HALOGEN DERIVATIVES

Class XII

CONCEPT MAP

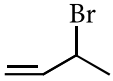
The substitution of chlorine atoms into a molecule of alkane results in a compound with anaesthetic properties *e.g.*, chloroform. Increasing the number of chlorine atoms in the compounds increases the depth of anaesthesia given but also increases toxicity. C–F bonds are very stable so their presence 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

When C—*X* carbon is sp^3 hybridised.

Allylic

C=C–C–*X*

e.g., 

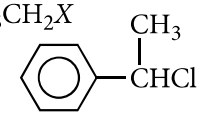
Alkyl

$C_nH_{2n+1}X$

e.g., $CH_3CH_2CH_2Cl$

Benzylic

$C_6H_5CH_2X$

e.g., 

When C—*X* carbon is sp^2 hybridised.

Vinylic

C=C–*X*

e.g., CH_2=CH–Cl

Aryl

Halogen is directly attached to the carbon atom of aromatic ring, *e.g.*, C_6H_5Cl

Methods of Preparation

(i) Direct halogenation of alkanes:

Free radical mechanism:

$R-H + X_2 \xrightarrow{h\nu} R-X + HX$

Reactivity order:

Allylic > 3° > 2° > 1° > CH_4

(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:

$3R-OH + PX_3 \rightarrow 3R-X + H_3PO_3$

$R-OH + HX \longrightarrow R-X + H_2O$

$R-OH + SOCl_2 \longrightarrow RCl + SO_2\uparrow + HCl\uparrow$

[Darzen's method]

(iv) Hunsdiecker reaction:

$RCOOAg + Br_2 \xrightarrow[\text{reflux}]{CCl_4} R-Br + CO_2 + AgBr$

(v) Finkelstein reaction:

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

Uses of Some Commercially Important Halogen Derivatives

(i) Chloroform ($CHCl_3$):
- 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 (CHI_3):
- 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, etc.

(iv) DDT:
- Used as a powerful insecticide.
- Effective against *Anopheles* mosquitoes which spread malaria.

(v) Teflon ($-CF_2-CF_2-)_n$:
- Used as non-stick coating for pans and other cookwares.
- Used in containers and pipework for corrosive chemicals.

Chemical Properties

Elimination Reactions

(i) Dehydrohalogenation:

$R-CH_2-CH_2-X \xrightarrow{\text{alc. KOH}} R-CH=CH_2$

- Elimination follows the Saytzeff's rule.
- Ease of dehydrohalogenation:

Tertiary > Secondary > Primary

(ii) Action of heat:

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

Nucleophilic Substitution Reactions

S_N1
- First order kinetics
- Reactivity: 3° > 2° > 1° > CH_3X

S_N2
- Second order kinetics
- Reactivity: CH_3X > 1° > 2° > 3°

(I) Hydrolysis with alkalies:

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

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

(ii) Williamson's synthesis:

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

(iii) $R-X + KCN \xrightarrow{\text{alc.}} KX + RCN \xrightarrow[\text{conc. HCl}]{H_3O^+} RCONH_2 \xrightarrow[\text{conc. HCl}]{H_3O^+} RCOOH + NH_3$

$RCN \xrightarrow[\text{or } LiAlH_4]{Na/C_2H_5OH} R-CH_2NH_2$

$RCN \xrightarrow{SnCl_2/HCl} R-CH=NH\cdot HCl \xrightarrow{H_3O^+} R-CHO + NH_4Cl$

(iv) $R-X + AgCN \xrightarrow[\Delta]{C_2H_5OH/H_2O} R-N\cong C$

Miscellaneous Reactions

(i) Reduction:

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

(ii) Wurtz reaction:

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

(iii) Reaction with metals:

$R-X + Mg \xrightarrow{\text{Dry ether}} R-MgX$ (Powder) (Grignard reagent)

$2R-X + 2Zn \xrightarrow{\text{Ether}} R_2Zn + ZnX_2$

$4C_2H_5Br + 4Pb/Na \xrightarrow{\text{Dry ether}} (C_2H_5)_4Pb + 4NaBr + 3Pb$

sod. lead alloy — Tetraethyl lead

(iv) Corey-House reaction:

$R_2CuLi + R'X \longrightarrow R-R' + R-Cu + LiX$

(This reaction can be used to prepare unsymmetrical alkanes.)

(v) Oxidation:

$R-CH_2X \xrightarrow{DMSO} R-\overset{O}{\overset{\|}{C}}-H$ (1° Alkyl halide → Aldehyde)

$R-\overset{X}{\overset{|}{C}}H-R \xrightarrow{DMSO} R-\overset{O}{\overset{\|}{C}}-R$ (2° Alkyl halide → Ketone)