CONCEPT MAP

HALOALKANES AND HALOARENES

Halogen Derivatives
Obtained by replacing one or more H-atoms of hydrocarbons.

Haloalkanes

Properties

Physical

- Water insoluble
- **M.P. and B.P. :** R–I > R–Br > R–Cl > R–F
- B.P. ∝ alkyl part size
- B.P. ∝ 1/branching
- **Bond strength :** CH_3–Cl > CH_3–F > CH_3–Br > CH_3–I
- **Stability of –X bond :** R—F > R–Cl > R–Br > R–I

Chemical

- Highly reactive undergoes.

Nucleophilic Substitution Reaction

S_N1 : I order reaction :

- Rate ∝ [substrate]
- Proceeds via carbonium ion formation.
- In 2 steps, I → formation of carbonium ion (slow → rate determining), II → Attack of nucleophile.
- Racemic mixture obtained.
- Most favourable substrate → 3° alkyl halide.

S_N2 : II order reaction :

- Rate ∝ [alkylhalide] [nucleophile]
- Converted reaction (in 1 step).
- Inversion of configuration occurs (walden inversion),
- Most favourable substrate → 1° alkyl halide.
- Favoured in non-polar solvent.

Elimination Reaction

E1 : In 2 steps.

- Reactivity of alkyl halides 3° > 2° > 1°

E2 : In 1 steps.

- via transition state.
- Favourable → 1° alkyl halide.

Optical Isomerism

Substances which can rotate the plane of polarized light → optically active.
Dextrorotatory (+) → rotates towards right.
Laevorotatory (–) → rotates towards left.

Haloarenes

Properties

Physical

- B.P. iodoarenes > bromoarenes > chloroarenes > fluoroarenes.
  B.P. isomeric dihalobenzenes → nearly same.
  M.P. of isomeric dihalobenzenes → $p > o > m$

Chemical

- Low reactivity due to lesser polar character.
- C–X bond acquires some double bond character and hence stronger.
- Presence of e^- withdrawing groups such as –NO_2, –CN etc. at o– and p– positions w.r.t. halogen → activates the halogen towards nucleophilic displacement.
- Halogen atom is slightly deactivating and o, p–directing (p-product usually predominates).

$$R\text{–}X + Mg \xrightarrow{\text{dry ether}} R\text{–}Mg\text{–}X \text{ Grignard's reagent}$$

$$R\text{–}X + NaCN \xrightarrow[\Delta]{C_2H_5OH\text{–}H_2O} R\text{–}CN{\equiv}C$$

$$AgCN \longrightarrow R\text{–}N{\equiv}C$$

$$R\text{–}I + AgNO_2 \xrightarrow[-AgI]{\text{Alcohol}, \Delta} \underset{\text{Alkyl nitrite}}{RONO} + \underset{\text{Nitro alkane}}{RNO_2}$$

$$R\text{–}X + R'ONa \longrightarrow ROR' + NaX$$

Polyhalogen Compounds

Dihalogens
Combounds with two halogen atoms

- **Vicinal dihalides**
  Both halogen atoms on different atoms
- **Geminal dihalides**
  Both halogen atoms on same carbon atom

Trihalogens
Compounds with three halogen atoms *e.g.* $CHCl_3$, CHI_3

Chlorofluorocarbons

- Freons
  Polychlorofluoro alkanes - CCl_2F_2, $C_2Cl_2F_4$
- Perfluoro carbons (PFC)
  C_nF_{2n+2}, CF_4, C_2F_6
- BHC
  Gammexane C_6H_6Cl