Unit

6

Haloalkane and Haloarene Compounds

6.1 Introduction

Amongst the elements included in the periodic table, maximum number of compounds are of carbon. If tetravalency of carbon element is satisfied by hydrogen then the compounds formed are called hyrdocarbons. If the hydrogen in the compounds of hydrocarbons is substituted by one or more halogen functional group (X = F, Cl, Br, I), then the compounds obtained are called halogen containing organic compounds. These compounds are also called organic halides.

By substitution of hydrogen atom in hydrocarbons of alkane series (methane, ethane, propane) by halogen atom, the compounds obtained are called **haloalkanes (alkyl halides);** while substitution of hydrogen atom by halogen atoms in the hydrocarbons of arene series are called **haloarenes (aryl halide).** In haloalkane and haloarene compounds covalent bond (C–X) is formed between carbon and halogen. These compounds are not available in free form in nature, but are chemically synthesised. These compounds are useful for introducing alkyl or aryl group in other organic compounds. These compounds have unique importance as initial reactant or as initial raw material to obtain organic compounds in the form of product. In addition, haloalkane and haloarene compounds are good solvents. These compounds are useful in obtaining immunity against diseases in human body, physical growth and as enzyme secretion in biochemical reactions in hormone (iodine in thyroxine), substance used as anesthesia in surgery of the body (chloroform), in drugs for the remedy of diseases like typhoid, malaria. Haloalkane and haloarene compounds are very important in everyday life and in industries. We will study about preparation, physical and chemical properties and uses of haloalkane and haloarene compounds. In addition, we will have information about the effect of polyhalogen compounds on enviornment.

6.2 Classification

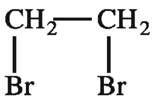
The classification of haloalkanes and haloarenes is carried out as follows :

(1) Classification on the basis of number of halogen atoms : On the basis of the number of same halogen element one, two, three or four or more combined with alkyl or aryl group, they are classified respectively as mono, di, tri, tetra or polyhalogen form. e.g., For haloalkane,

(i) R–X mono haloalkane → As only one halogen atom is present.

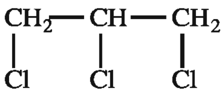
e.g., CH_3CH_2Cl monochloroethane → as only one chlorine atom is present.

(ii) $R{-}X_2$ Dihaloalkane → As there are two halogen atoms.

e.g., 

$\underset{Br}{CH_2}-\underset{Br}{CH_2}$ 1,2-dibromo ethane → as there are two bromine atoms.

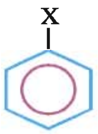
(iii) $R{-}X_3$ Trihaloalkane → As there are three halogen atoms.

e.g., 

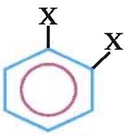
$\underset{Cl}{CH_2}-\underset{Cl}{CH}-\underset{Cl}{CH_2}$ 1, 2, 3-trichloropropane → As there are three chlorine atoms.

In aromatic compounds, the classification can be carried out as follows on the basis of halogen atoms.

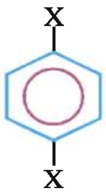
For haloarenes,



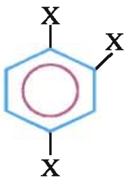
Monohalobenzene



or

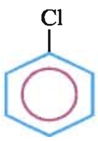


Dihalobenzene

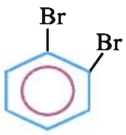


Trihalobenzene

e.g.,

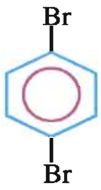


Chlorobenzene

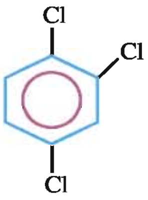


1,2-Dibromobenzene
(o-Dibromobenzene)

or



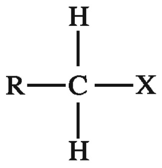
1,4-Dibromobenzene
(p-Dibromobenzene)



1,2,4-Trichlorobenzene

(2) Halogen attached to carbon possessing sp^3 hybridisation, in halogen containing organic compounds : In halogen containing organic compounds, halogen (X = F, Cl, Br, I) containing carbon is possessing sp^3 hybridisation, the compounds can be classified in three types as follows :

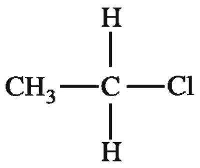
(a) Haloalkane or Alkyl halide : Halogen containing carbon which is sp^3 hybridised when attached to only one other carbon atom it is called **primary (1^0) alkyl halides.**



$$R-\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-X$$

Primary (1^0) haloalkane

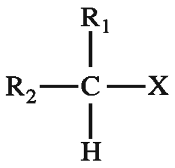
(Primary alkyl halide)



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

Primary (1^0) chloroethane.

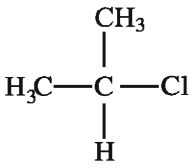
Halogen containing carbon atom which is sp^3 hybridised when combine with other two carbon atoms, it is called **secondary (2^0) alkyl halide.**



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

Secondary (2^0) haloalkane

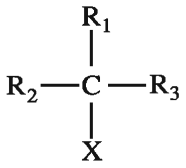
(Secondary alkyl halide)



$$H_3C-\overset{\displaystyle CH_3}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-Cl$$

Secondary (2^0) 2-chloro propane

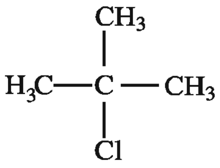
Halogen atom having carbon which is sp^3 hybridised when combine with other three carbon atoms, it is called **tertiary (3^0) alkyl halide.**



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

Tertiary (3^0) haloalkane

(Tertiary alkyl halide)



$$H_3C-\overset{\displaystyle CH_3}{\underset{\displaystyle Cl}{\overset{|}{\underset{|}{C}}}}-CH_3$$

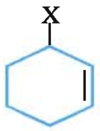
2-chloro-2-methyl propane

(Tertiary butyl chloride)

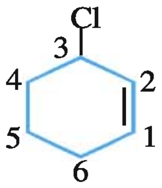
(b) Allylic halides : Halogen containing carbon atom which is sp^3 hybridised when combine with other carbon having double bond (–C=C–) then such compounds are called allylic halides.

e.g. (1) $CH_2=CH-CH_2-X$ Allylic halide (3-haloprop-1-ene)

(2) $CH_3-CH=CH-CH_2-Cl$ 1-Chlorobut-2-ene

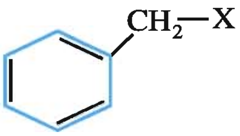


3-Halocyclohex-1-ene

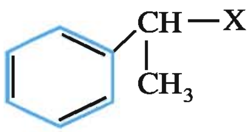


3-Chlorocyclohex-1-ene

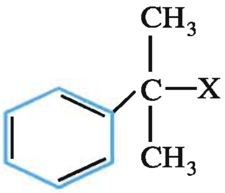
(c) Benzylic halide : Halogen containing carbon which is sp^3 hybridised when combine with carbon of benzene ring, then the compounds are called benzylic halides.



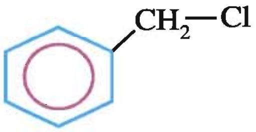
(1^0)



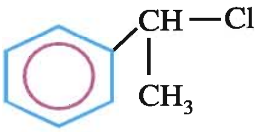
(2^0)



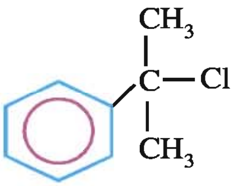
(3^0)



Benzyl chloride



(1-Chloroethyl)benzene

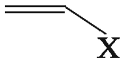


(1-Chloro-1-methylethyl)benzene

(3) Halogen attached to carbon possessing sp^2 hybridisation in halogen containing organic compounds : In halide compounds, carbon atom containing halogen (X = F, Cl, Br, I) possesses sp^2 hybridisation then the compounds can be classified in two types as follows :

(a) Vinyl halide : In this type of halide compounds halogen atom is combined with carbon atoms having (–C=C–) double bond carbon atom possessing sp^2 hybridisation.

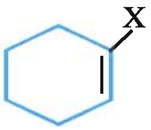
(1) $CH_2{=}CH{-}X$ **or**



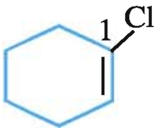
e. g. $CH_2{=}CH{-}Cl$

1-Chloro ethene (Vinyl chloride)

(2)

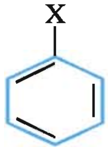


e.g.,

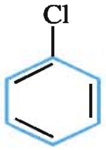


1-Chlorocyclo hex-1-ene

(b) Aryl halide : In this type of halide compounds halogen atoms are combined with sp^2 hybridised carbon atom of aromatic ring.



Halobenzene

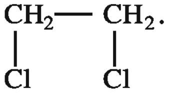


Chlorobenzene

6.3 Common and IUPAC Nomenclature of Haloalkane and Haloarene Compounds

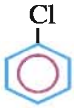
For IUPAC nomenclature of haloalkane and haloarene compounds, the longest carbon chain is decided to which halolgen atom is attached and the prefix halo is attached to the name of hydrocarbon. viz. for fluorine, chlorine, bromine, iodine; fluoro, chloro, bromo, iodo prefix are used respectively. For haloalkane containing three or more than three carbon atoms the least number showing the position of halogen is shown as prefix viz. 1-chloropropane ($CH_3–CH_2–CH_2–Cl$), 2-chloropropane ($CH_3–CHCl–CH_3$), etc.

If two, three, four or more same halogen atoms are present then the number showing the prefix di, tri, tetra etc. are used respectively viz 1,2-dichloro ethane



$\underset{Cl}{\underset{|}{CH_2}}—\underset{Cl}{\underset{|}{CH_2}}$.

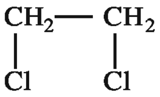
The common name of haloarene is aryl halide. For IUPAC nomenclature of haloarenes, after the corresponding halogen elements, the name of aromatic nucleus is joined after the name of corresponding prefix. e.g. chlorobenzene



For dihalogen derivatives, o, m and p prefix are used in common nomenclature, but in IUPAC nomenclature, 1, 2; 1, 3 and 1, 4 are used. The classification of dihalo compounds containing only one type of halogen atoms, is made as geminal halide and vicinal halide. Geminal halide means both the halogen atoms are on one carbon only and in vicinal halide both the halogen atoms are combined with adjacent carbon atoms. In common nomenclature method, geminal dihalide is called alkylidine halide and vicinal halide is called alkylene dihalides; while in IUPAC nomenclature method, they are called dihaloalkanes.

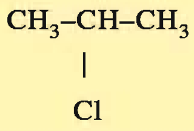
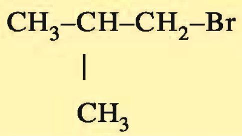
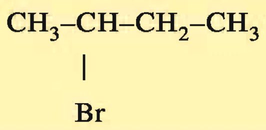
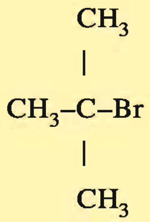
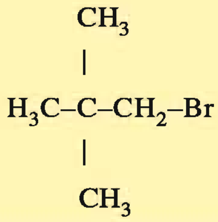
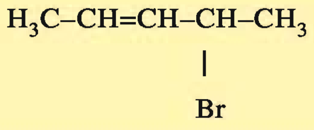
e.g. (1) The common name of $H_3C–CHCl_2$ is ethylidine chloride while IUPAC name is 1,1-dichloro ethane.

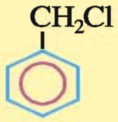
(2)



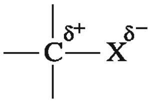
$\underset{Cl}{\underset{|}{CH_2}}—\underset{Cl}{\underset{|}{CH_2}}$ Common name is Ethylene dichloride and IUPAC name is 1, 2-dichloro ethane.

Table 6.1 Common and IUPAC names of Haloalkane and Haloarene compounds

Structural Formula	**IUPAC name**	**Common name**
CH_3Cl	Chloromethane	Methyl chloride
CH_3CH_2Cl	Chloroethane	Ethyl chloride
$CH_3CH_2CH_2Cl$	1-Chloropropane	n-Propyl chloride
 $CH_3-\underset{Cl}{CH}-CH_3$	2-Chloropropane	Iso propyl chloride or secondary(2^0) propylchloride
$CH_3-CH_2-CH_2-CH_2-Br$	1-Bromobutane	n-butyl bromide
 $CH_3-\underset{CH_3}{CH}-CH_2-Br$	1-Bromo 2-methylpropane	Iso butyl bromide
 $CH_3-\underset{Br}{CH}-CH_2-CH_3$	2-Bromobutane	Secondary (2^0) butyl bromide
 $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Br$	2-Bromo-2-methylpropane	Tert-butyl bromide
 $H_3C-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-Br$	1-Bromo-2, 2-dimethyl propane	Neopentyl bromide
$H_2C=CH-Cl$	Chloroethene	Vinyl chloride
 $H_3C-CH=CH-\underset{Br}{CH}-CH_3$	4-Bromopent-2-ene	–
$H_2C=CH-CH_2-Br$	3-Bromopropene	Allyl bromide

	Chlorobenzene	Phenyl chloride
	(Chloromethyl)benzene	Benzyl chloride

6.4 Nature of C–X Bond

As the electronegativity of halogen atom is more than that of carbon atom, the bond between carbon and halogen (C–X) becomes polar.  $-\overset{|}{\underset{|}{\overset{\delta+}{C}}}-\overset{\delta-}{X}$ as the electron pair of covalent bond is more attracted towards halogen nucleus having more electronegativity, partial negative electric charge (δ–) on halogen atom and partial positive electric charge (δ+) on the carbon atom is created.

The atomic sizes of halogens F, Cl, Br, and I present in haloalkane increases respectively, so the bond length of C–X increases successively and the bond enthalpy decreases successively.

$CH_3–F > CH_3–Cl > CH_3–Br > CH_3–I$

The changes in the values of bond length, bond enthalpy and bond polarity as we move from C–F to C–I are given in table 6.2.

Table 6.2 Values of bond length, bond enthalpy and bond polarity of some alkyl halide compounds

Bond	Bond length (pm)	Bond enthalpy ($kJ\ mol^{-1}$)	Polarity of bond (Debye)
$CH_3–F$	139	452	1.847
$CH_3–Cl$	178	351	1.860
$CH_3–Br$	193	293	1.830
$CH_3–I$	214	234	1.636

6.5 Preparation of Haloalkane and Haloarene Compounds

(1) From Alcohol : The method of formation of haloalkane from alcohol is simple. Haloalkane is obtained by substitution of hydroxyl group –OH of alcohol by halolgen. Some reactions of preparation of haloalkane from alcohol are as follows :

(a) Haloalkane is obtained by passing dry hydrogen halide gas from alcohol in presence of anhydrous zinc chloride or by heating alcohol and concentrated hydrogen halide at high temperature.

$$\underset{\text{Alcohol}}{R-OH} + \underset{\text{Hydrogen halide}}{H-X} \xrightarrow[\Delta]{\text{Anhydrous } ZnCl_2} \underset{\text{Haloalkane}}{R-X} + H_2O$$

$$\text{e.g.,}\quad \underset{\text{Ethanol}}{CH_3-CH_2-OH} + \underset{\text{Hydrochloric acid}}{HCl} \xrightarrow[\Delta]{\text{Anhydrous } ZnCl_2} \underset{\text{1 - Chloroethane}}{CH_3-CH_2-Cl} + H_2O$$

By reaction of ethanol with hydrochloric acid in presence of anhydrous zinc chloride at high temperature, molecule of water is liberated and chloroethane is obtained. Haloalkane is obtained by the above method from primary and secondary alcohols but haloalkane is obtained by mixing tertiary alcohol with concentrated HCl in presence of anhydrous $ZnCl_2$ at room temperature. The order of reactivity of alcohol with haloacid is $3^0 > 2^0 > 1^0$. On the basis of this reaction primary, secondary and tertiary alcohol can be identified by a test known as **Lucas test.**

For preparation of aryl halide, this method cannot be used because oxygen of the hydroxyl group in phenol is attached to carbon having double bond of benzene ring. Carbon-oxygen bond possesses partial double bond characteristic, which is very strong so it is difficult to break.

(b) Haloalkane is obtained by reaction of alcohol with sodium halide and concentrated sulphuric acid.

$$\underset{\text{Alcohol}}{R-OH} + \underset{\text{Sodium halide}}{NaX} + H_2SO_4 \longrightarrow \underset{\text{Haloalkane}}{R-X} + \underset{\text{Sodium hydrogen sulphate}}{NaHSO_4} + H_2O$$

e.g., Bromoethane is obtained by reaction of ethanol with sodium bromide and concentrated H_2SO_4.

$$\underset{\text{Ethanol}}{CH_3CH_2OH} + \underset{\text{Sodium bromide}}{NaBr} + H_2SO_4 \longrightarrow \underset{\substack{\text{1-bromoethane} \\ \text{(Ethyl bromide)}}}{CH_3CH_2Br} + NaHSO_4 + H_2O$$

(c) Haloalkane is obtained by reaction of alcohol with halides of phosphorus. By this reaction, high purity and more quantity of haloalkanes are obtained.

$$\underset{\text{Alcohol}}{3R-OH} + \underset{\text{Phosphorus trihalide}}{PX_3} \longrightarrow \underset{\text{Haloalkane}}{3R-X} + \underset{\text{Phosphorus acid}}{H_3PO_3} \quad (\text{where, } X = Cl,\ Br)$$

$$\underset{\text{Alcohol}}{R-OH} + \underset{\substack{\text{Phosphorus} \\ \text{Pentachloride}}}{PCl_5} \longrightarrow \underset{\text{Chloroalkane}}{R-Cl} + \underset{\substack{\text{Phosphorus} \\ \text{oxychloride}}}{POCl_3} + HCl$$

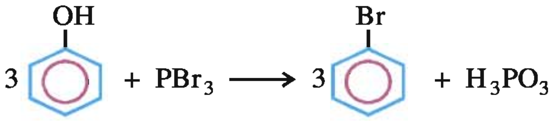
$$\underset{\text{Alcohol}}{R-OH} + \underset{\text{Dihalogen}}{X_2} \xrightarrow{\text{Red P}} \underset{\text{Haloalkane}}{R-X} \quad (\text{where, } X = Br, I)$$

(d) Haloalkane is obtained by reaction of alcohol with thionyl chloride.

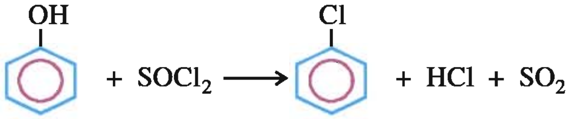
$$\underset{\text{Alcohol}}{R-OH} + \underset{\text{Thionyl chloride}}{SOCl_2} \longrightarrow \underset{\text{Haloalkane}}{R-Cl} + HCl + SO_2$$

$$\underset{\text{Propan-1-ol}}{CH_3-CH_2-CH_2-OH} + SOCl_2 \longrightarrow \underset{\text{1-Chloropropane}}{CH_3-CH_2-CH_2-Cl} + HCl + SO_2$$

(e) To prepare haloarene from phenol; phenol is reacted with reactants like PBr_3 or $SOCl_2$.



Phenol Phosphorus tribromide Bromo benzene Phosphorus acid



Chlorobenzene

The products bromobenzene and chlorobenzene obtained by above two reactions are in very less proportion.

(2) From Hydrocarbon :

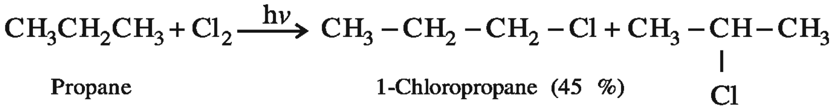
(a) Free radical halogenation : Haloalkane is obtained by substitution reaction of alkane compound with free radical X obtained by homolytic fission of dihalogen. e.g.,

(i) Chloromethane is obtained by doing reaction of methane with dichlorine gas in presence of ultraviolet light.

$$CH_4 + Cl_2 \xrightarrow{h\nu} CH_3Cl + HCl$$

Methane Chloromethane

(ii) Mixture of isomers of chloropropane is obtained by halogenation reaction of propane with dichlorine gas in presence of ultraviolet light.

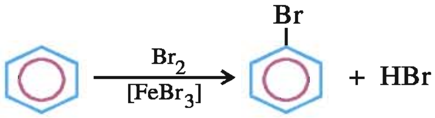


$$CH_3CH_2CH_3 + Cl_2 \xrightarrow{h\nu} CH_3-CH_2-CH_2-Cl + CH_3-\underset{\underset{Cl}{|}}{CH}-CH_3$$

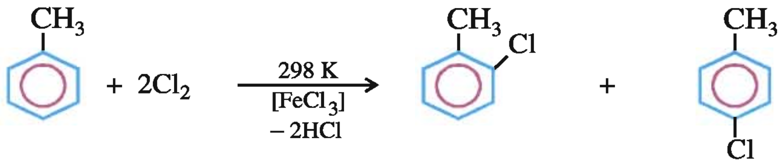
Propane 1-Chloropropane (45 %) 2-Chloropropane (55 %)

(b) By electrophilic substitution : In the chlorination or bromination reaction of benzene and toluene, first of all dihalogen gas (Cl_2 or Br_2) react with catalyst Fe or FeX_3 and gives electrophilic ion X^+ (Lewis acid). It is called electrophilic reagent. H^+ attached to carbon having π electron cloud of benzene is removed and X^+ enters in its place so electrophilic substitution reaction takes place.

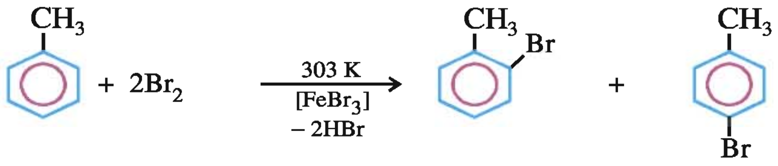
Bromobenzene is obtained by bromination reaction of benzene with Br_2 at 303 to 313 K temperature in presence of $FeBr_3$ catalyst.



Benzene Bromobenzene



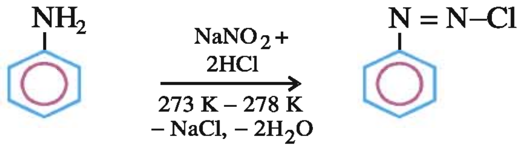
Toluene 1-Chloro-2-methylbenzene (o-Chlorotoluene) 1-Chloro-4-methylbenzene (p-Chlorotoluene)



Toluene 1-Bromo-2-methylbenzene (o-Bromotoluene) 1-Bromo-4-methylbenzene (p-Bromotoluene)

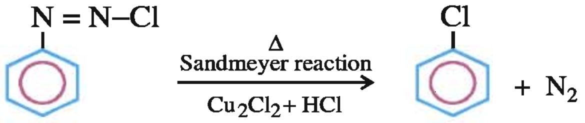
The ortho and para products obtained can be easily separated because of large difference between their boiling points. Since reactivity of difluorine is very high, fluoroarenes are not produced by this reaction.

(c) Sandmeyer reaction : Benzenediazoniumchloride is obtained by dissolving primary amine like aniline at low temperature (273 K to 278 K) in hydrochloric acid in presence of sodium nitrite $(NaNO_2)$.



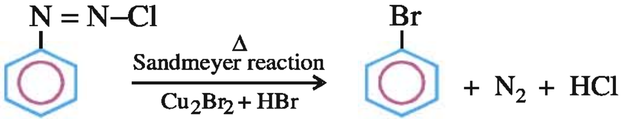
Aniline Benzenediazoniumchloride

Benzene diazonium chloride obtained is an unstable product at room temperature. Hence, chlorobenzene is obtained by heating freshly prepared benzenediazoniumchloride with solution of cuprous chloride prepared in hydrochloric acid. This reaction is called **Sandmeyer reaction.**



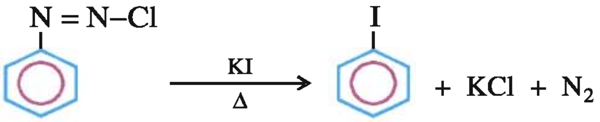
Benzenediazoniumchloride Chlororbenzene

In the solution of freshly prepared benzenediazoniumchloride if cuprous bromide is mixed in place of cuprous chloride, diazonium group is substituted by bromine.



Benzenediazoniumchloride Bromobenzene

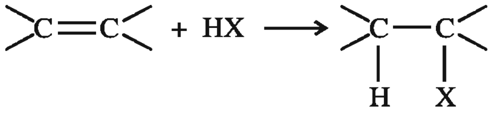
Iodobenzene is obtained by reaction of freshly prepared benzenediazoniumchloride with potassium iodide at higher temperature.



Benzenediazoniumchloride Iodobenzene

(d) From Alkenes :

(i) Addition reaction with hydrogen halide : In the reaction of alkene with hydrogen halide (HX) the π–bond between carbon-carbon atoms breaks and addition reaction takes place such that H is attached to one carbon and X to the other carbon. This reaction is called **hydrohalogenation.**



(Where, X = Cl, Br, I)

Alkene Hydrogen halide Haloalkane

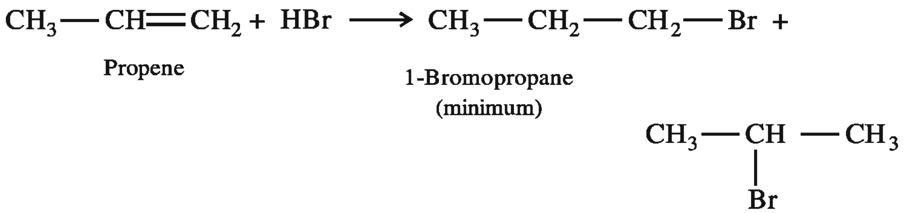
e.g., Chloroethane is obtained by reaction of ethane with hydrochloric acid.

$$CH_2{=}CH_2 + HCl \longrightarrow CH_3{-}CH_2{-}Cl$$

Ethene Hydrochloric acid Chloroethane

Two isomers of bromo propane are obtained by addition reaction of propene with hydrobromic acid.

According to Markonikov's rule, the product 2-bromopropane is obtained in maximum proportion (see Std-11, Semester II, Unit 6 Hydrocarbons)



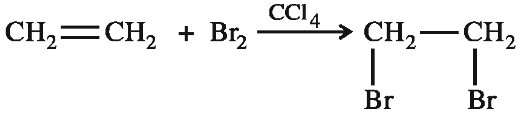
$$CH_3{-}CH{=}CH_2 + HBr \longrightarrow CH_3{-}CH_2{-}CH_2{-}Br + CH_3{-}\underset{\displaystyle Br}{\underset{|}{CH}}{-}CH_3$$

Propene

1-Bromopropane (minimum)

2-Bromopropane (maximum)

(ii) Addition reaction with dihalogen gas : Dihalogen containing alkane is obtained by addition of both the atoms of dihalogen molecule to an alkene and addition reaction occurs by breaking of π bond of ethylenic double bond. This reaction is called **halogenation reaction** e.g. 1,2-dibromoethane is obtained by addition reaction of ethene with solution of bromine prepared in CCl_4.



$$CH_2{=}CH_2 + Br_2 \xrightarrow{CCl_4} \underset{\displaystyle Br}{\underset{|}{CH_2}}{-}\underset{\displaystyle Br}{\underset{|}{CH_2}}$$

Ethene Dibromine 1,2-Dibromoethane

(4) By halogen exchange : Iodoalkane is obtained by the reaction of bromoalkane or chloroalkane with solution of sodium iodide prepared in dry acetone. This reaction is known as **Finkelstein reaction.**

$$\underset{\text{Haloalkane}}{R - X} \quad + \quad \underset{\text{Sodium iodide}}{NaI} \xrightarrow{\text{Acetone}} \underset{\text{Iodoalkane}}{R - I} + NaX \quad (\text{where, } X = Cl, Br)$$

e.g.,

$$\underset{\text{Chloromethane}}{CH_3 - Cl} \quad + \quad \underset{\text{Sodium iodide}}{NaI} \xrightarrow{\text{Acetone}} \underset{\text{Iodomethane}}{CH_3 - I} + NaCl$$

$$\underset{\text{Bromoethane}}{CH_3 - CH_2 - Br} + \underset{\text{Sodium iodide}}{NaI} \xrightarrow{\text{Acetone}} \underset{\text{Iodoethane}}{CH_3 - CH_2 - I} + NaBr$$

By reaction of bromomethane or chloromethane with metallic fluorides like AgF, Hg_2F_2, CoF_2 or SbF_3 fluoromethane is obtained. This reaction is called **Swartz reaction.**

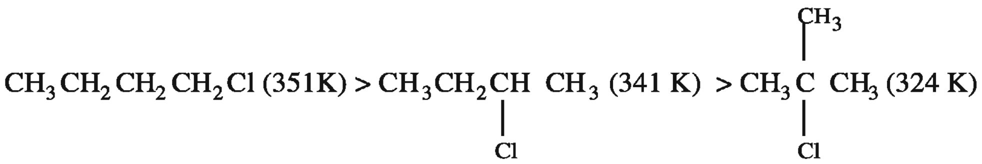
$$\underset{\text{Bromomethane}}{CH_3 - Br} \quad + \quad \underset{\text{Silver fluoride}}{AgF} \longrightarrow \underset{\text{Fluoromethane}}{CH_3 - F} \quad + \quad \underset{\text{Silver bromide}}{AgBr}$$

6.6. Physical Properties

- Pure haloalkane compounds are colourless.
- Bromide and iodide compounds are coloured in presence of light.
- Volatile halide compounds possess sweet smell.
- Halides having one, two or three carbon atoms are in gaseous state at normal temperature while halides having more than three carbon atoms are in liquid or solid state.
- In haloalkane and haloarene compounds $>\overset{\delta+}{C}-\overset{\delta-}{X}$ being polar, inter-moloecular forces (van der Waals) increases. As a result, the boiling points of haloalkanes are higher than their corresponding alkanes.

  e.g. CH_3Cl (249 K) > CH_4 (109 K)
- As the number of carbon atoms increases in monohaloalkanes, there is increase in their boiling points. e.g.,

  CH_3Cl (249 K) < CH_3CH_2Cl (285 K) < $CH_3CH_2CH_2Cl$ (320 K)
- There is decrease in boiling points of isomeric haloalkanes having equal number of carbon atoms and equal halogen atom, as we move from primary (1^0) to secondary (2^0) and secondary (2^0) to tertiary (3^0). e.g.,

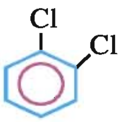


$$CH_3CH_2CH_2CH_2Cl\ (351K) > CH_3CH_2\underset{\displaystyle Cl}{\underset{|}{C}}H\ CH_3\ (341\ K) > CH_3\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle Cl}{\underset{|}{C}}}}\ CH_3\ (324\ K)$$

- The boiling points decrease in the following order as the halogen atoms change in haloalkane containing similar alkyl group.

  $CH_3I > CH_3Br > CH_3Cl > CH_3F$

- The boiling points of haloarene compounds are high because of the presence of strong bond because of short C–X bond length in haloarene compounds than haloalkane compounds.
- In dihaloarene compounds, there is much less difference in the boiling points of (1,2) ortho, (1,3) meta and (1,4) para isomers.

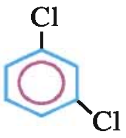


453 K

1,2-Dichloro benzene

448 K

1,4-Dichloro benzene



446 K

1,3-Dichloro benzene

- The densities of polychloroalkane, bromoalkane and iodoalkane are more than density of water and the density increases as the number of carbon atoms or halogen atoms or the atomic mass of halogen atom increases.

Table 6.3 Densities of some Haloalkanes (298 K)

Compound	Density gml^{-1}	Compound	Density gml^{-1}
n–C_3H_7Cl	0.89	CH_2Cl_2	1.336
n–C_3H_7Br	1.335	$CHCl_3$	1.489
n–C_3H_7I	1.747	CCl_4	1.595

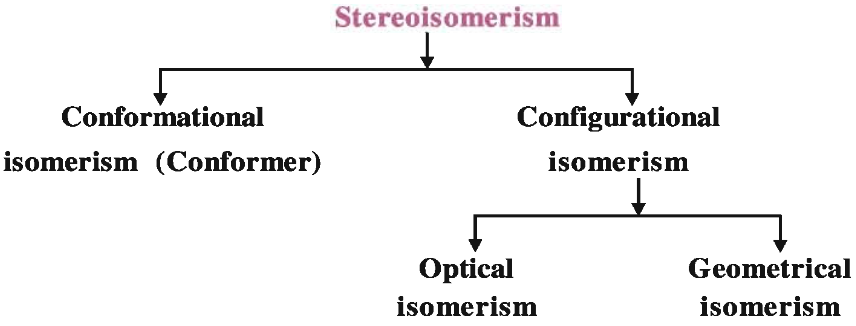
Haloalkane compounds are sparingly soluble in water, while they are soluble in organic solvents like acetone, ethanol.

To understand chemical properties of haloalkanes, some concepts of stereochemistry should be understood.

6.7 D, L (Relative configuration) and R,S (Absolute configuration) Nomenclature

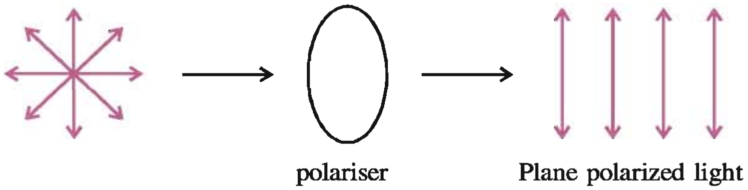
The branch of organic chemistry in which the study of three dimensional structure is carried out is called **stereochemistry.** Isomerism is the basic property in stereochemistry. Mainly two types of isomerism are there : (1) Structural isomerism and (2) Stereoisomerism

You have studied about structural isomerism in standard 11, Semester-I. The classification of stereoisomerism is as follows :



To understand optical isomerism, it is necessary to study the terms like plane polarised light, optical activity, chirality connected with it.

(1) Plane polarised light : There are seven colours in a white light. The light consisting the different wavelengths is vibrating in each possible plane. When such a light is passed through Nichol prism or polaroid, then the electromagnetic vibrations in the emerging light are found to be in the same plane. Such a light is called **polarised light.**



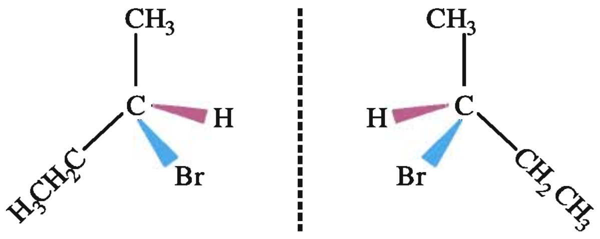
(2) Optical activity : The substance which has the capacity to rotate the plane of polarised light, is called **optically active substance.** Certain optically active substances which rotate the plane of polarised light towards left hand side are called **levo rotatory.** They are expressed by ***l*** **or (–)** symbol. The substances which rotate the plane of polarised light towards right hand side are called **dextro rotatory substance.** They are expressed by **d or (+)** symbol.

(3) Chirality : The main reason for optical activity is molecular asymmetry. There must be minimum one chiral carbon in each optically active compound. The carbon whose all the four valencies are satisfied by four different groups, is called **asymmetric carbon.** The substances whose images can not be superimspoed are called **chiral substances.** This property is called **chirality** e.g., the hand or foot, and English **alphabets like B, C, D, E** etc.

The substances which can be superimposed on their images, are called **achiral substances.** e.g., spoon, and English **alphabets like A, H, I, M** etc.

If one chiral carbon is present in a compound, then the following enantiomers are obtained which cannot be superimposed on one another.

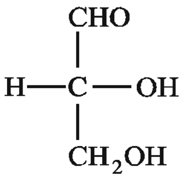
e.g. 2-Bromobutane is a chiral molecule. It gives following two enantiomers which can not be superimposed on each other.



2-bromobutane

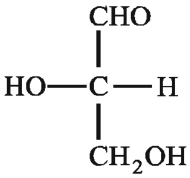
D and L configuration (Relative configuration) :

D and L terms are generally used to explain configuration of carbohydrates and amino acids. In the Fischer structure, if the –OH group is attached to the right hand side of the chiral carbon present at the end of the chain, then **D-configuration** and if attached on the left hand side, it is called **L-configuration.** In amino acids, D and L configurations are determined from the position of $-NH_2$ group e.g.,



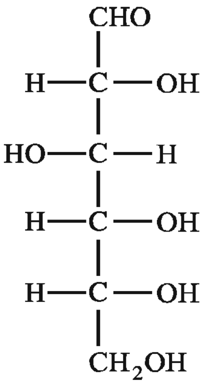
$$\begin{array}{c} \mathrm{CHO} \\ | \\ \mathrm{H-C-OH} \\ | \\ \mathrm{CH_2OH} \end{array}$$

D-Glyceraldehyde



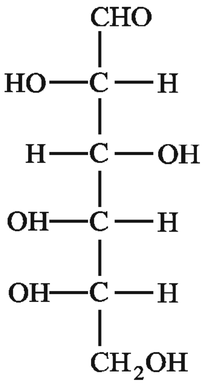
$$\begin{array}{c} \mathrm{CHO} \\ | \\ \mathrm{HO-C-H} \\ | \\ \mathrm{CH_2OH} \end{array}$$

L-Glyceraldehyde



$$\begin{array}{c} \mathrm{CHO} \\ | \\ \mathrm{H-C-OH} \\ | \\ \mathrm{HO-C-H} \\ | \\ \mathrm{H-C-OH} \\ | \\ \mathrm{H-C-OH} \\ | \\ \mathrm{CH_2OH} \end{array}$$

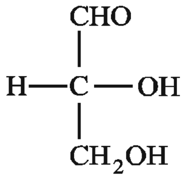
D-Glucose



$$\begin{array}{c} \mathrm{CHO} \\ | \\ \mathrm{HO-C-H} \\ | \\ \mathrm{H-C-OH} \\ | \\ \mathrm{OH-C-H} \\ | \\ \mathrm{OH-C-H} \\ | \\ \mathrm{CH_2OH} \end{array}$$

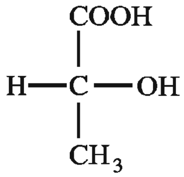
L-Glucose

Here, it is necessary to note that there is no direct relation of D with d and of L with *l*; that is compound having D-configuration can be of d or *l* type. Similarly compound having L-configuration can be of d or *l* type. e.g., D-Glyceraldehyde and D-Lactic acid are found experimentally to be d(+) and *l*(–).



$$\begin{array}{c} \mathrm{CHO} \\ | \\ \mathrm{H-C-OH} \\ | \\ \mathrm{CH_2OH} \end{array}$$

D-(+)-Glyceraldehyde



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

D-(–)-Lactic acid

D- or L-configuration of the compound are determined theoretically; while d or *l* configuration is determined experimentally with the help of polarimeter. D- and L-configurations of one substance are enantiomers.

R–S Nomenclature (Absolute configuration) : For the identifications of chiral compounds having asymmetric carbon R, S nomenclature method is well-known.

This R, S nomenclature method was proposed by Cahn, Ingold and Prelog. In this method the configurations are expressed as **R** (Latin word Rectus = right) and **S** (Latin word Sinister = left).

For this nomenclature, all the four groups attached with asymmetric carbon are given sequence order (1,2,3,4). For this methods two steps are used.

Step-1 : To determine sequence order of group attached with asymmetric carbon :

(1) To determine sequence order, the atomic number of first atom or group attached to an asymmetric carbon is taken into consideration. The atom whose atomic number is the highest will receive first sequence e.g., $-H$, $-NH_2$, $-CH_3$, $-Br$ are attached then sequence order is given as follows.

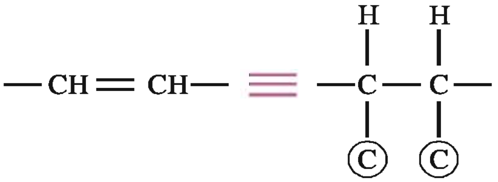
$-Br \rightarrow 1$, $-NH_2 \rightarrow 2$, $-CH_3 \rightarrow 3$, $-H \rightarrow 4$

$(Z = 35)$ $(Z = 7)$ $(Z = 6)$ $(Z = 1)$

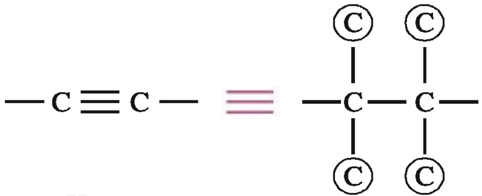
(2) If two isotopes are combined with asymmetric carbon atom, then the sequence number is given to isotope having more atomic mass in comparison to isotope having less atomic mass. e.g., H, Br, C, D (deuterium) atoms are attached with asymmetric carbon atom, then sequence order is given as 1,2,3, and 4 respectively to Br, C, D and H.

(3) If the first atom of two groups attached to asymmetric carbon atom, is same, then the atomic number of the second atom of the group is taken into consideration. e.g. If $-CH_2NH_2$, $-CH_3$, $-CH_2OH$, $-CH_2CH_3$ groups are attached to asymmetric carbon atom, then the sequence number 1,2,3,4 are given to $-CH_2OH$, $-CH_2NH_2$, $-CH_2CH_3$ and $-CH_3$ respectively.

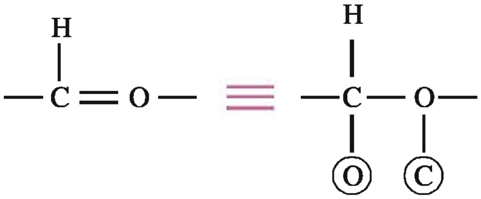
(4) In giving sequence number to groups having double bond or triple bond, imaganary atoms are assumed to be attached to each π bond after breaking them.



$$-CH=CH- \equiv -\overset{H}{\underset{\textcircled{C}}{C}}-\overset{H}{\underset{\textcircled{C}}{C}}-$$



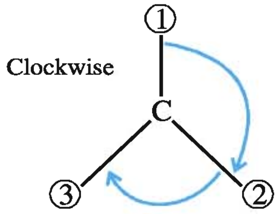
$$-C\equiv C- \equiv -\overset{\textcircled{C}}{\underset{\textcircled{C}}{C}}-\overset{\textcircled{C}}{\underset{\textcircled{C}}{C}}-$$



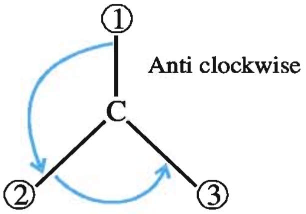
$$-\overset{H}{C}=O- \equiv -\overset{H}{\underset{\textcircled{O}}{C}}-\underset{\textcircled{C}}{O}-$$

On the basis of the above sequence rules, the order of some important groups can be shown as follows : $-I > -Br > -Cl > -SO_3H > -SH > -F > -OCOR > -OR > -OH > -NO_2 > -NR_2 > -NHR > -COOR > -COOH > -COR > -CHO > -CH_2OH > -CN > -CH_3 > -D > -H$

Step-2 To determine R and S configuration : After determination of selection of sequence number according to step 1, in the three dimensional structure, the group having lowest sequence, number i.e. group number 4 is placed away from the observer. Then, the molecule is observed such that, the group having minimum sequence goes on opposite side. Then the increasing order of the remaining three groups (1, 2 and 3) is in clockwise direction (right hand side), then configuration of isomer is considered as R but if this sequence is in anticlockwise direction (left side) then it is considered as S-configuration.

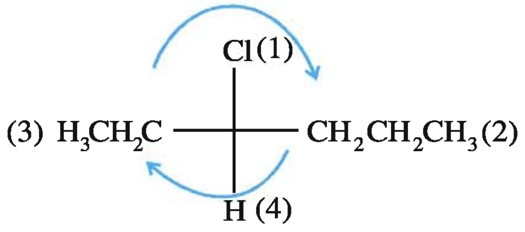


R - configuration

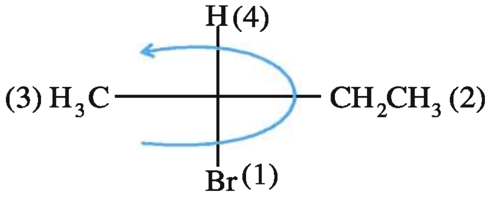


S - configuration

According to the rules discussed above, the three dimensional, structure is to be assumed, which is difficult. Generally, showing chiral compounds in two dimension Fischer structure is more convenient. In the Fischer structure, the group showing lowest sequence number (4) is placed in vertical line and 1→2→3 are in clockwise direction then it is R and if it is anticlockwise direction it is considered as S-configuration.

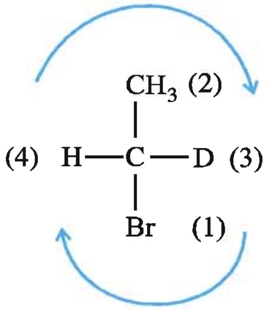


R-Configuration

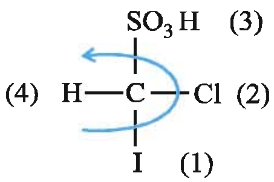


S-Configuration

In Fischer structure if group showing sequence number (4) is in horizontal line, then the configuration of the compound is determined as above is opposite to that configuration. i.e. in such cases if 1 → 2 → 3 is in clockwise direction then S and if in anticlockwise direction then R-configuration is considered. This explanation was given by Epling in 1982. e.g.,



S-Configuration



R-Configuration

6.8. Chemical Properties (Chemical Reactions)

6.8.1 Reactions of haloalkane compounds :

(1) Nucleophilic substitution reactions : As polar bond $C^{\delta+}–X^{\delta-}$ is present in haloalkane compounds, nucleophilic reagents ($:Nu^-$) are attracted by partially positively charged carbon atoms and substitutes halogen. Nucleophilic ions which are Lewis bases are called **nucleophilic reagents.**

The substitution reactions that take place through them are called **nucleophilic substitution reactions.** In short it is called **SN reaction.**

$$:Nu^- + \gt\overset{\delta+}{C}—\overset{\delta-}{X} \longrightarrow \gt C—Nu + :X^-$$

Some of the nucleophilic reagents are as follows :

$:OH^-$, $:OR^-$, $:X^-$, $:CN^-$, $RCOO^-:$, $:SH^-$, $:NH_2^-$, $^-O-\ddot{N}=O$ etc. Which are Lewis bases also.

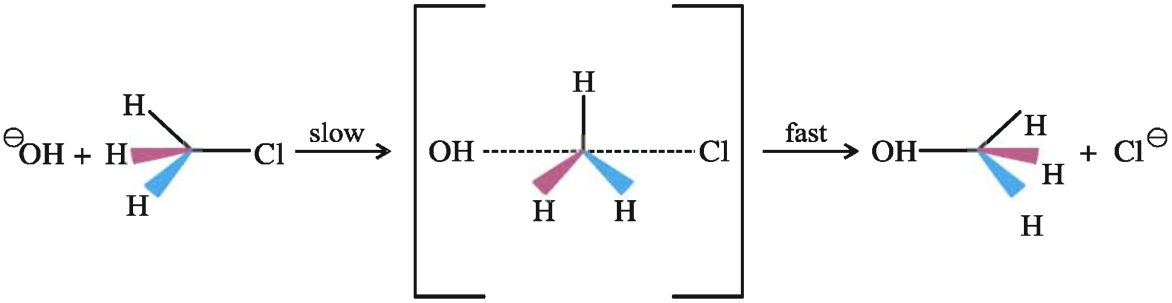
Nucleophilic reagents like cyanide and nitrite possess two nucleophilic centres. The structure of cyanide group is expressed in two ways. Cyanide group reacts as nucleophilic reagent in two different methods, In one of them carbon acts as a nucleophilic reagent. So that $(–C{\equiv}N)$ becomes nucleophilic ion and alkyl cynide product is obtained; while in second structures, nitrogen acts as a nucleophilic reagent; so isocyanide product is obtained by $(:C{=}N^-)$ nucleophilic ion.

In the same way, in the nucleophilic ion nitrite $(O^- - \ddot{N} = O)$ alkyl nitrite product is obtained but when nitrogen atom combines nitroalkane compound is obtained.

The reaction mechanism of nucleophilic substitution is classified in two ways as follows :

(a) Bimolecular Nucleophillic Substitution (SN^2) reaction : The reaction of chloromethane (CH_3Cl) with hydroxide ion $(:OH^-)$ is second order nucleophilic substitution reaction. According to the principle of chemical kinetics, the order of reaction depends on the concentrations of both the reactants and so it is second order reaction.

We will understand by following example.



For Information only

In the above reaction the bond shown by dark shading is outside the plane. Bond shown by light shading is on the rear side of plane. While bond shown by straight line is in the plane of paper.

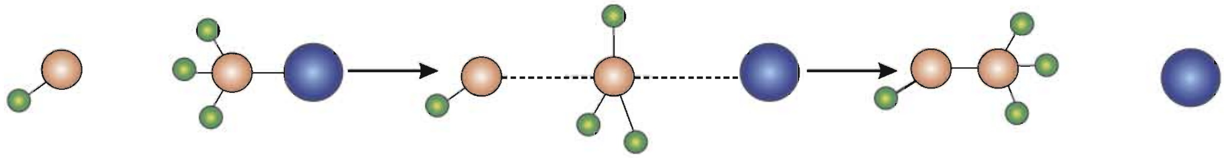


Fig. 6.2

Green dots indicate the entering hydroxyl group.

Blue sphere is the removing halide ion.

In 1937, scientist Edward Davies Hughes and Sir Christopher Ingold proposed the reaction mechanism of SN^2 reaction which can be studied from below :

Bimolecular Nucleophilic substitution reaction is called **SN^2 reaction.**

SN^2 reaction is the bimolecular reaction occurring between substrate (S) and nucleophilic reagent ($:Nu^-$). SN^2 reaction occurs in only one step without formation of intermediate product. In this reaction the substrate (reactant) does not undergo heterolytic fission. Carbon taking part in this reaction possesses sp^3 hybridisation; but at transition state it possesses sp^2 hybridisation. In transition state, the bonds are partially formed and broken. During the first step in the presence of realeased group Cl^-, nucleophilic reagent OH^- reacts with substrate and transition state is obtained. Thus, in transition state, both reagent and substrate combine.

At the transition state, the bond with Cl^- becomes weak and the formation of bond of nucleophilic OH^- starts. At this time, all the three hydrogen atoms with carbon are arranged in one plane only. As both the nucleophile OH^- and the group that is released, being negative, the nucleophile always combines in the direction totally opposite to the releasing group. The spatial arrangement of the obtained product is totally in opposite direction of the spatial arrangement of reactant. This means that, inverted product from substrate as a result of SN^2 reaction, is observed which is shown in fig 6.2.

The rate of SN^2 reaction depends on concentrations of both substrate and nucleophilic reagent.

Rate of reaction = $K\ [S]^1\ [Nu^-]^1$ where S = substrate

Nu^- = Nucleophilic reagent.

Hence, SN^2 reaction is a second order reaction. Thus, in rate determining step, when nucleophile reacts on carbon having less electron density, the rate controlling is done by both reacting agent and reagent in transition state; such substitution reactions are called bimolecular nucleophilic substitution (SN^2) reaction..

(b) Unimolecular Nucleophilic Substitution (SN^1) Reaction : SN^1 (unimolecular nucleophilic substitution) reaction takes place in two steps. In SN^1 reaction, firstly heterolytic fission of substrate takes place and carbocation (carbonium ion) is formed. The energy required to break C–X bond in the formation of carbocation is obtained from polar solvents like water, alcohol, acetic acid. In second step, nucleophile is attached to carbocation.

Tertiary butyl alcohol is obtained as product by reaction of tertiary butyl bromide with hydroxide ion.

This reaction is first order reaction from chemical kinetics point of view.

$$\underset{\text{Tertiarybutyl bromide}}{(CH_3)_3C-Br} + OH^- \longrightarrow \underset{\text{Tertiarybutylalcohol}}{(CH_3)_3-C-OH} + Br^-$$

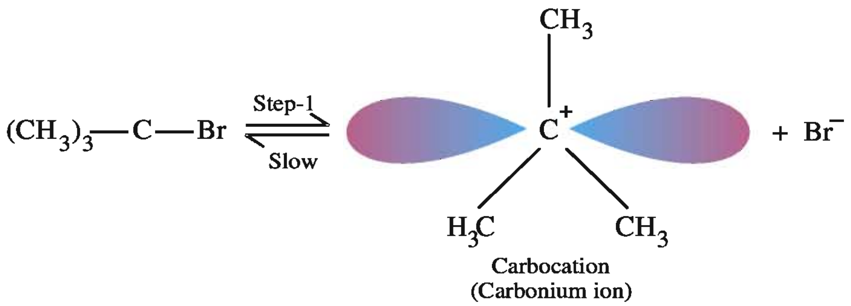
The order of this reaction depends only on the concentration of substrate and so it is a first order reaction.

$\therefore$ Rate of reaction α $[(CH_3)_3C{-}Br]$

$= K\ [C(CH_3)_3C{-}Br]$

The reaction mechanism of this reaction is in two steps as shown below :

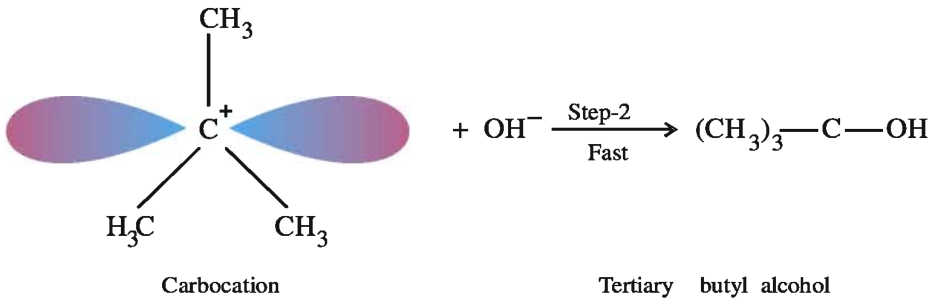
Step-1 :

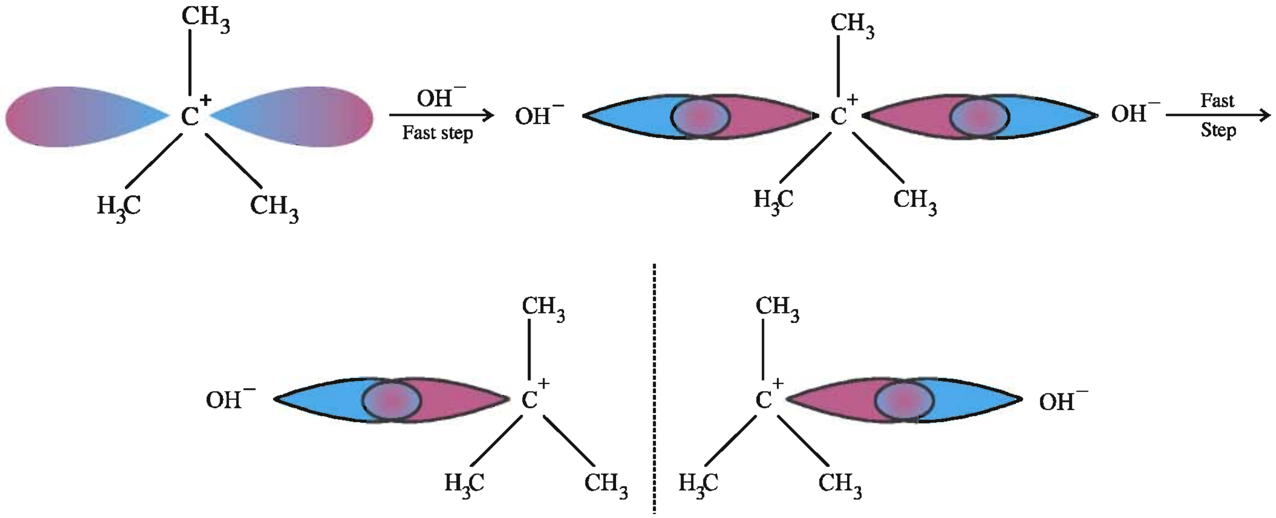


The polar C–Br bond breaks slowly and carbocation and bromide ion are formed. As this step is slow, it is rate determining step.

Step-2 :

Nucleophilic reagent completes the substitution reaction by attacking the carbocation.





Mirror image

As shown above, the nucleophilic reagent (OH^-) can attack carbocation from both the sides, they will be mirror image of eachother. In the above example substrate tertiary butylbromide is not optically active, hence the obtained product is optically inactive. If haloalkane substrate is optically active (e.g., secondarybutyl bromide) then product obtained will be optically active. As nucleophilic reagent OH^- can attack carbocation from both the sides, equal proportion of dextro and levorotatory optically active isomer which forms a **racemic mixture.**

In this second step of reaction carbocation readily combines with nucleophilic reagent (OH^-) and gives the product. Hence, the rate of reaction of SN^1 reaction does not depend at all on the concentration of nucleophilic reagent but it depends on the concentration of substrate.

Rate of reaction = $K[S]^1$ where S = substrate. Thus, SN^1 reaction is a first order reaction.

The rate of SN^1 reaction depends on concentration of substrate, easy formation of carbocation and stability of carbocation. In SN^1 reaction weak nucleophilic reagent also reacts easily. As the stability of carbocation is more, the rate of SN^1 reaction will be fast. As stable carbocation is formed on tertiary carbon SN^1 reaction becomes easy; while SN^2 reaction is difficult.

The order of case of SN^1 and SN^2 reactions in alkyl halides is as follows :

SN^2 reactions

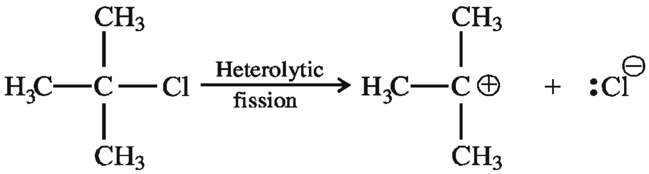
$\longrightarrow$

Tertiary halide, Secondary halide, Primary halide, CH_3X

$\longleftarrow$

SN^1 reactions

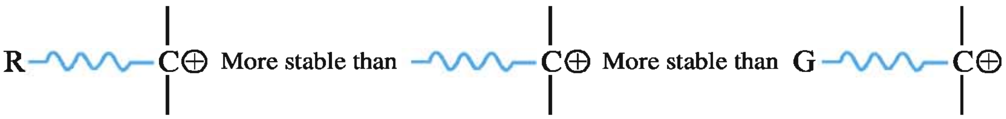
Stability of carbocation : 3^0-butyl carbocation is obtained as intermediate by heterolytic fission of C–Cl bond during nucleophilic substitution of 3^0-butylchloride as follows :



$$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-Cl \xrightarrow[\text{fission}]{\text{Heterolytic}} H_3C-\overset{CH_3}{\underset{CH_3}{C}}\oplus + :Cl^{\ominus}$$

3^0 butyl chloride $\qquad$ 3^0 butyl carbocation

The stability of carbocation increases because of distribution of positive charge on carbon, any factor which tends to distribute the positive charge of carbon having deficiency of electron and the positive charge is equally distributed on the remaining part of ion must increase the stability of carbocation. Hence, if electron donating group is attached with carbocation, the stability increases. As contrast to this if electron attracting group combines with carbo cation, the stability decreases.

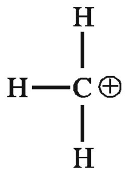


R = electron donating group

G = electron accepting group

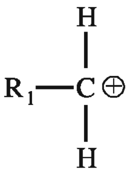
The alkyl group attached with carbon atom having positive charge possesses electron releasing inductive effect (I). Hence, the carbon to which alkyl group is attached the effect of positive charge of carbon will be less. Hence, alkyl group will be partially positively charged. The stability of carbocation will increase because of distribution of this positive charge.

e.g.,



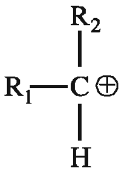
$H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}\oplus$

Methylcation



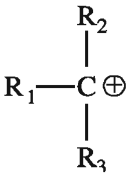
$R_1-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}\oplus$

1^0 (primary) carbocation



$R_1-\overset{\displaystyle R_2}{\underset{\displaystyle H}{C}}\oplus$

2^0 (Secondary carbocation)



$R_1-\overset{\displaystyle R_2}{\underset{\displaystyle R_3}{C}}\oplus$

3^0 (Tertiary carbocation)

Tertiary carbocation possesses maximum stability because three alkyl groups are attached to it; while two alkyl groups are attached with secondary carbocation. It possesses more stability than primary carbocation. The stability of the carbocation with which no alkyl group is attached has minimum stability.

Thus, the order of stability of carbocation can be shown as below :

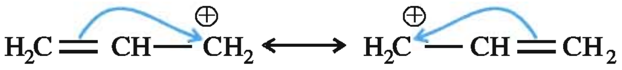
$3^0\ C^{\oplus} > 2^0\ C^{\oplus} > 1^0\ C^{\oplus} > C^{\oplus}H_3$ or

Tertiary $C^{\oplus}$ > Secondary $C^{\oplus}$ > Primary $C^{\oplus}$ > $C^{\oplus}H_3$. The rate of reaction depends on the stability of the carbocation obtained.

The stability of carbocation decreases if electron attracting atom or group is attached with carbocation having electron deficiency.

Resonance is also an important factor in deciding the stability of carbocation. The resonance structure can be drawn if electron pair deficient carbon is attached with unsaturated system in which positive charge is delocalized on the whole molecules.

The carbocation having possibility of resonance structure, is more than the carbocation having simple alkyl group; which can be made clear by the following example.



$$H_2C=CH-\overset{\oplus}{C}H_2 \longleftrightarrow H_2\overset{\oplus}{C}-CH=CH_2$$

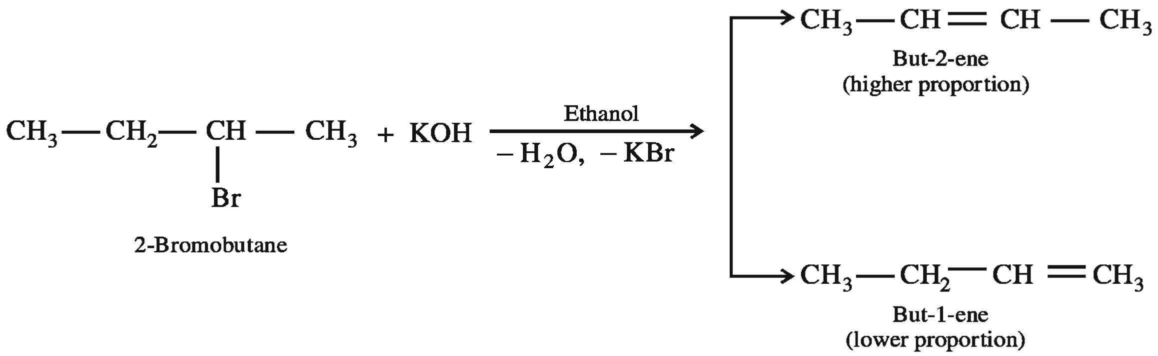
(2) Elimination Reactions : Alkene is formed by reaction of ethanolic solution of potassium hydroxide with haloalkanes containing hydrogen on β–carbon. Alkene compound is formed by formation of double bond betwen α and β–carbon atoms by releasing halogen atom of α–carbon atom and hydrogen atom of β–carbon atom of haloalkane. This reaction is called **β–elimination reaction.** This reaction is also called **dehydrohalogenation.**

$$^{\beta}CH_3-{}^{\alpha}CH_2-Cl+KOH \xrightarrow{\text{Ethanol}} CH_2=CH_2+KCl+H_2O$$

Chloroethane Ethene

When there are more than one β–hydrogen in haloalkane, then more than one alkenes are obtained as product. Generally one product of alkene whose proportion is more is called major product and whose proportion is less called minor product.

In 1875, Russian scientist Alexander Zaitsev (it is also pronounced as Saytzeff) gave one formula. In dehydrohalogenation reaction, the alkene product having more number of alkylgroups attached to carbon atom containing double bond is obtained in higher proportion e.g.



$$\underset{\text{2-Bromobutane}}{CH_3-CH_2-\underset{\underset{Br}{|}}{CH}-CH_3} + KOH \xrightarrow[-H_2O,\ -KBr]{\text{Ethanol}} \begin{cases} \underset{\substack{\text{But-2-ene}\\ \text{(higher proportion)}}}{CH_3-CH=CH-CH_3} \\ \underset{\substack{\text{But-1-ene}\\ \text{(lower proportion)}}}{CH_3-CH_2-CH=CH_3} \end{cases}$$

(3) Reactions with metals : By reaction of haloalkane with metals, chemical bond between carbon and metal are formed and the compounds obtained are known as organometallic compounds.

(a) Grignard reaction : In 1900, Victor Grignard discovered one important compound amongst organometallic compounds called alkyl magnesium halide. It became well known as **Grignard reagent RMgX.** Alkane is obtained by reaction of Grignard reagent with haloalkane.

$$\underset{\text{Halo alkane}}{R-X+Mg} \xrightarrow{\text{Dry ether}} \underset{\substack{\text{Alkyl magnesium halide}\\ \text{(Grignard reagent)}}}{R-Mg-X}$$

$$\underset{\text{Grignard reagent}}{R-Mg-X} \xrightarrow[\text{HX}]{\text{Aqueous}} \underset{\text{Alkane hydrocarbon}}{R-H} + \underset{\text{Magnesium dihalide}}{MgX_2}$$

$$\underset{\text{Chloroethane}}{CH_3-CH_2-Cl+Mg} \xrightarrow{\text{Dry ether}} \underset{\substack{\text{Ethyl magnesium chloride}\\ \text{(Grignard regent)}}}{CH_3-CH_2-Mg-Cl} \xrightarrow[-MgCl_2]{\text{Aqueous HCl}} \underset{\text{Ethane}}{CH_3-CH_3}$$

$$\underset{\text{Iodomethane}}{CH_3-I+Mg} \xrightarrow{\text{Dry Ether}} \underset{\substack{\text{Methyl magnesium iodide}\\ \text{(Grignard reagent)}}}{CH_3-Mg-I} \xrightarrow[\text{Aqueous acid}]{\text{Hydrolysis } H_2O} \underset{\text{Methane}}{CH_4} + Mg(OH)I$$

(b) Wurtz Reaction : Alkane having double the number of carbon atoms compared to initial haloalkane is obtained by reaction of haloalkane with sodium metal in dry ether. This reaction is called **Wurtz reaction.**

$$2R-X+2Na \xrightarrow{\text{Dry ether}} R-R+2NaX$$

e.g.

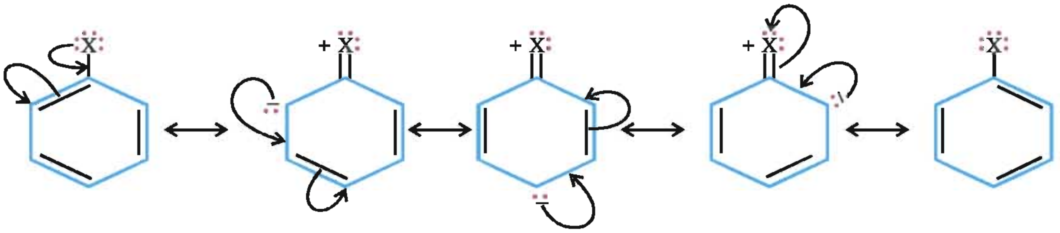
$$\underset{\text{Chloromethane}}{2CH_3Cl + 2Na} \xrightarrow{\text{dry ether}} \underset{\text{Ethane}}{CH_3 - CH_3} + 2NaCl$$

$$\underset{\text{Chloroethane}}{2CH_3CH_2Cl + 2Na} \xrightarrow{\text{Dry ether}} \underset{\text{n - Butane}}{CH_3CH_2CH_2CH_3} + 2NaCl$$

6.8.2 Reaction of Haloarene Compounds :

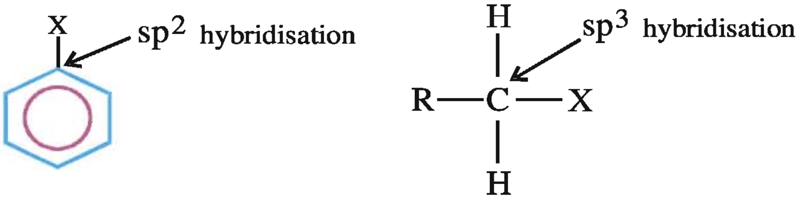
(1) Nucleophilic substitution reaction : The nucleophilic substitution reactions in haloarenes are not so easy as in haloalkanes. The reasons for nucleophilic substitution reactions in haloarene compounds being difficult are as under :

(i) Resonance effect : Halocation is formed because of electron pair on halogen atom in haloarene compound. The following resonance structures are possible for this cation.



C–X bond becomes shorter due to resonance structures. As a result, carbon-halogen bond is stronger in haloarenes as compared to haloalkanes. Hence, strong reaction conditions are essential for nucleophilic substitution reaction in haloarenes e.g., The bond length of C–Cl in chlorobenzene is 169 pm which is less than the C–Cl bond length in chloromethane which is 177 pm. Hence, nucleophilic substitution reactions in chlorobenzene are difficult.

(ii) Difference in hybridisation of carbon atom in C–X bond : Carbon atom attached with halogen in haloarene compounds possesses sp^2 hybridisation while carbon atom attached with halogen in haloalkane compounds possesses sp^3 hybridisation.

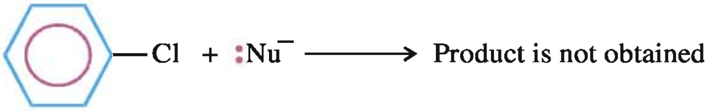


The carbon atom of haloarene, having sp^2 hybridisation possesses more electronegativity as compared to sp^3 hybridisation containing carbon atom in haloalkane; hence it attracts electron pair of C–X bond towards it. As a result the C–X bond length becomes shorter (169 pm). More energy will be required to break C–X bond which is shorter than C–X bond length in haloalkanes. As a result the reactivity of nucleophilic substitution of haloarene compounds is less in comparison to reactivity of haloalkane compounds.

(iii) Unstable phenyl cation : As phenyl cation is formed in haloarene compounds, generally self ionisation is not possible under general conditons. The resonance form of phenyl cation decreases the stability of self-ionisation reaction. Hence, SN^1 reaction is not possible in haloarene compounds.

$$CH_3-Cl + :Nu^- \longrightarrow CH_3-Nu + :Cl^-$$

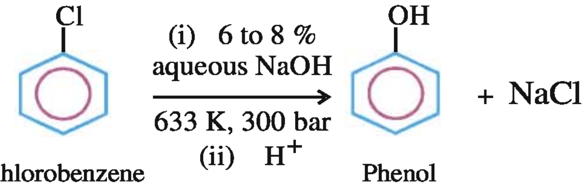
1-Chloromethane



Chlorobenzene

Reactions : The nucleophilic substitution reactions in haloarenes under, strong conditions are as follows :

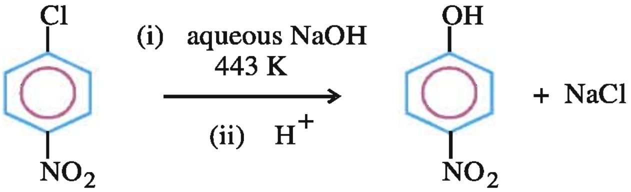
(i) Substitution by OH^- group : Phenol is formed by reaction of chlorobenzene with 6 to 8% aqueous NaOH at 633 K temperature and 300 bar pressure. This process called **Dow process.**



Chlorobenzene

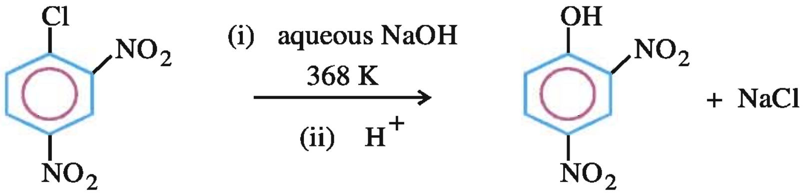
Phenol

(ii) Substitution of Cl atom by OH^- group in presence of electron attracting group $(-NO_2)$:



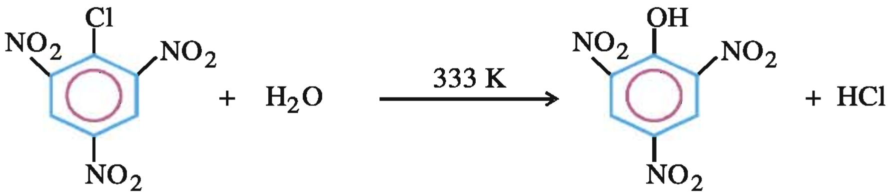
1-Chloro-4-nitrobenzene

4-Nitro phenol
(55 % product)



1-Chloro-2, 4-Dinitrobenzene

2, 4-Dinitrophenol
(76 % product)

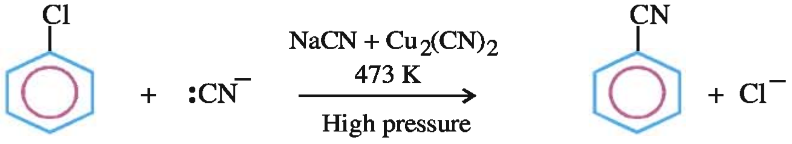


1-Chloro-2,4,6-trinitrobenzene

2,4,6-trinitrophenol
(93 % product)

If the electron attracting group $(-NO_2)$ is attached in ortho or para position of chlorobenzene, then in strong reaction conditions like high temperature about 443 K chloride (Cl^-) is substituted by $(:OH^-)$ group and 55% product is obtained. If the electron attracting group $(-NO_2)$ are in both ortho and para positions, then substitution of (Cl^-) by $(:OH^-)$ group takes place at high temperature like 368 K and 76 % product is obtained. But, when electron attracting group $(-NO_2)$ attached to two ortho and one para positions i.e. at all the three places, then by heating at 333 K temperature, chloride (Cl^-) is substituted easily by $(:OH^-)$ group and about 93 % 2,4,6 trinitrophenol (TNP) product is obtained.

(iii) Substitution by $:CN^-$ group : Phenyl cyanide is formed by reaction of chlorobenzene with NaCN in presence of $Cu_2(CN)_2$ at 473 K temperature.

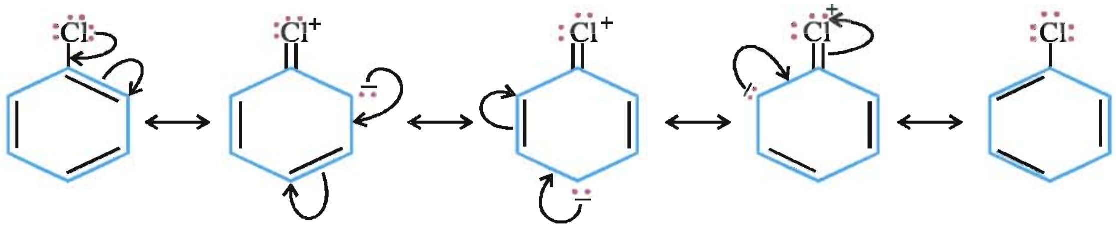


Chlorobenzene

Phenyl cyanide
(Cyanobenzene)

(2) Electrophilic substitution reactions : In haloarene compounds inspite of halogen group producing ortho-para directing effect, it decreases reactivity of benzene nucleus. Hence, halogen groups differ from other ortho-para directing group.

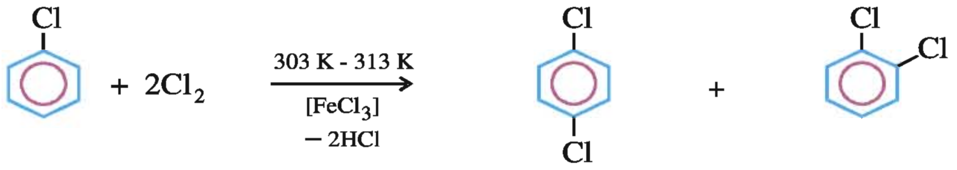
Negative inductive effect (–I effect) is produced in chlorobenzene because of eletronegative chlorine in chlorobenzene. The possibility of resonance structures increase because of non-bonding electron pairs on chlorine atom; which can be seen from the following structures :



Because of resonance, the electron density of ortho and para positions, increases more than meta position. Because of negative inductive effect (–I) of chlorine, attracts electron from phenyl nucleus. As a result the negative inductive effect (–I) increases more than the resonance. Because of this benzene ring tries to be inert. Hence electrophilic substitution in haloarene compounds by chlorine are slow. In relation to benzene, in chlorobenzene, strong reaction conditoins are necessary.

Certain electrophilic substitution reactions found in chlorobenzene such as halogenation, nitration, sulphonation and Friedel-Crafts reaction are shown below :

(a) Chlorination :

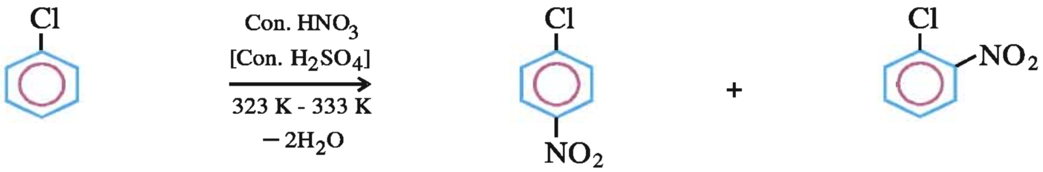


Chlorobenzene

1, 4-dichlorobenzene (p-dichlorobenzene)

1,2-dichlorobenzene (o-dichlorobenzene)

(b) Nitration :

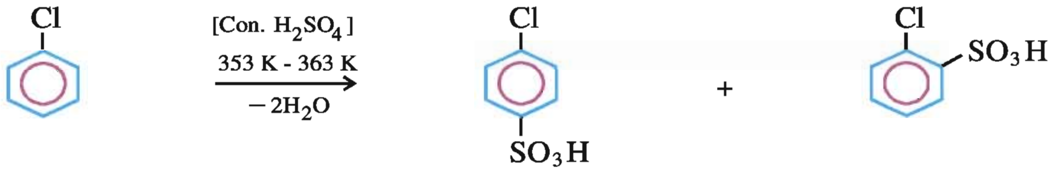


Chlorobenzene

1-Chloro-4-nitorbenzene (p-nitrochlorobenzene)

1-Chloro-2-nitorbenzene (o-nitrochlorobenzene)

(c) Sulphonation :

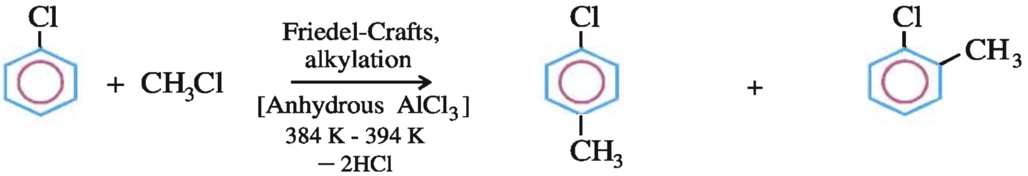


Chlorobenzene

4-Chlororbenzene sulphonic acid (p-Chlorobenzene sulphonic acid)

2-Chlororbenzene sulphonic acid (o-Chlorobenzene sulphonic acid)

(d) Friedel-Crafts Alkylation :

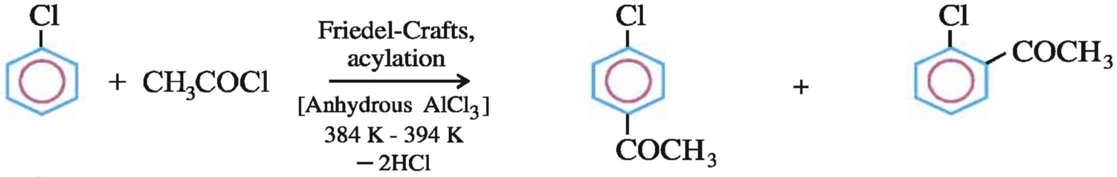


Chlorobenzene

1-Chloro-4-methylbenzene (p-Chlorotoluene)

1-Chloro-2-methylbenzene (o-Chlorotoluene)

(e) Friedel-Crafts Acylation :



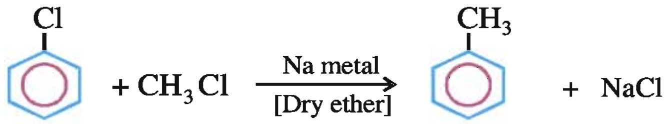
Chlorobenzene

1-(4-Chlorophenyl) ethan-1-one (p-Chloroacetophenone)

1-(2-Chlorophenyl) ethan-1-one (o-Chloroacetophenone)

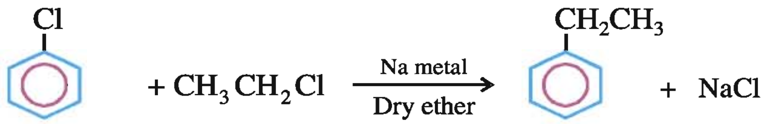
(3) Reaction with metal :

(i) Wurtz-Fittig reaction : Toluene is obtained by reaction of mixture of chlorobenzne and methyl chloride with sodium metal in dry ether. This reaction is called Wurtz-Fittig reaction.



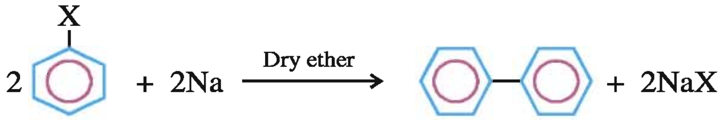
Chlorobenzene Toluene

Similarly ethyl benzene is obtained by the reaction of chlorobenzene with ethyl chloride.



Chlorobenzene 1- Chloroethane (ethyl chloride) ethylbenzene

(ii) Fittig reaction : When aryl halide is reacted with sodium metal in dry ether, two aryl groups combine and give the product. This reaction is called Fittig reaction.



Chlorobenzene Diphenyl

6.9 Polyhalogen Compounds

(1) Dichloromethane –CH_2Cl_2 (Methylene chloride) :

Preparation :

(i) Dichloromethane is formed by reduction of chloroform ($CHCl_3$) in presence of Zn + HCl.

$$CHCl_3 + 2[H] \xrightarrow{Zn + HCl} \underset{\substack{\text{Dichloromethane} \\ \text{(methylene chloride)}}}{CH_2Cl_2} + HCl$$

(ii) In recent time dichloromethane is prepared by chlorination of methane.

$$\underset{\text{Methane}}{CH_4} \xrightarrow[Cl_2\ \ -HCl]{\text{Chlorination } h\nu} \underset{\text{Chloromethane}}{CH_3Cl} \xrightarrow[Cl_2\ \ -HCl]{\text{Chlorination } h\nu} \underset{\text{Dichloromethane}}{CH_2Cl_2}$$

(iii) Dichloromethane is obtained by reduction of chloroform.

$$\underset{\text{Chloroform}}{CHCl_3} \xrightarrow[\text{[Ni]}]{\text{Reduction } H_2} \underset{\text{Dichloromethane}}{CH_2Cl_2} + HCl$$

Properties and Uses :

- Dichloromethane is a colourless liquid.
- Its boiling point is 313 K.
- It is useful as solvent in industries. Mostly it is used as solvent in the production of chemicals used in removal of colour. It is harmful to nervous system. If it comes in direct contact of eye it damages the cornea.
- In addition, if it comes in direct contact of skin, red rashes are formed.

(2) Trichloromethane $CHCl_3$ (Chloroform)

Preparation :

(i) Chloroform is obtained by reaction of ethanol with dichlorine gas in presence of bleaching powder.

$$\underset{\text{Ethanol}}{CH_3CH_2OH} + Cl_2 \xrightarrow[\substack{\text{Bleaching powder} \\ -2HCl}]{[O]} \underset{\substack{\text{Ethanal} \\ \text{(Acetaldehyde)}}}{CH_3CHO} \xrightarrow[\substack{\text{Bleaching powder} \\ -2HCl}]{3Cl_2} \underset{\text{Chloral}}{CCl_3CHO}$$

$$\underset{\text{Chloral}}{2CCl_3CHO} + \underset{\substack{\text{Calcium} \\ \text{hydroxide}}}{Ca(OH)_2} \longrightarrow \underset{\substack{\text{Trichloromethane} \\ \text{(Chloroform)}}}{2CHCl_3} + \underset{\text{Calcium formate}}{(HCOO)_2Ca}$$

(ii) Chloroform is formed by partial reduction of carbon tetrachloride with the help of water in the presence of iron.

$$\underset{\substack{\text{Tetrachloro methane} \\ \text{(Carbon tetrachloride)}}}{CCl_4 + H_2} \xrightarrow[H_2O]{[Fe]} \underset{\substack{\text{Trichloromethane} \\ \text{(Chloroform)}}}{CHCl_3} + HCl$$

(iii) Pure chloroform is obtained by reaction of chloral hydrate with concentrated alkali.

$$\underset{\text{Chloral hydrate}}{CCl_3CH(OH)_2} + \underset{\substack{\text{Concentrated} \\ \text{Sodium hydroxide}}}{NaOH} \longrightarrow \underset{\text{Chloroform}}{CHCl_3} + \underset{\text{Sodium formate}}{HCOONa} + H_2O$$

Properties and uses :

- Chloroform is a colourless liquid.
- Its boiling point is 334 K.

- Its vapour is combustible.
- It possesses sweet smell.
- It is soluble in alcohol and ether.
- If kept open in air, poisonous substance carbonyl chloride ($COCl_2$) is formed which is known as phosgene.
- Chloroform used as anesthetic should not be converted to phosgene and so alcohol is added to it.
- Chloroform is used as solvent. In addition, it is used as anesthetic for making patient unconcious during operation.

(3) Tetrachloromethane : CCl_4 (Carbon tetrachloride) :

(i) Tetrachloromethane is formed by reaction of carbon disulphide with dichlorine gas in presence of anhydorous $AlCl_3$ as catalyst.

$$\underset{\text{Carbon disulphide}}{CS_2} + 3Cl_2 \xrightarrow{[\text{Anhydrous}AlCl_3]} \underset{\substack{\text{Tetrachloromethane}\\\text{(Carbon tetra chloride)}}}{CCl_4} + \underset{\substack{\text{Sulphur}\\\text{dichloride}}}{S_2Cl_2}$$

(ii) Tetrachloro methane is formed by chlorination of methane.

$$CH_4 + 4Cl_2 \xrightarrow{h\nu} \underset{\substack{\text{Tetrachloro}\\\text{methane}}}{CCl_4} + 4HCl$$

Properties and uses :

- Carbon tetrachloride is a colourless, fragrant liquid heavier than water.
- It is insoluble in water; but is soluble in ethanol and ether.
- Its boiling point is 350 K.
- CCl_4 is used under the name of pyrene for extinguishing the fire in substances like oil, fat and petrol because its vapour is not combustible.

It is stable at higher temperature (about 773 K). When it comes in contact with water at high temperature, poisonous substance phosgene is formed. Hence, care is to be taken while extinguishing the fire. It is useful as solvent in industry and drycleaning.

(4) Triiodomethane CHI_3 (Iodoform) :

Preparation : Iodoform is formed by the reaction of alcohol containing CH_3CHOH–group or acetone with iodine and solution of sodium carbonate or dilute NaOH solution.

$$CH_3CH_2OH + 3Na_2CO_3 + 4I_2 \longrightarrow \underset{\substack{\text{Triiodomethane}\\\text{(Iodoforms)}}}{CHI_3} + 5NaI + HCOONa + 3CO_2 + 2H_2O$$

$$\mathrm{CH_3COCH_3 + 4NaOH + 3I_2 \longrightarrow \underset{\substack{\text{Triiodomethane}\\ \text{(Iodoform)}}}{CHI_3} + 3NaI + \underset{\text{Sodium acetate}}{CH_3COONa} + 3H_2O}$$

Properties and Uses :

- Iodoform is light yellow coloured crystalline, smell prosessing substance.
- Its melting point is 392 K. It is insoluble in water but dissolves in organic liquids like ethanol, ether etc.
- As iodine is liberated from iodoform, it is useful as antiseptic in medicines.

(5) Dichlorodifluoro methane (CCl_2F_2) Freon (Chlorofluorocarbon) :

Preparation : Chlorofluoro carbon is prepared by reaction between carbon tetrachloride and antimony trifluoride at high pressure in presence of antimony pentachloride.

$$\underset{\substack{\text{Carbon tetra}\\ \text{Chloride}}}{\mathrm{3CCl_4}} + \mathrm{2SbF_3} \xrightarrow[\text{High pressure}]{\mathrm{SbCl_5}} \underset{\substack{\text{Freon (CFC)}\\ \text{Dichlorodifluoromethane}}}{\mathrm{3CCl_2F_2}} + \mathrm{2SbCl_3}$$

These compounds have got a long series in which CCl_2F_2 is known as freon 12.

Properties and Uses :

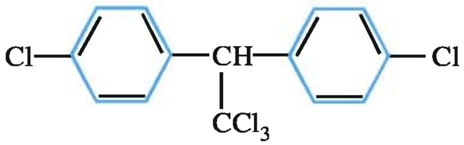
- Freon is a colourless, odourless gas.
- Its boiling point is 243 K.
- Metal does not corrode because of its effect.

It is more used in refrigerator and air conditioner. Freons CCl_2F_2 and $C_2Cl_2F_4$ series are used in them. Fragrant substances are used in aerosol mixtures of insecticide substances. In this, Freon-22, $CClF_3$, CCl_2F_2, CCl_3F etc. are also useful.

CFC is proved harmful to ozone layer.

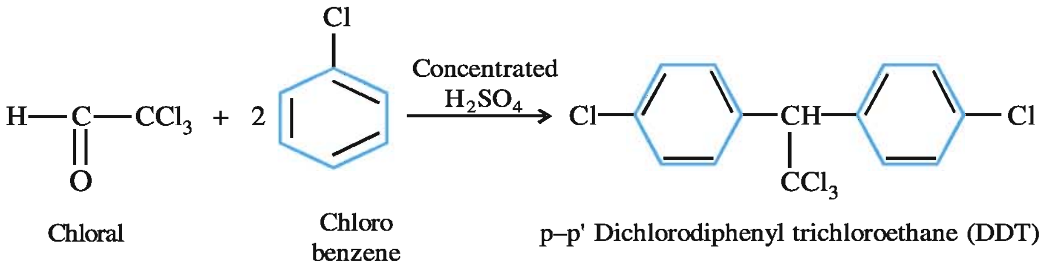
(6) p–p' Dichlorodiphenyl trichloro ethane (DDT) :

Structural formula :



p–p' Dichlorodiphenyl trichloroethane (DDT)

Preparation : DDT is formed by reaction of chloral and chlorobenzene in presence of concentrated sulphuric acid.



Properties and Uses :

- DDT is a white solid substance.
- It gives pungent smell of chlorine and the eyes get irritated, there is a possibility of cancer, if it enters the body.
- It is useful as household insecticides.

SUMMARY

The classification of haloalkane and haloarene compounds is made on the basis of one, two, three or more halogen atoms, respectively as mono, di,tri and polyform. They are classified into primary, secondary, and tertiary halides according to their characteristics combined with carbon with functional group halogen. In addition, the classification of halo compounds, halogen having carbon possessing sp^3 or sp^2 hybridisation as alkyl, allylic, benzylic, vinyl and aryl halide is also made.

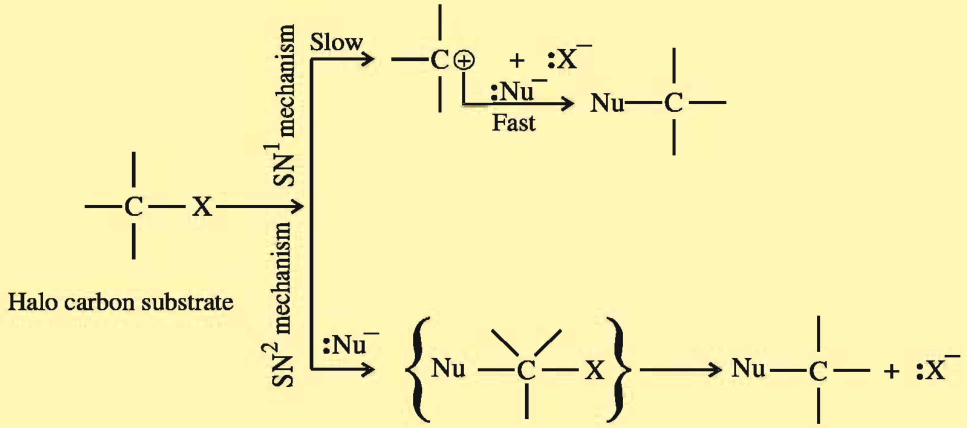
Prefix halo is used for IUPAC nomenclature of alkyl halide and aryl halide viz. for F, Cl, Br, I as fluoro, chloro, bromo, iodo respectively.

In these compounds, the electronegativity of halogen is more than that of carbon. $C^{\delta+}–X^{\delta-}$ bond becomes polar and partial positive charge on carbon and partial netagive charge on halogen are produced.

Preparation of haloalkane compounds can be made by substitution of hydroxyl–OH group by halogen –X. Alkyl halides, or aryl halides can be prepared in the same way by halogenation from hydrocarbon, by electrophilic substitution in cyclic hydrocarbon, by addition reaction in alkene, by exchange of halogen etc.

In halocarbon compounds $C^{\delta+}–X^{\delta-}$ bond being polar, intermolecular attraction forces are more and so their boiling points are found to be higher in comparison to their corresponding hydrocarbons. As C–X bond length is shorter in haloarene than in haloalkane, their boiling points are higher. Halocarbon compounds are sparingly soluble in water but becomes soluble in organic solvents.

In alkyl halide because of the polarity of $C^{\delta+}–X^{\delta-}$ bond in alkyl halide, nucleophilic reagents ($:Nu^-$) are attracted by carbon having partial positive charge, they give nucleophilic substitution reactions. The reaction mechanism of these substitution reactions are classified in two parts in the form of SN^1 and SN^2.



According to chemical kinetics principle, SN^1 is a first order reaction, while SN^2 is a second order reaction. The stability of carbocation depends on electron donating group, inductive effect (I) and resonance factor.

From stereochemistry point of view, because of the optical activity of chiral carbon produced from halocarbon componds, racemic mixture is obtained in the form of product.

On the basis of chemical characteristics of haloalkane compounds, elimination reaction, Grignard reaction with metals, Wurtz reaction, different products can be obtained.

The reactions carried out by haloarene compounds viz. in nucleophilic substitution reactions, resonance effect, difference in hybridisation of C–X bond, effect of unstable phenyl cation, different products can be obtained.

Haloarene compounds give electrophilic substitution reactions. In addition, under strong reaction conditions gives nucleophililic reactions also.

Phenol can be obtained by substitution of functional group –X of haloarene by –OH group. Similarly arylcyanide can be obtained by substitution of –X by –CN. Electrophilic substitution reactions occurring in phenyl nucleus of haloarene, are more stable because of their resonance structures. In these reactions the ortho-para products of halogenation, nitration, sulphonation, Friedel-Crafts explains ortho-para directing effect of halogen functional group.

Haloarene with sodium metal gives different reactions like Wurtz, Fittig reaction.

In certain important halocarbon compounds dichloromethane (CH_2Cl_2), trichloromethane ($CHCl_3$), Chloral (CCl_3CHO), tetrachloromethane (CCl_4), iodoform (CHI_3), freon, DDT etc. are included. Most of these compounds are not easily decomposed and so they are harmful to ozone layer; they are proved to be dangerous for environment.

EXERCISE

1. Select the proper choice from the given multiple choices :

(1) In haloalkane .... bond is formed between carbon and halogen.

(A) Ionic (B) van der Waals (C) Covalent (D) Hydrogen

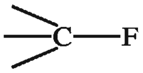
(2) In haloarene compounds, halogen combines with carbon having which hybridisation ?

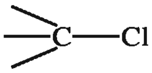
(A) sp^2 (B) sp^3 (C) sp (D) dsp^2

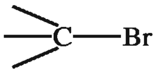
(3) In haloalkane, carbon in C–X bond possesses which partial electric charge ?

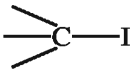
(A) Chargeless (B) Positive (C) Negative (D) Anionic

(4) Which of the following bonds is the strongest ?

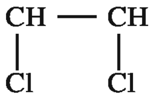
(A) 

(B) 

(C) 

(D) 

(5) Which of the folloiwng is vinyl halide ?

(A) CH_2Cl_2 (B) $CH_2=CH–Cl$ (C) $CH≡C–Cl$ (D) 

$CH(Cl)—CH(Cl)$

(6) What is B in R–OH + PX_5 → R–X + B + HX ?

(A) $HPOX_3$ (B) H_3PO_3 (C) POX_3 (D) H_3PO_2

(7) Which catalyst is used in preparation of bromobenzene by bromination of benzene ?

(A) $FeBr_3$ (B) HBr (C) $AlBr_3$ (D) Br_2

(8) By which name the reaction $CH_3–Br + Ag–F \rightarrow CH_3F + AgBr$ is known ?

(A) Grignard (B) Wurtz (C) Fittig (D) Swartz

(9) What are nucleophilic reagents according to Lewis theory ?

(A) Acid (B) Base (C) Neutral molecules (D) Positive ions

(10) On which of the following factors the stability of carbocation depends ?

(A) Resonance (B) Temperature (C) Transition state (D) Reaction rate

(11) What is called an optically active substbnce ?

(A) Which reflects polarised light

(B) Which rotates the plane of polarised light

(C) Which increases rate of polarised light

(D) Which absorbs polarised light

(12) Arrange giving the sequence order to Br, Cl, F and H combined with asymmetric carbon.

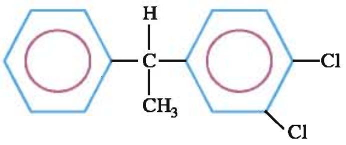
(A) H, Cl, Br, F (B) H, Cl, F, Br (C) Br, Cl, F, H (D) H, F, Br, Cl

(13) $2C_6H_5{-}X + 2Na \xrightarrow{\text{Dry ether}} A + 2NaX$. What will be the product A obtained in the reaction ?

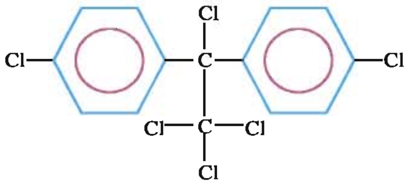
(A) C_6H_5Cl (B) $C_{12}H_{10}$ (C) $C_6H_5{-}C_6H_5$ (D) C_6H_5Na

(14) Which is the structural formula of DDT ?

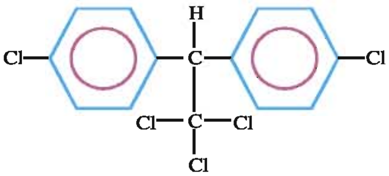
(A)



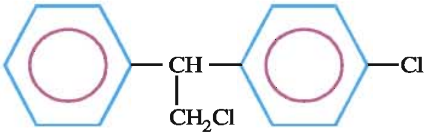
(B)



(C)



(D)



(15) Which substance is inflamable ?

(A) DDT (B) Freon (C) CHI_3 (D) $CHCl_3$

2. Answer the following questions in short :

(1) Write IUPAC names of the following substances.

(i) $(CH_3)_2{-}CH{-}CH(Cl){-}CH_3$

(ii) $CH_3{-}CH(CH_3){-}CH(CH_3){-}Cl$

(iii) $CH_3{-}C(C_2H_5)_2{-}CH_2{-}Cl$

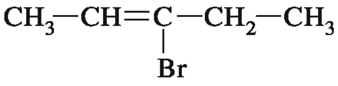
(iv) $CH_3{-}C(ClC_2H_5){-}CH_2{-}Br$

(v) $Cl{-}CH_2{-}C{\equiv}C{-}CH_2{-}Cl$

(2) Classify the following compounds in the form as alkyl, allylic, benzylic, vinyl or aryl halide.

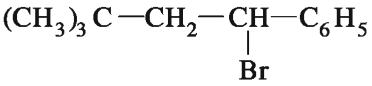
(i) $C_6H_5CH_2Br$

(ii) $CH_3{-}CH{=}CH{-}Cl$

(iii) 

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

(iv) $CH_3-CH_2-CH_2-Br$

(v) 

$(CH_3)_3C-CH_2-\underset{\overset{|}{Br}}{CH}-C_6H_5$

(3) Write the structural formulas of the following :

(i) 2-bromo-3 methyl pentane

(ii) 1-chloro-4-methyl cyclohexane

(iii) 1, 4-dichlorobut-2-ene

(iv) 1-chloro-4-secondary butyl-2-methyl benzene

(4) Give examples of 1^0, 2^0, 3^0 haloalkanes.

(5) Give reason for polarity of C–X bond in haloalkane.

(6) Give examples of 1^0, 2^0, 3^0 benzyl halide.

(7) What is meant by chirality ?

(8) In haloalkanes intermolecular attraction forces are more than those in alkanes ? Why ?

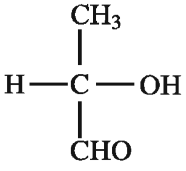
(9) What is called SN^1 reaction ?

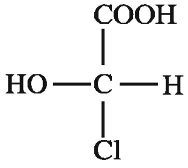
(10) Why SN^2 reaction is called bimolecular substitution reaction ?

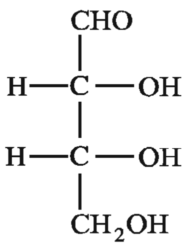
(11) Which poisonous substance is formed by keeping chloroform open in air ?

(12) On which factor, the stability of carbocation depends ?

(13) Mention D or L configurations in following compounds :

(1) 

(2) 

(3) 

3. Write answers of the following questions :

(1) Mention the classification of haloalkanes on the basis of number of halogen atoms giving suitable examples.

(2) Explain the reaction for preparation of haloalkane from alcohol giving reaction equation.

(3) Describe Zaitsev's formula giving suitable example.

(4) Give only equations of substitution reaction in haloarenes by OH^- group.

(5) Write preparation of methylene chloride.

(6) Mention properties of dichloromethane.

(7) Is 2, 3-dibromobutane optically active ?

(8) Explain the factors affecting the rate of reaction in SN^1 and SN^2 reactions.

(9) Write physical properties and uses of chloroform.

(10) Write a note on resonance effect in the nucleophilic substitution reaction of haloarenes.

4. Give answers of the following questions in detail :

(1) Explain classification of haloalkane and haloarene compounds on the basis of number of halogen atoms.

(2) Write a note on C–X bond.

(3) Write a note on β–elimination reaction in haloalkane.

(4) Give following electrophilic reactions :

(i) Chlorination (ii) Nitration (iii) Sulphonation

(iv) Friedel-Crafts acylation (v) Friedel-Crafts alkylation

(5) Explain in detail Fittig reaction of haloarene.

(6) Explain in detail SN^1 reaction.

(7) Write a note on SN^2 reaction.

(8) Mention preparation, properties and uses of tetrachloromethane.

(9) Give preparation of iodoform and its importance in medical field.

(10) Mention types of freon and explain freon as coolant.

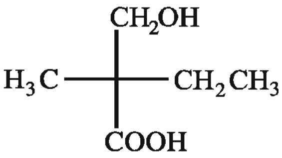
(11) Explain stability of carbocation.

(12) Explain the two steps to determine R–S nomenclature.

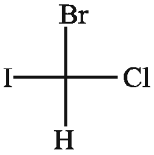
(13) Explain D–L nomenclature.

(14) Write a note about any three polyhalogen compounds.

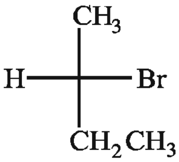
(15) Mention R or S configuration of following compounds :

(1) 

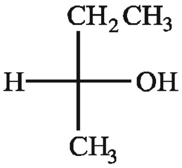
$$\begin{array}{ccc} & CH_2OH & \\ & | & \\ H_3C - & + & - CH_2CH_3 \\ & | & \\ & COOH & \end{array}$$

(2) 

$$\begin{array}{ccc} & Br & \\ & | & \\ I - & + & - Cl \\ & | & \\ & H & \end{array}$$

(3) 

$$\begin{array}{ccc} & CH_3 & \\ & | & \\ H - & + & - Br \\ & | & \\ & CH_2CH_3 & \end{array}$$

(4) 

$$\begin{array}{ccc} & CH_2CH_3 & \\ & | & \\ H - & + & - OH \\ & | & \\ & CH_3 & \end{array}$$