Unit 10

Haloalkanes and Haloarenes

Objectives

After studying this Unit, you will be able to

- name haloalkanes and haloarenes according to the IUPAC system of nomenclature from their given structures;
- describe the reactions involved in the preparation of haloalkanes and haloarenes and understand various reactions that they undergo;
- correlate the structures of haloalkanes and haloarenes with various types of reactions;
- use stereochemistry as a tool for understanding the reaction mechanism;
- appreciate the applications of organo-metallic compounds;
- highlight the environmental effects of polyhalogen compounds.

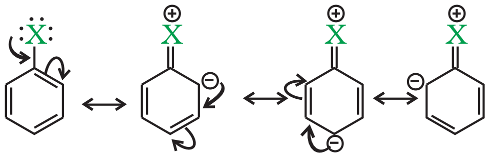
Halogenated compounds persist in the environment due to their resistance to breakdown by soil bacteria.

The replacement of hydrogen atom(s) in a hydrocarbon, aliphatic or aromatic, by halogen atom(s) results in the formation of alkyl halide (haloalkane) and aryl halide (haloarene), respectively. Haloalkanes contain halogen atom(s) attached to the sp^3 hybridised carbon atom of an alkyl group whereas haloarenes contain halogen atom(s) attached to sp^2 hybridised carbon atom(s) of an aryl group. Many halogen containing organic compounds occur in nature and some of these are clinically useful. These classes of compounds find wide applications in industry as well as in day-to-day life. They are used as solvents for relatively non-polar compounds and as starting materials for the synthesis of wide range of organic compounds. Chlorine containing antibiotic, *chloramphenicol*, produced by soil microorganisms is very effective for the treatment of typhoid fever. Our body produces iodine containing hormone, *thyroxine*, the deficiency of which causes a disease called *goiter*. Synthetic halogen compounds, *viz.* chloroquine is used for the treatment of malaria; halothane is used as an anaesthetic during surgery. Certain fully fluorinated compounds are being considered as potential blood substitutes in surgery.

In this Unit, you will study the important methods of preparation, physical and chemical properties and uses of organohalogen compounds.

2. Electrophilic substitution reactions

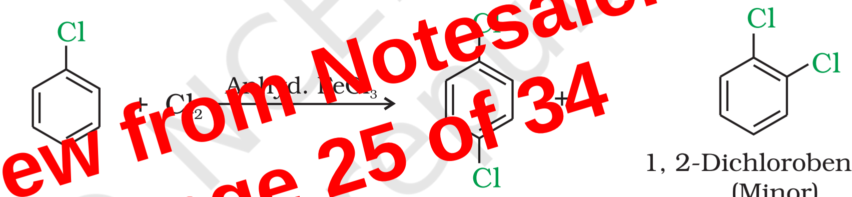
Haloarenes undergo the usual electrophilic reactions of the benzene ring such as halogenation, nitration, sulphonation and Friedel-Crafts reactions. Halogen atom besides being slightly deactivating is *o, p*-directing; therefore, further substitution occurs at *ortho*- and *para*-positions with respect to the halogen atom. The *o, p*-directing influence of halogen atom can be easily understood if we consider the resonating structures of halobenzene as shown:



I II III IV

Due to resonance, the electron density increases more at *ortho*- and *para*-positions than at *meta*-positions. 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 electrophilic substitution reactions in haloarenes occur slowly and require more drastic conditions as compared to those in benzene.

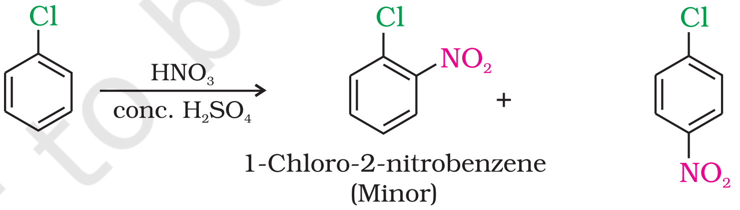
(i) Halogenation



1, 4-Dichlorobenzene
(Major)

1, 2-Dichlorobenzene
(Minor)

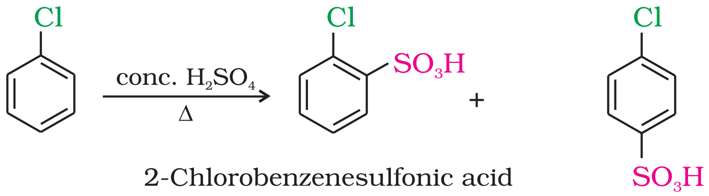
(ii) Nitration



1-Chloro-2-nitrobenzene
(Minor)

1-Chloro-4-nitrobenzene
(Major)

(iii) Sulphonation



2-Chlorobenzenesulfonic acid
(Minor)

4-Chlorobenzenesulfonic acid
(Major)

Summary

Alkyl/ Aryl halides may be classified as mono, di, or polyhalogen (tri-, tetra-, etc.) compounds depending on whether they contain one, two or more halogen atoms in their structures. Since halogen atoms are more electronegative than carbon, the carbon-halogen bond of alkyl halide is polarised; the carbon atom bears a partial positive charge, and the halogen atom bears a partial negative charge.

Alkyl halides are prepared by the **free radical halogenation** of alkanes, addition of halogen acids to alkenes, replacement of –OH group of alcohols with halogens using phosphorus halides, thionyl chloride or halogen acids. Aryl halides are prepared by **electrophilic substitution** to arenes. Fluorides and iodides are best prepared by halogen exchange method.

The boiling points of organohalogen compounds are comparatively higher than the corresponding hydrocarbons because of strong dipole-dipole and van der Waals forces of attraction. These are slightly soluble in water but completely soluble in organic solvents.

The polarity of carbon-halogen bond of alkyl halides is responsible for their **nucleophilic substitution, elimination** and their reaction with metal atoms to form **organometallic compounds**. Nucleophilic substitution reactions are categorised into **S_N1** and **S_N2** on the basis of their kinetic properties. **Chirality** has a profound role in understanding the reaction mechanisms of S_N1 and S_N2 reactions. S_N2 reactions of chiral alkyl halides are characterised by the inversion of configuration while S_N1 reactions are characterised by racemisation.

A number of polyhalogen compounds e.g., **dichloromethane**, **chloroform**, **iodoform**, **carbon tetrachloride**, **freon** and **DDT** have many industrial applications. However, some of these compounds cannot be easily decomposed and even cause depletion of ozone layer and are proving **environmental hazards**.

Exercises

10.1 Name the following halides according to IUPAC system and classify them as alkyl, allyl, benzyl (primary, secondary, tertiary), vinyl or aryl halides:

(i) $(CH_3)_2CHCH(Cl)CH_3$ (ii) $CH_3CH_2CH(CH_3)CH(C_2H_5)Cl$
(iii) $CH_3CH_2C(CH_3)_2CH_2I$ (iv) $(CH_3)_3CCH_2CH(Br)C_6H_5$
(v) $CH_3CH(CH_3)CH(Br)CH_3$ (vi) $CH_3C(C_2H_5)_2CH_2Br$
(vii) $CH_3C(Cl)(C_2H_5)CH_2CH_3$ (viii) $CH_3CH=C(Cl)CH_2CH(CH_3)_2$
(ix) $CH_3CH=CHC(Br)(CH_3)_2$ (x) *p*-$ClC_6H_4CH_2CH(CH_3)_2$
(xi) *m*-$ClCH_2C_6H_4CH_2C(CH_3)_3$ (xii) *o*-Br-$C_6H_4CH(CH_3)CH_2CH_3$

10.2 Give the IUPAC names of the following compounds:

(i) $CH_3CH(Cl)CH(Br)CH_3$ (ii) $CHF_2CBrClF$ (iii) $ClCH_2C\equiv CCH_2Br$
(iv) $(CCl_3)_3CCl$ (v) $CH_3C(p\text{-}ClC_6H_4)_2CH(Br)CH_3$ (vi) $(CH_3)_3CCH=CClC_6H_4I$-*p*

10.3 Write the structures of the following organic halogen compounds.

(i) 2-Chloro-3-methylpentane (ii) *p*-Bromochlorobenzene
(iii) 1-Chloro-4-ethylcyclohexane (iv) 2-(2-Chlorophenyl)-1-iodooctane
(v) 2-Bromobutane (vi) 4-tert-Butyl-3-iodoheptane
(vii) 1-Bromo-4-sec-butyl-2-methylbenzene (viii) 1,4-Dibromobut-2-ene

(iii) 1-Bromobutane, 1-Bromo-2,2-dimethylpropane, 1-Bromo-2-methylbutane, 1-Bromo-3-methylbutane.

10.17 Out of $C_6H_5CH_2Cl$ and $C_6H_5CHClC_6H_5$, which is more easily hydrolysed by aqueous KOH.

10.18 *p*-Dichlorobenzene has higher m.p. than those of *o*- and *m*-isomers. Discuss.

10.19 How the following conversions can be carried out?

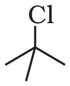
(i) Propene to propan-1-ol
(ii) Ethanol to but-1-yne
(iii) 1-Bromopropane to 2-bromopropane
(iv) Toluene to benzyl alcohol
(v) Benzene to 4-bromonitrobenzene
(vi) Benzyl alcohol to 2-phenylethanoic acid
(vii) Ethanol to propanenitrile
(viii) Aniline to chlorobenzene
(ix) 2-Chlorobutane to 3, 4-dimethylhexane
(x) 2-Methyl-1-propene to 2-chloro-2-methylpropane
(xi) Ethyl chloride to propanoic acid
(xii) But-1-ene to n-butyliodide
(xiii) 2-Chloropropane to 1-propanol
(xiv) Isopropyl alcohol to iodoform
(xv) Chlorobenzene to *p*-nitrophenol
(xvi) 2-Bromopropane to 1-bromopropane
(xvii) Chloroethane to butane
(xviii) Benzene to diphenyl
(xix) *tert*-Butyl bromide to isobutyl bromide
(xx) Aniline to phenylisocyanide

10.20 The treatment of alkyl chlorides with aqueous KOH leads to the formation of alcohols but in the presence of alcoholic KOH, alkenes are major products. Explain.

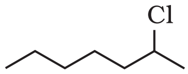
10.21 Primary alkyl halide C_4H_9Br (a) reacted with alcoholic KOH to give compound (b). Compound (b) is reacted with HBr to give (c) which is an isomer of (a). When (a) is reacted with sodium metal it gives compound (d), C_8H_{18} which is different from the compound formed when n-butyl bromide is reacted with sodium. Give the structural formula of (a) and write the equations for all the reactions.

10.22 What happens when

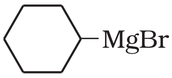
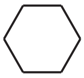
(i) n-butyl chloride is treated with alcoholic KOH,
(ii) bromobenzene is treated with Mg in the presence of dry ether,
(iii) chlorobenzene is subjected to hydrolysis,
(iv) ethyl chloride is treated with aqueous KOH,
(v) methyl bromide is treated with sodium in the presence of dry ether,
(vi) methyl chloride is treated with KCN?

10.8 (i) 

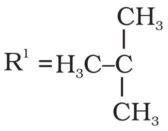
Tertiary halide reacts faster than secondary halide because of the greater stability of tert-carbocation.

(ii) 

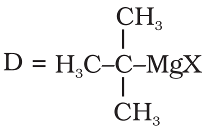
Because of greater stability of secondary carbocation than primary.

10.9 A =  B = 

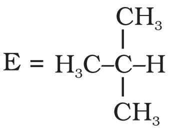
C = RMgBr R = $CH_3\underset{|}{C}HCH_3$



$R^1 = H_3C-\overset{CH_3}{\underset{CH_3}{C}}$



$D = H_3C-\overset{CH_3}{\underset{CH_3}{C}}-MgX$



$E = H_3C-\overset{CH_3}{\underset{CH_3}{C}}-H$