

HALOGEN DERIVATIVES

Class XII

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.

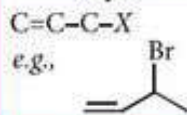
CONCEPT MAP

When C—X carbon is sp^3 hybridised.

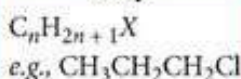
Halogen Derivatives

When C—X carbon is sp^2 hybridised.

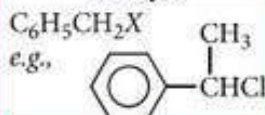
Allylic



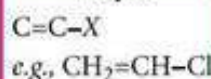
Alkyl



Benzylic



Vinyllic



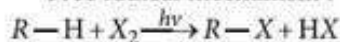
Aryl

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

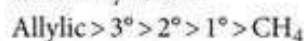
Methods of Preparation

(i) Direct halogenation of alkanes:

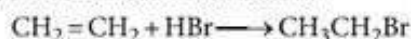
Free radical mechanism:



Reactivity order:



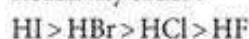
(ii) Addition of HX to alkenes:



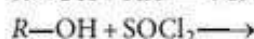
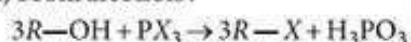
- Unsymmetrical alkenes follow Markovnikov's rule during electrophilic addition.

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

Reactivity order:

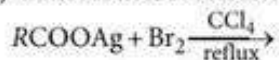


(iii) From alcohols:

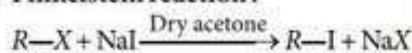


[Darzen's method]

(iv) Hunsdiecker reaction:



(v) Finkelstein reaction:



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.

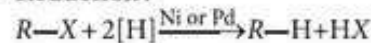
(iv) DDT:

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

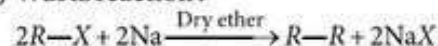
(v) Teflon ($-CF_2-CF_2-$)_n:

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

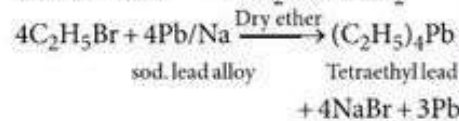
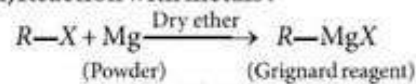
(i) Reduction:



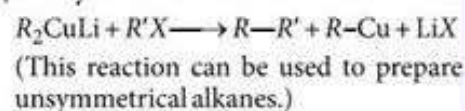
(ii) Wurtz reaction:



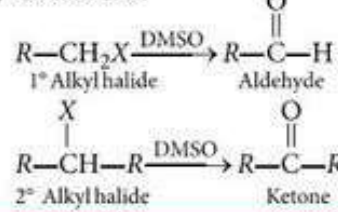
(iii) Reaction with metals:



(iv) Corey-House reaction:



(v) Oxidation:



Chemical Properties

Elimination Reactions

S_N1

- First order kinetics
- Reactivity: $3^\circ > 2^\circ > 1^\circ > CH_3X$

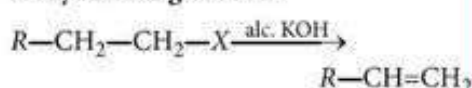
Nucleophilic Substitution Reactions

Miscellaneous Reactions

S_N2

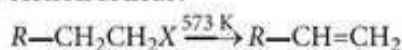
- Second order kinetics
- Reactivity: $CH_3X > 1^\circ > 2^\circ > 3^\circ$

(i) Dehydrohalogenation:

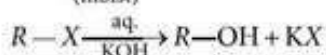


- Elimination follows the Saytzeff's rule.
- Ease of dehydrohalogenation: Tertiary > Secondary > Primary

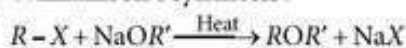
(ii) Action of heat:



(I) Hydrolysis with alkalis:



(ii) Williamson's synthesis:



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

