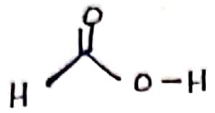
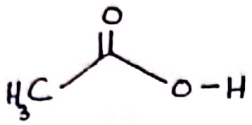
CARBOXYLIC ACID

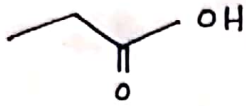
Classification of mono and di carboxylic acids



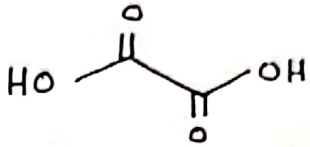
Methanoic acid
(Formic acid)



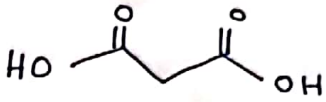
Ethanoic acid
(Acetic acid)



Propanoic acid



Ethane-1,2-dioic acid
(oxalic acid)



Propane-1,3-dioic acid
(Malonic acid)

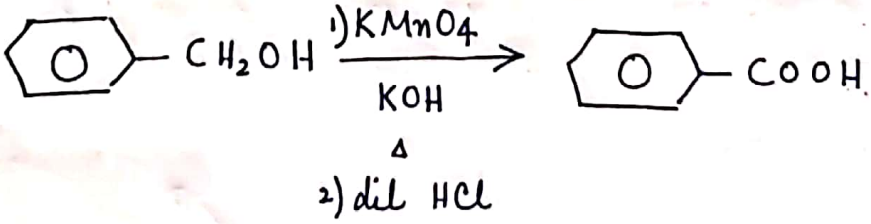
Preparation of aliphatic and aromatic carboxylic acid :-

① From alcohol and aldehyde

By oxidation of primary alcohol and aldehyde

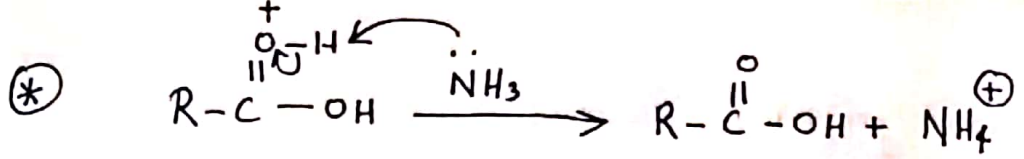
$$RCH_2OH \xrightarrow[H_2SO_4]{K_2Cr_2O_7/} RCHO \xrightarrow[H_2SO_4]{K_2Cr_2O_7/} RCOOH$$

[O] [O]



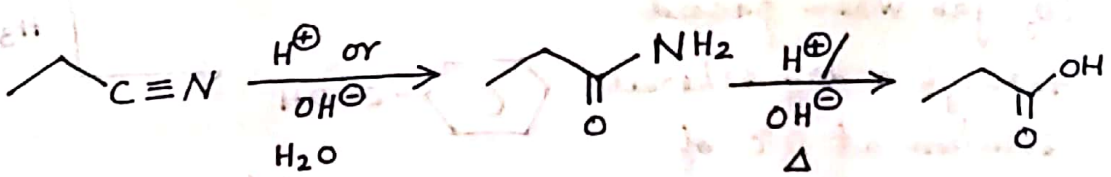
By oxidation of secondary alcohol or ketones

$$R-\underset{\underset{OH}{|}}{CH}-R' \xrightarrow[H_2SO_4]{K_2Cr_2O_7/} R-\underset{\underset{O}{\|}}{C}-R' \xrightarrow[H_2SO_4]{K_2Cr_2O_7/} R-COOH + R''COOH$$



② From nitriles

Nitriles are hydrolysed in acidic or basic medium first to amide and then to acid.

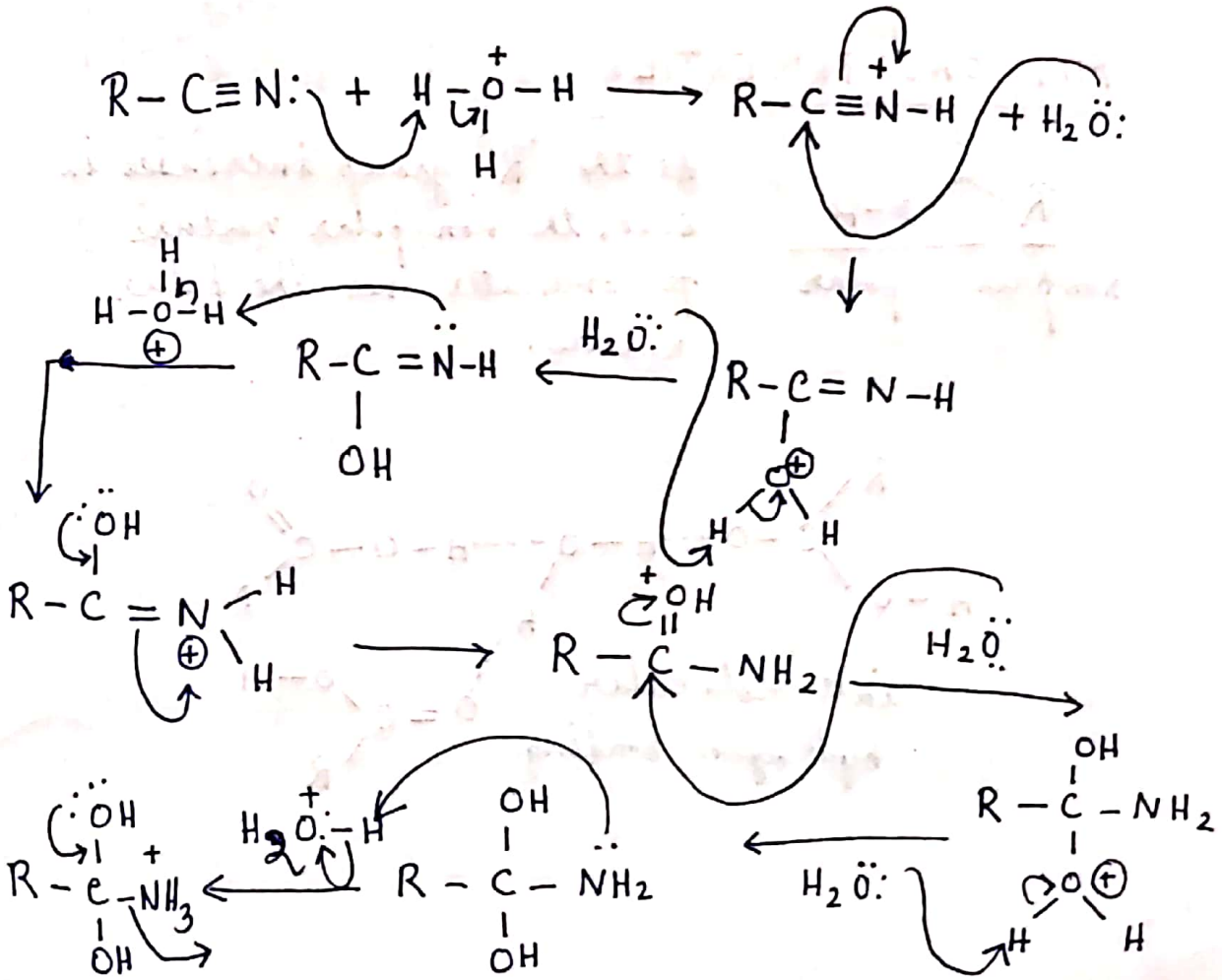


$$R-C\equiv N + 2H_2O \xrightarrow[\Delta]{\text{dil HCl}} RCOOH + NH_4Cl$$

$$R-C\equiv N + H_2O \xrightarrow[\Delta]{\text{dil NaOH}} RCOONa + NH_3\uparrow$$

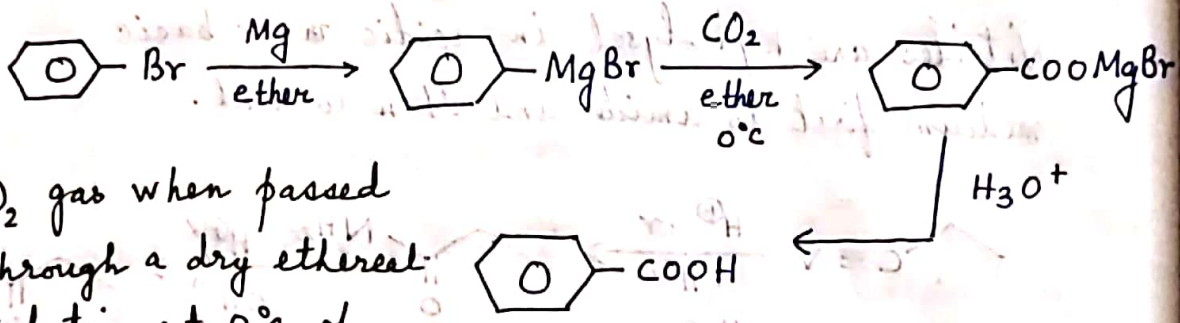
$$\downarrow HCl$$

$$RCOOH + NaCl.$$

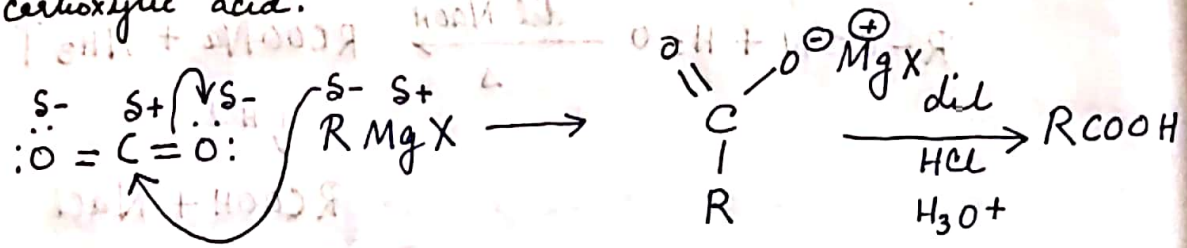


3) From Grignard Reagent

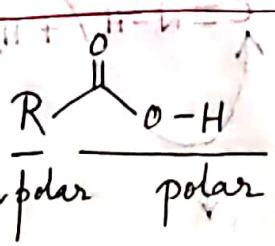
$$CH_3MgBr + CO_2 \xrightarrow[0^\circ c]{\text{dry ether}} CH_3-\underset{\underset{OMgBr}{|}}{\overset{\overset{O}{\|}}{C}} \xrightarrow[HCl]{\text{dil}} CH_3COOH + Mg(OH)Br$$



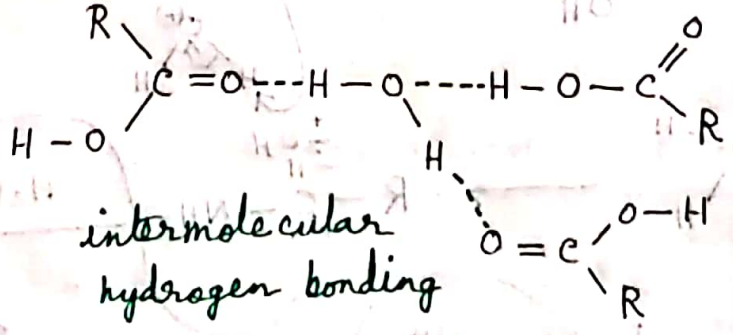
CO_2 gas when passed through a dry ethereal solution at 0°c of Grignard reagent, at first an addition compound is obtained which on hydrolysis will get the carboxylic acid.



PHYSICAL PROPERTIES

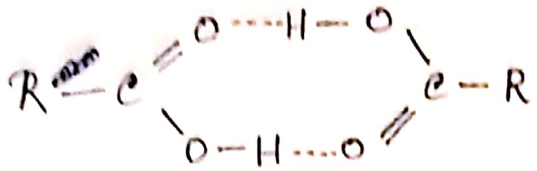


As the 'R' group increases in size, the non-polar nature predominates over the polar nature.

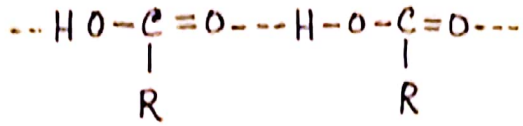


intermolecular hydrogen bonding

Boiling Point



Strong H-bond in cyclic dimer of carboxylic acid (in vapour state and in aprotic solvent)

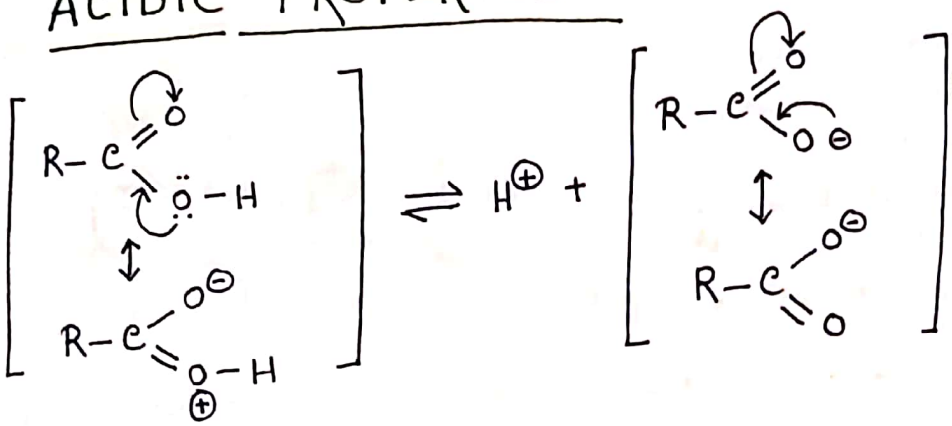


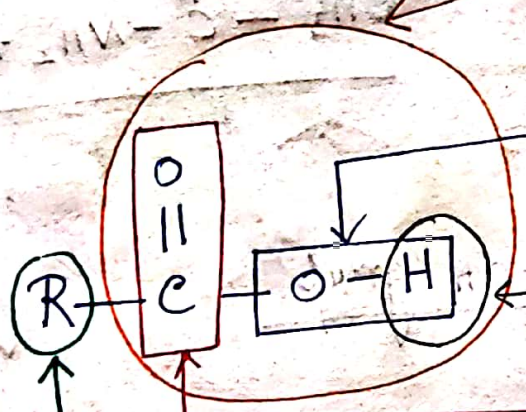
Polymeric form of carboxylic acid in liquid state.

Melting Point

The melting point of an acid containing even number of carbon atoms is higher than the next higher homologue containing odd number of C-atoms.

ACIDIC PROPERTIES





Replacement of the -COOH grp (Decarboxylation Rx^{n}).

Replacement of the -OH grp (Formation of acid derivatives)

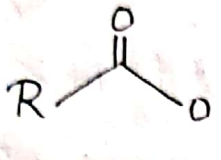
Replacement of the H-atom of the -COOH group (Acidic Property)

Reactions of the carbonyl grp. (Reduction Rx^{n})

Replacement of the H-atom in the 'R' group (HVZ Reaction)

Chemical Properties of Carboxylic acid

1) Substitution of H-atom of carboxylic group



← H-atom of the carboxylic group.

a) $2CH_3COOH + 2Na \longrightarrow 2CH_3COONa + H_2\uparrow$

b) $CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

c) $2CH_3COOH + Na_2CO_3 \rightarrow 2CH_3COONa + H_2O + CO_2\uparrow$

d) $2CH_3COOH + Na_2SO_3 \rightarrow 2CH_3COONa + H_2O + SO_2\uparrow$

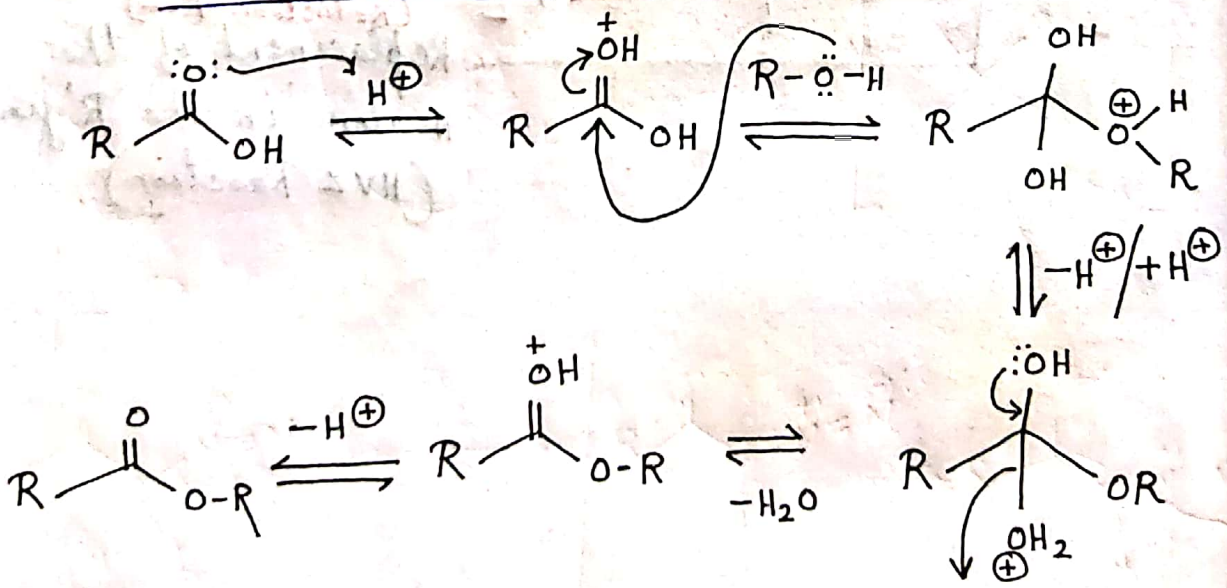
e) $CH_3COOH + NH_3 \longrightarrow CH_3COONH_4$

$\downarrow \Delta$

$CH_3 - \overset{O}{\overset{\|}{C}} - NH_2 + H_2O$

2) Substitution of the -OH group

A) Formation of ester



$$CH_3-\overset{O}{\overset{\|}{C}}\boxed{-O-H+H}-O-C_2H_5 \xrightarrow[H_2SO_4]{conc} CH_3-\overset{O}{\overset{\|}{C}}-O-C_2H_5$$

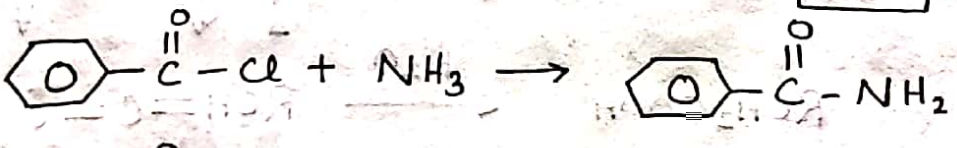
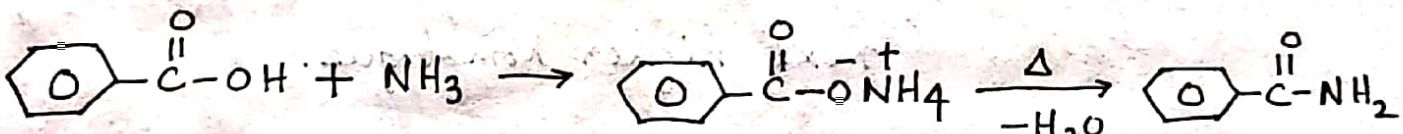
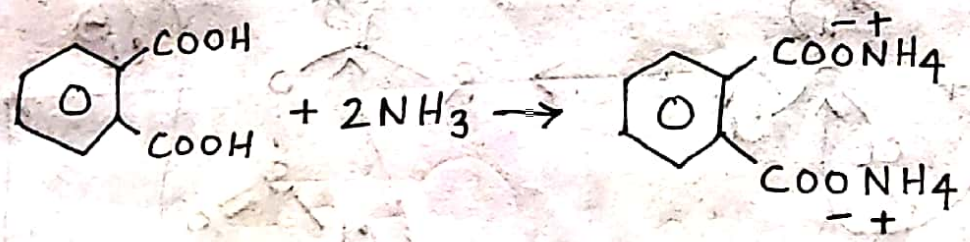
Ethyl acetate

Order of reactivity :-

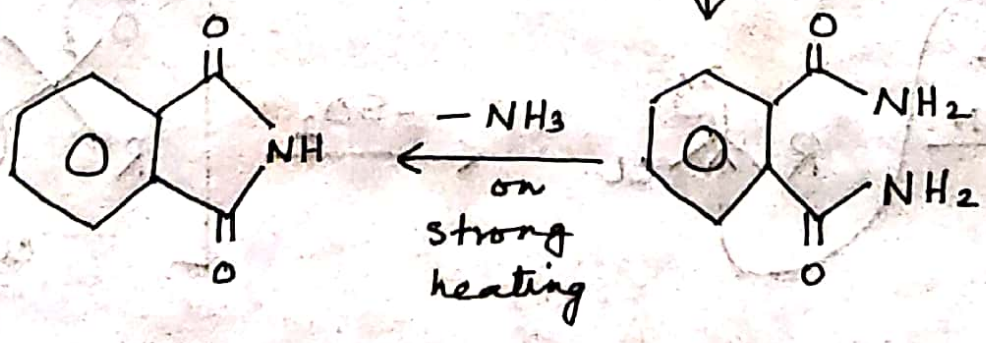
methyl alcohol > 1° alcohol > 2° alcohol > 3° alcohol.

$CH_3COOH > RCH_2COOH > R_2CHCOOH > R_3CCOOH$.

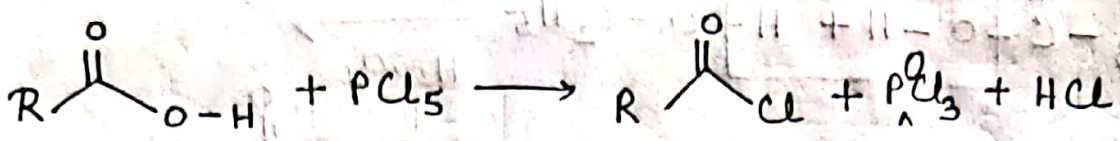
B) Formation of acid amide

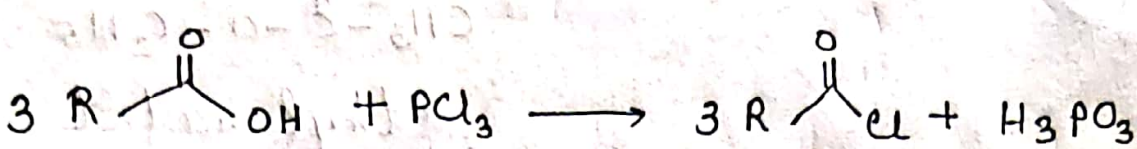
- $RCOOH + NH_3 \longrightarrow RCOONH_4 \xrightarrow{\Delta} RCONH_2 + H_2O$.
- $RCOCl + NH_3 \longrightarrow RCONH_2 + HCl \longrightarrow NH_4Cl$.
- 
- 
- 

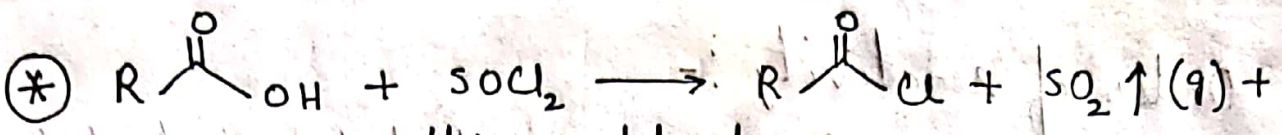
$-2H_2O \downarrow \Delta$



c) Formation of Acid Chloride

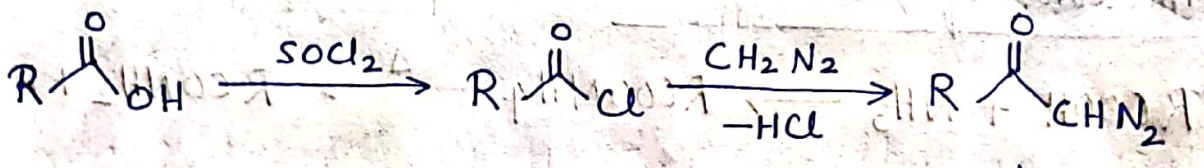




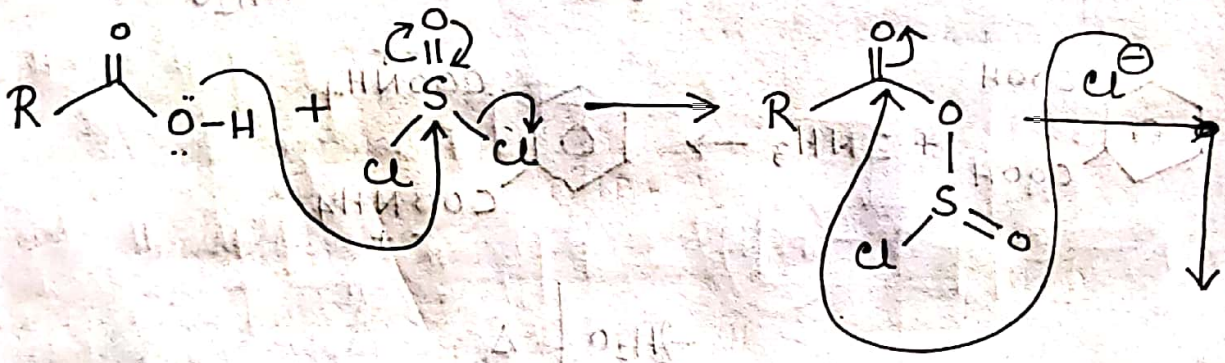
(*) 

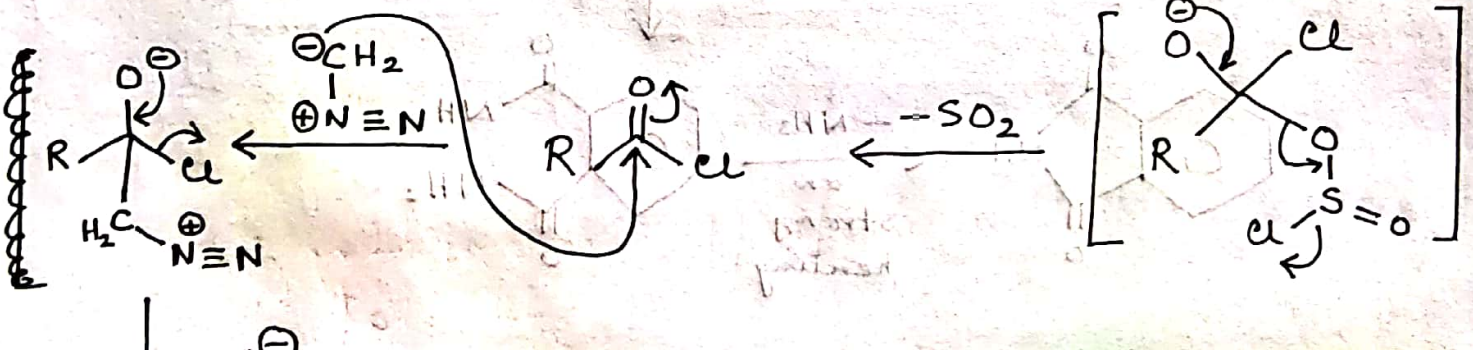
thionyl chloride

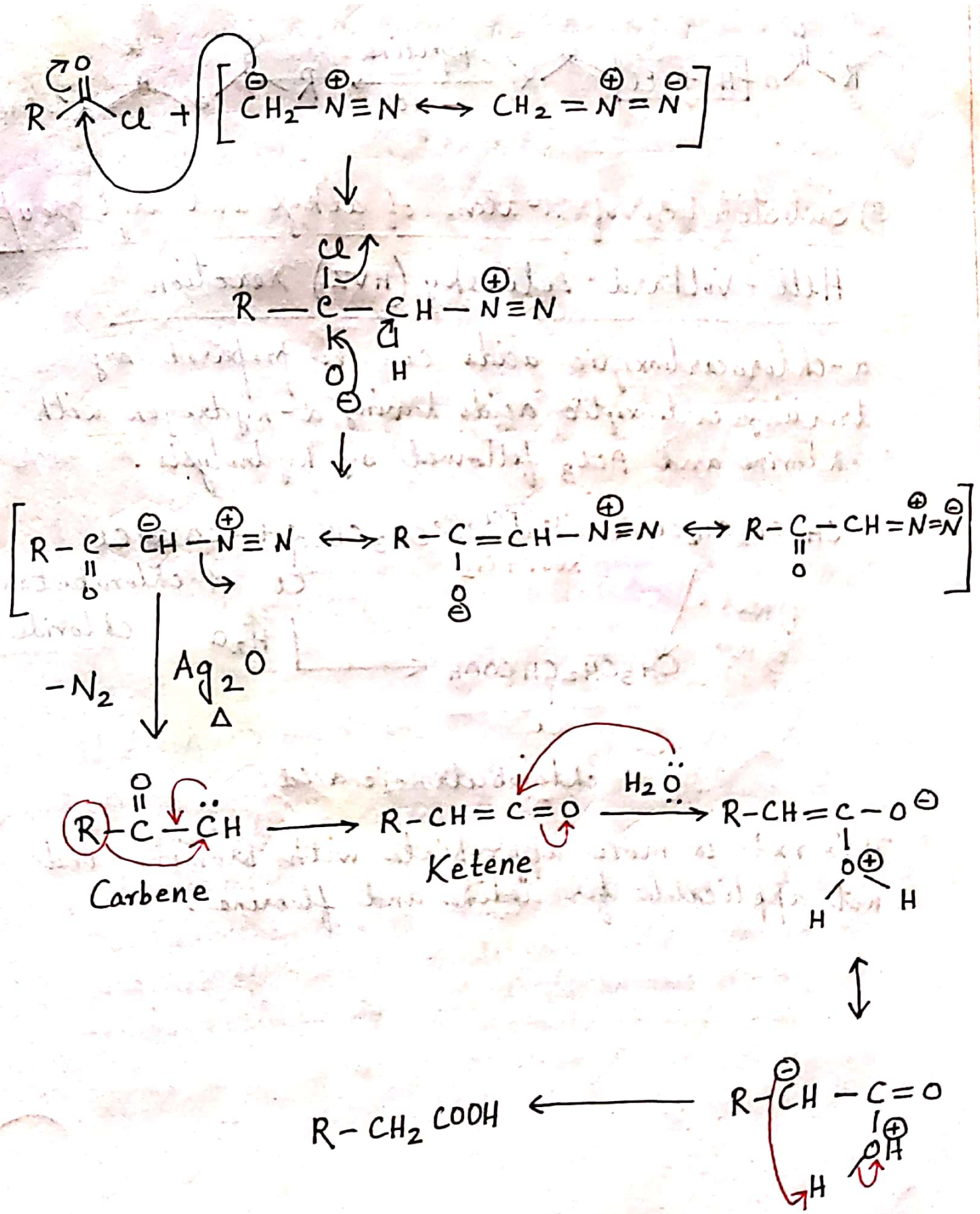
ARNDT-EISTERT SYNTHESIS



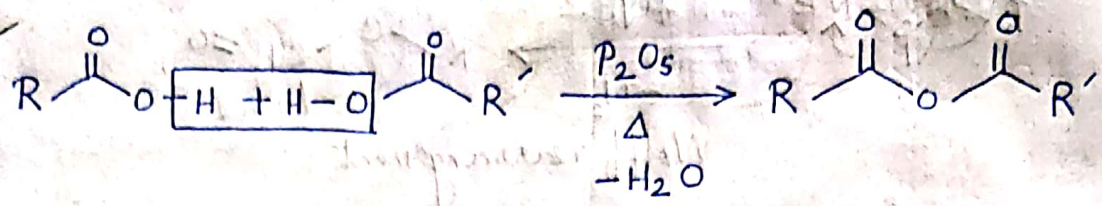
next higher homologue.



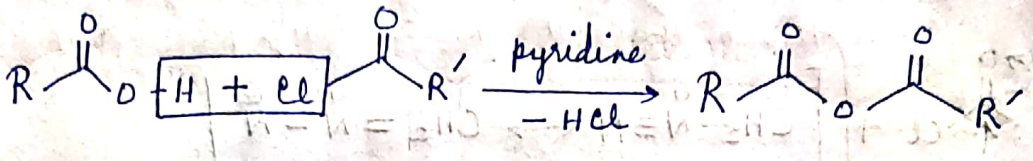




D) Formation of acid anhydride



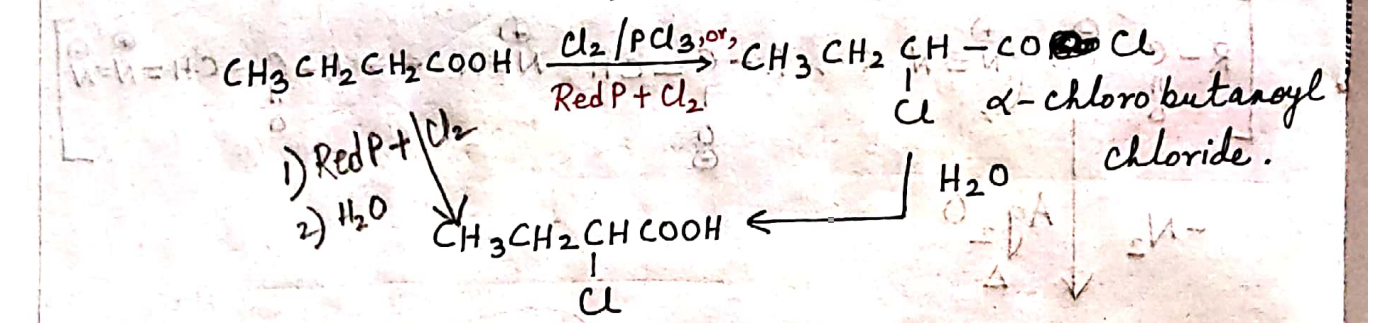
Carboxylic acids also react with acid chloride in presence of pyridine to form acid anhydride.



3) Substitution of H-atom of alkyl and aryl group

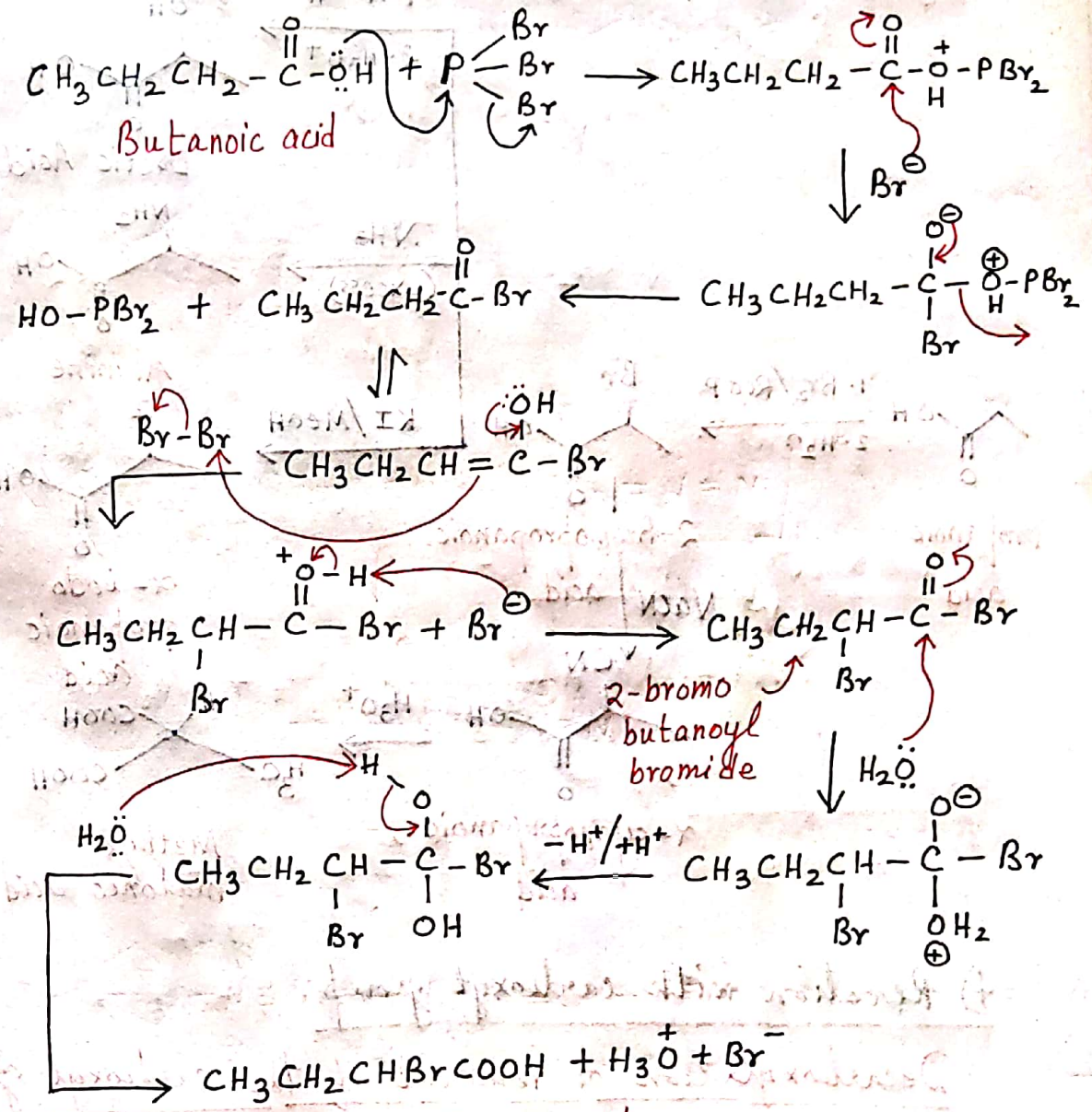
Hell - Volhard - Zelinsky (HVZ) reaction

α-chlorocarboxylic acids can be prepared by treating carboxylic acids having α-hydrogen with chlorine and PCl_3 followed by hydrolysis.



This rxn is more appropiate with bromine and not applicable for iodine and fluorine.

Mechanism :-



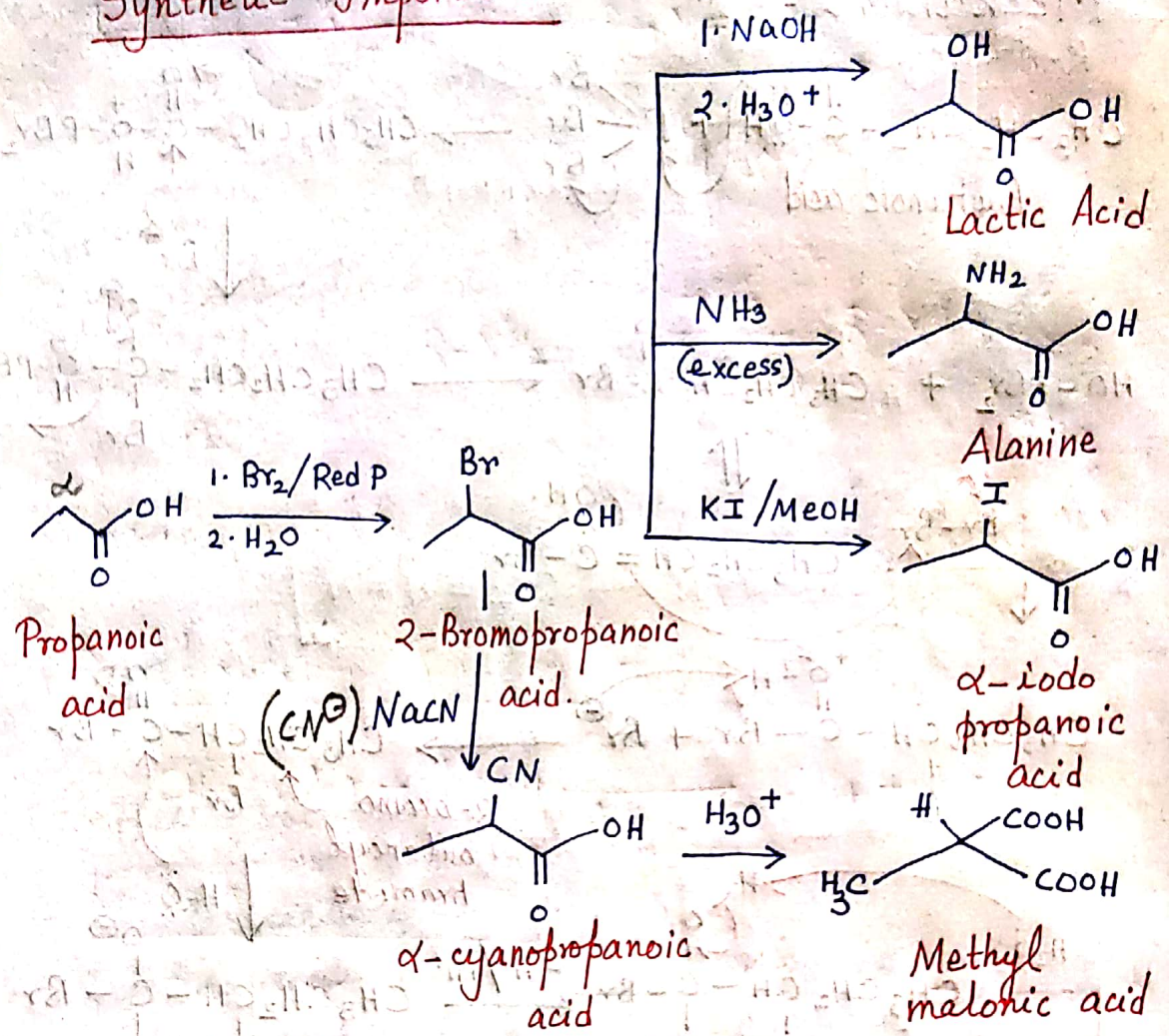
$CH_3CH_2CH_2CHBrCOOH + H_3\overset{+}{O} + Br^-$

2-Bromobutanoic acid.

If there is more than one α-H atom, like in butanoic acid there are 2 α-H atoms, both of them will be replaced to give 2,2-dibromo-butanoic acid.

This reaction can be utilized to detect the presence of α-H in acids since the reaction occurs exclusively with acids having α-H.

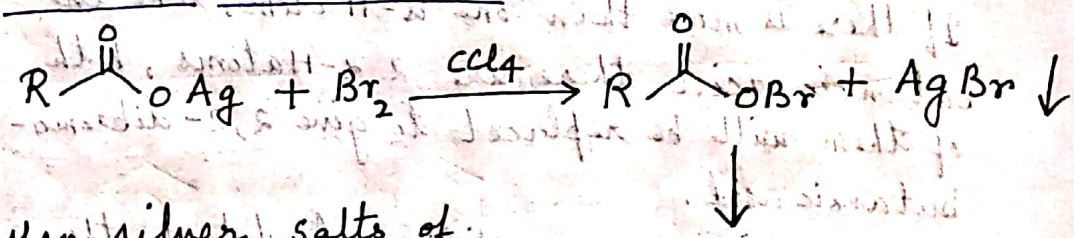
Synthetic Importance



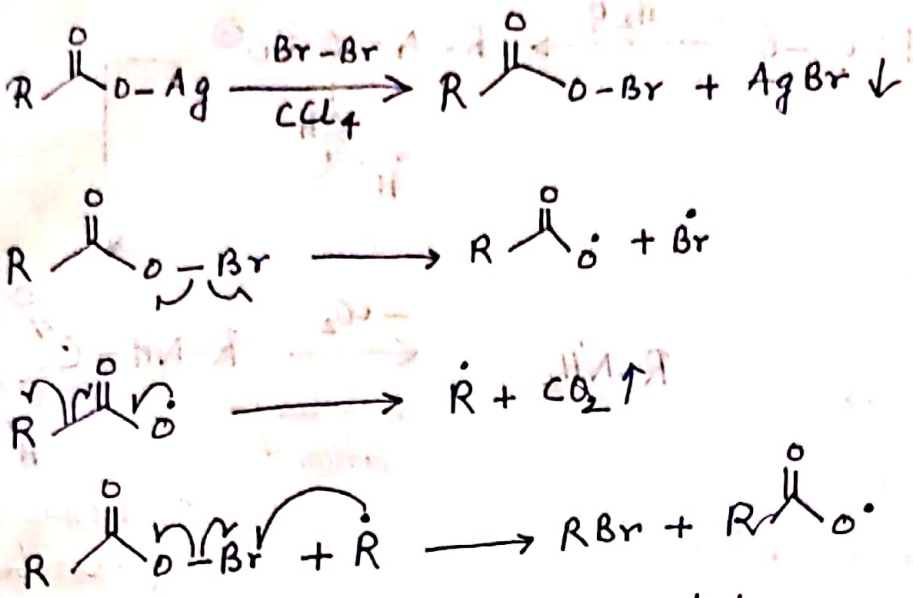
4) Reaction with carboxyl group

Decarboxylation or removal of the carboxyl grp

Hundsdiecker Reaction



When silver salts of carboxylic acids dissolved in carbon tetrachloride are treated with bromine, alkyl or aryl bromides are formed containing one carbon less.



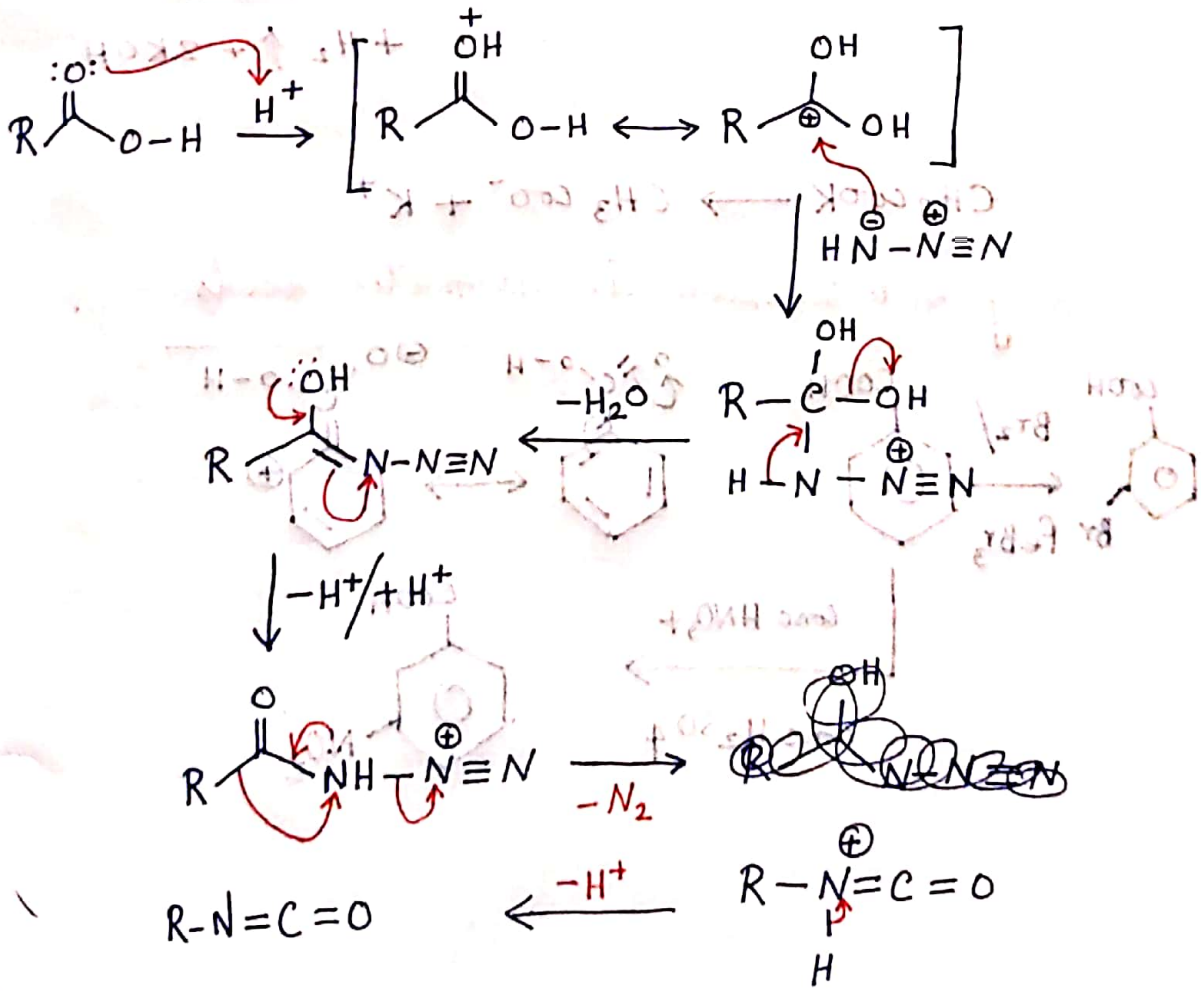
Then, again the steps are repeated.

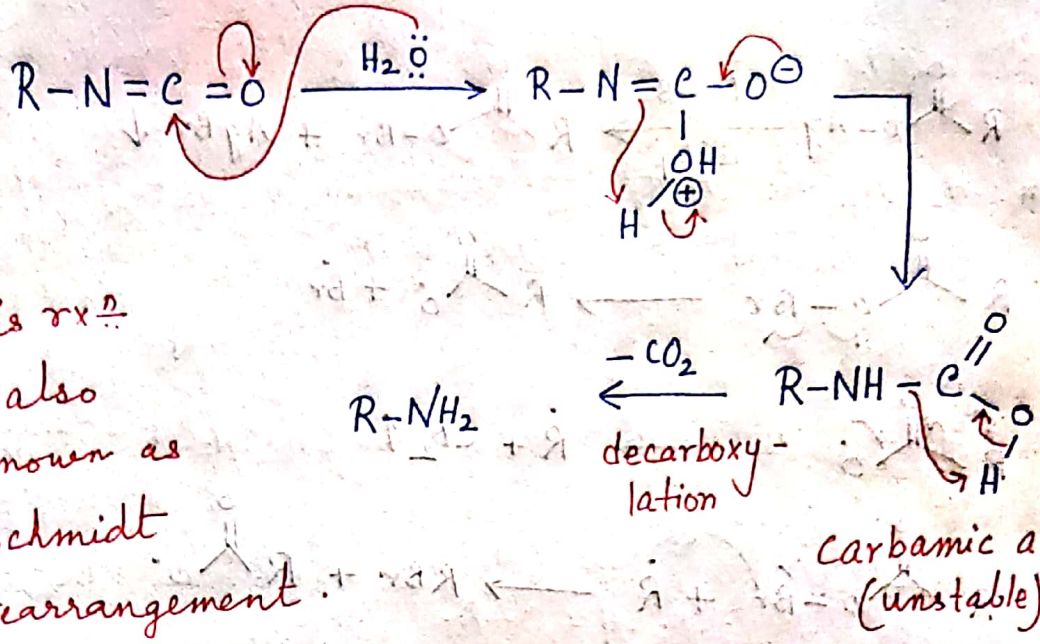
Schmidt Reaction

$$CH_3COOH + HN_3 \xrightarrow[H_2SO_4,\ \Delta]{conc} CH_3NH_2 + CO_2\uparrow + N_2\uparrow$$

hydrazoic acid

Conversion of carboxylic acid to primary amine.





This rxn is also known as Schmidt rearrangement.

Decarboxylation Reaction :-

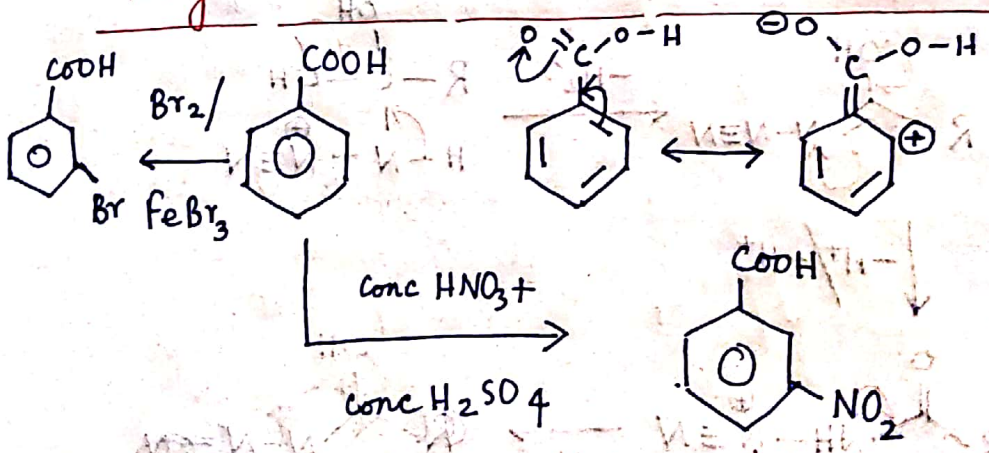
$$CH_3COONa + NaOH \xrightarrow[\Delta]{CaO} CH_4 + Na_2CO_3$$

Kolbe's Electrolysis :-

$$2CH_3COOK + 2H_2O \xrightarrow{\text{electrolysis}} \underset{\text{ethane}}{CH_3-CH_3} + 2CO_2\uparrow + H_2\uparrow + 2KOH$$

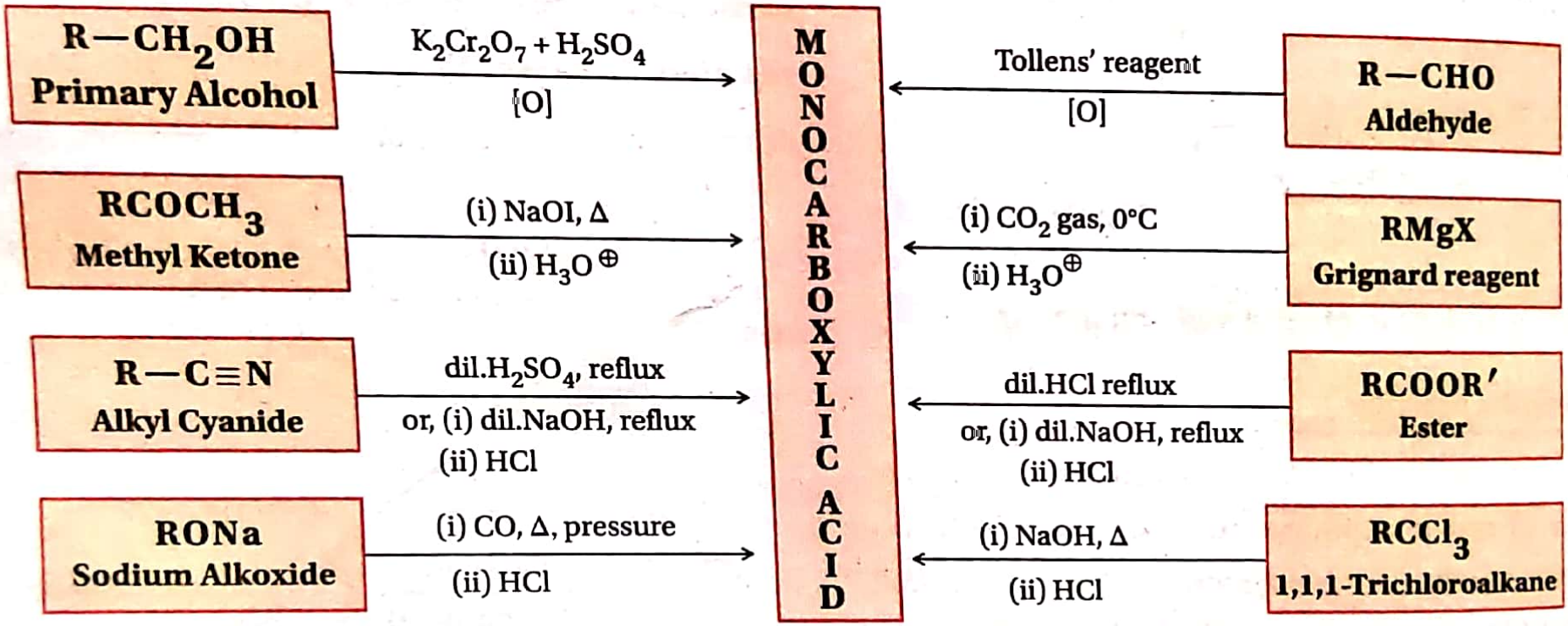
$$CH_3COOK \longrightarrow CH_3COO^- + K^+$$

Ring Substitution in aromatic acids

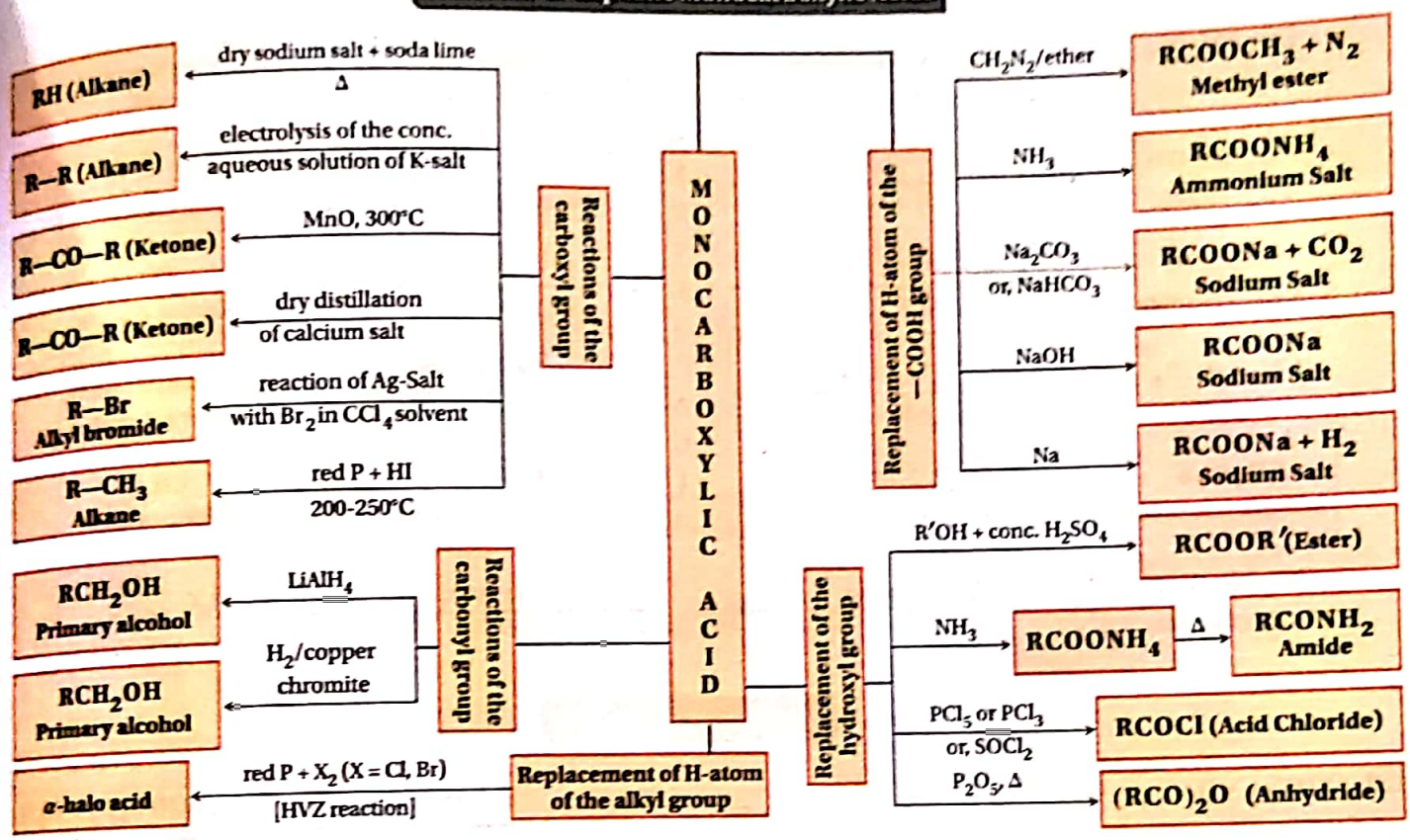


paration & Reactions of Carboxcylic Acids

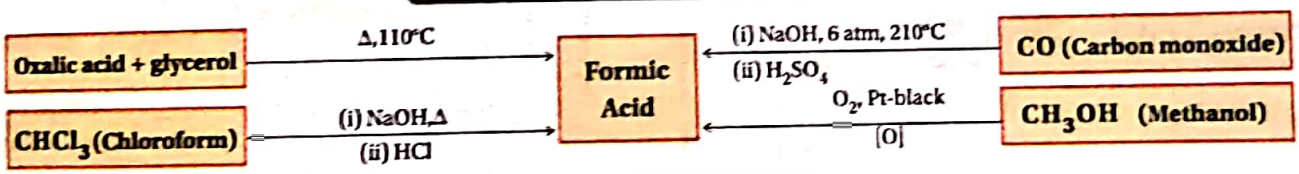
Preparation of Aliphatic Monocarboxylic Acids



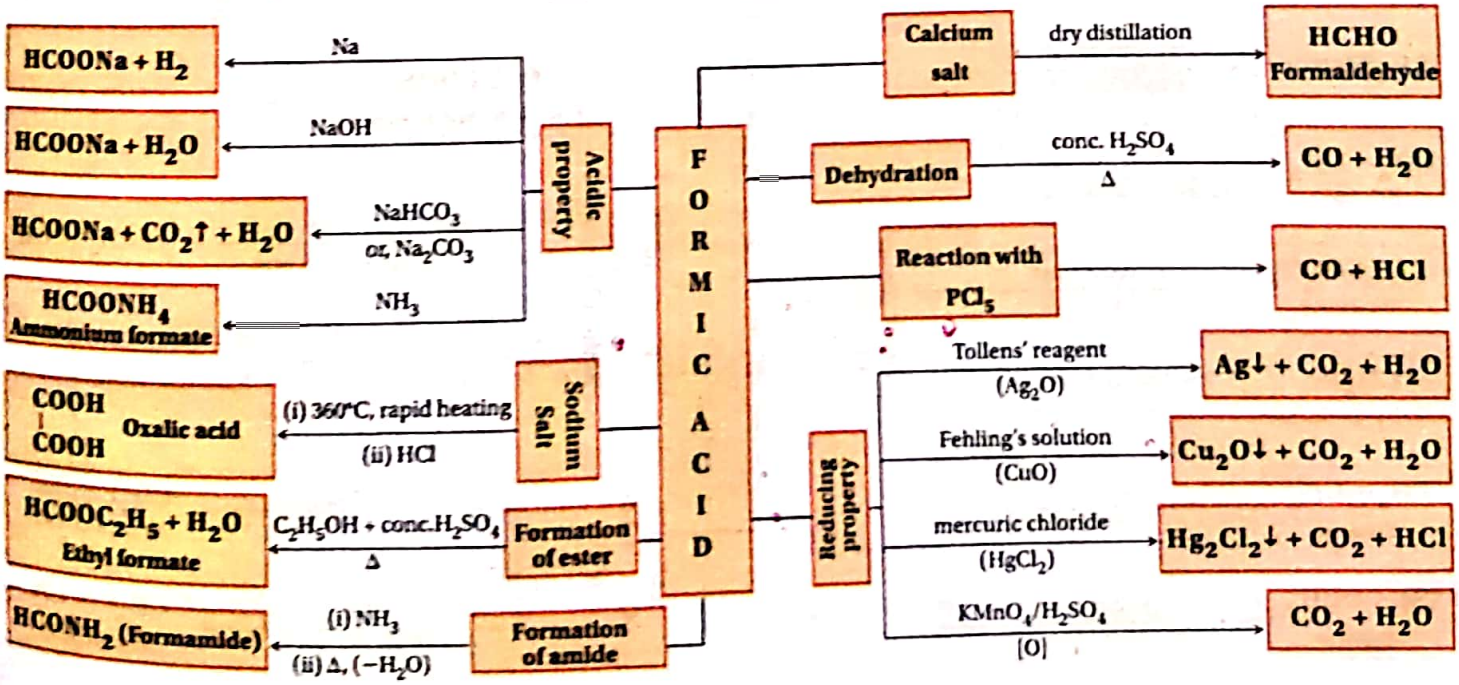
Reactions of Aliphatic Monocarboxylic Acids



Preparation of Formic Acid (HCOOH)



Reactions of Formic Acid



Preparations of Acetic Acid

ACETIC ACID

- CH_3CH_2OH (Ethyl alcohol) → Quick vinegar process (aerobic oxidation in the presence of bacteria)
- CH_3CH_2OH (Ethyl alcohol) → $Na_2Cr_2O_7 + H_2SO_4$ [O]
- CH_3CN (Methyl cyanide) → dil. H_2SO_4, reflux
- CH_3COCH_3 (Acetone) → (i) $NaOH + I_2$, Δ (ii) $H_3O^{\oplus}$
- CH_3ONa (Sodium methoxide) → (i) CO, Δ, pressure (ii) HCl
- $CH_3COOC_2H_5$ (Ethyl acetate) → (i) NaOH, reflux (ii) HCl
- Pyroligneous acid → removal of methanol and acetone
- $HC\equiv CH$ (Acetylene) → (i) 20% H_2SO_4, 1% $HgSO_4$, 60-80°C or O_2, Mn-acetate, 60-70°C
- CO_2 (Carbon dioxide) → (i) CH_3MgI, ether, 0°C (ii) $H_3O^{\oplus}$
- $CH_3CH(OH)CH_3$ (Isopropyl alcohol) → (i) $NaOH + I_2$, Δ (ii) $H_3O^{\oplus}$
- CH_3I (Methyl iodide) → (i) KCN (ii) dil. HCl, reflux
- $H_2C(COOH)_2$ (Malonic acid) → 150-200°C [$-CO_2$]

Reactions of Acetic Acid

ACETIC ACID

Replacement of the H-atom of the —COOH group

- Na → $CH_3COONa + H_2\uparrow$
- NaOH → $CH_3COONa + H_2O$
- $NaHCO_3$ or, Na_2CO_3 → $CH_3COONa + CO_2\uparrow + H_2O$
- NH_3 → CH_3COONH_4
- CH_2N_2/ether → $CH_3COOCH_3 + N_2\uparrow$

Replacement of the hydroxyl group

- C_2H_5OH + conc. H_2SO_4, Δ → $CH_3COOC_2H_5 + H_2O$ (Ethyl acetate)
- NH_3 → CH_3COONH_4 → Δ, ($-H_2O$) → CH_3CONH_2 (Acetamide)
- PCl_5, PCl_3 or, $SOCl_2$ → CH_3COCl (Acetyl chloride)
- P_2O_5, Δ → $CH_3CO-O-COCH_3$ (Acetic anhydride)

Reactions of the carboxyl group

- dry sodium salt + soda lime, Δ → CH_4 (Methane)
- electrolysis of aqueous solution of K-salt → CH_3-CH_3 (Ethane)
- dry distillation of the Ca-salt → CH_3COCH_3 (Acetone)
- reaction of Ag-salt with Br_2 in CCl_4 solvent → CH_3Br (Methyl bromide)
- red P + HI, 200-250°C → CH_3-CH_3 (Ethane)
- MnO, 300°C → CH_3COCH_3 (Acetone)

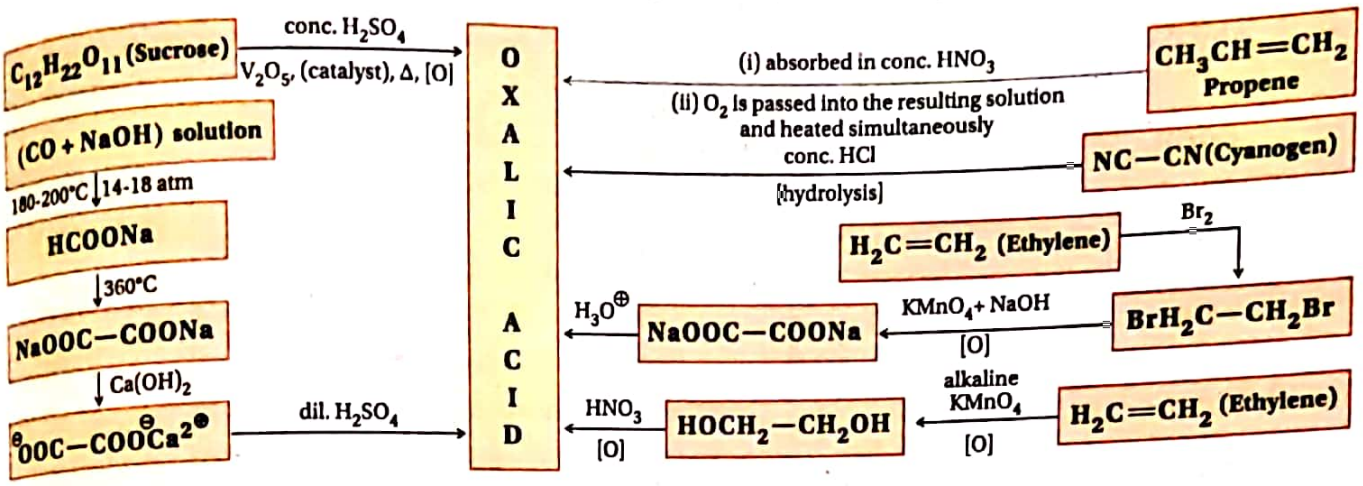
Replacement of H-atom of the alkyl group

- Cl_2 → $CHCl_2COOH$ → Cl_2 → $ClCH_2COOH$ → Cl_2 → CCl_3COOH (Trichloro acetic acid)
- Cl_2 gas is passed through boiling acetic acid → $ClCH_2COOH$
- red P + X_2 (X = Cl, Br) [HVZ reaction] → $X-CH_2-COOH$ (Monohaloacetic acid)

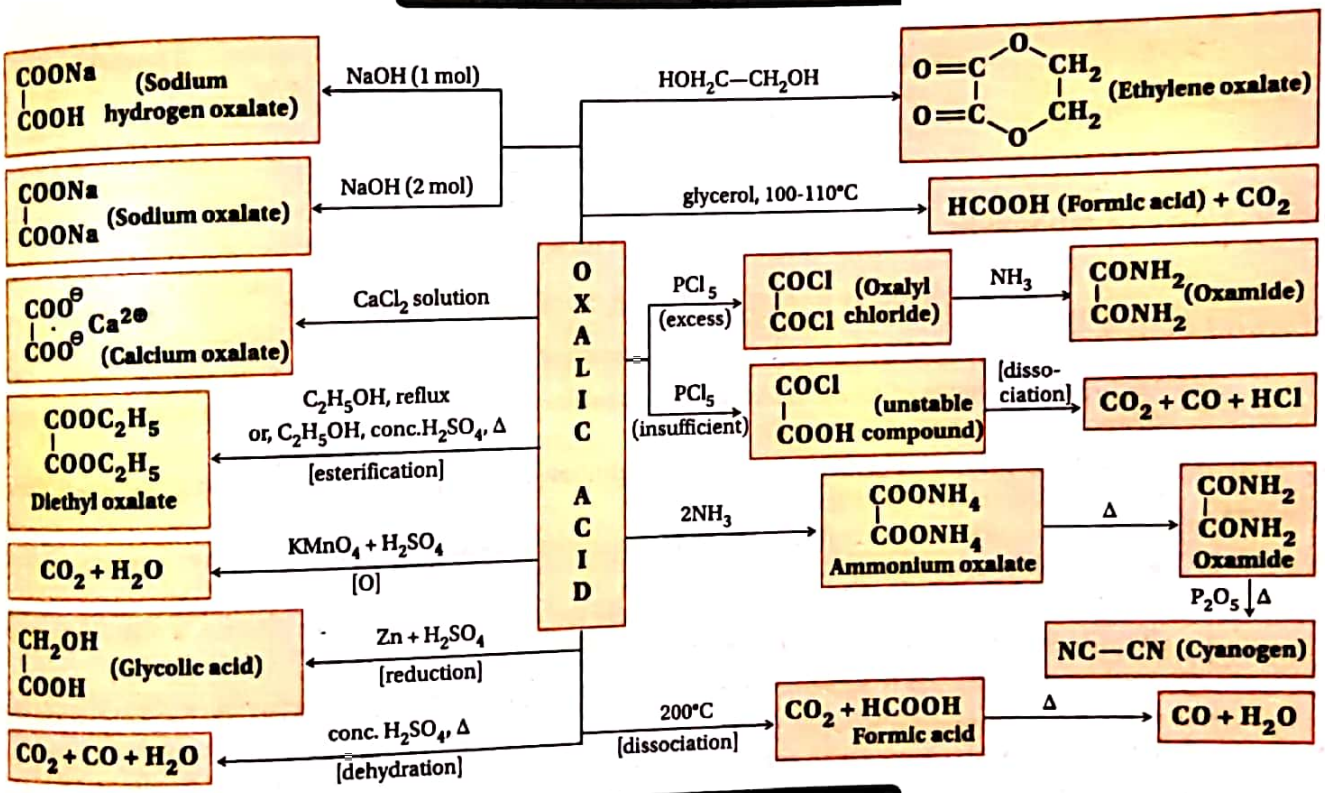
Reduction of the carbonyl group

- $LiAlH_4$ → CH_3CH_2OH (Ethyl alcohol)
- H_2, copper chromite → CH_3CH_2OH (Ethyl alcohol)

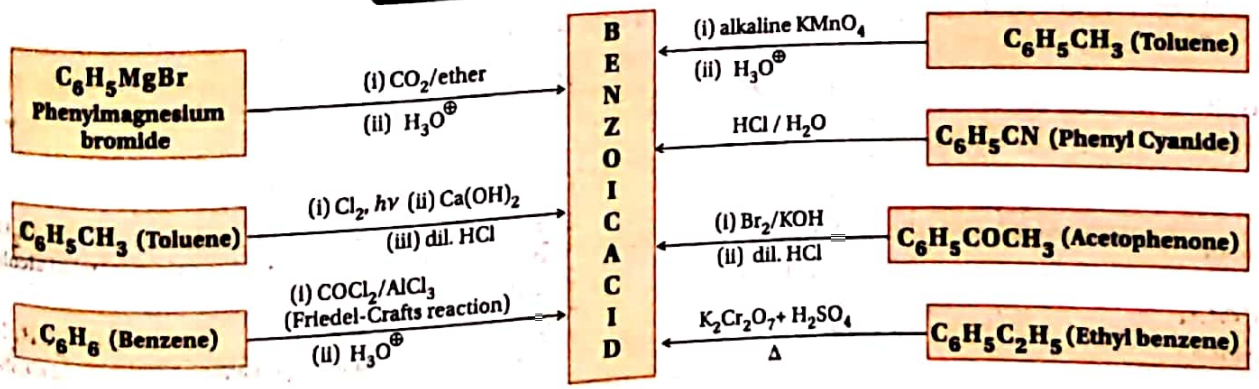
Preparations of Oxalic Acid (HOOC—COOH)



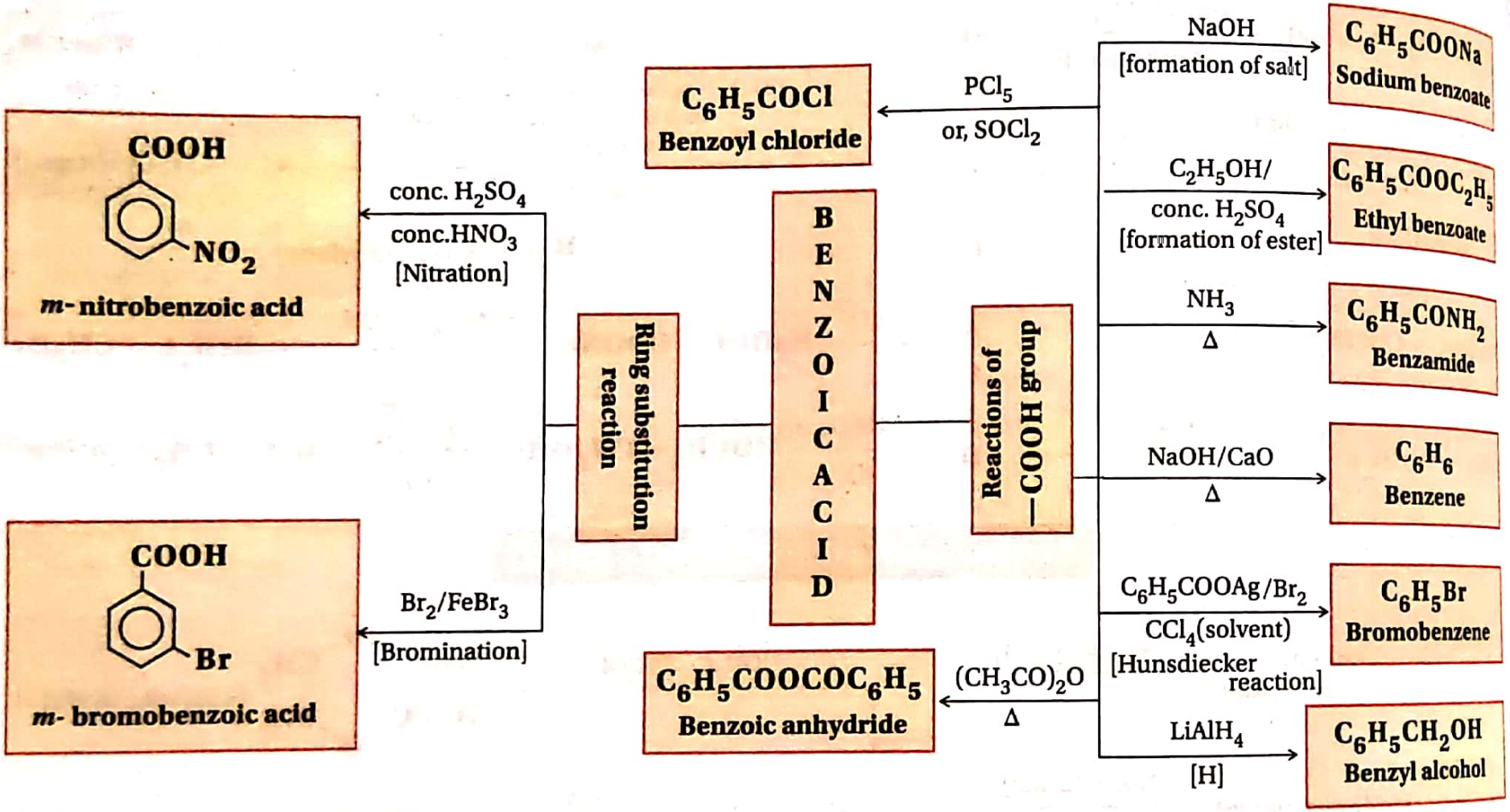
Reactions of Oxalic Acid (HOOC—COOH)



Preparations of Benzoic Acid (C_6H_5COOH)



Reactions of Benzoic Acid (C_6H_5COOH)



...ous smell is evolved.

Acetic acid and Acetone

Test	Acetic acid	Acetone
Reaction with $NaHCO_3$ solution	CO_2 gas is evolved in the form of bubbles.	CO_2 gas is not evolved.
conc. NaOH solution + I_2 dissolved in KI solution + heat	Yellow crystals are not produced.	Yellow crystals of iodoform having characteristic smell are produced.
Brady's reagent (2, 4-DNP) + heat	Orange or yellow precipitate is not produced.	Orange precipitate is produced.

Ethanol and Acetic acid

Test	Ethanol	Acetic acid
Reaction with $NaHCO_3$ solution	No gaseous substance is evolved.	CO_2 gas is evolved in the form of bubbles.
conc. NaOH solution + I_2 dissolved in KI solution + heat	Yellow crystals of iodoform having characteristic smell are produced.	No yellow precipitate is produced.

Formaldehyde and Formic acid

Test	Formaldehyde	Formic acid
Reaction with $NaHCO_3$ solution	No gas is evolved.	CO_2 gas is evolved in the form of bubbles.
Brady's reagent (2,4-DNP) + heat	Orange precipitate is obtained.	No characteristic precipitate is formed.

Oxalic acid and Acetic acid

Test	Oxalic acid	Acetic acid
Reaction with $CaCl_2$ solution	A white precipitate of calcium oxalate is produced. $\begin{matrix}COOH\\ \mid \\ COOH\end{matrix} + CaCl_2 \rightarrow \begin{matrix}COO^-\\ \mid \\ COO^-\end{matrix} Ca^{2+}\downarrow + 2HCl$	No precipitate is obtained.
Cacodyl oxide test	No characteristic change occurs.	Cacodyl oxide gas having obnoxious smell is evolved.

Phenol and Acetic acid

Test	Phenol	Acetic acid
Reaction with $NaHCO_3$ solution	No gas is evolved.	CO_2 gas is evolved in the form of bubbles.
Reaction with neutral $FeCl_3$ solution	Violet colour developes.	The solution turns red and on boiling gives brown precipitate.

Benzoic acid and Salicylic acid

Test	Phenol	Salicylic acid
Reaction with neutral $FeCl_3$ solution	No characteristic colouration is produced.	Violet colouration is produced.
Reaction with methanol in the presence of conc. H_2SO_4	Smell of wintergreen oil is not produced.	Methyl salicylate having smell of wintergreen oil is produced.

Benzoic acid and Phenol

Test	Benzoic acid	Phenol
Reaction with $NaHCO_3$ solution	CO_2 gas is evolved in the form of bubbles.	No gas is evolved.
Reaction with neutral $FeCl_3$ solution	Violet colouration is not produced.	Violet colouration is produced.

Transformations

1. **Higher acid (acetic acid) from lower acid (formic acid):**

$$\underset{\text{Formic acid}}{HCOOH} \xrightarrow[\text{[reduction]}]{LiAlH_4} \underset{\text{Methanol}}{CH_3OH} \xrightarrow{\text{red P + } I_2} \underset{\text{Methyl iodide}}{CH_3I} \xrightarrow[\text{alcohol}]{KCN} \underset{\text{Methyl cyanide}}{CH_3CN} \xrightarrow[\text{reflux}]{\text{dil. } H_2SO_4} \underset{\text{Acetic acid}}{CH_3COOH}$$

Alternative method: acetic acid to propionic acid:

$$\underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{PCl_5} \underset{\text{Acetyl chloride}}{CH_3COCl} \xrightarrow[\text{ether}]{CH_2N_2} \underset{\text{Diazoketone}}{CH_3COCHN_2} \xrightarrow[\text{(ii) } H_2O]{\text{(i) } Ag_2O,\ \Delta} \underset{\text{Propionic acid}}{CH_3CH_2COOH}$$

2. **Lower acid (formic acid) from higher acid (acetic acid):**

$$\underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{PCl_5} \underset{\text{Acetyl chloride}}{CH_3COCl} \xrightarrow{NH_3} \underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow{Br_2/KOH} \underset{\text{Methylamine}}{CH_3NH_2} \xrightarrow{HNO_2} \underset{\text{Methanol}}{CH_3OH} \xrightarrow[\text{[O]}]{K_2Cr_2O_7,\ H_2SO_4} \underset{\text{Formic acid}}{HCOOH}$$

[NS '07]

3. **Ethanoic acid from propanoic acid:**

$$\underset{\text{Propanoic acid}}{CH_3CH_2COOH} \xrightarrow{PCl_5} \underset{\text{Propanoyl chloride}}{CH_3CH_2COCl} \xrightarrow{NH_3} \underset{\text{Propanamide}}{CH_3CH_2CONH_2} \xrightarrow[KOH]{Br_2} \underset{\text{Ethylamine}}{CH_3CH_2NH_2} \xrightarrow{HNO_2} \underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[\text{[O]}]{K_2Cr_2O_7/H_2SO_4} \underset{\text{Ethanoic acid}}{CH_3COOH}$$

4. **Isopropyl alcohol from propionic acid:**

$$\underset{\text{Propionic acid}}{CH_3CH_2COOH} \xrightarrow{PCl_5} \underset{\text{Propanoyl chloride}}{CH_3CH_2COCl} \xrightarrow{NH_3} \underset{\text{Propanamide}}{CH_3CH_2CONH_2} \xrightarrow{Br_2/KOH} \underset{\text{Ethylamine}}{CH_3CH_2NH_2} \xrightarrow{HNO_2} \underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[\text{[O]}]{K_2Cr_2O_7/\text{ conc.}H_2SO_4} \underset{\text{Acetic acid}}{CH_3COOH}$$

$$\underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{Ca(OH)_2} \underset{\text{Calcium acetate}}{(CH_3COO)_2Ca} \xrightarrow[\text{distillation}]{\text{dry}} \underset{\text{Acetone}}{CH_3COCH_3} \xrightarrow[\text{or, } LiAlH_4]{Na/C_2H_5OH} \underset{\text{Isopropyl alcohol}}{CH_3CH(OH)CH_3}$$