Methods of Preparation of Monocarboxylic acid.

(1) **By oxidation of alcohols, aldehydes and ketones**

$$\underset{\text{alcohol}}{RCH_2OH} \xrightarrow[K_2Cr_2O_7]{[O]} RCHO \xrightarrow[K_2Cr_2O_7]{[O]} \underset{\text{Carboxylic acid}}{RCOOH}$$

$$\underset{\text{Aldehyde}}{RCHO} \xrightarrow{[O]} RCOOH$$

Ketones and secondary alcohols form acid with fewer carbon atoms.

$$\underset{\text{Sec. Alcohol}}{\begin{matrix} R \\ R'CH_2 \end{matrix}} CHOH \xrightarrow{[O]} \boxed{C=O} \xrightarrow[H_2SO_4]{K_2Cr_2O_7} RCOOH + R'COOH$$

Note:❑Aldehyde can be oxidized to carboxylic acid with mild oxidizing agents such as ammonical silver nitrate solution $[Ag_2O \text{ or } Ag(NH_3)_2^+OH^-]$

❑Methanoic acid cannot be prepared by oxidation method.

❑ Ketones can be oxidized under drastic conditions using strong oxidizing agent like $K_2Cr_2O_7$.

❑ Methyl ketones can also be converted to carboxylic acid through the haloform reaction.

$$R-\underset{\underset{O}{\|}}{C}-CH_3 + 3I_2 + 3NaOH \xrightarrow[H_2O]{\Delta} R-\underset{\underset{O}{\|}}{C}-OH + CHI_3 + 3NaI + 3H_2O$$

(2) **By Hydrolysis of nitriles, ester, anhydrides and acid chloride**

(i) **Hydrolysis of nitriles**

$$R-C\equiv N + HOH \xrightarrow[\text{or } NaOH]{HCl} \left[R-C\begin{matrix} OH \\ NH \end{matrix}\right] \xrightarrow{\text{Rearrangement}} R-C\begin{matrix} O \\ NH_2 \end{matrix} \xrightarrow[HCl]{H_2O} RCOOH + NH_4Cl$$

(ii) **Hydrolysis of Esters:** $\underset{\text{Ester}}{RCOOR'} + HOH \xrightarrow[OH^-]{HCl} \underset{\text{Acid}}{RCOOH} + \underset{\text{Alcohol}}{R'OH}$

(iii) **Hydrolysis of Anhydrides:** $\underset{\text{Ethanoic anhydride}}{\begin{matrix} CH_3-\overset{\overset{O}{\|}}{C} \\ CH_3-\underset{\underset{O}{\|}}{C} \end{matrix}} O + HOH \xrightarrow{H^+/OH^-} \underset{\text{Ethanoic acid}}{2CH_3COOH}$

(iv) **Hydrolysis of acid chloride and nitro alkane**

$$R-\underset{\underset{O}{\|}}{C}-Cl+HOH \xrightarrow{H^+/OH^-} RCOOH + HCl$$

$$R-CH_2-NO_2 \xrightarrow{85\%H_2SO_4} RCOOH$$

(v) **Hydrolysis of Trihalogen:**

$$R-C\begin{matrix}X\\X\\X\end{matrix} + 3NaOH \rightarrow \left[R-C\begin{matrix}OH\\OH\\OH\end{matrix}\right] \xrightarrow{-H_2O} R-C\begin{matrix}O\\OH\end{matrix} + 3NaX$$

(3) **From Grignard Reagent**

$$O=C=O + \overset{\delta-\delta+}{RMgX} \xrightarrow{\text{Dry ether}} R-\overset{\overset{O}{\|}}{C}-OMgX \xrightarrow{H^+/H_2O} RCOOH + Mg(OH)X$$

$(R = CH_3, C_2H_5, (CH_3)_2CH-, (CH_3)_3C-$

(4) **From Alkene or Hydro-carboxy-addition (koch reaction)**

When a mixture of alkene, carbon monoxide and steam is heated under pressure at 350°C in presence of phosphoric acid (H_3PO_4) monocarboxylic acid is formed.

$$CH_2=CH_2 + CO + H_2O \xrightarrow[\substack{500-1000\ atm\\ \&350\,^\circ C}]{H_3PO_4} CH_3CH_2COOH$$

Mechanism:

(i) $C=C + H^+ \rightarrow -C\overset{\oplus}{C}-$ (Carbocation)

(ii) $-\overset{H}{\overset{|}{C}}-\overset{+}{C}- \xrightarrow{C\equiv O} -\overset{H}{\overset{|}{C}}-C(-C\equiv O^{\oplus}) \xrightarrow[-H^{\oplus}]{H_2O}$ (Acyl cation)

$-\overset{H}{\overset{|}{C}}-\overset{OH}{\overset{|}{C}}=O$ (Carboxylic acid)

(5) **Special Methods**

(i) **Carboxylation of sodium alkoxide:** $\underset{\text{Sod. alkoxide}}{RONa} + CO \rightarrow \underset{\text{Sod. salt}}{RCOONa} \xrightarrow{HCl} \underset{\text{Acid}}{RCOOH}$

(ii) **Action of heat on dicarboxylic acid:** $\underset{\text{Substitute d malonic acid}}{R-CH\begin{matrix}COOH\\COOH\end{matrix}} \xrightarrow[\text{heat}]{-CO_2} \underset{\text{Monocarbox ylic acid}}{R-CH_2COOH}$

(iii) **From Acetoacetic ester:** $\begin{matrix}CH_3CO & CHRCO & OC_2H_5\\ OH & H & OH \quad H\end{matrix} \xrightarrow{\text{Hydrolysis}} \begin{matrix}CH_3COOH\\ +RCH_2COOH + C_2H_5OH\end{matrix}$

(iv) **Oxidation of alkene and alkyne**

$$\underset{\text{Alkene}}{RCH=CHR'} \xrightarrow[\substack{\text{Hot alkalne}\\ KMnO_4}]{[O]} RCOOH + R'COOH$$

$$\underset{\text{Alkyne}}{R-C\equiv C-R'} \xrightarrow[(ii)H_2O]{(i)O_3} R-COOH + R'COOH$$

(v) **The Arndt-Eistert Synthesis:**

$$R-\underset{\underset{O}{||}}{C}-Cl + CH_2N_2 \rightarrow R-\underset{\underset{O}{||}}{C}-CHN_2 \xrightarrow[Ag_2O]{H_2O} R-CH_2-COOH$$

(vi) **From acid amides:** $\underset{\text{Amide}}{RCONH_2} + H_2O \xrightarrow[\text{or } Alkali]{\text{Acid}} \underset{\text{Acid}}{RCOOH} + NH_3$

$$\underset{\text{Amide}}{RCONH_2} + \underset{\text{Nitrous acid}}{HNO_2} \rightarrow RCOOH + N_2 + H_2O$$