995 ; A.I.S.B. 1998 ; P.S.B. 1998)*

4. Give reasons in one or two sentences for the following :

(*i*) Alkyl halides are better solvents than aryl halides. *(H.P.S.B. 1993 S)*

(*ii*) Organic halogen compounds used as solvents in industry are chlorides rather than bromides and iodides.

(*iii*) *p*-Dichlorobenzene has a higher melting point than *o*- and *m*-isomers but the boiling points of these isomers are nearly the same.

5. Give a brief account of the following with one example of each.

(*i*) Friedel-Crafts reaction *(A.I.S.B. 1990, H.S.B. 1990)*
(*ii*) Friedal-Crafts acylation. *(H.S.B. 2001)*
(*iii*) Friedal-Crafts alkylation.
(*iv*) Wurtz reaction *(A.I.S.B. 1990, H.S.B. 1990 ; P.S.B. 2000)*
(*v*) Reimer-Tiemann reaction *(A.I.S.B. 1990)*
(*vi*) Markovnikov's rule *(A.I.S.B. 1990)*
(*vii*) Sandmeyer reaction *(H.S.B. 1990 ; H.P.S.B. 1993 S ; D.S.B. 1996, 99 ; A.I.S.B. 1998 ; P.S.B. 1998, 2000, 2001)*
(*viii*) Kharasch effect *(A.I.S.B. 1998)*
(*ix*) Balz-Schiemann reaction.

6. Identify the compounds X, Y and Z in each of the following sequence of reactions :

(*i*) $C_2H_4 \xrightarrow{HBr} X \xrightarrow{aq.\ KOH} Y \xrightarrow{I_2\ .\ NaOH} Z$

(*ii*) $C_2H_5Br \xrightarrow{alc.\ KOH} X \xrightarrow{Br_2} Y \xrightarrow{alc.\ KOH} Z$

(*iii*) $C_6H_6 \xrightarrow{Cl_2/Fe} X \xrightarrow[pyridine,\ \Delta]{CuCN} Y \xrightarrow{H^+,\ H_2O} Z$

(*iv*) $C_6H_5NH_2 \xrightarrow[273-278\ K]{NaNO_2,\ HCl} X \xrightarrow{CuBr/HBr} Y \xrightarrow[+\ Anhyd.\ AlCl_3]{(CH_3CO)_2O} Z$ (major product)

(*v*) $C_6H_6 \xrightarrow[+Anhyd.\ AlCl_3]{CH_3Cl} X \xrightarrow[sunlight]{Cl_2\ (1\ mole)} Y \xrightarrow{KOH} Z$

Long Answer Questions CARRYING 5 or more MARKS

Sec. 17.1. to 17.7.

1. What are haloalkanes ? How are they named according to IUPAC system. How can haloalkanes be prepared from (*i*) alcohols (*ii*) alkenes and (*iii*) alkanes?

2. What are haloarenes ? How are they classified ? Give one method each for the preparation of nuclear and side chain substituted haloarenes.

Sec. 17.8. to 17.11.

3. Describe the synthetic reactions of alkyl halides, illustrating how a wide variety of organic compounds can be synthesized from them ? *(H.S.B. 1988)*

4. Write eight synthetic reactions of haloalkanes taking iodomethane for the purpose. *(H.S.B. 1991)*

5. Write any five chemical properties of alkyl halides to show their synthetic importance. *(P.S.B. 1993)*

Sec.17.12. to 17.22.

6. Why are haloarenes less reactive than alkyl halides ? Discuss some important nucleophilic substitution reactions of haloarenes.

7. Comment upon low reactivity of haloarenes. How can this low reactivity be increased ?

8. How is chloroform prepared from (*i*) ethyl alcohol (*ii*) methane and (*iii*) carbon tetrachloride ? Starting from chloroform, how will you prepare the following : (*i*) phosgene (*ii*) chloretone (*iii*) chloropicrin (*iv*) formic acid (*v*) phenyl isocyanide and (*vi*) salicylaldehyde?

9. Give the preparation and uses of chloropicrin, chloretone, Freon-12, *p*-dichlorobenzene, BHC, DDT, carbon tetrachloride, iodoform and perfluorocarbons. *(N.C.E.R.T.)*

COMPETITION FOCUS

ADDITIONAL USEFUL INFORMATION

1. Analysis of Alkyl and Aryl Halides

The presence of halogen in organic compounds is tested by the following two tests :

(i) **Beilstein test.** In this test, a copper strip is heated strongly in the bunsen flame till it ceases to impart any greenish or bluish green flame. A pinch of the organic halide is then placed on this hot copper strip and then reintroduced into the flame.

If a green or bluish green flame reappears, it indicates the presence of halogen in the organic compound.

This test is very sensitive but does not indicate the nature of halogen (i.e. chlorine, bromine or iodine).

(ii) **Lassaigne's test.** In this test, a fleshly cut pea- size sodium metal is placed in a fusion tube and strongly heated till it forms a shining globule. The fusion tube is withdrawn from the flame and a pinch of the organic halide added. The fusion tube is again heated in the flame to red-heat and then plunged into distilled water and filtered. The filtrate thus obtained is called **Lassaigne's extract.**

The Lassaigne's extract is then boiled with dil. HNO_3 to expel gases, if evolved. The solution is then cooled and $AgNO_3$ solution added to it.

(a) A white precipitate soluble in NH_4OH indicates the presence of chlorine.

(b) A pale yellow precipitate partially soluble in NH_4OH indicates the presence of bromine.

(c) A bright yellow precipitate insoluble in NH_4OH indicates the presence of iodine.

In principle, the organic halides contain the following three types of halogens.

(i) **Ionic halogen** *as in benzenediazonium halides and quaternary ammonium halides* **i.e.,**

$C_6H_5\overset{+}{N_2}X^-$ and $R_4\overset{+}{N}X^-$ (where X=Cl, Br or I)

(ii) **Labile halogen** *as in alkyl, allyl and benzyl halides, i.e.*

$$R\text{—}X,\ CH_2 = CH\text{—}CH_2X\ ;\ C_6H_5\text{—}CH_2X \quad (\text{where } X = Cl, Br \text{ or } I).$$

(iii) **Inert halogen** *as in aryl halides, i.e. chlorobenzene, bromobenzene, iodobenzene etc. and vinyl halides, i.e., vinyl chloride, vinyl bromide etc.*

A distinction between these types of halogens is carried out on the basis of **$AgNO_3$ test.**

(i) **$AgNO_3$ test in the cold.** An aqueous solution of the organic halide is acidified with dil. HNO_3 and then treated with $AgNO_3$ solution in the cold. *The appearance of a white or yellow precipitate indicates* **ionic halogen.**

(ii) **$AgNO_3$ test in the hot.** The organic halide is boiled with aqueous KOH solution. The reaction mixture is cooled, acidified with dil. HNO_3 and then treated with $AgNO_3$ solution. *The appearance of a white or yellow ppt. indicates* **labile halogen.**

If both the above tests are negative, the presence of **inert halogen** *is indicated.*

C.B.S.E.-P.M.T. (MAINS) SPECIAL

A. Subjective Questons (Common with I.I.T.)

Q. 1. Explain why alkyl halides are generally not prepared in the laboratory by free radical halogenation of alkanes.

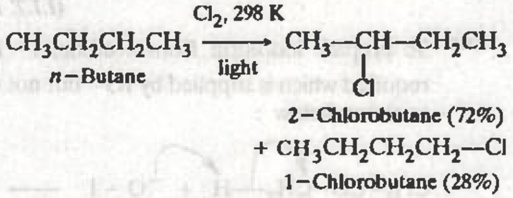
Ans. Free radical halogenation is not a suitable method for laboratory synthesis of alkyl halides because of the following two reasons :

(*i*) It gives a mixture of isomeric monohalogenated products whose boiling points are so close that they cannot be easily separated in the laboratory.

(*ii*) Polyhalogenation may also occur to some extent thereby making the mixture more complex and hence more difficult to separate.

Q. 2. Explain why chlorination of *n*-butane in presence of light at 298 K gives a mixture of 72% of 2-chlorobutane and 28% of 1-chlorobutane.

Ans. According to the question,



$$\underset{n-\text{Butane}}{CH_3CH_2CH_2CH_3} \xrightarrow[\text{light}]{Cl_2,\ 298\ K} \underset{2-\text{Chlorobutane (72\%)}}{CH_3-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_2CH_3} + \underset{1-\text{Chlorobutane (28\%)}}{CH_3CH_2CH_2CH_2-Cl}$$

The relative ratios of these two isomeric chlorobutanes can be easily calculated by knowing: (*i*) the number and type of hydrogens (*i.e.* 1°, 2° or 3°) to be substituted and (*ii*) their relative rates of substitution (*i.e.* 1 : 3·8 : 5·0 for Cl_2 at 298 K). Thus,

$$\frac{1-\text{Chlorobutane}}{2-\text{Chlorobutane}} = \frac{\text{No. of } 1^\circ \text{ H}}{\text{No. of } 2^\circ \text{ H}} \times \frac{\text{Reactivity of } 1^\circ \text{ H}}{\text{Reactivity of } 2^\circ \text{ H}}$$

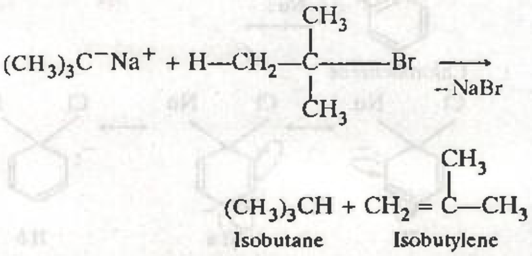
$$= \frac{6}{4} \times \frac{1}{3\cdot 8}$$

$$= \frac{6}{15\cdot 2} = \frac{28\%}{72\%}$$

Q. 3. Wurtz reaction fails in case of *tert*-alkyl halides. Explain.

Ans. *tert*-Alkyl halides prefer to undergo dehydrohalogenation in presence of a strong base such as Na metal instead of undergoing Wurtz reaction as shown below :

$$\underset{tert-\text{Butyl bromide}}{(CH_3)_3C-Br} + 2\,Na \longrightarrow \underset{tert-\text{Butylsodium}}{(CH_3)_3C^-Na^+} + NaBr$$

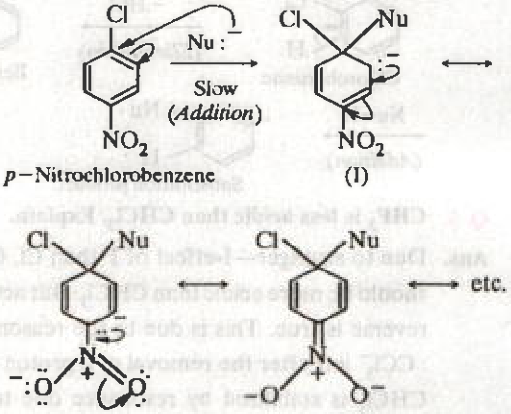


$$(CH_3)_3C^-Na^+ + H-CH_2-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-Br \xrightarrow[-NaBr]{} \underset{\text{Isobutane}}{(CH_3)_3CH} + \underset{\text{Isobutylene}}{CH_2=\overset{\displaystyle CH_3}{\overset{|}{C}}-CH_3}$$

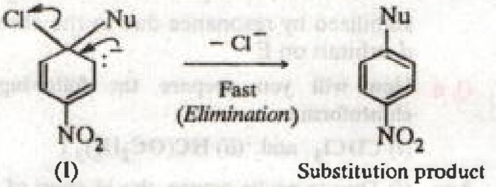
Thus, only 1° and 2° alkyl halides undergo Wurtz reaction while 3° alkyl halides prefer to undergo dehydrohalogenation to form alkenes.

Q. 4. Why does nucleophilic substitution reaction of chlorobenzene take place through benzyne mechanism and that of *p*-nitrochlorobenzene proceeds *via* addition-elimination mechanism ? Explain.

Ans. In *p*-nitrochlorobenzene, the carbanion (I) resulting through initial attack of the nucleophile is stabilized by electron-withdrawing $-NO_2$ group as well as by the benzene ring as shown below :

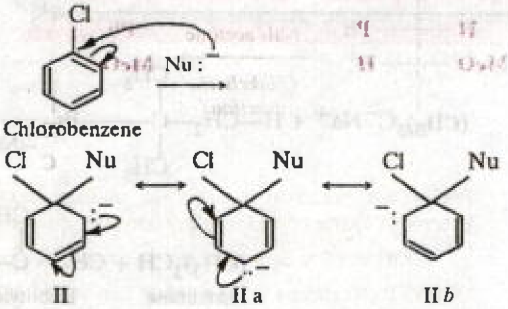


In the second step, the carbanion (I) loses a chloride ion to complete the substitution.



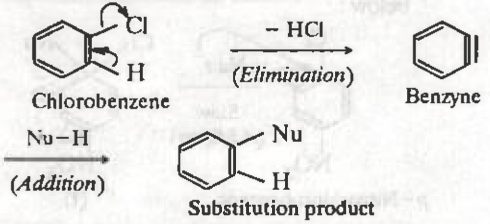
This two-step bimolecular aromatic nucleophilic substitution mechanism is also called **addition-elimination mechanism.**

In contrast, the carbanion (II) resulting through nucleophilic attack on chlorobenzene is stabilized only by the benzene ring.



Stabilized by benzene ring

Since stabilization by NO_2 group is much greater than that by benzene ring, therefore, carbanion (I) is easily formed and hence *p*-nitrochlorobenzene undergoes substitution *via* **addition-elimination** mechanism. In contrast, the carbanion (II) is only slightly stabilized and hence is not easily formed. Therefore, chlorobenzene undergoes nucleophilic substitution by an alternate mechanism involving **benzyne intermediate** or **elimination-addition mechanism** as shown below :



Q. 5. CHF_3 is less acidic than $CHCl_3$. Explain.

Ans. Due to stronger—I-effect of F than Cl, CHF_3 should be more acidic than $CHCl_3$. But actually reverse is true. This is due to the reason that $:CCl_3^-$ left after the removal of a proton from $CHCl_3$ is stabilized by resonance due to the presence of *d*-orbitals on Cl but : CF_3^- left after the removal of a proton from CHF_3 is not stabilized by resonance due to the absence of *d*-orbitals on F.

Q. 6. How will you prepare the following from chloroform :

(*i*) $CDCl_3$ and (*ii*) $HC(OC_2H_5)_3$?

Ans. (*i*) Due to acidic nature, the H-atom of $CHCl_3$ can easily undergo deuterium exchange on treatment with D_2O in alkaline solution.

$$CHCl_3 + OH^- \rightleftharpoons H_2O + :CCl_3^-$$

$$\xrightleftharpoons{D_2O} \underset{\text{Deuterated chloroform}}{CDCl_3} + OD^-$$

$CDCl_3$ is widely used as a solvent in NMR spectroscopy.

(*ii*) When $CHCl_3$ is heated with sodium ethoxide, it forms ethyl orthoformate as shown below :

$$C_2H_5O^- + CHCl_3 \rightleftharpoons :CCl_3^- + C_2H_5OH$$

$$:CCl_3^- \xrightarrow{\text{Slow}} \underset{\text{Dichlorocarbene}}{:CCl_2} + Cl^-$$

$$:CCl_2 + 2\,C_2H_5O^- \longrightarrow :C(OC_2H_5)_2 + 2\,Cl^-$$

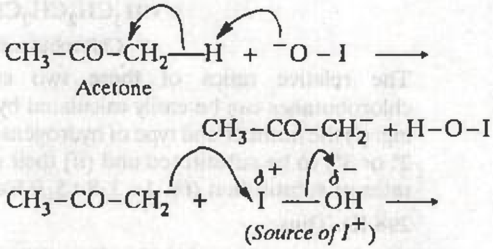
$$:C(OC_2H_5)_2 + C_2H_5OH \longrightarrow \underset{\text{Triethyl orthoformate}}{HC(OC_2H_5)_3}$$

Q. 7. Give reasons in one or two sentences for the following :

Iodoform is obtained by the reaction of acetone with hypoiodite but not with iodide ion.

(I.I.T. 1991)

Ans. To prepare iodoform from acetone, I^+ ion is required which is supplied by IO^- but not by I^- as shown below :



$$\underset{\text{Acetone}}{CH_3-CO-CH_2-H} + {}^-O-I \longrightarrow$$

$$CH_3-CO-CH_2^- + H-O-I$$

$$CH_3-CO-CH_2^- + \underset{(\textit{Source of } I^+)}{\overset{\delta+}{I}-\overset{\delta-}{OH}} \longrightarrow$$

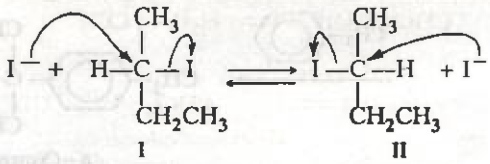
$$CH_3-CO-CH_2I + OH^-$$

$$CH_3\,COCH_2I \xrightarrow[-OH^-]{+IO^-} CH_3COCHI_2 \xrightarrow[-OH^-]{+IO^-}$$

$$CH_3COCI_3 \xrightarrow{OH^-} CHI_3 + CH_3COO^-$$

Q. 8. Optically active 2-iodobutane on treatment with NaI in acetone gives a product which does not show optical activity. *(I.I.T. 1995)*

Ans. Optically active 2-iodobutane on treatment with NaI in acetone undergoes racemization and hence the product does not show optical activity as explained below :



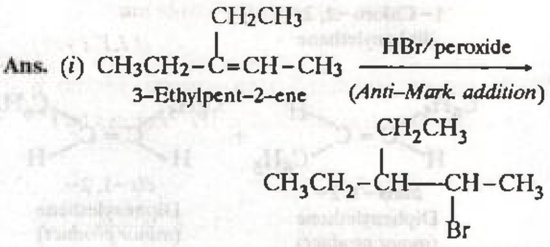
I
2–Iodobutane
(say dextrorotatory)

II
2–Iodobutane
(laevorotatory)

When 2-iodobutane (I) is treated with I^- ion, it undergoes *Walden inversion* (S_N2 reaction) to give 2-iodobutane (II) which is the enantiomer of I. Now 2- iodobutane (II) undergoes Walden inversion to give enantiomer I. As a result of these two Walden inversions, ultimately a 50 : 50 mixture of the two enantiomers is obtained. In other words, optically active 2- iodobutane undergoes reacemization.

Q. 9. Give the structures of the major organic products from 3-ethylpent-2-ene under each of the following conditions.
(*a*) HBr in presence of peroxide
(*b*) Br_2 / H_2O *(I.I.T. 1996)*

Ans. (*i*)

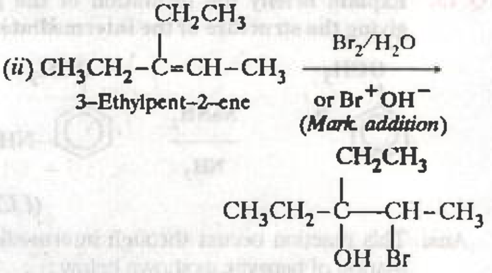


$$CH_3CH_2-\overset{CH_2CH_3}{\overset{|}{C}}=CH-CH_3 \xrightarrow[\textit{(Anti–Mark. addition)}]{HBr/peroxide} CH_3CH_2-\overset{CH_2CH_3}{\overset{|}{CH}}-\underset{Br}{\underset{|}{CH}}-CH_3$$

3–Ethylpent–2–ene

2–Bromo–3–ethylpentan–3–ol

(*ii*)

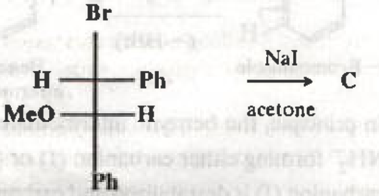


$$CH_3CH_2-\overset{CH_2CH_3}{\overset{|}{C}}=CH-CH_3 \xrightarrow[\textit{or } Br^+OH^- \textit{ (Mark. addition)}]{Br_2/H_2O} CH_3CH_2-\underset{OH}{\underset{|}{\overset{CH_2CH_3}{\overset{|}{C}}}}-\underset{Br}{\underset{|}{CH}}-CH_3$$

3–Ethylpent–2–ene

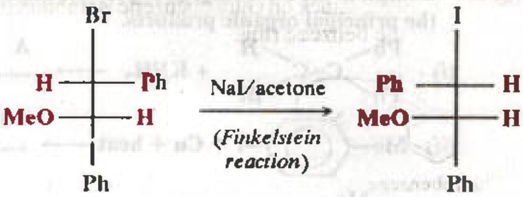
2–Bromo–3–ethylpentan–3–ol

Q. 10. Predict the structure of the product in the following reaction.



(I.I.T. 1996)

Ans.

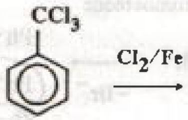


C

Finkelstein reaction is used to convert alkyl bromides to the corresponding alkyl iodides. It is an example of a S_N2 reaction in which I^- ion attacks from the *back side* giving the iodide (C) with *inversion of configuration* (note that the position of H and Ph have been exchanged) at the upper chiral carbon undergoing nucleophilic attack.

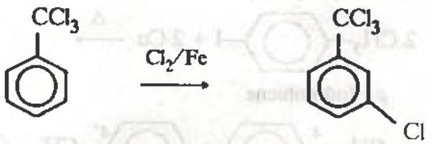
Q. 11. Predict the major product in each of the following reactions :—

(*i*)



(***ii***) $CH_3CH_2—Br \xrightarrow{AgCN}$ *(I.I.T. 1997)*

Ans. (*i*) **CCl_3 is *m*-directing.**



Benzotrichloride *m*-Chlorobenzotrichloride

(*ii*) AgCN reacts with ethyl bromide to give ethyl isocyanide as the major product.

$$CH_3CH_2—Br \xrightarrow[-AgBr]{AgCN} CH_3CH_2—N \overset{\rightarrow}{=} C$$

Ethyl bromide Ethyl isocyanide

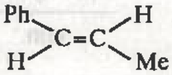
Q. 12. Write down the structures of A and B.

$$PhC \equiv CH \xrightarrow{NaNH_2,\ MeI} A \xrightarrow{Na/NH_3\ (l)} B$$

(I.I.T. 1997)

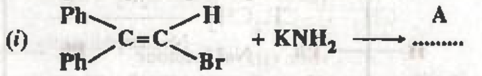
Ans. $$\underset{\text{Phenylacetylene}}{PhC \equiv CH} \xrightarrow[-NH_3]{NaNH_2} \underset{\text{Sod. phenyl acetylide}}{PhC \equiv C\,Na^+} \xrightarrow[-NaI]{MeI}$$

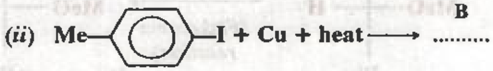
$$\underset{\text{1–Phenylprop–1–yne (A)}}{PhC \equiv CMe} \xrightarrow[\textit{(Birch reduction)}]{Na/NH_3\ (I)}$$

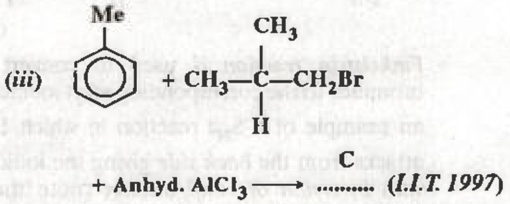


trans–1–Phenylprop–1–ene (B)

Q. 13. **Complete the following, giving the structures of the principal organic products.**

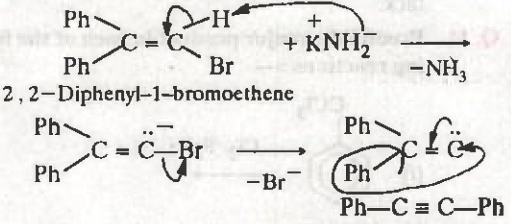






(I.I.T. 1997)

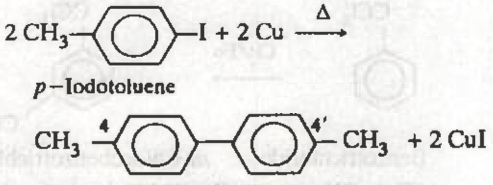
Ans. (*i*) Dehydrobromination occurs with the migration of the phenyl group to give diphenylacetylene.



2, 2−Diphenyl−1−bromoethene

Ph—C ≡ C—Ph Diphenylacetylene

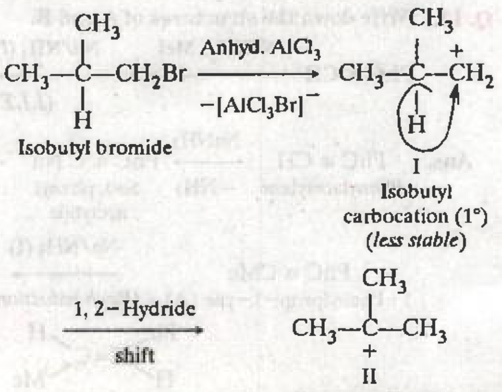
(*ii*) *p*-Iodotoluene when heated with copper undergoes *Ullmann biaryl synthesis reaction* to give 4, 4′-dimethyldiphenyl.



p−Iodotoluene

4, 4′−Dimethyldiphenyl

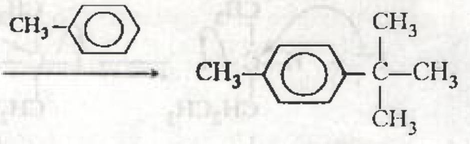
(*iii*) The initially formed less stable 1° carbocation (I) undergoes rearrangement by 1, 2-hydride shift to form more stable 3° carbocation (II) which then attacks the toluene ring to form *p*-cymene



Isobutyl bromide

Isobutyl carbocation (1°) (*less stable*)

tert−Butyl carbocation (3°) (*more stable*)



p−Cymene

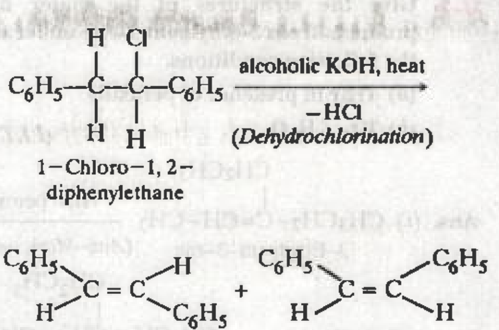
Q.14. **The following reaction gives two products.**

$$C_6H_5CH_2CHClC_6H_5 \xrightarrow{\text{alcoholic KOH, heat}}$$

Write the structures of the products.

(I.I.T. 1998)

Ans. $C_6H_5CH_2CHClC_6H_5$ upon heating with alcoholic KOH, undergoes dehydrochlorination to yield 1, 2-diphenylethene (*stilbene*) which exhibits geometrical isomerism. Thus, the two products formed are : *trans*-1, 2-diphenylethene and *cis*-1, 2-diphenylethene.

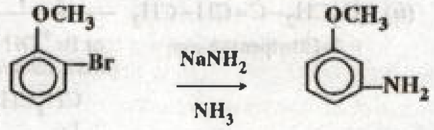


1−Chloro−1, 2−diphenylethane

trans−1, 2−Diphenylethene (*major product*)

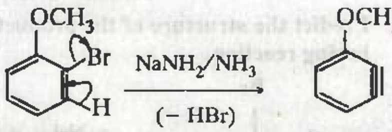
cis−1, 2−Diphenylethene (*minor product*)

Q. 15. **Explain briefly the formation of the product giving the structure of the intermediate.**



(I.I.T. 1999)

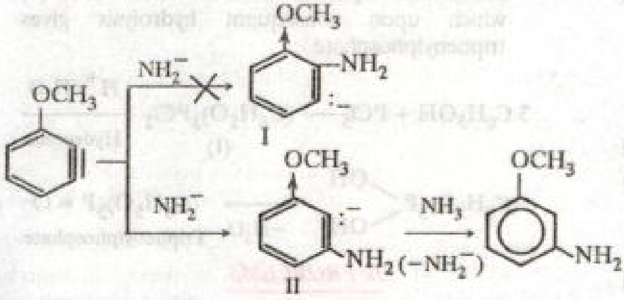
Ans. This reaction occurs through intermediate formation of benzyne as shown below :



o−Bromoanisole

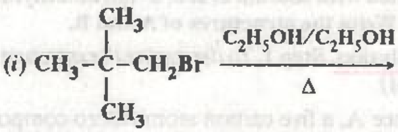
Benzyne intermediate

In principle, the benzyne intermediate may add NH_2^- forming either carbanion (I) or (II). Since carbanion (I) is destabilized and carbanion (II) is stabilized by −I-effect of the $-OCH_3$ group, therefore, only carbanion (II) is formed. This then abstracts a proton from NH_3 to form *m*-anisidine.



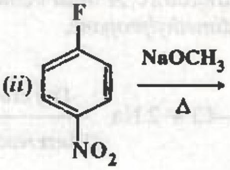
m−Anisidine

Q.16. What would be the major products in the following reactions ?

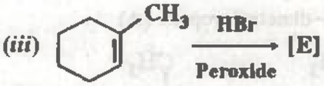


$$(i)\ \mathrm{CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-CH_2Br} \xrightarrow[\Delta]{C_2H_5OH/C_2H_5OH}$$

(I.I.T. 2000 ; C.B.S.E. P.M.T. 2004)

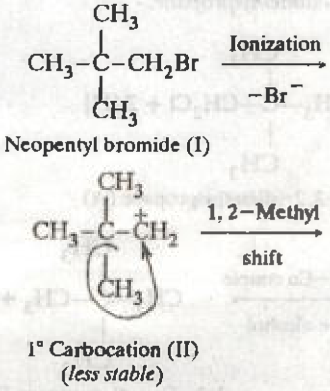


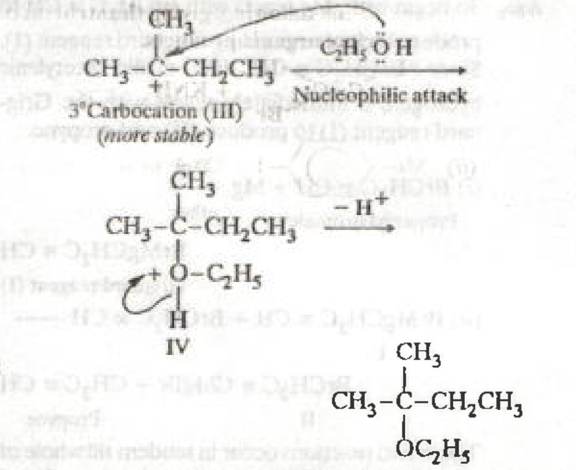
(I.I.T. 2000)



(Roorkee 2000)

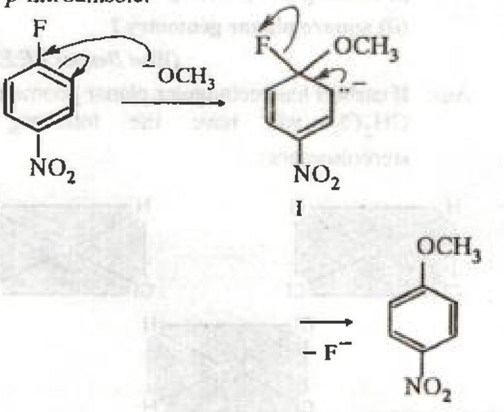
Ans. (*i*) Neopentyl bromide (I) first undergoes ionization to give 1° carbocation (II) which rearranges to a more stable 3° carbocation (III). III then undergoes nucleophilic attack by C_2H_5OH to give IV which subsequently loses a proton to give 2-ethoxy-2-methylbutane (V).





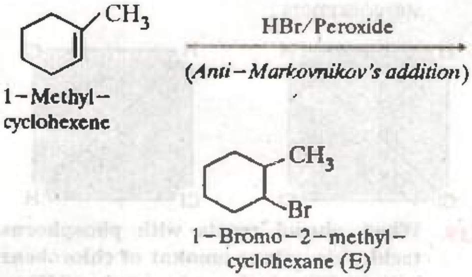
2−Ethoxy−2−methylbutane (V)

(*ii*) F is activated towards nucleophilic substitution by the electron-withdrawing effect of the NO_2 group. Nucleophilic attack by CH_3O^- first gives carbanion (I) which then loses a F^- to give *p*-nitroanisole.



p−Nitroanisole

(*iii*) In presence of peroxides, addition of HBr to alkenes occurs *anti* to Markovnikov's rule. Thus,



Q. 17. Explain why Grignard reagent from $BrCH_2C \equiv CH$ cannot be prepared ?

(West Bengal J.E.E. 2001)

Ans. To begin with, Mg reacts with $BrCH_2C \equiv CH$ to produce the corresponding Grignard reagent (I). Since $BrCH_2C \equiv CH$ has acidic acetylenic hydrogen, it immediately reacts with the Grignard reagent (I) to produce (II) and propyne.

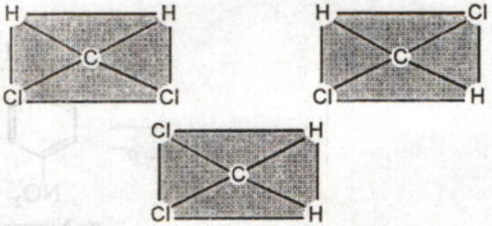
$$(i)\ \underset{\text{Propargyl bromide}}{BrCH_2C \equiv CH} + Mg \xrightarrow[\text{ether}]{\text{Dry}} \underset{\text{Grignard reagent (I)}}{BrMgCH_2C \equiv CH}$$

$$(ii)\ \underset{\text{I}}{BrMgCH_2C \equiv CH} + BrCH_2C \equiv CH \longrightarrow \underset{\text{II}}{BrCH_2C \equiv CMgBr} + \underset{\text{Propyne}}{CH_3C \equiv CH}$$

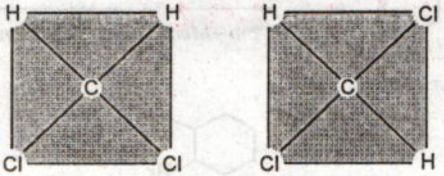
These two reactions occur in tandem till whole of propargyl bromide is consumed. It is because of this reason that Grignard reagent from $BrCH_2C \equiv CH$ cannot be prepared.

Q. 18. How many isomers are possible for CH_2Cl_2 assuming carbon to have
***(i)* rectangular planar geometry and**
***(ii)* square planar geometry ?**
(West Bengal J.E.E. 2001)

Ans. If carbon has rectangular planar geometry, then CH_2Cl_2 will have the following three stereoisomers :



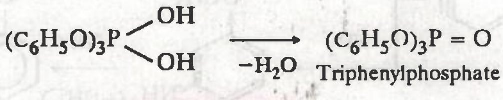
And if carbon has square planar geometry, then CH_2Cl_2 will have the following two stereoisomers :



Q. 19. When phenol reacts with phosphorus pentachloride, minor amount of chlorobenzene is formed. What is the major product ? Write down its structure. ***(West Bengal J.E.E. 2003)***

Ans. Because of resonance, C—OH bond in phenols is much stronger than C—OH bond in alcohols and hence cannot be displaced by Cl. Instead phenol acts as a nucleophile and brings about a nucleophilic displacement reaction on PCl_5. However due to steric hindrance only three Cl atoms are displaced to form intermediate (I) which upon subsequent hydrolysis gives triphenylphosphate

$$3\,C_6H_5OH + PCl_5 \longrightarrow \underset{\text{(I)}}{(C_6H_5O)_3PCl_2} \xrightarrow[\text{Hydrolysis}]{H^+/H_2O}$$



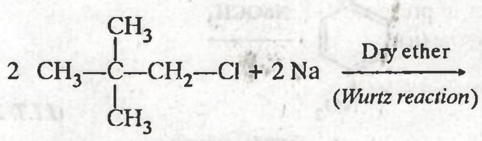
$$(C_6H_5O)_3P(OH)_2 \xrightarrow{-H_2O} \underset{\text{Triphenylphosphate}}{(C_6H_5O)_3P = O}$$

B. PROBLEMS

Problem 1. **A chloro compound (A) on reduction with Zn—Cu couple and alcohol gives the hydrocarbon (B) with five carbon atoms. When A is dissolved in ether and treated with sodium 2, 2, 5, 5- tetramethylhexane is formed. Write the structures of A and B.**

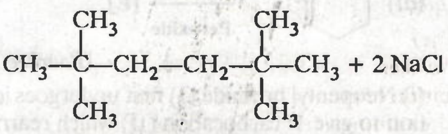
Solution. Step 1. *To determine the structure of compound (A)*

Since A, a five carbon atom chloro compound, on reaction with sodium in ether (*Wurtz reaction*) gives 2, 2, 5, 5- tetramethylhexane, therefore, *A must be neopentyl chloride or 1-chloro-2, 2-dimethylpropane.*



$$2\ CH_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}{-}CH_2{-}Cl + 2\,Na \xrightarrow[\textit{(Wurtz reaction)}]{\text{Dry ether}}$$

1-Chloro-2, 2-dimethylpropane (A)

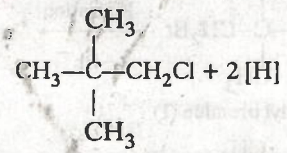


$$CH_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}{-}CH_2{-}CH_2{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}{-}CH_3 + 2\,NaCl$$

2, 2, 5, 5-Tetramethylhexane

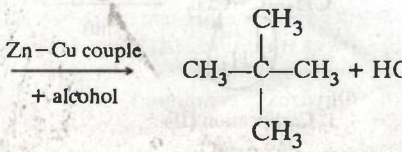
Step 2. *To determine the structure of compound (B)*

Since A on reduction with Zn—Cu couple and alcohol gives a hydrocarbon (B), therefore, *B must be neopentane or 2, 2- dimethylpropane.*



$$CH_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}{-}CH_2Cl + 2\,[H]$$

1-Chloro-2, 2-dimethylpropane (A)



$$\xrightarrow[\text{+ alcohol}]{\text{Zn-Cu couple}} CH_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}{-}CH_3 + HCl$$

2, 2-Dimethylpropane (B)

Thus, A = 1-chloro-2, 2-dimethylpropane and B = 2, 2- dimethylpropane.

Problem 2. **A sweet smelling organic compound A is slowly oxidisied by air in presence of light to a highly poisonous gas. On warming with silver powder, it forms a gaseous substance B, which is also produced by the action of calcium carbide on water. Identify A and B and write the chemical equations of the reactions involved.** *(C.B.S.E. Sample Paper 1997)*

Solution. **Step 1.** *To determine the structure of compound (B)*

$$\underset{\text{Cal. carbide}}{CaC_2} + 2\,H_2O \longrightarrow \underset{\text{Acetylene (B)}}{HC \equiv CH} + Ca(OH)_2$$

Step 2. *To determine the structure of compound (A)*

Since compound (B), *i.e.*, acetylene is produced by warming compound (A) with silver powder, therefore, *compound (A) must be chloroform*

$$\underset{\text{Chloroform (A)}}{CH\,Cl_3 + 6\,Ag + Cl_3\,CH} \xrightarrow{\Delta} \underset{\text{Acetylene (B)}}{HC \equiv CH} + 6AgCl$$

The fact that compound (A) is actually chloroform is confirmed by the observation that (A) is slowly oxidised by air in presence of light to a highly poisonous gas, *i.e., phosgene.*

$$\underset{\text{Chloroform (A)}}{2\,CHCl_3} + O_2 \xrightarrow{h\nu} \underset{\substack{\text{Phosgene}\\ \textit{(Poisonous gas)}}}{2\,COCl_2} + 2\,HCl$$

Thus, A = $CHCl_3$ (chloroform) and B = $HC \equiv CH$ (acetylene)

Problem 3. **n-Butane is produced by monobromination of ethane followed by Wurtz reaction. Calculate the volume of ethane at NTP required to produce 55 g of n-butane, if the bromination takes place with 90 per cent yield and Wurtz reaction with 85 per cent yield.** *(I.I.T. 1989)*

Solution. Reactions involved herein are :

$$\underset{\substack{\text{Ethane}\\22\cdot4\text{ litres at NTP}}}{CH_3CH_3} + Br_2 \xrightarrow[\text{Monobromination}]{h\nu} \underset{\substack{\text{Ethyl bromide}\\109\text{ g}}}{CH_3CH_2Br} + HBr \quad ...(i)$$

$$\underset{\substack{\text{Ethyl bromide}\\2 \times 109 = 218\text{ g}}}{2\,CH_3CH_2Br} + 2\,Na \xrightarrow[\text{reaction}]{\text{Wurtz}} \underset{\substack{n-\text{Butane}\\58\text{ g}}}{CH_3CH_2{-}CH_2CH_3} + 2\,NaBr \quad ...(ii)$$

From Eqn. (*ii*) using weight-weight relationship, we have,

58 g of *n*-butane are obtained from

$CH_3CH_2Br = 218$ g

∴ 58 g of *n*-butane will be obtained from

$$CH_3CH_2Br = \frac{218 \times 55}{58}\text{ g}$$

But the yield of Wurtz reaction is only 85%

∴ Amount of CH_3CH_2Br actually required

$$= \frac{100}{85} \times \frac{218}{58} \times 55 = 243\cdot2\text{ g}$$

From Eqn. (*i*) using weight-volume relationship, we have,

109 g of CH_3CH_2Br are obtained from ethane = 22·4 litres at NTP

∴ 243·2 g of CH_3CH_2Br will be obtained from ethane

$$= \frac{22\cdot4 \times 243\cdot2}{109}\text{ litres at NTP}$$

But the yield of bromination is only 90%

∴ Volume of ethane actually required

$$= \frac{100}{90} \times \frac{22\cdot4 \times 243\cdot2}{109} = 55\cdot53\text{ litres at NTP}$$

I.I.T. (MAINS) SPECIAL

Q. 1. **An organic compound (X), on analysis gives 24.24% C and 4.04% H. Further, sodium extract of 1.0 g of (X) gives 2.90 g of silver chloride with acidified silver nitrate solution. The compound (X) can be represented by two isomeric structures (Y) and (Z). (Y) on treatment with aqueous potassium hydroxide solution gives a dihydroxy compound, while (Z) on similar treatment gives ethanal. Find out the molecular formula of (X) and give the structures of (Y) and (Z).** *(I.I.T. 1989)*

Ans. (*a*) $$\%\,Cl = \frac{\text{At. wt. of Cl}}{\text{Mol. wt. of AgCl}} \times \frac{\text{Mass of AgCl formed}}{\text{Mass of substance taken}} \times 100$$

$$= \frac{35\cdot5}{143\cdot5} \times \frac{2\cdot90}{1\cdot0} \times 100 = 71\cdot74\%$$

$$\text{Now C : H : Cl} = \frac{24\cdot24}{12\cdot0} : \frac{4\cdot04}{1\cdot0} : \frac{71\cdot74}{35\cdot5}$$

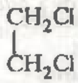
$$= 1 : 2 : 1$$

∴ E.F. of X = CH_2Cl

Since CH_2Cl is not a stable compound, therefore, lowest possible M.F.

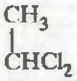
$$= 2 \times CH_2Cl = C_2H_4Cl_2.$$

(*b*) The two possible isomers of $C_2H_4Cl_2$. (X) *i.e.* (Y) and (Z) are :



$$\begin{array}{l} CH_2Cl \\ | \\ CH_2Cl \end{array}$$

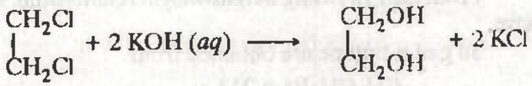
Ethylene dichloride



$$\begin{array}{l} CH_3 \\ | \\ CHCl_2 \end{array}$$

Ethylidene dichloride

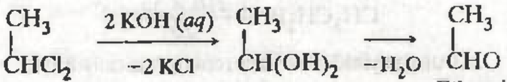
(*c*) Since (Y) on treatment with aqueous KOH gives a dihydroxy compound while (Z) on similar treatment gives ethanal, therefore, (Y) must be ethylene dichloride and (Z) must be ethylidene dichloride.



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

Ethylene dichloride (Y)

Ethylene glycol (*a dihydroxy compound*)



$$\begin{array}{l} CH_3 \\ | \\ CHCl_2 \end{array} \xrightarrow[-2\,KCl]{2\,KOH\,(aq)} \begin{array}{l} CH_3 \\ | \\ CH(OH)_2 \end{array} \xrightarrow[-H_2O]{} \begin{array}{l} CH_3 \\ | \\ CHO \end{array}$$

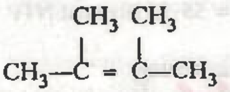
Ethylidene dichloride (Z)

(*unstable*)

Ethanal

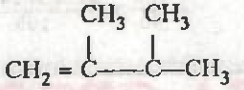
Q. 2. **An alkyl halide, X, of formula $C_6H_{13}Cl$ on treatment with potassium *tert*-butoxide gives two isomeric alkenes Y and Z (C_6H_{12}). Both alkenes on hydrogenation give 2, 3-dimethylbutane. Predict the structures of X, Y and Z.** (*I.I.T. 1996*)

Ans. (*a*) Since the two isomeric alkenes Y and Z (C_6H_{12}) on catalytic hydrogenation give the same 2,3- dimethylbutane, therefore, Y and Z must differ in the position of the double bond, *i.e.*,



$$CH_3-\overset{\overset{CH_3}{|}}{C}=\overset{\overset{CH_3}{|}}{C}-CH_3$$

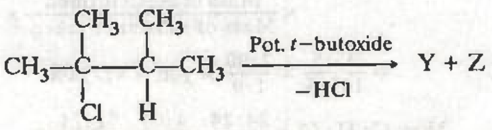
2, 3-Dimethylbut-2-ene (Y)



$$CH_2=\overset{\overset{CH_3}{|}}{C}-\overset{\overset{CH_3}{|}}{C}-CH_3$$

2, 3-Dimethylbut-1-ene (Z)

If this is so, then the alkyl halide X ($C_6H_{13}Cl$) must have a H-atom on either side of Cl atom, *i.e.*, X must be 2-chloro-2, 3-dimethylbutane



$$CH_3-\underset{\underset{Cl}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 \xrightarrow[-HCl]{Pot.\ t\text{-butoxide}} Y + Z$$

2-Chloro-2, 3-dimethylbutane (X)

Q. 3. **(W) and (X) are optically active isomers of C_5H_9Cl. (W) on treatment with one mole of H_2 is converted to an optically inactive compound (Y), but (X) gives an optically active compound (Z) undeer the same conditions. Give structure of (Y) and configuration of (W), (X) and (Z) in Fischer projections.** (*Roorkee 2000*)

Ans. (*i*) No. of double bond equivalents (D.B.E.)

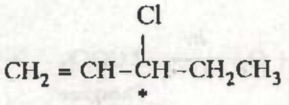
$$= \frac{\Sigma n\,(v-2)}{2} + 1$$

where n = no. of atoms, v = valency of the atom. Substituting the values of n and v for each atom in the formula, C_5H_9Cl, we have,

$$\text{D.B.E.} = \frac{5\,(4-2) + 9\,(1-2) + 1\,(1-2)}{2} + 1$$

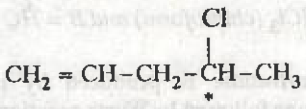
$$= 0 + 1 = 1$$

Thus, the formula C_5H_9Cl suggests that (W) and (X) are either saturated chlorocycloalkanes or chloroalkenes. Since both (W) and (X) undergo hydrogenation, therefore, they are chloroalkenes and not chlorocycloalkanes. Further since both (W and X) are optically active chloroalkenes, therefore, they must contain at least one chiral carbon atom, and hence their probable structures are :



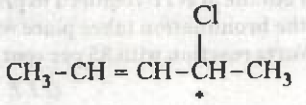
$$CH_2=CH-\underset{*}{\overset{\overset{Cl}{|}}{C}H}-CH_2CH_3$$

I



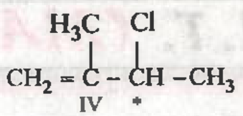
$$CH_2=CH-CH_2-\underset{*}{\overset{\overset{Cl}{|}}{C}H}-CH_3$$

II



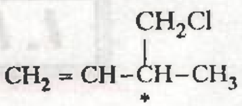
$$CH_3-CH=CH-\underset{*}{\overset{\overset{Cl}{|}}{C}H}-CH_3$$

III



$$CH_2=\overset{\overset{H_3C}{|}}{C}-\underset{*}{\overset{\overset{Cl}{|}}{C}H}-CH_3$$

IV

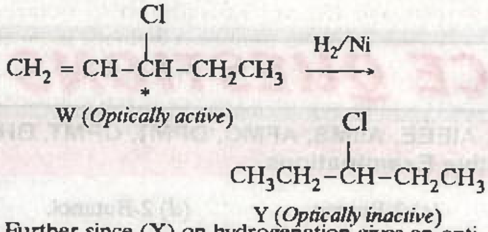


$$CH_2=CH-\underset{*}{\overset{\overset{CH_2Cl}{|}}{C}H}-CH_3$$

V

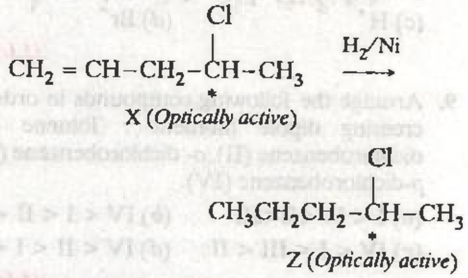
(*ii*) Now (W) $\xrightarrow{H_2}$ optically inactive (Y) and (X) $\xrightarrow{H_2}$ optically active (Z).

An inspection of the five formulae given above suggests that only structure (I) on hydrogenation gives optically inactive compound (Y). Therefore,



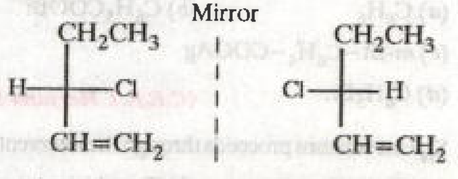
$$\underset{\text{W (Optically active)}}{CH_2=CH-\underset{*}{\overset{Cl}{\overset{|}{C}H}}-CH_2CH_3} \xrightarrow{H_2/Ni} \underset{\text{Y (Optically inactive)}}{CH_3CH_2-\overset{Cl}{\overset{|}{C}H}-CH_2CH_3}$$

Further since (X) on hydrogenation gives an optically active compound (Z), therefore, (X) can have any of the four structures (II to V). If we assume that formula II represents compound (X), then the structure of compound (Z) is as under :

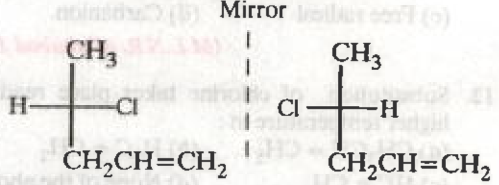


$$\underset{\text{X (Optically active)}}{CH_2=CH-CH_2-\underset{*}{\overset{Cl}{\overset{|}{C}H}}-CH_3} \xrightarrow{H_2/Ni} \underset{\text{Z (Optically active)}}{CH_3CH_2CH_2-\underset{*}{\overset{Cl}{\overset{|}{C}H}}-CH_3}$$

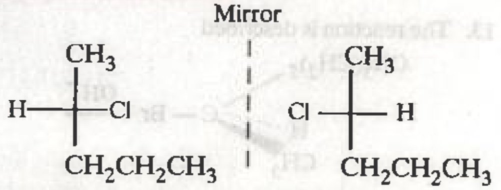
(*iii*) Knowing the structures of (W), (X) and (Z), their Fischer Projections may be written as follows :



Enantiomers of (W)



Enantiomers of (X)

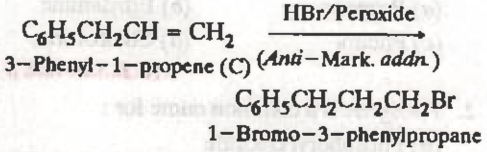


Enantiomers of (Z)

Q. .. **A Grignard reagent [A] and a haloalkene [B] react together to give [C]. Compound (C) on heating with KOH yields a mixture of two geometrical isomers, (D) and (E), of which (D) predominates. (C) and (E) have the same molecular formula but (C) gives 1-bromo-3-phenylpropane on reaction with HBr in the presence of a peroxide. Give structures of (A), (B) and (C) and configuration of (D) and (E) with reasons.** ***(Roorkee 2001)***

Ans. Step 1. *To determine the structure of compound (C).*

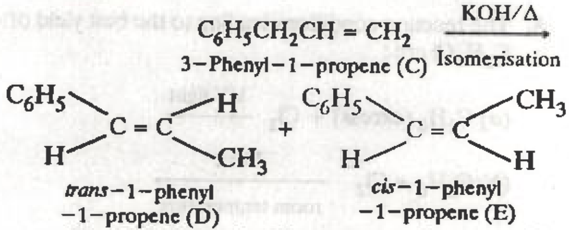
(*i*) Since (C) on treatment with HBr in presence of peroxide (*anti-Markovnikov's addition*) gives 1-bromo-3- phenylpropane, therefore, *(C) must be 3-phenyl-1-propene.*



$$\underset{\text{3-Phenyl-1-propene (C)}}{C_6H_5CH_2CH=CH_2} \xrightarrow[\text{(Anti-Mark. addn.)}]{\text{HBr/Peroxide}} \underset{\text{1-Bromo-3-phenylpropane}}{C_6H_5CH_2CH_2CH_2Br}$$

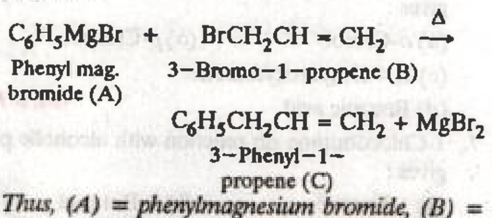
Step 2. *To determine the structures of compounds (D) and (E).*

Now (C), *i.e.*, 3-phenyl-1-propene being a terminal alkene does not show geometrical isomerism. However, when (C) is heated with KOH, it gives a mixture of two geometrical isomers, (D and E). Since (C) has the same M.F. as (E), therefore, (D) and (E) are isomers of (C), *i.e.*, on heating with KOH (C) undergoes isomerisation to give the more stable 1-phenyl-1-propene. Further since out of (D) and (E), (D) predominates, therefore, (D) must be the more stable *trans-* isomer, *i.e.*, *trans*-1-phenyl-1-propene and (E) must be the less stable *cis*-isomer, *i.e.*, *cis*-1-phenyl-1-propene isomer.



Step 3. *To determine the structures of compounds (A) and (B).*

Since (C), *i.e.*, 3-phenyl-1-propene is obtained by the reaction between a Grignard reagent (A) and a haloalkene (B), therefore, *(A) must be phenylmagnesium bromide and (B) must be 3-bromo-1-propene.*



$$\underset{\text{Phenyl mag. bromide (A)}}{C_6H_5MgBr} + \underset{\text{3-Bromo-1-propene (B)}}{BrCH_2CH=CH_2} \xrightarrow{\Delta} \underset{\text{3-Phenyl-1-propene (C)}}{C_6H_5CH_2CH=CH_2} + MgBr_2$$

Thus, (A) = phenylmagnesium bromide, (B) = 3-bromo-1-propene, (C) = 3-phenyl-1-propene, (D) = trans-1-phenyl-1-propene and (E) = cis-1-phenyl-1-propene.

MULTIPLE CHOICE QUESTIONS

For CBSE– PMT (Preliminary), IIT Screening, AIEEE, AIIMS, AFMC, DPMT, CPMT, BHU and All Other Competitive Examinations

1. Which of the following compounds does not react with bromine ?
   (*a*) Propene (*b*) Ethylamine
   (*c*) Phenol (*d*) Chloroform.
   (C.B.S.E. P.M.T. 1988)

2. Phosgene is a common name for :
   (*a*) Phosphoryl chloride
   (*b*) Carbon dioxide and phosphine
   (*c*) Carbonyl chloride
   (*d*) Carbon tetrachloride. *(C.B.S.E. P.M.T. 1988)*

3. When hydrochloric acid gas is treated with propene in presence of benzoyl peroxide, it gives
   (*a*) 2-Chloropropane (*b*) Allyl chloride
   (*c*) No reaction (*d*) *n*-Propyl chloride.
   (C.B.S.E. P.M.T. 1993)

4. The reaction of toluene with chlorine in presence of ferric chloride gives predominantly :
   (*a*) Benzoyl chloride (*b*) *m*-Chlorotoluene
   (*c*) Benzyl chloride (*d*) *o*-and *p*-Chlorotoluene.
   (I.I.T. 1986)

5. The reaction conditions leading to the best yield of C_2H_5Cl are :
   (*a*) $C_2H_6 \text{ (excess)} + Cl_2 \xrightarrow{\text{UV light}}$
   (*b*) $C_2H_6 + Cl_2 \xrightarrow[\text{room temperature}]{\text{Dark}}$
   (*c*) $C_2H_6 + Cl_2 \text{ (excess)} \xrightarrow{\text{UV light}}$
   (*d*) $C_2H_6 + Cl_2 \xrightarrow{\text{UV light}}$ *(I.I.T. 1986)*

6. Chlorination of toluene in presence of light and heat followed by treatment with aqueous NaOH gives :
   (*a*) *o*-Cresol (*b*) *p*-Cresol
   (*c*) 2, 4-Dihydroxytoluene
   (*d*) Benzoic acid. *(I.I.T. 1990)*

7. 1-Chlorobutane on reaction with alcoholic potash gives :
   (*a*) 1-Butene (*b*) 1-Butanol
   (*c*) 2-Butene (*d*) 2-Butanol.
   (I.I.T. 1991)

8. In the addition of HBr to propene in the absence of peroxides, the first step involves the addition of
   (*a*) H^+ (*b*) Br^-
   (*c*) $H^\bullet$ (*d*) $Br^\bullet$
   (I.I.T. 1993)

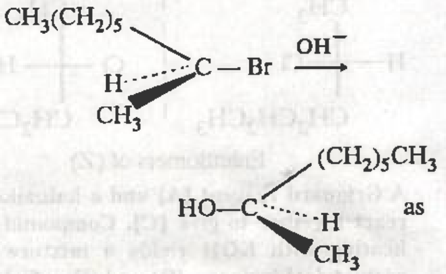
9. Arrange the following compounds in order of increasing dipole moment : Toluene (I), *m*-dichlorobenzene (II), *o*-dichlorobenzene (III) and *p*-dichlorobenzene (IV).
   (*a*) I < IV < II < III (*b*) IV < I < II < III
   (*c*) IV < I < III < II (*d*) IV < II < I < III.
   (I.I.T. 1996)

10. Silver benzoate reacts with bromine to
    (*a*) C_6H_6 (*b*) C_6H_5COOBr
    (*c*) *m*-$Br{-}C_6H_4{-}COOAg$
    (*d*) C_6H_5Br. *(C.E.E.T. Haryana 1996)*

11. **S_N2 mechanism proceeds through the intervention of**
    (*a*) Carbonium ion (*b*) Transition state
    (*c*) Free radical (*d*) Carbanion.
    (M.L.N.R. Allahabad 1996)

12. Substitution of chlorine takes place readily at higher temperature in :
    (*a*) $CH_3CH = CH_2$ (*b*) $H_2C = CH_2$
    (*c*) $HC \equiv CH$ (*d*) None of the above.
    (M.L.N.R. Allahabad 1996)

13. The reaction is described



as

ANSWERS

1. *d* 2. *c* 3. *a* 4. *d* 5. *a* 6. *d* 7. *a* 8. *a* 9. *b* 10. *d*
11. *b* 12. *a*

(*a*) S_E2 (*b*) S_N1
(*c*) S_N2 (*d*) S_N0.

(C.B.S.E. P.M.T. 1997)

14. The alkyl halide is converted into an alcohol by
(*a*) addition (*b*) substitution
(*c*) dehydrohalogenation
(*d*) elimination. *(C.B.S.E. P.M.T. 1997)*

15. The replacement of chlorine of chlorobenzene to give phenol requires drastic conditions but chlorine of 2, 4-dinitrochlorobenzene is readily replaced since
(*a*) NO_2 makes the ring electron rich at *ortho* and *para*.
(*b*) NO_2 withdraws electrons from the *meta*-position
(*c*) NO_2 donates electrons at *meta*- position
(*d*) NO_2 withdraws electrons from *ortho*/*para* positions. *(C.B.S.E. P.M.T. 1997)*

16. $C_3H_8 + Cl_2 \xrightarrow{\text{Light}} C_3H_7Cl + HCl$ is an example of
(*a*) Substitution
(*b*) Elimination
(*c*) Addition
(*d*) Rearrangment reaction. *(A.F.M.C. 1997)*

17. In the following groups :
$-OAc$ (I) , $-OMe$ (II)
$-OSO_2Me$ (III) , $-OSO_2CF_3$ (IV)
the order of leaving group ability is
(*a*) I > II > III > IV (*b*) IV > III > I > II
(*c*) III II > I > IV (*d*) II > III > IV > I.

(I.I.T. 1997)

18. The intermediate during the addition of HCl to propene in presence of peroxide is
(*a*) $CH_3\dot{C}HCH_2Cl$ (*b*) $CH_3\overset{+}{C}HCH_3$
(*c*) $CH_3CH_2\dot{C}H_2$ (*d*) $CH_3CH_2\overset{+}{C}H_2$

(I.I.T. 1997)

19. In the reaction of *p*-chlorotoluene with KNH_2 in liq. NH_3, the major product is
(*a*) *o*-toluidine (*b*) *m*-toluidine
(*c*) *p*-toluidine (*d*) *p*-chloroaniline.

(I.I.T. 1997)

20. $(CH_3)_3CMgBr$ on reaction with D_2O produces
(*a*) $(CH_3)_3CD$ (*b*) $(CH_3)_3COD$
(*c*) $(CD_3)_3CD$ (*d*) $(CD_3)_3OD$

(I.I.T. 1997)

21. Which of the following reactions is most suitable for the preparation of *n*-propylbenzene
(*a*) Friedel-Crafts alkylation
(*b*) Wurtz reaction
(*c*) Wurtz-Fitting reaction
(*d*) Grignard reaction *(M.P.P.M.T. 1998)*

22. 2-Bromopentane is heated with potassium ethoxide in ethanol. The major product obtained is
(*a*) 2-Ethoxypentane (*b*) Pentene-1
(*c*) *cis*-Pentene-2 (*d*) *trans*-Pentene-2

(C.B.S.E. P.M.T. 1998)

23. Which of the following is an example of S_N2 reaction ?
(*a*) $CH_3Br + OH^- \longrightarrow CH_3OH + Br^-$
(*b*) $(CH_3)_2CHBr + OH^- \longrightarrow (CH_3)_2CHOH + Br^-$
(*c*) $CH_3CH_2OH \xrightarrow{-H_2O} CH_2 = CH_2$
(*d*) $(CH_3)_3C-Br + OH^- \longrightarrow (CH_3)_3COH + Br^-$.

(C.P.M.T. 1999)

24. Which of the following possesses highest melting point ?
(*a*) Chlorobenzene (*b*) *o*-Dichlorobenzene
(*c*) *m*-Dichlorobenzene (*d*) *p*-Dichlorobenzene.

(C.P.M.T. 1999)

25. Which of the following will not give iodoform test ?
(*a*) Ethanol (*b*) Ethanal
(*c*) Isopropyl alcohol (*d*) Benzyl alcohol.

(C.P.M.T. 1999)

26. Gammexane is
(*a*) Chlorobenzene (*b*) Benzyl chloride
(*c*) Bromobenzene (*d*) Benzene hexachloride.

(C.B.S.E. P.M.T. 1999)

27. If H is replaced by a Cl atom in C_4H_9Cl, the total number of structural isomers will be
(*a*) 4 (*b*) 5
(*c*) 7 (*d*) 10

(J.I.P.M.E.R. 2000)

ANSWERS

13. *c* **14.** *b* **15.** *d* **16.** *a* **17.** *b* **18.** *b* **19.** *b* **20.** *a* **21.** *c* **22.** *d*
23. *a* **24.** *d* **25.** *d* **26.** *d* **27.** *d*

28. The conversion of $Cl—CH = CH—Cl$ to $Cl_2CH-CHCl_2$ can be carried out with

(*a*) Cl_2 (*b*) $Cl_2/h\nu$

(*c*) $Cl_2/AlCl_3$ (*d*) Cl_2/aq. NaOH.

(D.C.E. 2000)

29. 1, 2-Dibromopropane on treatment with X moles of $NaNH_2$ followed by treatment with ethyl bromide gives a pentyne. The value of X is

(*a*) One (*b*) Two

(*c*) Three (*d*) Four. *(D.C.E. 2000)*

30. The compound,

$$C_7H_8 \xrightarrow{3\,Cl_2/\Delta} A \xrightarrow{Br_2/Fe} B \xrightarrow{Zn/HCl} C$$

The compound C is

(*a*) *o*-Bromotoluene

(*b*) *m*-Bromotoluene

(*c*) *p*-Bromotoluene

(*d*) 3-Bromo-2, 4, 6-trichlorotoluene.

(D.C.E. 2000)

31. Two isomeric alkenes A and B having molecular formula C_5H_9Cl on adding H_2, A gives optically inactive compound while B gives a chiral compound. The two isomers are :

(*a*) A is 3-chloro-1-pentene and B is 4-chloro-2-pentene

(*b*) A is 4-chloro-1-pentene and B is 2-chloro-2-pentene

(*c*) A is 3-chloro-2-pentene and B is 1-chloro-2-pentene

(*d*) A is 1-chloro-1-pentene and B is 5-chloro-1-pentene. *(D.C.E. 2000)*

32. The conversion of 2, 3-dibromobutane to 2-butene with Zn and alcohol is

(*a*) Redox reaction (*b*) α-Elimination

(*c*) β-Elimination

(*d*) Both β-elimination and redox reaction.

(D.C.E. 2000)

33. When chlorine is passed through propene at 400°C, which of the following is formed ?

(*a*) PVC (*b*) Allyl chloride

(*c*) Vinyl chloride (*d*) 1, 2-Dichloroethane.

(Haryana C.E.E.T. 2000)

34. Nucleophilicity order is correctly represented by

(*a*) $CH_3^- < NH_2^- < HO^- < F^-$

(*b*) $CH_3^- \simeq NH_2^- > OH^- \simeq F^-$

(*c*) $CH_3^- > NH_2^- > HO^- > F^-$

(*d*) $NH_2^- > F^- > HO^- > CH_3^-$.

(J.I.P.M.E.R. 2000)

35. Which among MeX, RCH_2X, R_2CHX, R_3CX is most reactive towards S_N2 reaction :

(*a*) MeX (*b*) RCH_2X

(*c*) R_2CHX (*d*) R_3CX.

(J.I.P.M.E.R. 2000)

36. S_N1 **reaction of optically active alkyl halides leads to**

(*a*) retention of configuration

(*b*) racemisation

(*c*) inversion of configuration

(*d*) none of these. *(J.I.P.M.E.R. 2000)*

37. The addition of HBr is easiest with

(*a*) $CH_2 = CHCl$ (*b*) $ClCH = CHCl$

(*c*) $CH_3-CH = CH_2$ (*d*) $(CH_3)_2C = CH_2$.

(M.P.P.M.T. 2000)

38. Iodoform on heating with KOH gives

(*a*) CH_3CHO (*b*) CH_3COOK

(*c*) HCOOK (*d*) HCHO.

(M.P. P.M.T. 2000)

39. Unpleasant smelling carbylamines are formed by heating alkali and chloroform with

(*a*) Any aliphatic amine (*b*) Any aromatic amine

(*c*) Any amine (*d*) Any primary amine.

(K.C.E.T. 2000)

40. Chloroform on reaction with zinc and HCl forms.

(*a*) formic acid (*b*) chloropicrin

(*c*) methylene chloride (*d*) phosgene.

(M.P. C.E.E. 2000)

41. The order of reactivities of the following alkyl halides for a S_N2 reaction is

(*a*) RF > RCl > RBr > RI

(*b*) RF > RBr > RCl > RI

(*c*) RCl > RBr > RF > RI

(*d*) RI > RBr > RCl > RF *(I.I.T. 2000)*

42. Which of the following has the highest nucleophilicity ?

(*a*) F^- (*b*) OH^-

ANSWERS

28. *a* **29.** *c* **30.** *b* 31. *a* 32. *d* 33. *b* 34. *c* **35.** *a* **36.** *b* **37.** *d*
38. *c* 39. *d* 40. *c* 41. *d*

(*c*) CH_3^- (*d*) NH_2^- (*I.I.T. 2000*)

43. The addition of propene with HOCl proceeds via the addition of

(*a*) H^+ in the first step

(*b*) Cl^+ in the first step

(*c*) OH^- in the first step

(*d*) Cl^+ and OH^- in a single step. (*I.I.T. 2001*)

44. An S_N2 reaction at an asymmetric carbon of a compound always gives

(*a*) an enantiomer of the substrate

(*b*) a product with opposite optical rotation

(*c*) a mixture of diastereomers

(*d*) a single stereoisomer. (*I.I.T. 2001*)

45. In the presence of peroxide, hydrogen chloride and hydrogen iodide do not give anti-Markovnikov's addition to alkenes because

(*a*) both are highly ionic

(*b*) one is oxidising and the other is reducing

(*c*) one of the steps is endothermic in both the cases

(*d*) all the steps are exothermic in both the reactions. (*I.I.T. 2001*)

46. The reactivity order of halides for dehydrohalogenation is

(*a*) R—F > R—Cl > R—Br > R—I

(*b*) R—I > R—Br > R—Cl > R—F

(*c*) R—I > R—Cl > R—Br > R—F

(*d*) R—F > R—I > R—Br > R—Cl

(*C.B.S.E. P.M.T. 2002*)

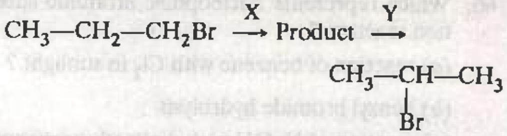
47. When primary amine reacts with chloroform in ethanolic KOH, then the product is

(*a*) an isocyanide (*b*) an aldehyde

(*c*) a cyanide (*d*) an alcohol

(*A.I.E.E.E. 2002*)

48. Identify the set of reagent/reaction conditions 'X' and 'Y' in the following set of transformations :



$$CH_3—CH_2—CH_2Br \xrightarrow{X} \text{Product} \xrightarrow{Y} \underset{\displaystyle Br}{CH_3—\underset{|}{CH}—CH_3}$$

(*a*) X = dil. aqueous NaOH, 20°C ;
Y = HBr/acetic acid, 20°C

(*b*) X = conc. alcoholic NaOH, 80°C ;
Y = HBr/acetic acid, 20°C

(*c*) X = dil. aqueous NaOH, 20°C ;
Y = $Br_2/CHCl_3$, 0°C

(*d*) X = conc. alcoholic NaOH, 80°C
Y = $Br_2/CHCl_3$, 0°C (*I.I.T. 2002*)

49. Among the following, the molecule with the highest dipole moment is

(*a*) CH_3Cl (*b*) CH_2Cl_2

(*c*) $CHCl_3$ (*d*) CCl_4 (*I.I.T. 2003*)

50. Bottles containing C_6H_5I and $C_6H_5CH_2I$ lost their original labels. They were labelled as A and B for testing. A and B were separately taken in test tubes and boiled with NaOH solution. The end solution in each tube was made acidic with dilute HNO_3 and some $AgNO_3$ solution was added. Substance B gave a yellow precipitate. Which one of the following statements is true for this experiment ?

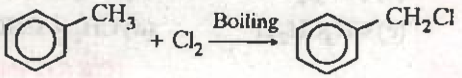
(*a*) Addition of HNO_3 was unnecessary

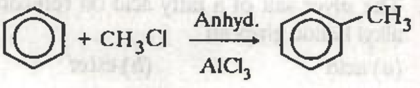
(*b*) A was C_6H_5I

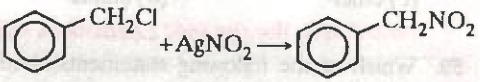
(*c*) A was $C_6H_5CH_2I$

(*d*) B was C_6H_5I (*A.I.E.E.E. 2003*)

51. Which of the following is a free radical substitution reaction ?

(*a*)


(*b*)


(*c*)


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

(*C.B.S.E. P.M.T. 2003*)

52. Which of the following are arranged in the decreasing order of dipole moment ?

(*a*) CH_3Cl, CH_3Br, CH_3F

(*b*) CH_3Cl, CH_3F, CH_3Br

(*c*) CH_3Br, CH_3Cl, CH_3F

(*d*) CH_3Br, CH_3F, CH_3Cl (*A.I.I.M.S. 2003*)

53. The most reactive nucleophile among the following is

(*a*) CH_3O^- (*b*) $C_6H_5O^-$

A N S W E R S

42. *c* 43. *b* 44. *d* 45. *c* 46. *c* 47. *a* 48. *b* 49. *a* 50. *b* 51. *a*
52. *b*

(*c*) $(CH_3)_2CHO^-$ (*d*) $(CH_3)_3CO^-$

(A.I.I.M.S. 2003)

54. To prevent chloroform to form phosgene gas (poisonous gas) what is added ?

(*a*) CH_3COCH_3 (*b*) C_2H_5OH

(*c*) CH_3COOH (*d*) CH_3OH

(M.G.I.M.S. Wardha 2003)

55. Chloropicrin is obtained by the reaction of

(*a*) Steam on carbon tetrachloride

(*b*) nitric acid on chlorobenzene

(*c*) chlorine on picric acid

(*d*) nitric acid on chlorofrm *(C.B.S.E. P.M.T. 2004)*

56. Which of the following will not form a yellow precipitate on heating with an alkaline solution of iodine ?

(*a*) $CH_3CHOHCH_3$ (*b*) $CH_3CH_2CHOHCH_3$

(*c*) CH_3OH (*d*) CH_3CH_2OH

(C.B.S.E. P.M.T. 2004)

57. Which of the following is least reactive in a nucleophilic substitution reaction ?

(*a*) $(CH_3)_3C{-}Cl$ (*b*) $CH_2 = CHCl$

(*c*) CH_3CH_2Cl (*d*) $CH_2 = CHCH_2Cl$

(C.B.S.E. P.M.T. 2004)

58. The silver salt of a fatty acid on refluxing with an alkyl halide gives an

(*a*) acid (*b*) ester

(*c*) ether (*d*) amine

(M.G.I.M.S. Wardha 2002 ; Karnatka C.E.T. 2004)

59. Which of the following statements about benzyl chloride is *incorrect* ?

(*a*) It is less reactive than alkyl halides

(*b*) It can be oxidised to benzaldehyde by boiling with copper nitrate solution

(*c*) It is a lachrymatory liquid and answers Beilstein's test

(*d*) It gives a while precipitate with alcoholic silver nitrate *(Karnataka C.E.T. 2004)*

60. An alkyl bromide produces a single alkene when it reacts with sodium ethoxide and ethanol. This alkene on hydrogenation produces 2-methylbutane. What is the identity of the alkyl halide ?

(*a*) 1-Bromo-2, 2-dimethyl propane

(*b*) 1-Bromobutane

(*c*) 1-Bromo-2-methylbutane

(*d*) 2-Bromo-2-methylbutane

(*e*) 2-Bromopentane *(Kerala M.E.E. 2004)*

61. Acetone is mixed with bleaching powder to give

(*a*) chloroform (*b*) acetaldehyde

(*c*) ethanol (*d*) phosgene

(A.F.M.C. 2004)

62. Which of the following cannot be used in Friedel-Crafts reactions ?

(*a*) $FeCl_3$ (*b*) $FeBC_3$

(*c*) $AlCl_3$ (*d*) NaCl

(A.F.M.C. 2004)

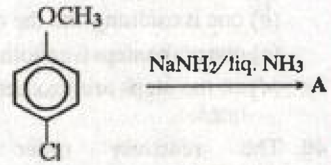
63. Which of the following reacts fastest with N-bromo succinimide ?

(*a*) C_6H_6 (*b*) CH_4

(*c*) Pyridine (*d*) Toluene

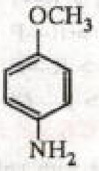
(J & K C.E.T. 2004)

64. In the reaction :

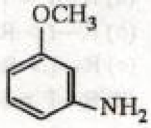


The major product is

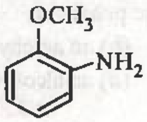
(*a*)



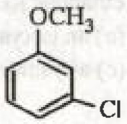
(*b*)



(*c*)



(*d*)



(J & K C.E.T. 2004)

65. Which represents nucleophilic aromatic substitution reaction ?

(*a*) reaction of benzene with Cl_2 in sunlight ?

(*b*) benzyl bromide hydrolysis

(*c*) reaction of NaOH with dinitrofluorobenzene

(*d*) Sulphonation of benzene

(Orissa J.E.E. 2004)

ANSWERS

53. *a* 54. *b* 55. *d* 56. *c* 57. *b* 58. *b* 59. *a* 60. *c* 61. *a* 62. *d*
63. *d* 64. *a* 65. *c*

HINTS/EXPLANATIONS to Multiple Choice Questions

3. Peroxide effect is observed only in case of HBr. With HCl, even in the presence of peroxides, only Markovnikov's product, *i.e.*, 2-chloropropane is obtained.

8. In absence of peroxides, electrophilic addition occurs, *i.e.*, H^+ adds first

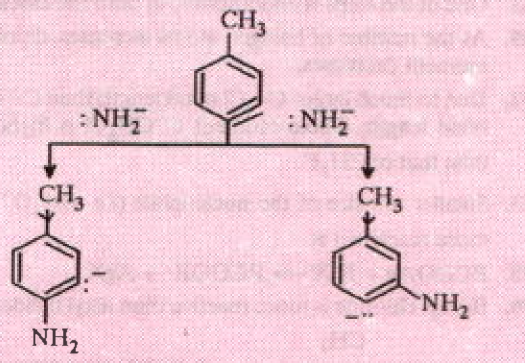
12. Allylic chlorination.

13. Inversion of configuration occurs is S_N2 reactions.

17. Weaker the base better is the leaving group. Now acidity increases in the order $CF_3SO_2OH > MeSO_2OH > AcOH > MeOH$, therefore, basicity of their conjugate bases increases in the reverse direction, *i.e.*, $CF_3SO_2O^-$ (IV) < $MeSO_2O^-$ (III) < AcO^- (I) < MeO^- (II). Thus, the correct order is : IV > III > I > II, *i.e.*, option (*b*) is correct.

18. *Anti-* Markovnikov's addition is observed only with HBr. Therefore, with HCl, even in the presence of peroxides, reaction occurs through a more stable carbocation intermediate, *i.e.* option (*b*) is correct.

19. The benzyne formed as an intermediate gives a more stable carbanion when the nucleophilic attack by the amide occurs at the *m*-position than at the *p*-position.



Destablized by +I-effect of the CH3 group

Stabilized by +I-effect of the CH3 group

20. $(CH_3)_3CMgBr + D{-}OD \longrightarrow (CH_3)_3CD + Mg(OD)Br$

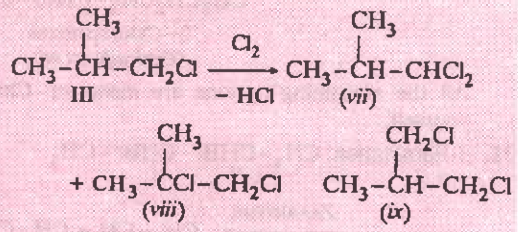
21. Friedel-Crafts alkylation of benzene with *n*- propyl bromide will give isopropylbenzene as the major product. Therefore, Wurtz-Fittig reaction is the right choice.

22. Heating with alc. C_2H_5OK brings about dehydrobromination to give *trans*-pentene-2 as the major product.

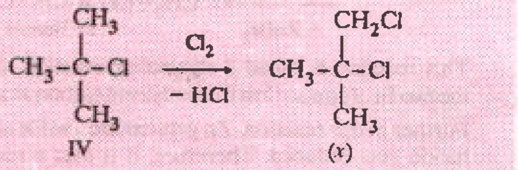
27. C_4H_9Cl has four isomers (I, II, III, IV). These on further chlorination will give 10 isomers as shown below :

$$\underset{\text{I}}{CH_3CH_2CH_2CH_2Cl} \xrightarrow[-\,HCl]{Cl_2} \underset{(i)}{CH_3CH_2CH_2CHCl_2} + \underset{(ii)}{CH_3CH_2CHClCH_2Cl} + \underset{(iii)}{CH_3CHClCH_2CH_2Cl} + \underset{(iv)}{ClCH_2CH_2CH_2CH_2Cl}$$

$$\underset{\text{II}}{CH_3-CHCl-CH_2CH_3} \xrightarrow[-\,HCl]{Cl_2} \underset{(ii)}{CH_3CH_2CHClCH_2Cl} + \underset{(v)}{CH_3-CCl_2-CH_2CH_3} + \underset{(vi)}{CH_3-CHCl-CHCl-CH_3}$$



$$\underset{\text{III}}{CH_3-\overset{\overset{CH_3}{|}}{C}H-CH_2Cl} \xrightarrow[-\,HCl]{Cl_2} \underset{(vii)}{CH_3-\overset{\overset{CH_3}{|}}{C}H-CHCl_2} + \underset{(viii)}{CH_3-\overset{\overset{CH_3}{|}}{C}Cl-CH_2Cl} \quad \underset{(ix)}{CH_3-\overset{\overset{CH_2Cl}{|}}{C}H-CH_2Cl}$$



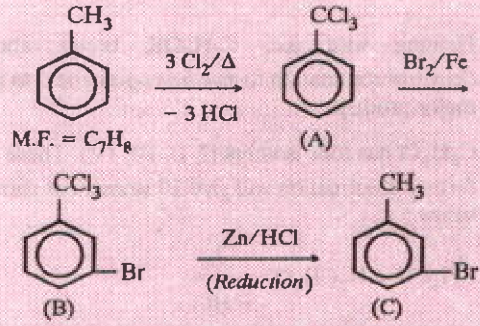
$$\underset{\text{IV}}{CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-Cl} \xrightarrow[-\,HCl]{Cl_2} \underset{(x)}{CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_2Cl}{|}}{C}}-Cl}$$

29. Three. $CH_3-CHBr-CH_2Br + 2\,NaNH_2 \longrightarrow CH_3C\equiv CH + 2\,NaBr + 2\,NH_3$

$CH_3C\equiv CH + NaNH_2 \longrightarrow CH_3C\equiv C^-\,Na^+ + NH_3$

and $CH_3C\equiv C^-\,Na^+ + CH_3CH_2Br \longrightarrow \underset{\text{2-Pentyne}}{CH_3C\equiv CCH_2CH_3} + NaBr$

30. *m*-Bromotoluene



31. $CH_2 = CH-\overset{*}{C}HCl-CH_2CH_3 \xrightarrow{H_2}$
3–Chloro–1–pentene (A)
(Optically active)

$CH_3CH_2-CHCl-CH_2CH_3$
3–Chloropentane
(Optically inactive)

$CH_3CH = CH-\overset{*}{C}HCl-CH_3 \xrightarrow{H_2}$
4–Chloro–2–pentene (B)
(Optically active)

$CH_3CH_2CH_2-\overset{*}{C}HCl-CH_3$
2–Chloropentane
(Optically active)

All the remaining options are incorrect. Check yourself.

32. *β*-Elimination. $CH_3-\underset{\beta}{C}HBr-\underset{\alpha}{C}HBr-CH_3$

$$\xrightarrow[-\ ZnBr_2]{Zn/alcohol} \underset{2-Butene}{CH_3-CH = CH-CH_3}$$

This reaction is called *β*-elimination reaction since the two Br atoms are lost from adjacent carbon atoms. Further in this reaction, Zn gets oxidised while alkyl halide gets reduced. Therefore, it is also a redox reaction. Thus, option (*d*) is correct.

33. Allyl chloride. $CH_3CH = CH_2 + Cl_2 \xrightarrow{400°C}$
$ClCH_2CH = CH_2 + HCl.$

34. As the electronegativity of the atom decreases (F > O > N > C), its tendency to donate electrons increases, *i.e.*, nucleophilicity increases. Thus, option (*c*) is correct.

35. As the number of substituents on the carbon atom carrying halogen increases, steric hindrance increases and hence the rate of S_N2 reaction decreases. Thus MeX having least steric hindrance is most reactive towards S_N2 reactions.

37. Greater the number of electron-donating groups attached to the double bond, more is the *π*-electron-density and hence easiest is the addition. Thus, option (*d*) is correct.

41. Reactively decreases as the C-X bond energy increases.

42. As the elecronegativity of the atom decreases (F>O>N>C), its tendency to donate a pair of electrons, i.e., nucleophilicity increases. Thus CH_3^- has he highest *nucleophilicity*.

43. Since O is more electronegative than Cl, therefore, heterolytic fission of HO—Cl gives HO^- and Cl^+.

$$HO-Cl \longrightarrow HO^- + Cl^+$$

Since alkenes undergo electrophilic addition reactions, therefore, the electrophile (Cl^+) attacks first to generate a more stable carbocation which then undergoes nucleophlic attack by HO^- to give propylene chlorohydrin.

$$CH_3CH{=}CH_2 + Cl^+ \longrightarrow CH_3 - \overset{+}{C}H - CH_2Cl$$

$$\xrightarrow{OH^-} CH_3-CHOH-CH_2Cl$$

44. In S_N2 reactions, inversion of configuration occurs. Since the reactant and the product are not enantiomers, therefore, the sign of optical rotation may or may not change and hence a single stereoisomer is obtained, *i.e.*, option (*d*) is correct option.

45. One of the steps is endothermic in both the cases.

49. As the number of halogen atoms increases, dipole moment decreases.

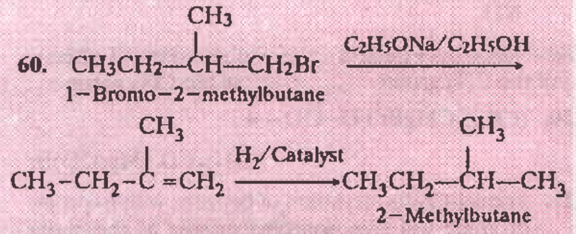
52. Due to much larger C—Cl bond length than C—F bond length, dipole moment of CH_3Cl is higher than that of CH_3F.

53. Smaller the size of the nucleophile (*i.e.* CH_3O^-) more reactive it is.

58. $RCOOAg + R'X \longrightarrow RCOOR' + AgX$

59. Benzyl chloride is more reactive than alkyl halides.

60.



$$\underset{1-Bromo-2-methylbutane}{CH_3CH_2-\overset{\overset{CH_3}{|}}{C}H-CH_2Br} \xrightarrow{C_2H_5ONa/C_2H_5OH}$$

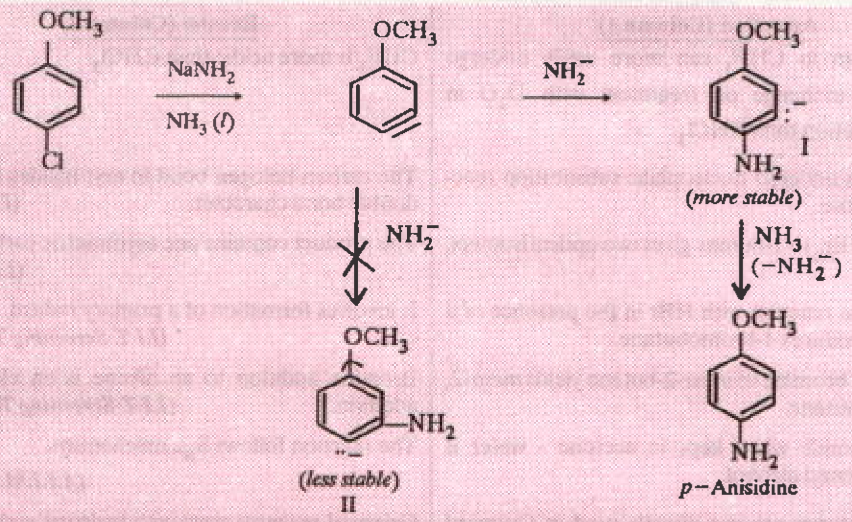
$$CH_3-CH_2-\overset{\overset{CH_3}{|}}{C}=CH_2 \xrightarrow{H_2/Catalyst} \underset{2-Methylbutane}{CH_3CH_2-\overset{\overset{CH_3}{|}}{C}H-CH_3}$$

62. NaCl is not a Lewis acid.

63. NBS reacts fastest with allylic/benzylic hydrogens, *i.e.*, toluene which contains benzylic hydrogens.

$$\underset{Toluene}{C_6H_5CH_3} \xrightarrow{NBS,\ h\nu\ or\ \Delta} \underset{Benzyl\ bromide}{C_6H_5CH_2Br} + HBr$$

64.



Since carbocation (II) is destabilized and carbanion (I) is stabilized by –I effect of the OCH_3 group, therefore, *p*-anisidine and (not *m*-anisidine) is formed.

ADDITIONAL QUESTIONS

For All Competitive Examinations

Assertion-Reason Type Questions

The questions given below consist of an "Assertion" in column 1 and the "Reason" in column 2. Use the following key to choose the appropriate answer.

(*a*) If both assertion and reason are CORRECT, and reason is the CORRECT explanation of the assertion.

(*b*) If both assertion and reason are CORRECT, but reason is NOT the CORRECT explanation of the assertion.

(*c*) If assertion is CORRECT, but reason is INCORRECT.

(*d*) If assertion is INCORRECT, but reason is CORRECT.

(*e*) If both assertion and reason are FALSE.

	Assertion (Column 1)	**Reason (Column 2)**
1.	*p*-Dichlorobenzene is less soluble in organic solvents than the corresponding *o*-isomer.	*o*-Dichlorobenzene is polar while *p*-dichlorobenzene is *non*-polar.
2.	2, 3, 4-Trichloropentane can exhibit optical isomerism	2, 3, 4-Trichloropentane has two chiral one pseudo-chiral carbon atom.
3.	*tert*-Butyl chloride on treatment with sodium metal in dry ether gives 2, 2, 3, 3-tetramethyl butane.	*tert*-Alkyl halides readily undergo Wurtz reaction.
4.	Alkyl halides are not soluble in water.	Although polar in nature yet alkyl halides are not able to form H-bonds with water molecules.
5.	Chlorobenzene is less reactive than chloroethane towards nucleophilic substitution reactions.	The reason for low reactivity of aryl halides over alkyl halides is their low polar character.
6.	In comparison to ethyl chloride, it is difficult to carry out nucleophilic substitution on vinyl chloride.	Vinyl group is electron-donating
7.	Methylmagnesium iodide should be prepared under perfectly anhydrous conditions.	Grignard reagents readily react with water.

	Assertion (Column 1)	Reason (Column 2)
8.	The H-atom in CHF_3 can more easily undergo deuterium exchange on treatment with D_2O in alkaline solution than $CHCl_3$.	CHF_3 is more acidic than $CHCl_3$.
9.	Aryl halides undergo nucleophilic substitution reactions with ease.	The carbon-halogen bond in aryl halides has partial double bond character. *(I.I.T. 1991)*
10.	Addition of Br_2 to 1-butene gives two optical isomers.	The product contains one asymmetric carbon. *(I.I.T. 1998)*
11.	1-Butene on reaction with HBr in the presence of a peroxide produces 1-bromobutane.	It involves formation of a primary radical. *(I.I.T. Screening Test 2000)*
12.	Addition of bromine to *trans*-2-butene yields *meso*-2, 3-dibromobutane.	Bromine addition to an alkene is an electrophilic addition. *(I.I.T. Screening Test 2001)*
13.	Benzyl bromide when kept in acetone - water it produces benzyl alcohol.	The reaction follows S_N2 mechanism. *(A.I.I.M.S. 2003)*
14.	Hydroxy ketones are not directly used in Grignard reaction.	Grignard reagents react with hydroxyl group. *(A.I.I.M.S. 2003)*
15.	2-Bromobutane on reaction with sodium ethoxide in ethanol gives 1-butene as a major product.	1-Butene is more stable than 2-butene. *(A.I.I.M.S. 2004)*

True/False Statements

1. Chlorobenzene and benzyl chloride can be distinguished by boiling with aqueous KOH followed by acidification with dil. HNO_3 and subsequent treatment with $AgNO_3$ solution.

2, 4, 6-Trinitrochlorobenzene can be obtained by treatment of picric acid with PCl_5.

3. 2, 4-Dinitrochlorobenzene is less reactive than chlorobenzene towards nucleophilic substitution reactions.
4. The correct chemical name of DDT is *p*, *p*′-dichlorodiphenyltrichloroethane.
5. Carbon tetrachloride burns in air when lighted to give phosgene. *(I.I.T. 1983)*
6. Carbon tetrachloride is inflammable. *(I.I.T. 1985)*
7. *m*-Chlorobromobenzene is an isomer of *m*-bromochlorobenzene. *(I.I.T. 1985)*
8. Iodide ion is a better nucleophile than bromide ion. *(I.I.T. 1985)*
9. The reaction of vinyl chloride with hydrogen iodide to give 1- chloro-1-iodoethane is an example of anti-Markownikov's rule. *(I.I.T. 1989)*
10. 2, 3, 4-Trichloropentane has three asymmetric carbon atoms. *(I.I.T. 1990)*
11. The formation of CH_3Cl by the gas phase ultraviolet irradiation of a mixture of CH_4 and Cl_2 involves free radical intermediate. *(M.L.N.R. 1991)*
12. The dipole moment of CH_3F is greater than CH_3Cl. *(I.I.T. 1993)*
13. Photobromination of 2-methylpropane gives a mixture of 1-bromo-2- methylpropane and 2-bromo-2-methylpropane in the ratio 9 : 1. *(I.I.T. 1993)*

Fill In The Blanks

1. The boiling point of an alkyl halide is higher than that of the corresponding alkane because of ....
2. Alkyl halides are insoluble in water because they do not form .... with water.
3. Small quantity of .... is added to chloroform to avoid oxidation of chloroform into phosgene.
4. Phenyl isocyanide is formed when chloroform is treated with .... in presence of alcoholic potash.
5. Formation of phenol from chlorobenzene is an example of .... aromatic substitution. *(I.I.T. 1989)*
6. Benzenediazonium chloride is formed when .... is treated with aqueous sodium nitrite and hydrochloric acid.
7. The well known refrigerant freon has the structure, ... *(M.L.N.R. Allahabad, 1994)*

8. Preparation of chlorobenzene from benzene diazonium chloride and aq. HCl is known as......... reaction. *(G.A.T.E. 1994)*

9. Carbon tetrachloride is used as a fire extinguisher since it is a .... liquid.

10. .... is used to eradicate malaria.

11. When phenol is heated with chloroform in presence of ethanolic KOH at 340 K .... is formed as the major product.

12. 1, 3-Butadiene with bromine in molar ratio generates predominantly.................. *(I.I.T. 1997)*

13. Vinyl chloride on reaction with dimethyl copper gives........... *(I.I.T. 1997)*

14. Total number of isomers of 3, 4-dichlorohexane is 3. *(Roorkee 2001)*

15. Addition of HI to 3, 3-dimethyl-1-butene not only gives 1- iodo-3, 3-dimethylbutane, but also 2-iodo-2, 3- dimethylbutane. *(Roorkee 2001)*

Matching Type Questions

Match the entries in column A with those in column B.

	A	**B**
1.	Iodoform	(*a*) Copolymer of vinyl chloride and vinylidene dichloride
2.	Saran	(*b*) Used for refrigeration
3.	DDT	(*c*) Insecticide
4.	Grignard reagent	(*d*) RMgX
5.	Freon	(*e*) Antiseptic

ANSWERS

ASSERTION-TYPE QUESTIONS

1. (*b*) **2.** (*c*) **3.** (*e*) **4.** (*a*) **5.** (*a*) **6.** (*c*) **7.** (*a*) **8.** (*e*) **9.** (*d*) **10.** (*a*) **11.** (*c*) **12.** (*b*) **13.** (*c*) **14.** (*a*). **15.** (*e*)

TRUE/FALSE STATEMENTS

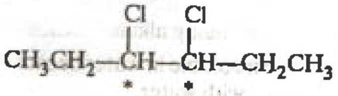
1. True **2.** True **3.** False, more reactive **4.** False, 2, 2-bis(4-chlorophenyl)-1, 1, 1-trichloroethane **5.** False, non-inflammable **6.** False, is non-inflammable **7.** False, same compound **8.** True **9.** True **10.** False, only two since the third (or middle) carbon atom is symmetrically substituted. **11.** True **12.** False, dipole moment of CH_3F is lower than that of CH_3Cl because of the much smaller C—F (1.38 Å) bond length than C—Cl (1.77 A) bond length. **13.** False, approx. 0.6% : 99.4%. This is due to the reason that the relative rates of abstraction of 1°, 2° and 3° H-atoms by bromine radicals is 1 : 82 : 1600. Since there are *nine* 1°-H atoms and only *one* 3°-H atom, therefore, the ratio of the products formed, *i.e.*, 1-bromo-2-methylpropane to 2-bromo-2- methylpropane should be approx. 9 × 1 : 1600 × 1 or approx. 0.6% : 99.4%.

FILL IN THE BLANKS

1. dipole-dipole interactions. **2.** hydrogen bonds. **3.** ethyl alcohol. **4.** aniline. **5.** nucleophilic. **6.** aniline **7.** CCl_2F_2 **8.** Gattermann **9.** non-inflammable. **10.** DDT. **11.** 2-hydroxybenzaldehyde (salicylaldehyde). **12.** 1, 4-dibromobut-2-ene is obtained by 1, 4-addition of Br_2 to 1,3-butadiene. **13.** $CH_3CH = CH_2$ (propene). The reaction is

$$CH_2 = CHCl + (CH_3)_2Cu \longrightarrow CH_2 = CHCH_3 + CH_3CuBr$$

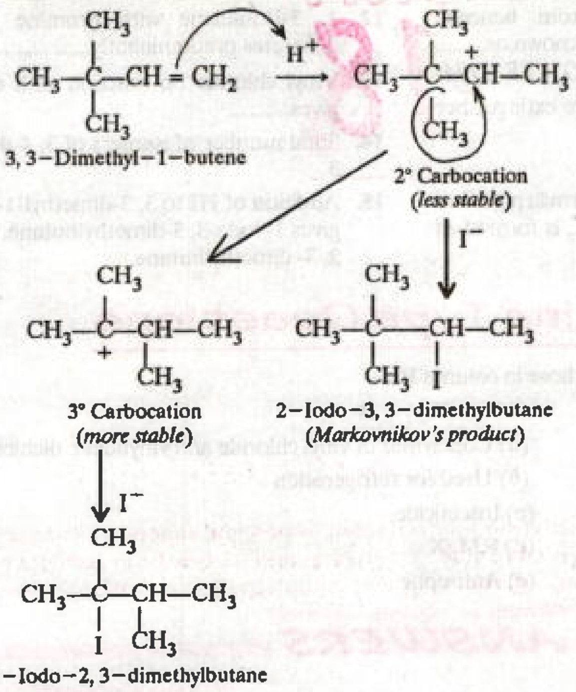
14. False, 3, 4-dichlorohexane has two similar chiral carbon atoms,



$$CH_3CH_2-\overset{Cl}{\overset{|}{\underset{*}{C}H}}-\overset{Cl}{\overset{|}{\underset{*}{C}H}}-CH_2CH_3$$

therefore, like tartaric acid, it has three stereoisomers, *i.e.* (+), (—) and meso and two optical isomers, *i.e.* (+) and (—)-3, 4-dichlorohexane.

15. False, addition of HI to 3, 3-dimethyl-1-butene not only gives 2-iodo-3, 3-dimethylbutane (*Markovnikov's product*) but also the rearranged product, *i.e.*, 2-iodo-2, 3- dimethylbutane as show below :



MATCHING TYPE QUESTIONS

1. (*e*) **2.** (*a*) **3.** (*c*) **4.** (*d*) **5.** (*b*).

HINTS/EXPLANATIONS to Assertion-Reason Type Questions

2. $\overset{1}{C}H_3-\underset{*}{\overset{2}{C}}HCl-\underset{*}{\overset{3}{C}}HCl-\underset{*}{\overset{4}{C}}HCl-\overset{5}{C}H_3$

Carbon atoms 2 and 4 are chiral carbon atoms but the central carbon atom is attached to not only two different atoms (H and Cl) but also to two similar chiral carbon atoms (2 and 4). Such a carbon atom is called **pseudo chiral carbon** atom. For the purpose of calculating the total number of stereoisomers, optical isomers and mesoforms, pseudochiral carbon atoms are also considered as chiral carbon atoms. thus 2, 3, 4-trichloropentane has three chiral carbon atoms.

12. Although addition of Br_2 to an alkene is an electrophilic addition reaction yet it is due to *trans*-addition of Br_2 to *trans*-2-butene that gives *meso*-2, 3-dibromobutane.

13. *Correct reason :* Benzyl halides undergo hydrolysis by S_N1 mechanism.