

The substitution of chlorine atoms into a molecule of alkane results in a compound with anaesthetic properties e.g., chloroform. Increasing the number of chlorine atoms in the compounds increases the depth of anaesthesia given but also increases toxicity. C-F bonds are very stable so their presence leads to non-flammable and unreactive properties. Organofluorine compounds find diverse applications from oil to water repellents to pharmaceuticals, refrigerants and reagents in catalysts.

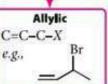
HALOGEN DERIVATIVES





Halogen Derivatives

When C-X carbon is sp^2 hybridised.



Alkyl

Benzylic C6H5CH5X CH₂ e.g.,

Vinylic

Halogen is directly attached to the carbon atom of aromatic ring, e.g., C₆H₅Cl

Methods of Preparation

(i) Direct halogenation of alkanes:

Free radical mechanism: $R - H + X_2 \xrightarrow{hv} R - X + HX$

Reactivity order:

Allylic > 3° > 2° > 1° > CH4

(ii) Addition of HX to alkenes:

 $CH_2 = CH_2 + HBr \longrightarrow CH_3CH_2Br$

- Unsymmetrical alkenes follow Markovnikov's rule during electrophilic addition.
- If the addition occurs in presence of peroxide, the product will be opposite to Markovnikov's addition (free radical mechanism).

Reactivity order:

HI>HBr>HCl>HF

(iii) From alcohols:

$$3R$$
—OH + PX₃ \rightarrow $3R$ — X + H₃PO₃
 R —OH + HX \longrightarrow R — X + H₂O
 R —OH + SOCl₂ \longrightarrow
 R Cl + SO₂ \uparrow + HCl \uparrow

[Darzen's method]

(iv) Hunsdiecker reaction:

R—Br + CO₂ + AgBr

(v) Finkelstein reaction:

$$R - X + \text{Nal} \xrightarrow{\text{Dry acetone}} R - I + \text{NaX}$$

Uses of Some Commercially Important Halogen Derivatives

(i) Chloroform (CHCl₃):

- Earlier it was used as anaesthetic but due to its harmful effects it is no longer used for the purpose.
- Used for preparation of chloretone and chloropicrin.
- Used as a solvent for fats, waxes, rubber, resins, etc.

(ii) Iodoform (CHI₃):

- Used as disinfectant.
- Effective as chemical antiseptic.

(iii) Freons or chlorofluorocarbons:

- Used as refrigerants.
- Used as propellant in aerosols such as body spray, hair spray, cleansers,

(iv) DDT:

- Used as a powerful insecticide.
- Effective against Anopheles mosquitoes which spread malaria.

(v) Teflon (-CF₂-CF₂-)_n:

- Used as non-stick coating for pans and other cookwares.
- Used in containers and pipework for corrosive chemicals.

(i) Reduction:

$$R - X + 2[H] \xrightarrow{\text{Ni or Pd}} R - H + HX$$

(ii) Wurtz reaction:

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

(iii) Reaction with metals:

$$R \longrightarrow X + Mg \xrightarrow{Dry \text{ ether}} R \longrightarrow MgX$$
(Powder) (Grignard reagent)
 $2R \longrightarrow X + 2Zn \xrightarrow{Ether} R_2Zn + ZnX_2$

$$2R-X+2Zn \longrightarrow R_2Zn+ZnX_2$$

 $4C_2H_5Br+4Pb/Na \xrightarrow{Dry ether} (C_2H_5)_4Pb$

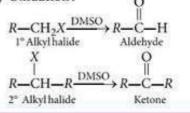
Tetraethyl lead

+4NaBr+3Pb

(iv) Corey-House reaction:

 R_2 CuLi + $R'X \longrightarrow R - R' + R - Cu + LiX$ (This reaction can be used to prepare unsymmetrical alkanes.)

(v) Oxidation:



Chemical Properties

Elimination Reactions

Nucleophilic Substitution Reactions

Miscellaneous Reactions

- First order kinetics
- Reactivity: 3°>2°>1°>CH₃X
- Second order kinetics Reactivity: CH₃X>1°>2°>3°

(i) Dehydrohalogenation:

$$R$$
-CH₂-CH₂- X alc. KOH \rightarrow

R-CH=CH3

- Elimination follows the Saytzeff's rule.
- Ease of dehydrohalogenation: Tertiary > Secondary > Primary
- (ii) Action of heat:

$$R$$
— $CH_2CH_2X \xrightarrow{573 \text{ K}} R$ — $CH=CH_2$

(I) Hydrolysis with alkalies:

$$RX + AgOH \longrightarrow ROH + AgX$$
(moist)

 $R - X \xrightarrow{\text{aq.}} R - OH + KX$

(ii) Williamson's synthesis:

 $R - X + \text{NaOR'} \xrightarrow{\text{Heat}} ROR' + \text{NaX}$

(iii)
$$R - X + KCN \xrightarrow{alc.} KX + RCN$$

(iv) $R - X + AgCN \xrightarrow{C_2H_5OH/H_2O} R - N \stackrel{\supseteq}{\longrightarrow} C$

$$\begin{array}{c} H_3O^* \\ \hline conc. \ HCl \end{array} \longrightarrow RCONH_2 \xrightarrow{H_3O^*} \hline conc. \ HCl \\ \hline RCOOH + NH_3 \\ \hline Na/C_2H_5OH \\ \hline or \ LiAlH_4 \\ \hline SnCl_2/HCl \longrightarrow R - CH_2NH_2 \\ \hline \downarrow H_3O^* \\ \hline R-CHO + NH_4Cl \\ \hline \end{array}$$