Preparations and properties of Dihalides.

- (1) Methods of preparation of dihalides
- (i) Methods of preparation of gemdihalide
- (a) From alkyne (Hydrohalogenation) :

$$R - C \equiv C - H + HX \xrightarrow{R} R - C = C - H \xrightarrow{+HX} R - C = C - H \xrightarrow{+HX} R - C = C - CH_{3}$$

(b) From carbonyl compound: $RCHO + PCl_5 \longrightarrow RCHCl_2 + POCl_3$ [Terminal dihalide]

Note: If ketone is taken internal dihalide formed.

- (ii) Methods of preparation of vicinal dihalide
- (a) From alkene [By halogenation] : $R CH = CH_2 + Cl_2 \longrightarrow R CH CH_2$

(b) From vicinal glycol:
$$\begin{array}{c} R - CH - OH \\ | \\ CH_2 - OH \end{array} + 2PCl_5 \longrightarrow \begin{array}{c} R - CH - Cl \\ | \\ CH_2 - Cl \end{array} + 2HCl + 2POCl_3 \end{array}$$

 \mathbf{v}

(2) Properties of dihalides

(i) Physical properties

(a) Dihalide are colourless with pleasant smell liquid. Insoluble in water, soluble in organic solvent.

- (b) M.P and B.P \propto -molecular mass.
- (c) Reactivity of vicinal dihalides > Gem dihalide.
- (ii) Chemical properties of dihalide

(a) Reaction with aqueous KOH:
$$RCHX_2 + 2KOH(aq.) \xrightarrow{-KX} RCH(OH)_2 \xrightarrow{-H_2O} RCHO$$

(b) Reaction with alcoholic KOH: $RCH_2 - CHX_2 \xrightarrow{\text{Alc.KOH}} R - \stackrel{H}{C} = \stackrel{X}{C} - H \xrightarrow[-(NaX + NH_3)]{} R - C \equiv CH$

(c) Reaction with Zn dust

Gem halide (di) form higer symmetrical alkene.

□ Vicinal dihalide form respective alkene.

(d) Reaction with KCN: $R - CHX_2 + 2KCN \xrightarrow{-2KX} RCH(CN)_2 \xrightarrow{H_3O^{\oplus}} RCH(COOH)_2$

(e) Other substitution reaction

$$\Box_{L}^{CH_2-X} \xrightarrow{NH_3/373 K} CH_2-NH_2 \\
 CH_2-X \xrightarrow{H_3/373 K} CH_2-NH_2 \\
 CH_2-X \xrightarrow{CH_2-NH_2} CH_2-OCOCH_3 \\
 CH_2-X \xrightarrow{CH_3COONa} CH_2-OCOCH_3 + 2NaX.$$