HALO ACIDS [α, β, γ]

Preparation:- ① **HVZ Reaction:-** $R CH_2 COOH + X_2 \xrightarrow{Red\ P} R\underset{X\ (Br)}{\underset{|}{CH}}\ COOH$

② **From Acid halide:-**

$R-CH_2-\overset{O}{\overset{\|}{C}}-Cl$ + NBS (N-bromosuccinimide) $\longrightarrow R-\underset{Br}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{H_3O^{\oplus}}$

③ **From alkyl malonic acid:-**

$R-CH(COOH)_2 + Br_2 \longrightarrow R-\underset{Br}{\underset{|}{C}}(COOH)_2 \xrightarrow{\Delta} R-\underset{Br}{\underset{|}{CH}}-COOH + CO_2$

④ **From unsaturated aldehyde:-**

$R CH=CH CHO + HX \longrightarrow R\underset{X}{\underset{|}{CH}}-CH_2CHO \xrightarrow[[O]]{Conc.\ HNO_3} R-\underset{H}{\underset{|}{\overset{Br}{\overset{|}{C}}}}-CH_2COOH$

$R-\underset{\beta}{\underset{|}{\overset{I}{\overset{|}{CH}}}}-\underset{\alpha}{CH_2}\underset{O}{COOH}$ (β-haloacid)

⑤ **From α, β-unsaturated acid**

$R CH=CH COOH + HX \xrightarrow{CH_3COOH} R-\underset{X}{\underset{|}{CH}}\ CH_2\ COOH$ [β-haloacid]

⑥ **Action of Sulphuryl chloride (SO_2Cl_2) on carboxylic acid**

$CH_3CH_2COOH + 2\,SO_2Cl_2 \xrightarrow{I_2} CH_3-\underset{Cl}{\underset{|}{CH}}-COCl + 2SO_2 + 2HCl$

$CH_3-\underset{Cl}{\underset{|}{CH}}-COOH + HCl \xleftarrow{H_2O,\ Boil} CH_3-\underset{Cl}{\underset{|}{CH}}-COOH$

⑦ **By the action of HX or PX_3, PX_5 on α-Hydroxy acid**

$CH_3CH(OH)COOH + HBr \longrightarrow CH_3\underset{Br}{\underset{|}{CH}}\ COOH + H_2O$

⑧ **From alkene cyanohydrin**

$\underset{OH}{\underset{|}{CH_2}}-\underset{CN}{\underset{|}{CH_2}} + 2HBr + H_2O \longrightarrow \underset{Br}{\underset{|}{CH_2}}-\underset{COOH}{\underset{|}{CH_2}} + NH_4Br$

⑨ **From Amino acid**

$R-\underset{NH_2}{\underset{|}{CH}}-COOH \xrightarrow{NOCl} R-\underset{Cl}{\underset{|}{CH}}-COOH + N_2 + H_2O$

Properties of Haloacids

① $R-\underset{CN}{\underset{|}{CH}}-COOH \xrightarrow{H_3O^{\oplus}} R-\underset{COOH}{\underset{|}{CH}}-COOH$

If R = CH_3 then Methyl Malonic acid

$R-\underset{NO_2}{\underset{|}{CH}}-COOH$

$R-\underset{Br}{\underset{|}{CH}}-COOH \xrightarrow{NaCN\ or\ KCN} R-\underset{CN}{\underset{|}{CH}}-COOH \xrightarrow{H_3O^{\oplus}} R-\underset{COOH}{\underset{|}{CH}}-COOH$

$R-\underset{Br}{\underset{|}{CH}}-COOH \xrightarrow{AgNO_2} R-\underset{NO_2}{\underset{|}{CH}}-COOH$

$R-\underset{Br}{\underset{|}{CH}}-COOH \xrightarrow{AgOH\ or\ NaOH} R-\underset{OH}{\underset{|}{CH}}-COOH$ [If $R = CH_3$, Lactic acid]

$R-\underset{Br}{\underset{|}{CH}}-COOH \xrightarrow{NaI} R-\underset{I}{\underset{|}{CH}}-COOH$

$R-\underset{Br}{\underset{|}{CH}}-COOH \xrightarrow{HNH_2\ (2)} R-\underset{NH_2}{\underset{|}{CH}}-COOH$ (Amino acid) $+ NH_4Br$

[If $R = CH_3$, = Alanine]

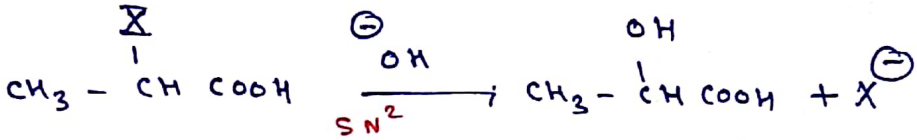
If $R = C_6H_5$ ✓ mandelic acid

$Cl-\underset{Cl}{\underset{|}{C}}-\overset{O}{\overset{\|}{C}}-O-H \xrightarrow{-H^{\oplus}} Cl-\underset{Cl}{\underset{|}{C}}-\overset{O}{\overset{\|}{C}}-O^{\ominus} \xrightarrow{-CO_2} Cl-\underset{Cl}{\underset{|}{\overset{Cl}{\overset{|}{C}}}}:^{\ominus} \xrightarrow{H^{\oplus}} CHCl_3$

HALO ACIDS

Action of alkali on α, β, γ- & δ- Halo acid

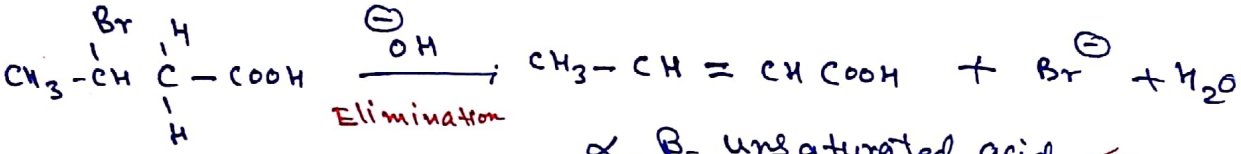
1- α- Halo acid



Lactic acid

α-hydroxy acid

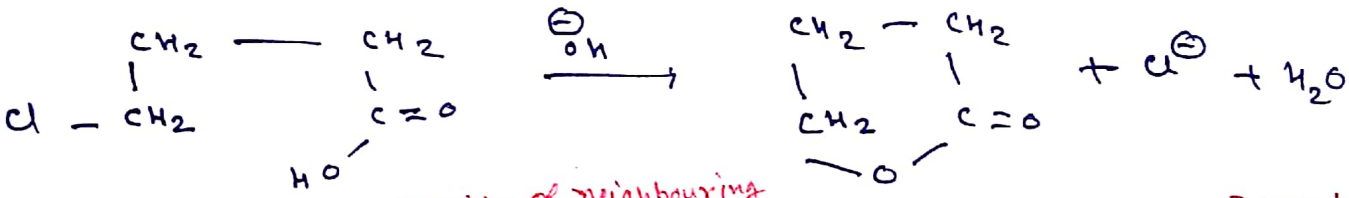
2- β- Halo acid



α, β- unsaturated acid

[crotonic acid]

3- γ and δ- Halo acid



This reaction is an example of neighbouring group participation.

γ- Butyrolactone [5 membered ring = Stable]

∴ In some cases, the β- Halo acids for internal ester (lactones). ex–