HALOGEN DERIVATIVES

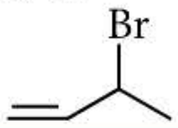
Class XII

CONCEPT MAP

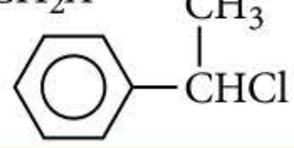
The substitution of chlorine atoms into a molecule of alkane results in a compound with anaesthetic properties *e.g.*, chloroform. Increasing the number of chlorine atoms in the compounds increases the depth of anaesthesia given but also increases toxicity. C–F bonds are very stable so their presence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

(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

$$R-\underset{X}{\underset{|}{CH}}-R \xrightarrow{DMSO} R-\overset{O}{\overset{\|}{C}}-R$$

2° Alkyl halide — Ketone

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

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

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

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

Miscellaneous Reactions