CHEMISTRY OF FUNCTIONAL GROUP-I

Halogen Compounds

→ Replacement of a H atom from alkane by halogen gives alkyl halide

→ classified as 1°, 2° & 3° - based on whether halogen is attached to 1° carbon, 2° carbon etc

(1°)

$CH_3-CH_2-CH_2-CH_2-Cl$

n-butyl chloride

1-chlorobutane

(1°)

$CH_3-CH(CH_3)-CH_2-Cl$

Isobutyl chloride

1-chloro-2-methylpropane

(2°)

$CH_3-CH(Cl)-CH_2-CH_3$

sec-butyl chloride

2-chlorobutane

(3°)

$CH_3-C(CH_3)_2-Cl$

Tert-butyl chloride

2-chloro-2-methyl-propane

Preparation:

(A) From alkanes by radical halogenation

Order of reactivity of halogens in halogenation is

$$F_2 > Cl_2 > Br_2 > I_2$$

① Chlorination

Alkane react with Cl_2 either in presence of UV light / upon heating at 250–400°C

$$CH_4 + Cl_2 \xrightarrow[(or\ 250^\circ C)]{Light} CH_3-Cl + HCl$$

Chloromethane

$$CH_3-CH_3 + Cl_2 \xrightarrow[(or\ 250^\circ C)]{Light} CH_3-CH_2-Cl + HCl$$

Chloroethane

→ Extent of chlorination depend upon the amount of Cl_2 used. If sufficient Cl_2 is taken, instead of monochloro derivative successive replacement of H atoms by Cl atoms occur.

Eg:

$$CH_4 + Cl_2 \xrightarrow[(or\ \Delta)]{UV\ light} CH_3Cl + HCl$$

Chloromethane

$$CH_3Cl + Cl_2 \longrightarrow CH_2Cl_2 + HCl$$

Dichloromethane

$$CH_2Cl_2 + Cl_2 \longrightarrow CHCl_3 + HCl$$

Trichloromethane (chloroform)

$$CHCl_3 + Cl_2 \longrightarrow CCl_4 + HCl$$

Tetrachloromethane
(Carbon tetrachloride)

→ Chlorination of higher alkanes yield isomeric product

Eg $CH_3-CH_2-CH_3 \xrightarrow[\text{Light}]{Cl_2} CH_3-CH_2-CH_2-Cl + CH_3-\underset{Cl}{CH}-CH_3$

1-chloropropane (45%) 2-chloropropane (55%)

$CH_3-CH_2-CH_2-CH_3 \xrightarrow[\text{Light}]{Cl_2} CH_3-CH_2-CH_2-CH_2-Cl +$

1-chlorobutane (72%)

$CH_3-\underset{Cl}{CH}-CH_2-CH_3$

2-chlorobutane (28%)

(2) Bromination

Br_2 react with alkanes either in presence of UV light or at 250-400°C

$CH_4 + Br_2 \xrightarrow[(\text{or } \Delta)]{\text{Light}} CH_3Br + HBr$

Bromomethane

$CH_3-CH_3 + Br_2 \xrightarrow[(\text{or } \Delta)]{h\nu} CH_3-CH_2Br + HBr$

Bromoethane

(3) From Alkenes

A halogen acid, HX (HCl, HBr or HI) adds to an alkene to yield the corresponding alkyl halide

$CH_2 = CH_2 + HBr \longrightarrow CH_3 - CH_2 - Br$

Ethyl bromide

$CH_3 - CH = CH - CH_3 + HI \longrightarrow CH_3 - CH_2 - \underset{I}{CH} - CH_3$

2- Iodobutane

Markownikoff's rule

→ Addition of HX to an unsymmetrical alkene takes place by this rule

"The rule states that, the addition of an unsymmetrical reagent to an unsymmetrical alkene, the +ve part of the adding molecule goes to that carbon atom which bears the greater number of H atoms"

Eg: $CH_3 - CH = CH_2 + HCl \longrightarrow CH_3 - \underset{Cl}{CH} - CH_3$

Propene

2- chloropropane

$CH_3 - \underset{CH_3}{C} = CH_2 + HCl \longrightarrow CH_3 - \underset{Br}{\overset{CH_3}{C}} - CH_3$

2-methyl propene

2-Bromo-2-methyl propane

Order of reactivity of HX for a given alkene

$HCl < HBr < HI$

→ The addition of HBr (not HCl or HI) to an unsymmetrical alkene in the presence of a peroxide occurs by "anti-markownikoff's addition" is known as peroxide effect or Kharasch effect

Eg: $CH_3-CH=CH_2 + HBr \xrightarrow{\text{Benzoyl peroxide}} CH_3-CH_2-CH_2-Br$

1-Bromopropane

Reactions of alkyl halides

① Nucleophilic Substitution Reactions

→ Attacking reagent is a nucleophile

→ Alkyl halides undergo this reaction because the greater electronegativity of the halogen makes the C-X bond polar & C atom acquire partial +ve charge & hence nucleophile is attacked.

$$Nu^{(-)} + -\overset{|}{\underset{|}{C}}-\overset{\delta+}{}\overset{\delta-}{X} \longrightarrow -\overset{|}{\underset{|}{C}}-Nu + X^{(-)}$$

Nucleophile — Alkyl halide — Product — leaving group

Eg:

* Substitution of halogen by:

① By hydroxyl group – Action of aq. alkali or moist silver oxide (formation of alcohols)

$$R-X + KOH \xrightarrow{\Delta} R-OH + KX$$

$$R-X + AgOH \xrightarrow{\Delta} R-OH + AgX$$

Eg: $CH_3-I + KOH \xrightarrow{\Delta} CH_3-OH + AgI$

$$CH_3-CH_2-Br + AgOH \xrightarrow{\Delta} CH_3CH_2OH + AgBr$$

② By alkoxy group – Action of sodium/potassium alkoxide or dry silver oxide (formation of ethers)

(a) Williamson's synthesis

$$R-X + NaOR' \xrightarrow{\Delta} R-O-R' + NaX$$

Ether

Eg: $CH_3-Br + NaOCH_3 \xrightarrow{\Delta} CH_3-O-CH_3 + NaBr$

Methoxymethane

$$C_2H_5-I + NaOCH_3 \xrightarrow[-NaI]{\Delta} CH_3-CH_2-O-CH_3$$

Methoxyethane

(IV) : Alkyl halide are heated with sodium/potassium alkoxide, ethers are obtained

(b) When heated with dry silver oxide

$$R-X + Ag_2O \xrightarrow{\Delta} ROR + 2AgX$$

$$CH_3-I + Ag_2O + CH_3-I \xrightarrow{\Delta} CH_3OCH_3 + 2AgI$$

(3) By cyano group — Action of alcoholic KCN

(formation of alkyl cyanide or alkanenitriles) ~~alkyl nit~~

$$R-X + KCN \xrightarrow[\Delta]{\text{Alcohol}} R-CN + KX$$

$$CH_3CH_2-Br + KCN \xrightarrow[\Delta]{\text{Alcohol}} CH_3CH_2CN + KBr$$

Propanenitrile
(Ethyl cyanide)

(4) By Isocyanide group — Action of Alcoholic AgCN

(formation of alkyl isocyanide or alkylcarbylamine)

$$R-X + AgCN \xrightarrow[\Delta]{\text{Alcohol}} R-CN + AgX$$

$$CH_3-I + AgCN \xrightarrow[\Delta]{\text{Alcohol}} CH_3-CN + AgI$$

Methyl Isocyanide
(Methyl carbylamine)

nitrile

⑤ By nitrito group – Action of alcoholic KNO_2

(formation of alkyl nitrites)

$$R-X + KNO_2 \xrightarrow[\Delta]{\text{Alcohol}} R-O-NO + KX$$

$$CH_3CH_2-Br + KNO_2 \xrightarrow[\Delta]{\text{Alcohol}} CH_3CH_2-O-NO + KBr$$

Ethyl nitrite

⑥ By nitro group – Action of alcoholic $AgNO_2$

(formation of nitroalkanes)

$$R-X + AgNO_2 \xrightarrow[\Delta]{\text{Alcohol}} R-NO_2 + AgX$$

Nitroalkane

$$CH_3CH_2I + AgNO_2 \xrightarrow[\Delta]{\text{Alcohol}} CH_3-CH_2-NO_2 + AgI$$

Nitroethane

⑦ By carboxylate group – Action of alcoholic solution of silver salt of fatty acids

(formation of esters)

$$R'-COOAg + X-R \xrightarrow[\Delta]{\text{Alcoholic}} R'-COO-R + AgX$$

$$CH_3COOAg + BrC_2H_5 \xrightarrow[\Delta]{\text{Alcohol}} CH_3COOCH_2CH_3 + AgBr$$

Ethyl acetate

⑧ By alkynyl group – Action of sodium alkynide (formation of higher alkynes)

$$R-X + Na\,C\equiv C-R' \longrightarrow R-C\equiv C-R' + NaX$$

Alkyne

$$CH_3-I + Na\,C\equiv C-H \longrightarrow CH_3-C\equiv C-H + NaI$$

Propyne

⑨ By amino group – Action of alcoholic NH_3 (formation of amines)

$$R-X + HNH_2 \xrightarrow[\text{Pressure}]{\text{Alcohol},\ \Delta} R-NH_2 \xrightarrow[-HX]{R-X} R_2NH \xrightarrow[-HX]{R-X} R_3N \xrightarrow{R-X} R_4N^+X^-$$

$R-NH_2$: 1° amine; R_2NH: 2° amine; R_3N: 3° amine; $R_4N^+X^-$: Quaternary salt

$$CH_3-Br + HNH_2 \xrightarrow[\text{Pressure}]{\text{Alcohol},\ \Delta} CH_3-NH_2 \xrightarrow[-HBr]{CH_3Br} (CH_3)_2NH \xrightarrow[-HBr]{CH_3Br} (CH_3)_3N \xrightarrow{CH_3Br} (CH_3)_4N^+Br^-$$

CH_3-NH_2: Methanamine; $(CH_3)_2NH$: N-methyl methanimine; $(CH_3)_3N$: N,N-dimethyl methanamine; $(CH_3)_4N^+Br^-$: Tetramethyl ammonium bromide