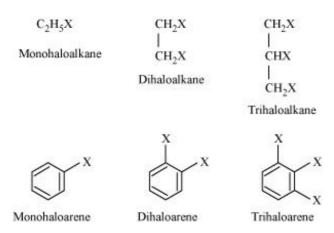


Haloalkanes and Haloarenes

Classification: Mono, di and polyhalogen (tri, tetra, etc.)



- (i) Alkyl halides or haloalkanes $(R-X) \rightarrow They$ form homologous series of general formula $C_nH_{2n+1}X$. They are further classified into primary, secondary, and tertiary.
- (ii) Allylic halides → Compounds containing halogen atom bonded to an allylic carbon
- (iii) Benzylic halides \rightarrow Compounds containing halogen atom bonded to an sp^3 hybridised carbon atom next to an aromatic ring

Methods of preparation:

• From alcohols -

$$\begin{split} R - OH + HX & \xrightarrow{ZnCl_2} R - X + H_2O \\ 3R - OH + PX_3 & \longrightarrow 3R - X + H_3PO_3 (X = Cl_1Br) \\ R - OH + PCl_5 & \longrightarrow R - Cl + POCl_3 + HCl \\ R - OH & \xrightarrow{red P:X_2 \\ X_2 = Br_2l_2} \to R - X \\ R - OH + SOCl_2 & \longrightarrow R - Cl + SO_2 + HCl \end{split}$$

• From hydrocarbons -

By free radical halogenations- Yields a complex mixture of isomeric mono- and polyhaloalkanes

$$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \xrightarrow{\text{Cl}_2/\text{UV light}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH} + \text{CH}_3\text{CH}_2\text{CHClCH}_3$$

• By electrophilic substitution

• Sandmeyer's reaction -

$$\frac{\text{NaNO}_2 + \text{HX}}{273 - 278 \text{ K}}$$
Benzenediazonium halide
$$Cu_2X_2$$

$$X = \text{Cl, Br}$$

From alkenes –

Addition of hydrogen halides to unsaturated hydrocarbons (Markovnikov's rule)

$$CH_3CH = CH_2 + H - I \longrightarrow CH_3CH_2CH_2I + CH_3CHICH_3$$
(Minor) (Major)

Addition of halogens

(Method used for detecting double bond in a molecule)

In this method, a reddish-brown colour is discharged.

$$H C = C H + Br_2 C H_2 BrCH_2 CH_2 Br$$
 vic -Dibromide

• Halogen exchange -

Finkelstein reaction

$$R - X + NaI \xrightarrow{dry \ acetone} R - I + NaX$$

 $X = CI, Br$

Swarts reaction (synthesis of alkyl fluoride) –

$$H_3C - X + AgF \longrightarrow H_3C - F + AgX$$

 $X = Cl, Br$

Physical properties:

- Melting and boiling points –
- Halides have higher boiling points than hydrocarbons of comparable molecular mass because of having stronger dipole—dipole and van der Waals' forces of attraction.
- The order of increasing boiling points of the different haloalkanes is:

 The boiling points of isomeric haloalkanes decrease with increase in branching. The order of branching is

$$\begin{array}{c|c} & Br & CH_3 \\ \hline | & | & CH_3CH_2CH_2CH_2Br & CH_3CH_2CHCH_3 & CH_3CCH_3 \\ \hline | & | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | & | \\ \hline | & | & | &$$

Hence, order of boiling points is opposite.

• Density -

The density of halides increases with increase in the number of carbon atoms, halogen atoms and atomic mass of the halogen atoms.

• Solubility -

Soluble in organic solvents, but only slightly soluble in water

Reactions of haloalkanes -

Nucleophilic substitution reaction:

$$N_u^- + \frac{\lambda^+}{C} X^- \longrightarrow C \longrightarrow N_u + X^-$$

Mechanism

• Substitution nucleophilic bimolecular (S_N2) (Inversion of configuration)

The increasing order of reactivity is

(Due to increase in hindrance by bulky substituent in the case of 2° and 3° halides)

• Substitution nucleophilic unimolecular (S_N1) (Two-step mechanism)

Step I is the slowest; it is reversible and rate-determining step

$$(CH_3)_3CBr$$
 $Step I$
 H_3C
 CH_3
 CH_3
 CH_3
 CH_3

$$H_3C$$
 CH_3
 $+$
 OH
 $Step II$
 $CH_3)_3COH$

The increasing order of reactivity

• In both the mechanisms, for a given alkyl group, the increasing order of reactivity is

$$R - F \ll R - CI \ll R - Br \ll R - I$$

• Elimination reactions (β – elimination):

$$H_3C$$
— CH_2 — CH_2 — CH_2 — CH_2 — CH_3 — CH_3 — CH_3 — CH_4 — CH_5 — CH_5 — CH_5 — CH_5 — CH_6 — CH_7 — CH_8 — CH_8 — CH_8 — CH_8 — CH_9 —

- Reaction with metals:
- Grignard reagent –

$$RX + Mg \xrightarrow{dry \text{ ether}} RMgX$$

Grignard reagent

Wurtz reaction –

(Preparation of hydrocarbons containing double the number of carbon atoms)

$$2RX + Na \xrightarrow{\text{dry ether}} R - R + NaX$$

Nucleophilic substitution reaction:

- Aryl halides are less reactive towards nucleophilic substitution due to
- i. Resonance effect
- ii. sp^2 hybridisation
- III Instability of about setion

III. Instability of prienty cation

iv. Repulsion

Replacement by alkyl group

Presence of electron-withdrawing group at *o*-and *m*-positions increases the reactivity of haloarenes.

$$O_2N$$
 O_2
 O_2N
 O_2
 O_2N
 O_2
 O_2N
 O_2
 O_2N
 O_2
 O_2N
 O_2
 O_2

• Electrophilic substitution reaction:

The electron density at ortho-and para-position is more than at meta-position

Halogenation

$$\begin{array}{c} Cl \\ + Cl_2 \end{array} \xrightarrow{Anhyd. FeCl_3} \begin{array}{c} Cl \\ + Cl_2 \end{array} (Minor)$$

$$(Major)$$

Nitration

$$\begin{array}{c|c}
CI & CI & CI \\
\hline
HNO_3 & NO_2 \\
NO_2 & (Major)
\end{array}$$
(Minor)

Sulphonation

$$\begin{array}{c|c}
CI & Conc. H_2SO_4 \\
\hline
\Delta & SO_3H \\
\hline
(Major)
\end{array}$$

$$\begin{array}{c}
CI \\
SO_3H \\
\hline
(Minor)
\end{array}$$

Friedel-Crafts reaction

$$\begin{array}{c} Cl \\ + CH_3Cl \end{array} \xrightarrow{Anhyd. AlCl_3} \begin{array}{c} Cl \\ CH_3 \\ (Minor) \end{array}$$

Reaction with metals:

Wurtz-Fitting reaction

Fitting reaction

Polyhalogen compounds:

- Dichloromethane (CH₂Cl₂) Industrially used as a solvent
- Trichloromethane (Chloroform, CHCl₃) -
 - Used as a solvent for fats, alkaloids, iodine
 - Causes damage to lever, kidneys and skin
 - Stored in closed, dark-coloured container as it is oxidised to an extremely poisonous gas, phosgene, when exposed to light.

• Triiodomethane (iodoform, CHI₃) -

- o Earlier, used as an antiseptic
- Its antiseptic properties are due to the liberation of free iodine

• Tetrachloromethane -

- Used in the manufacture of refrigerants, chlorofluorocarbons
- Causes liver cancer in humans
- Causes depletion of ozone layer
- Freons Collective chlorofluorocarbon compounds of methane and ethane
 - Stable, unreactive, non-toxic, non-corrosive and easily liquefiable gas
 - Used as refrigerants
 - Upset the natural ozone balance
- p, p'-Dichlorodiphenyltrichloroethane (DDT) -

$$\begin{array}{c|c} Cl & Cl \\ \hline \\ Cl & H \\ \hline \\ DDT \end{array}$$

The first chlorinated organic insecticide