General methods of preparation of Alkyl Halides.

(1) From alkanes

(i) By halogenation: $\underset{\text{Ethane}}{C_2H_6}$ (Excess) + $Cl_2 \xrightarrow{hv} \underset{\text{Ethyl chloride (Major product)}}{C_2H_5Cl} + HCl$

$$\underset{\text{Propane}}{CH_3CH_2CH_3} \xrightarrow[UV\ light]{Cl_2} \underset{1-\text{Chloroprop ane (45\%)}}{CH_3CH_2CH_2Cl} + \underset{\underset{\text{2- Chloroprop ane (55\%)}}{Cl}}{CH_3\overset{|}{C}HCH_3}$$

This reaction proceed through free radical mechanism.

Note: Order of reactivity of X_2 for a given alkane is, $F_2 > Cl_2 > Br_2 > I_2$.

The reactivity of the alkanes follows the order : 3°alkane > 2°alkane > 1°alkane.

(ii) With sulphurylchloride: $R-H + SO_2Cl_2 \xrightarrow[Organic\ peroxide\ (R'CO_2)_2]{hv} R-Cl + SO_2 + HCl$

Note: In presence of light and trace of an organic peroxide the reaction is fast.

(2) From alkenes (Hydrohalogenation)

$$\underset{\text{But}-2-\text{ene}}{CH_3-CH=CH-CH_3} + HBr \longrightarrow CH_3CH_2-\underset{\underset{\text{2-Bromobutan e}}{Br}}{\overset{|}{C}H}-CH_3 \longrightarrow \text{Electrophillic addition.}$$

Note: Addition of HBr to alkene in the presence of organic peroxide take place due to peroxide effect or Kharasch's effect.

This addition take place by two mechanism,

Peroxide initiates free radical mechanism.

Markownikoff's addition by electrophillic mechanism.

From alkyne we cannot obtain mono alkyl halide.

The order of reactivity of halogen acids is, $HI > HBr > HCl$.

(3) From alcohols

(i) By the action of halogen acids

Groove's process $\underset{\text{Alcohol}}{R-OH} + H-X \xrightarrow[300\,^{\circ}C]{Anhy.\,ZnCl_2} \underset{\text{Haloalkane}}{RX} + H_2O$

Note: The reactivity order of HX in the above reaction is : $HI > HBr > HCl > HF$.

Reactivity order of alcohols $3^{\circ} > 2^{\circ} > 1^{\circ} > MeOH$.

2° and 3° alcohols undergo SN^1 ; where as 1° and MeOH undergo SN^2 mechanism.

Concentrated HCl + anhy. $ZnCl_2$ is known as lucas reagent.

(ii) Using PCl_5 and PCl_3 : $CH_3CH_2OH + \underset{\substack{\text{Phosphorus}\\\text{pentachlor ide}}}{PCl_5} \longrightarrow \underset{\text{Chloroetha ne}}{CH_3CH_2Cl} + \underset{\substack{\text{Phosphorus}\\\text{Oxychlorid e}}}{POCl_3} + HCl$

$3CH_3CH_2OH + PCl_3 \longrightarrow 3\underset{\text{Chloroetha ne}}{CH_3CH_2Cl} + \underset{\text{Phosphorus acid}}{H_3PO_3}$

Note: Bromine and iodine derivatives cannot be obtain from the above reaction, because PBr_5 or PI_5 are unstable.

This method gives good yield of primary alkyl halides but poor yields of secondary and tertiary alkyl halides.

(iii) By the action of thionyl chloride

(Darzan's process) $CH_3CH_2OH + SOCl_2 \xrightarrow{\text{Pyridine}} CH_3CH_2Cl + SO_2 + HCl$

Note: Reaction takes place through SN^2 mechanism.

(4) From silver salt of carboxylic acids (Hunsdiecker reaction, Decarboxylation)

(Free radical mechanism) $R-\underset{\underset{O}{\|}}{C}-O-Ag + Br-Br \xrightarrow[\text{Decarboxyl ation}]{CCl_4} R-Br + CO_2 \uparrow + AgBr \downarrow$

Note: The reactivity of alkyl group is $1° > 2° > 3°$

Not suitable for chlorination because yield is poor.

In this reaction iodine forms ester instead of alkyl halide and the reaction is called Birnbourn-Simoninireaction, $2R-COOAg + I_2 \longrightarrow RCOOR' + 2CO_2 + 2AgI$.

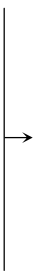
(5) From alkyl halide (Halide exchange method): $R-X + NaI \xrightarrow[\text{Reflux}]{\text{Acetone}} R-I + NaX (X = Cl, Br)$

Note: Alkyl fluorides cannot be prepared by this method. They can be obtained from corresponding chlorides by the action of Hg_2F_2 or antimony trifluoride.

$2CH_3Cl + Hg_2F_2 \rightarrow \underset{\text{Methyl fluoride}}{2CH_3F} + Hg_2Cl_2$

(6) Other method

(i) $ROH \xrightarrow{KI, H_3PO_4}$



(ii) $ROH \xrightarrow[\text{Rydon method}]{X_2+(PhO)_3P}$

(iii) Dihalide $\xrightarrow[HCl]{Zn-Cu} R-X$

(iv) $RMgX \xrightarrow{X_2}$

(v) $ROR \xrightarrow{PCl_5}$