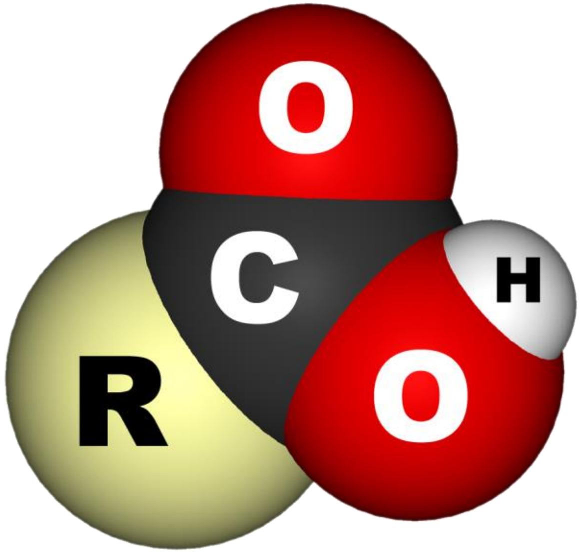
Shri Lemdeo Patil Mahavidyalaya, Mandhal

B.Sc III Sem

Paper II : Organic Chemistry

Unit IV : Carboxylic Acid and its Derivatives



Presented By

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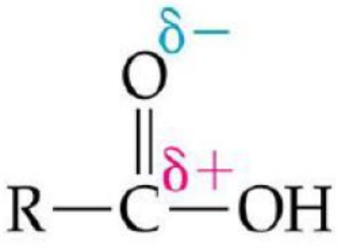
Chemistry Department

A. Carboxylic Acids

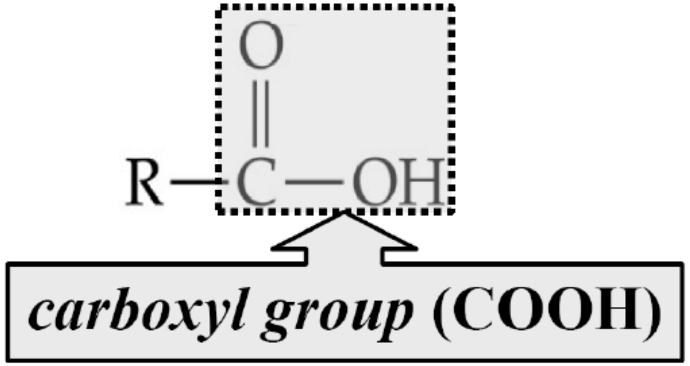
Defination:

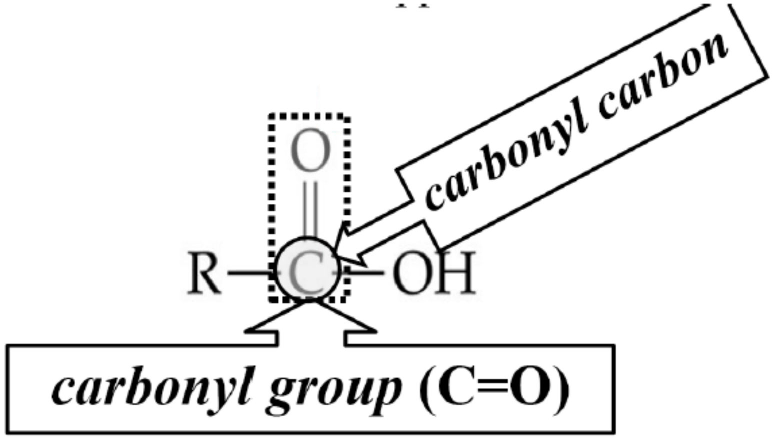
The organic compounds containing functional group –COOH are called as Carboxylic acids.

A **carboxylic acid** is an organic acid that contains a **carboxyl group** (-COOH) attached to an R-group. The general formula of a carboxylic acid is **R–COOH**, with R referring to the alkyl, alkenyl, aryl, or other group.



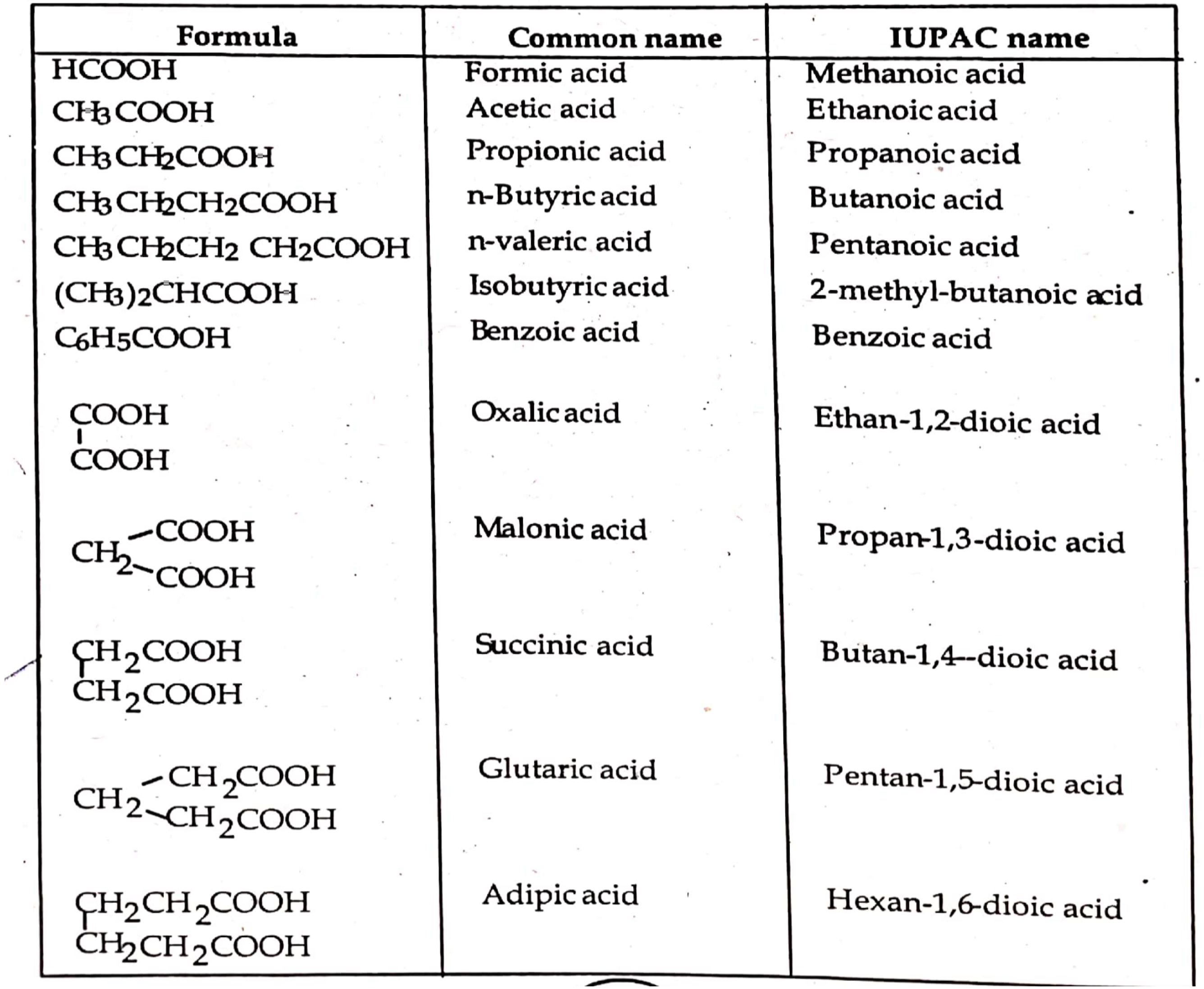
Carboxylic Acid





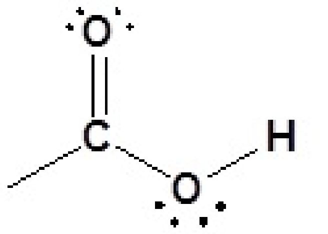
Nomenclature

The IUPAC system of nomenclature carboxylic acids named as the derivatives of hydrocarbons corresponding to the longest carbon chain containing the carboxylic group. The **–e** ending is removed from the name of the parent chain and is replaced **-oic acid**. Since a carboxylic acid group must always lie at the end of a carbon chain.



Formula	Common name	IUPAC name
$HCOOH$	Formic acid	Methanoic acid
CH_3COOH	Acetic acid	Ethanoic acid
CH_3CH_2COOH	Propionic acid	Propanoic acid
$CH_3CH_2CH_2COOH$	n-Butyric acid	Butanoic acid
$CH_3CH_2CH_2CH_2COOH$	n-valeric acid	Pentanoic acid
$(CH_3)_2CHCOOH$	Isobutyric acid	2-methyl-butanoic acid
C_6H_5COOH	Benzoic acid	Benzoic acid
$\begin{array}{l}COOH\\ \vert\\ COOH\end{array}$	Oxalic acid	Ethan-1,2-dioic acid
$CH_2\begin{array}{l}\diagup COOH\\ \diagdown COOH\end{array}$	Malonic acid	Propan-1,3-dioic acid
$\begin{array}{l}CH_2COOH\\ \vert\\ CH_2COOH\end{array}$	Succinic acid	Butan-1,4--dioic acid
$CH_2\begin{array}{l}\diagup CH_2COOH\\ \diagdown CH_2COOH\end{array}$	Glutaric acid	Pentan-1,5-dioic acid
$\begin{array}{l}CH_2CH_2COOH\\ \vert\\ CH_2CH_2COOH\end{array}$	Adipic acid	Hexan-1,6-dioic acid

Structure of Carboxylic Group



Carboxyl Group

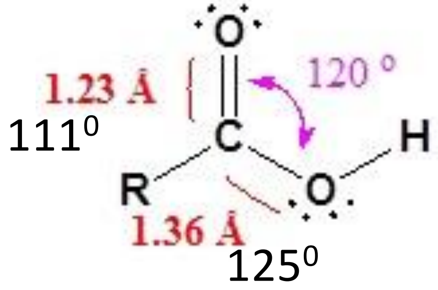
1. Electron configuration of carbon and Oxygen atom

$$C_6 :- 1s^2\,\underbrace{2s^1\,2p_x^1\,2p_y^1}_{sp^2}\,\underbrace{2p_z^1}.$$

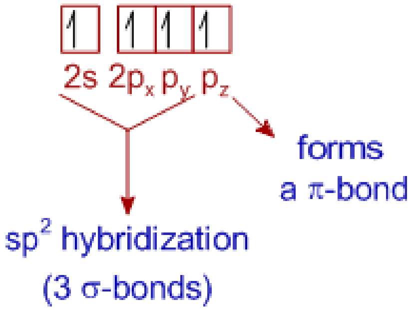
$$O_8 :- 1s^2\,\underbrace{2s^2\,2p_x^2\,2p_y^1}_{sp^2}\,\underbrace{2p_z^1}.$$

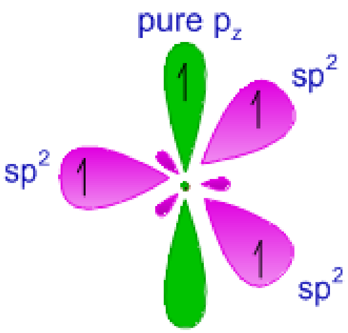
$$O_8 :- 1s^2\,\underbrace{2s^2\,2p_x^2\,2p_y^1}_{sp^2}\,\underbrace{2p_z^1}.$$

Unhybridized



2. Both Carbon and oxygen atom undergo sp^2 hybridization forming 3 hybrid orbitals. The $2p_z$ orbitals remain unhybridized and are perpendicular to plane of sp^2 hybrid orbitals





Acidity of Carboxylic Acid

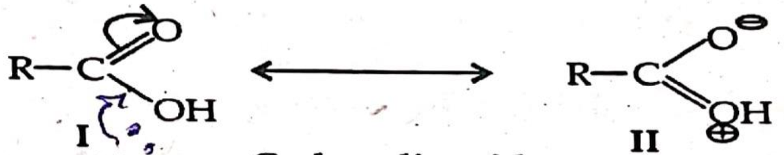
The tendency of donating proton (H^+) is called as acidity. Carboxylic acid in aqueous medium lose proton and gives an anion.

$$RCOOH \longrightarrow RCOO^- + H^+$$

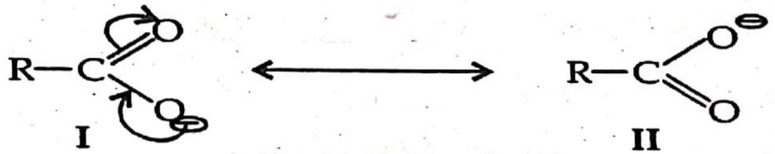
The acidic strength is given in terms of dissociation constant as-

$$K_a = \frac{[RCOO^-][H^+]}{[RCOOH]}$$

Higher is the value of Ka, more is the concentration of hydronium ions and more acidic is the acid. The acidity depends on the structure of carboxylate anion which can be explained on the basis of resonance phenomenon. According to resonance, the carboxylate anion is considered to be a resonance hybrid of the two structures I and II.



Carboxylic acid



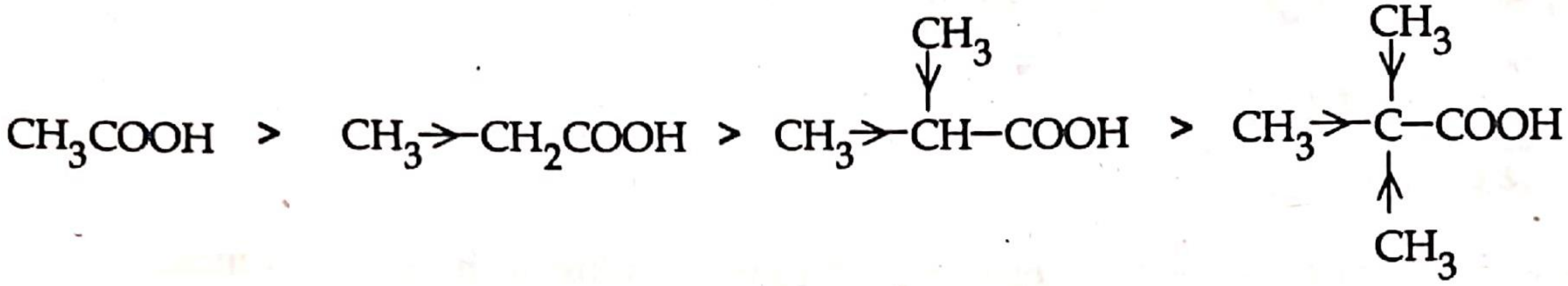
Carboxylate ion

In case of carboxylic acid, structure II has separation of ions and also oxygen bears positive charge which is more electronegative. Hence, it is highly unstable structure. On the other hand, carboxylate ion has delocalization of negative charge and so it is resonance stabilized. Hence, carboxylic acid has a tendency to loose proton and get converted into carboxylate ion. So, it is acidic in nature.

Effect of substituents on acid strength : Strength of carboxylic acid is expressed in term of dissociation constant (Ka). Higher is the value of dissociation constant, more is the acidic strength. The dissociation constant depends on stability of carboxylate ion. Higher is the stability of carboxylate ion, more is the acidic strength of carboxylic acid.

1. If the substituent on -COOH group is electron releasing in nature, it increases the electron density and so the acidic strength goes on decreasing. For example,

$$HCOOH > CH_3COOH > CH_3CH_2COOH$$

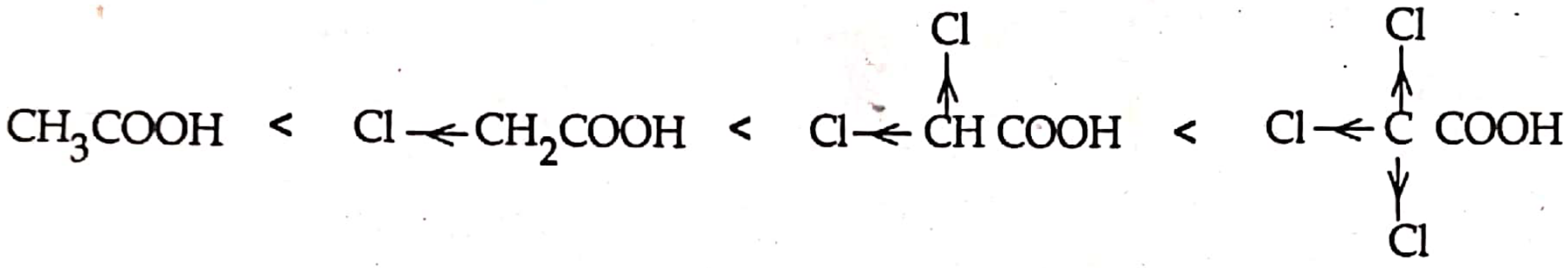


$$CH_3COOH > CH_3 \rightarrow CH_2COOH > CH_3 \rightarrow \overset{\overset{CH_3}{\downarrow}}{CH}-COOH > CH_3 \rightarrow \underset{\underset{CH_3}{\uparrow}}{\overset{\overset{CH_3}{\downarrow}}{C}}-COOH$$

2. If substituent is electron withdrawing in nature, it decreases the charge density on carboxylate and so increases the acidic strength. Higher is the electronegativity of such group, more is the acidic strength.

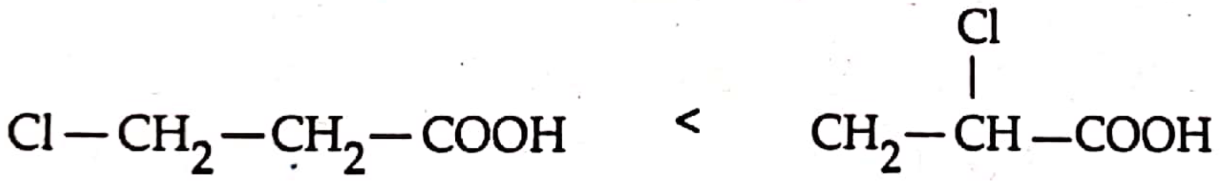
$$F \leftarrow CH_2COOH > Cl \leftarrow CH_2COOH > Br \leftarrow CH_2COOH > I \leftarrow CH_2COOH$$

3. More is the number of electron withdrawing groups, higher is the acidic strength.



$$CH_3COOH < Cl \leftarrow CH_2COOH < Cl \leftarrow \overset{\overset{Cl}{\uparrow}}{C}H\ COOH < Cl \leftarrow \underset{\underset{Cl}{\downarrow}}{\overset{\overset{Cl}{\uparrow}}{C}}\ COOH$$

4. Closer is the position of electron withdrawing group from -COOH group, more is the acidic strength.



$$Cl-CH_2-CH_2-COOH < CH_2-\overset{\overset{Cl}{|}}{CH}-COOH$$

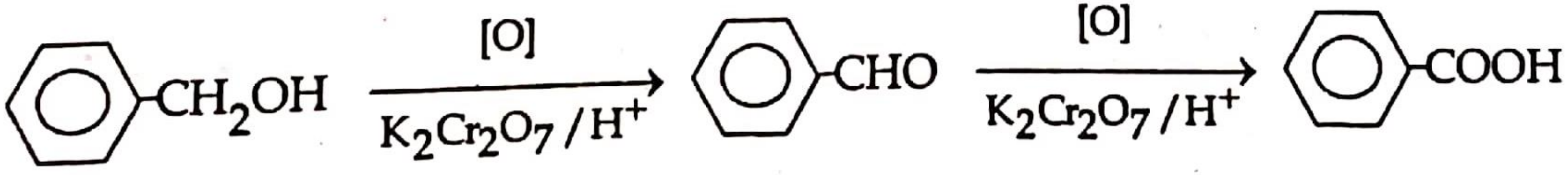
Preparation of Carboxylic Acid:

Preparation

1. **From primary alcohol and aldehydes:** Primary alcohol or aldehydes undergo oxidation with acidified potassium dichromate or potassium permanganate to form carboxylic acids. The alcohol is first oxidized to an aldehyde and then to a carboxylic acid.

$$RCH_2OH \xrightarrow[K_2Cr_2O_7/H^+]{[O]} RCHO \xrightarrow[K_2Cr_2O_7/H^+]{[O]} RCOOH$$

$$\underset{\text{Ethylalcohol}}{CH_3CH_2OH} \xrightarrow[K_2Cr_2O_7/H^+]{[O]} \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow[K_2Cr_2O_7/H^+]{[O]} \underset{\text{Acetic acid}}{CH_3COOH}$$

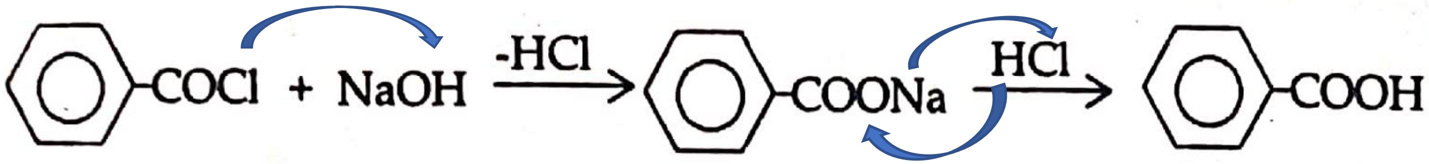


Benzyl alcohol Benzaldehyde Benzoic acid

2. **From acid chloride:** Acetyl chloride on acid hydrolysis gives acetic acid. Benzoyl chloride is first treated with NaOH to give sodium benzoate. This on acidification gives benzoic acid.

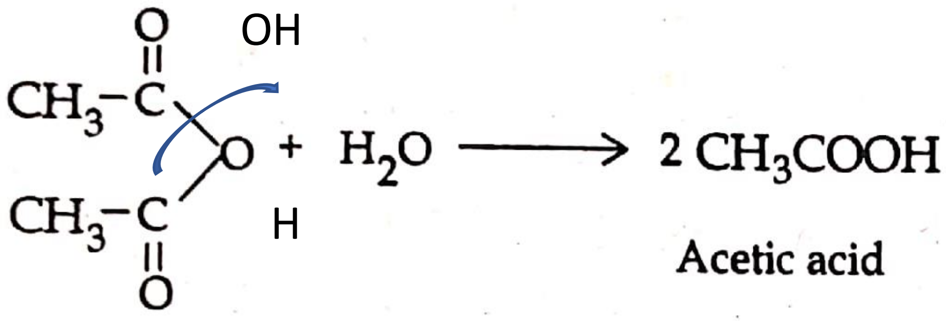
$$CH_3COCl + H_2O \xrightarrow{HCl} CH_3COOH$$

Acetyl chloride — Acetic acid



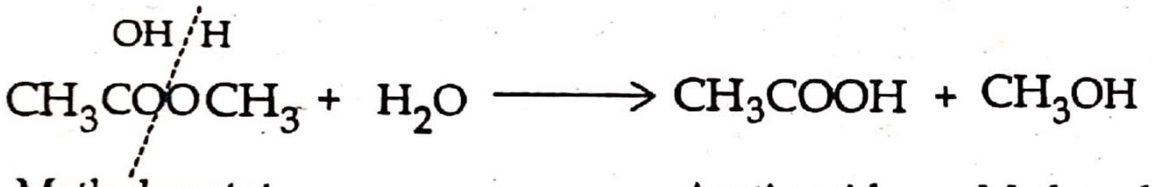
Benzoyl chloride — Sodium benzoate — Benzoic acid

3. **From anhydride:** Acetic anhydride when boiled with dilute HCl undergo hydrolysis forming acetic acid.



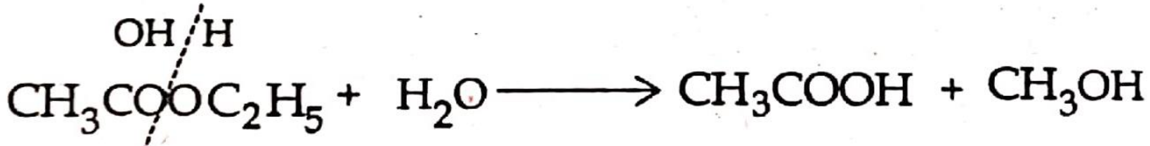
Acetic anhydride — Acetic acid

4. **From ester:** Ester on acid hydrolysis gives carboxylic acid.



$$CH_3COOCH_3 + H_2O \longrightarrow CH_3COOH + CH_3OH$$

Methyl acetate — Acetic acid — Methanol



$$CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + CH_3OH$$

Ethyl acetate — Acetic acid — Ethanol

5. **From amide:** Amide is boiled with NaOH solution to give sodium salt of carboxylic acid. This on acidification gives carboxylic acid.

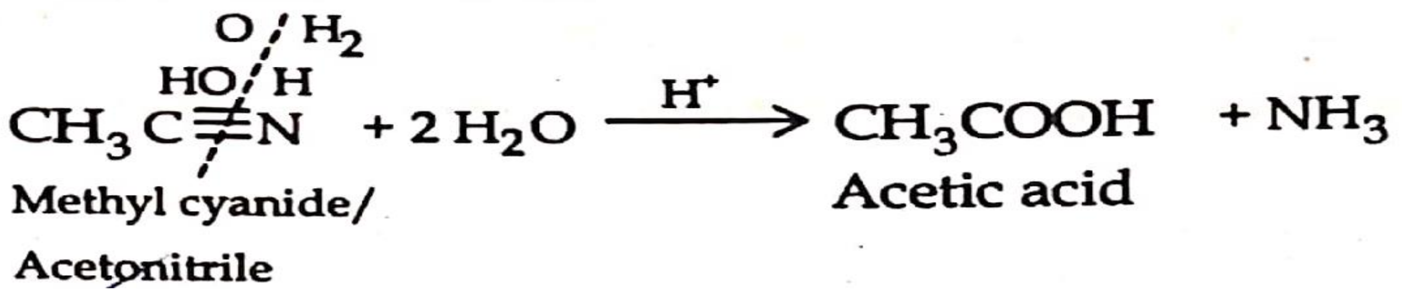
$$CH_3\,CONH_2 + NaOH \xrightarrow{-NH_3} CH_3COONa \xrightarrow{HCl} CH_3COOH$$

Acetamide — Acetic acid

$$C_6H_5\,CONH_2 + NaOH \xrightarrow{-NH_3} C_6H_5COONa \xrightarrow{HCl} C_6H_5COOH$$

Benzamide — Benzoic acid

6. From Nitrile (Cyanide): Alkyl cyanide on hydrolysis in the presence of acid or base carboxylic acid

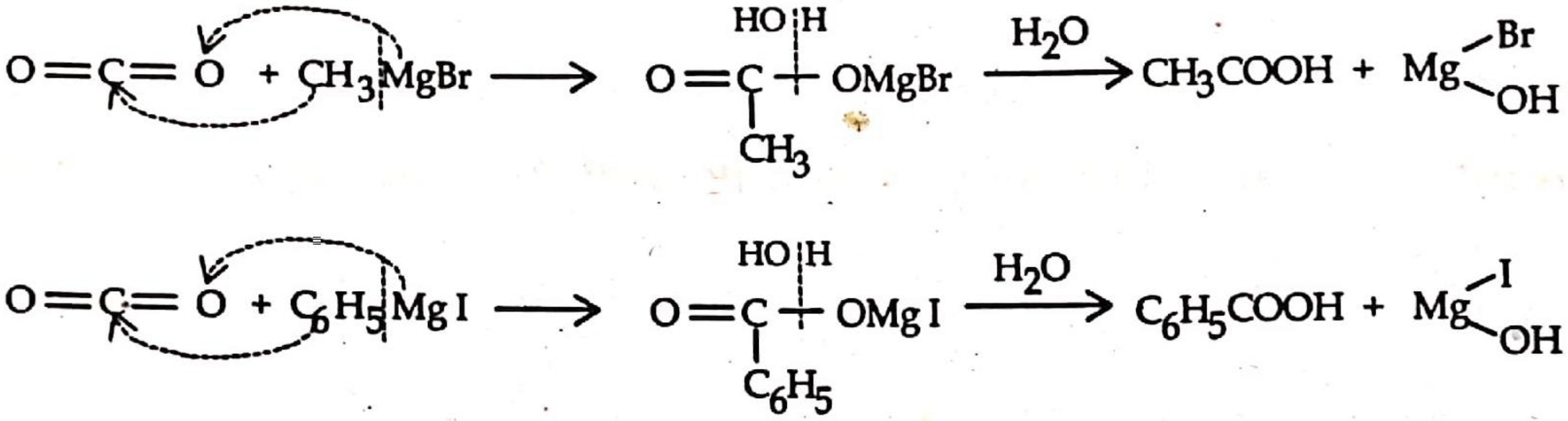


$$\overset{\overset{O\,/\,H_2}{HO\,/\,H}}{CH_3C\equiv N} + 2H_2O \xrightarrow{H^+} CH_3COOH + NH_3$$

Methyl cyanide/ Acetonitrile

Acetic acid

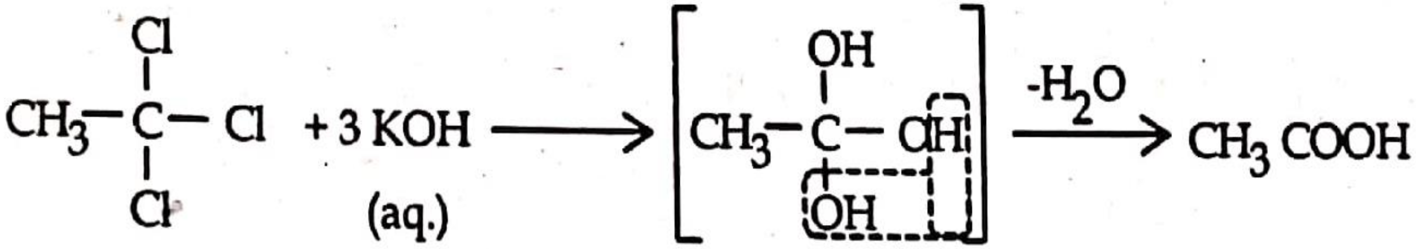
7. From dry ice (solid carbondioxide): Dry ice is treated with Grignard Reagent to give an addition product which on hydrolysis gives carboxylic



$$O=C=O + CH_3MgBr \longrightarrow O=\underset{CH_3}{C}\overset{HO\,|\,H}{-}OMgBr \xrightarrow{H_2O} CH_3COOH + Mg\begin{smallmatrix}Br\\OH\end{smallmatrix}$$

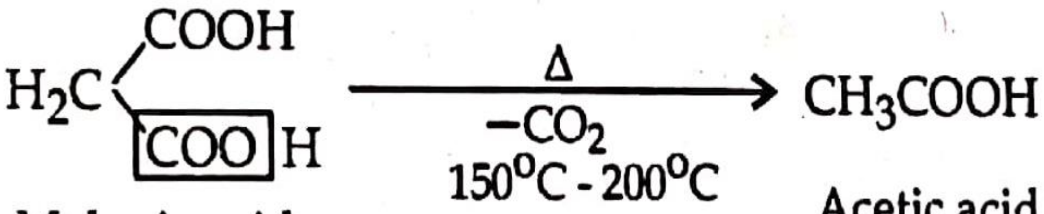
$$O=C=O + C_6H_5MgI \longrightarrow O=\underset{C_6H_5}{C}\overset{HO\,|\,H}{-}OMgI \xrightarrow{H_2O} C_6H_5COOH + Mg\begin{smallmatrix}I\\OH\end{smallmatrix}$$

8. **From geminal trihalide:** Geminal trihalide when boiled with aqueous KOH gives an unstable inermediate which further gives carboxylic acid.



$$CH_3-CCl_3 + 3\,KOH_{(aq.)} \longrightarrow \left[CH_3-C(OH)_3\right] \xrightarrow{-H_2O} CH_3COOH$$

9. **From malonic acid:** Malonic acid on heating decarboxylates to acetic acid.



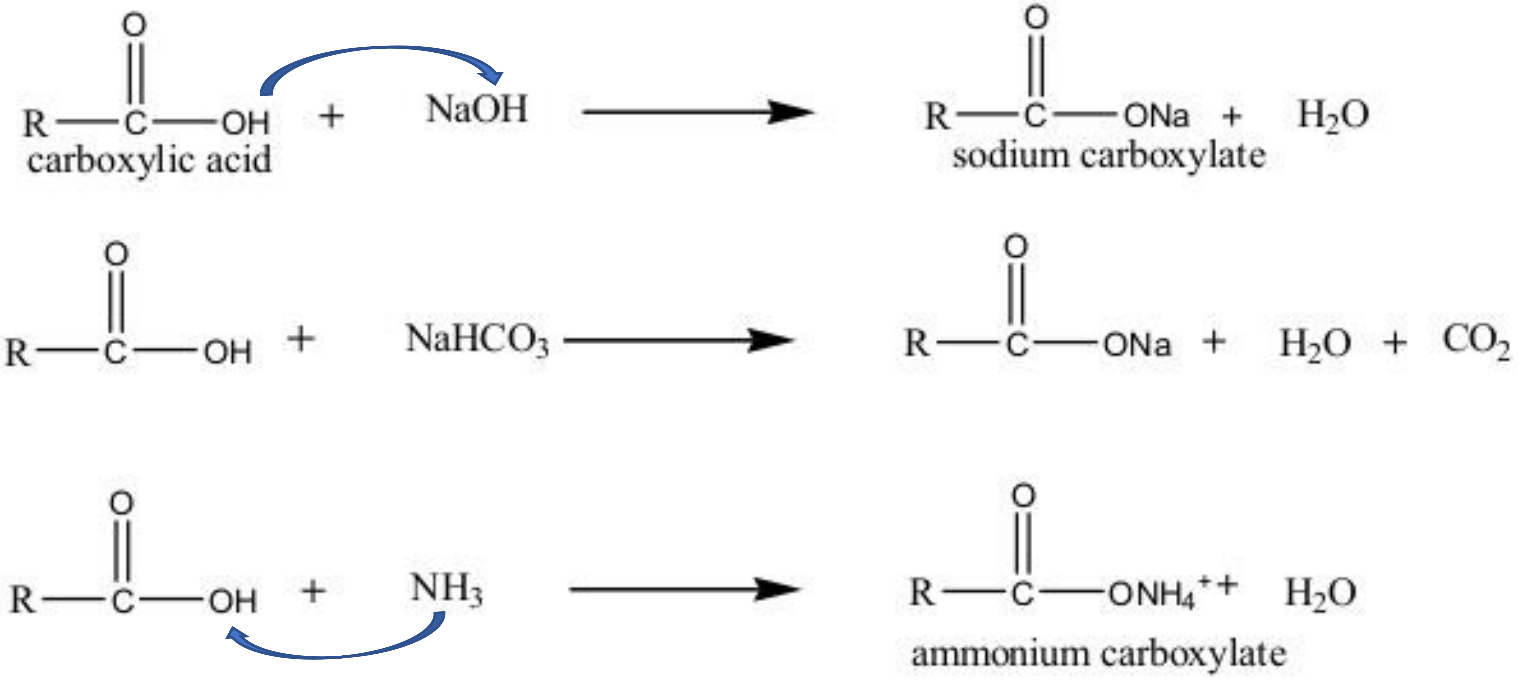
$$H_2C(COOH)_2 \xrightarrow[-CO_2,\ 150^\circ C - 200^\circ C]{\Delta} CH_3COOH$$

Malonic acid

Acetic acid

Chemical Reaction

1. Salt formation

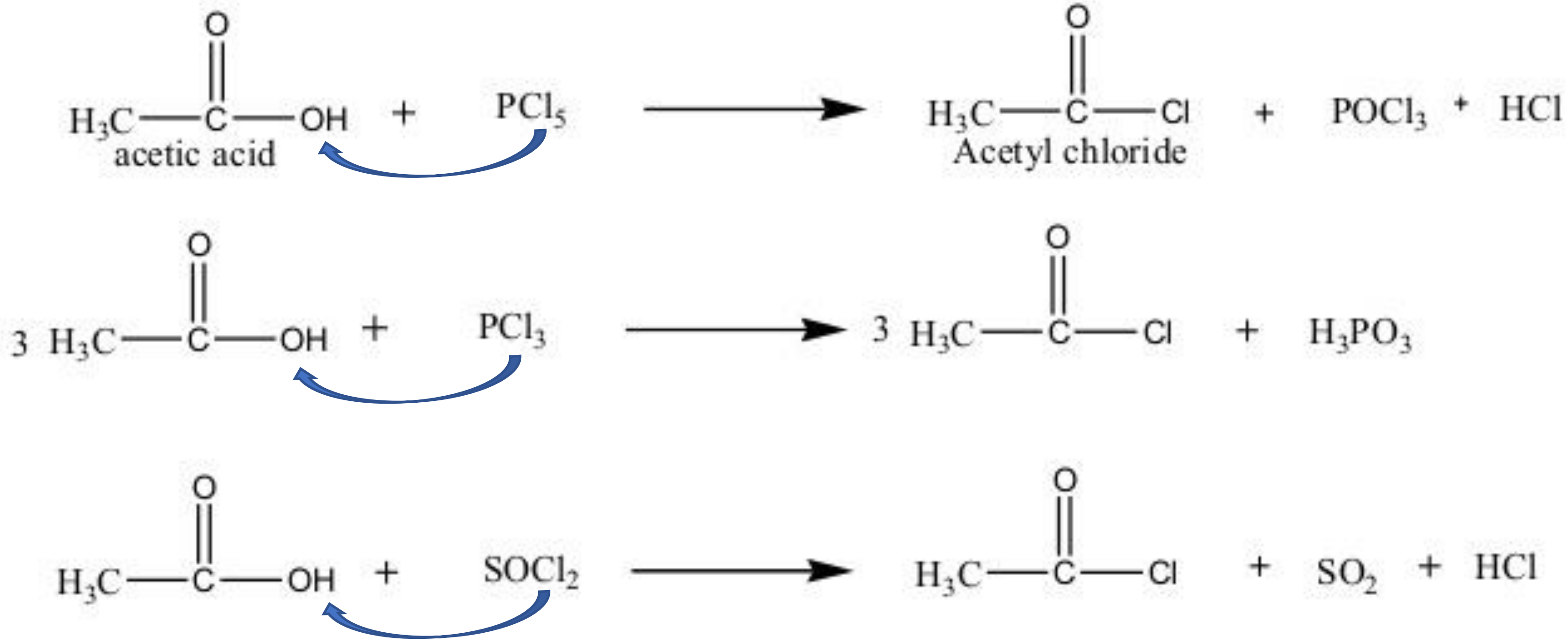


$$R-\overset{\overset{O}{\|}}{C}-OH + NaOH \longrightarrow R-\overset{\overset{O}{\|}}{C}-ONa + H_2O$$

$$R-\overset{\overset{O}{\|}}{C}-OH + NaHCO_3 \longrightarrow R-\overset{\overset{O}{\|}}{C}-ONa + H_2O + CO_2$$

$$R-\overset{\overset{O}{\|}}{C}-OH + NH_3 \longrightarrow R-\overset{\overset{O}{\|}}{C}-ONH_4^{+} + H_2O$$

2. Formation of Acyl halides



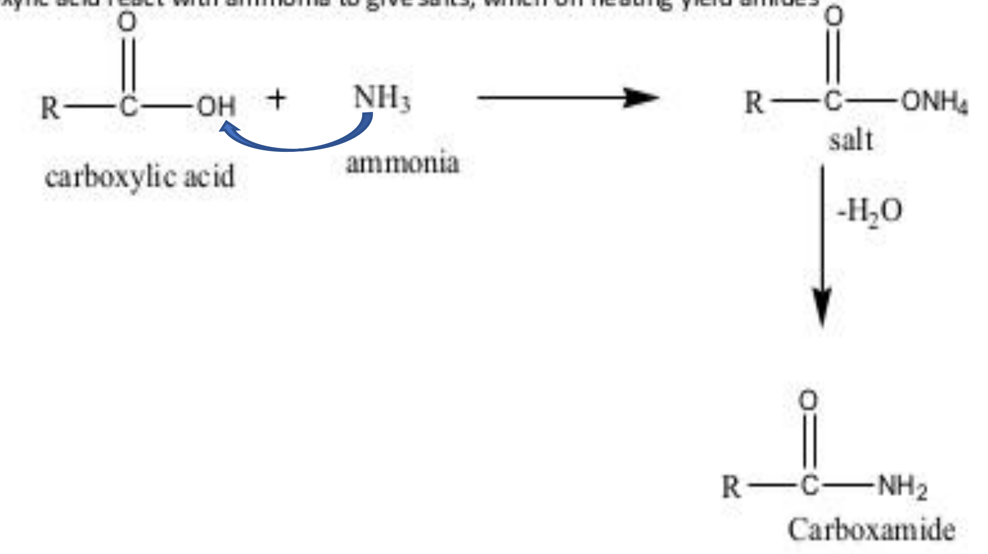
$$H_3C-C(=O)-OH + PCl_5 \longrightarrow H_3C-C(=O)-Cl + POCl_3 + HCl$$

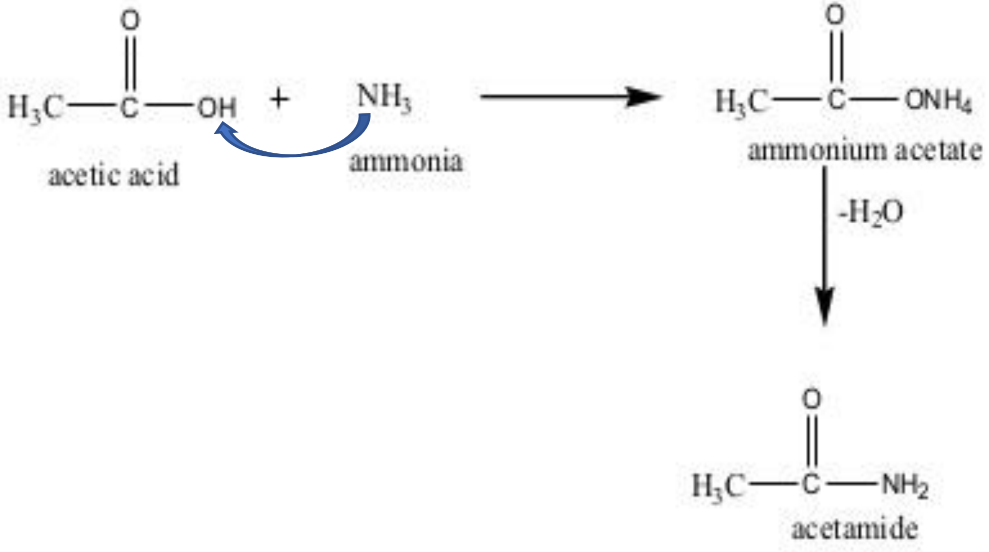
$$3\ H_3C-C(=O)-OH + PCl_3 \longrightarrow 3\ H_3C-C(=O)-Cl + H_3PO_3$$

$$H_3C-C(=O)-OH + SOCl_2 \longrightarrow H_3C-C(=O)-Cl + SO_2 + HCl$$

3. Formation of amide

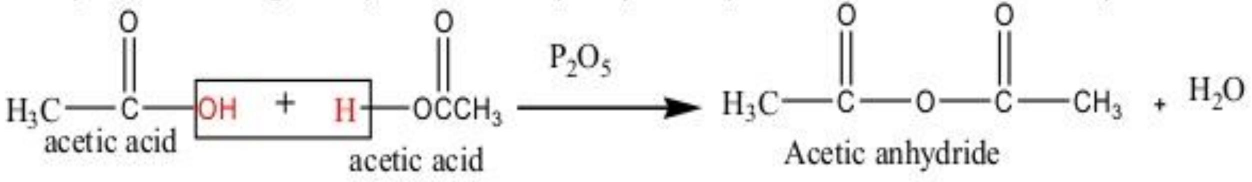
- Carboxylic acid react with ammonia to give salts, which on heating yield amides





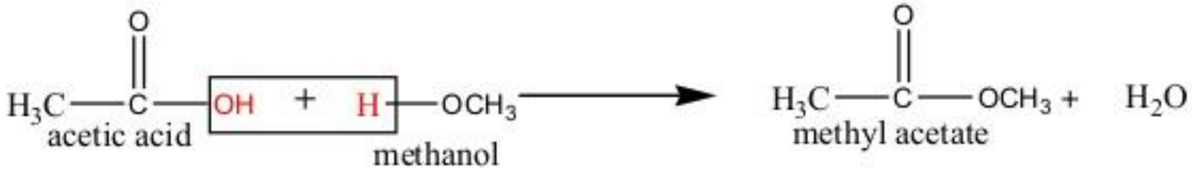
4. Formation of anhydride

Carboxylic acid undergo dehydration with phosphorus pentoxide to form acid anhydride



$$H_3C-\overset{O}{\overset{\|}{C}}-\boxed{OH + H}-O\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow{P_2O_5} H_3C-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3 + H_2O$$

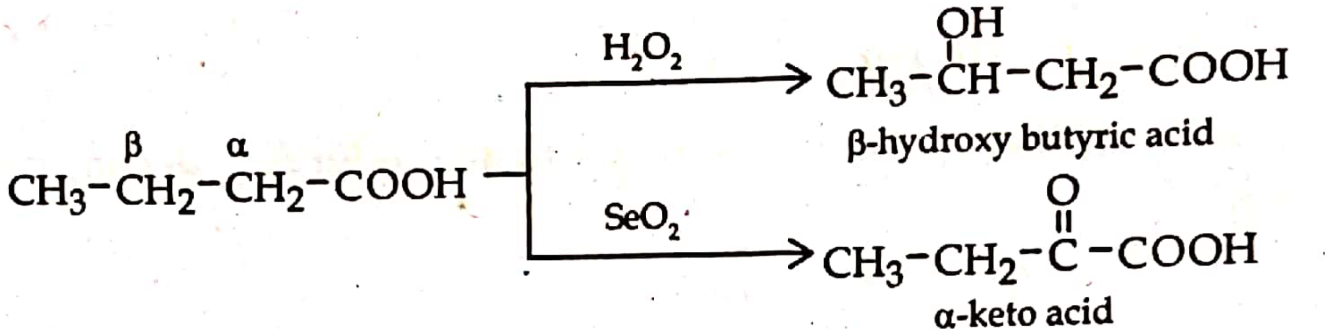
5. Formation of ester



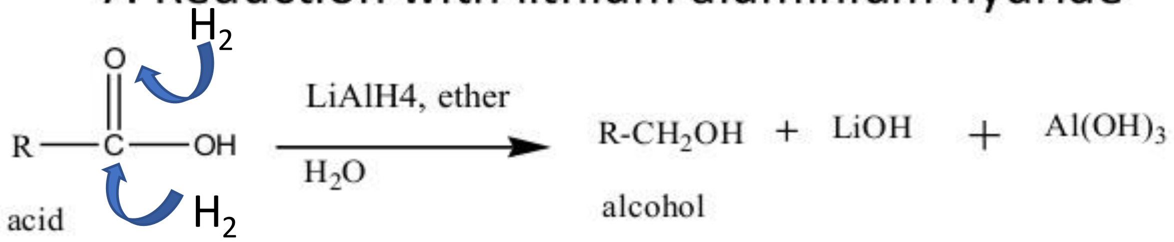
$$H_3C-\overset{O}{\overset{\|}{C}}-\boxed{OH + H}-OCH_3 \longrightarrow H_3C-\overset{O}{\overset{\|}{C}}-OCH_3 + H_2O$$

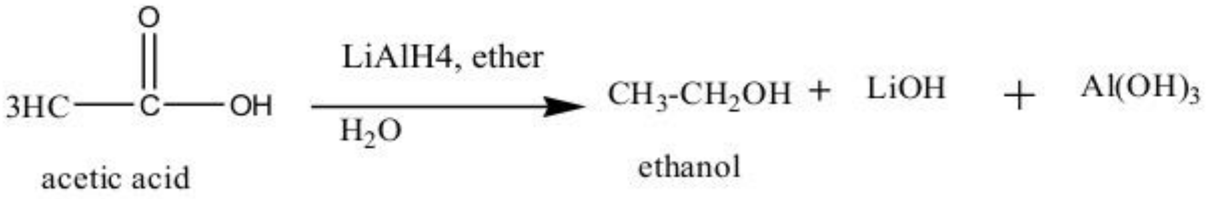
Carboxylic acid react with alcohols in the presence of strong acid to form esters

6. Oxidation : When carboxylic acid is oxidized with H_2O_2, β-hydroxyl acid is formed. If oxidized with SeO_2, α- keto acid is formed.



7. Reduction with lithium aluminium hydride

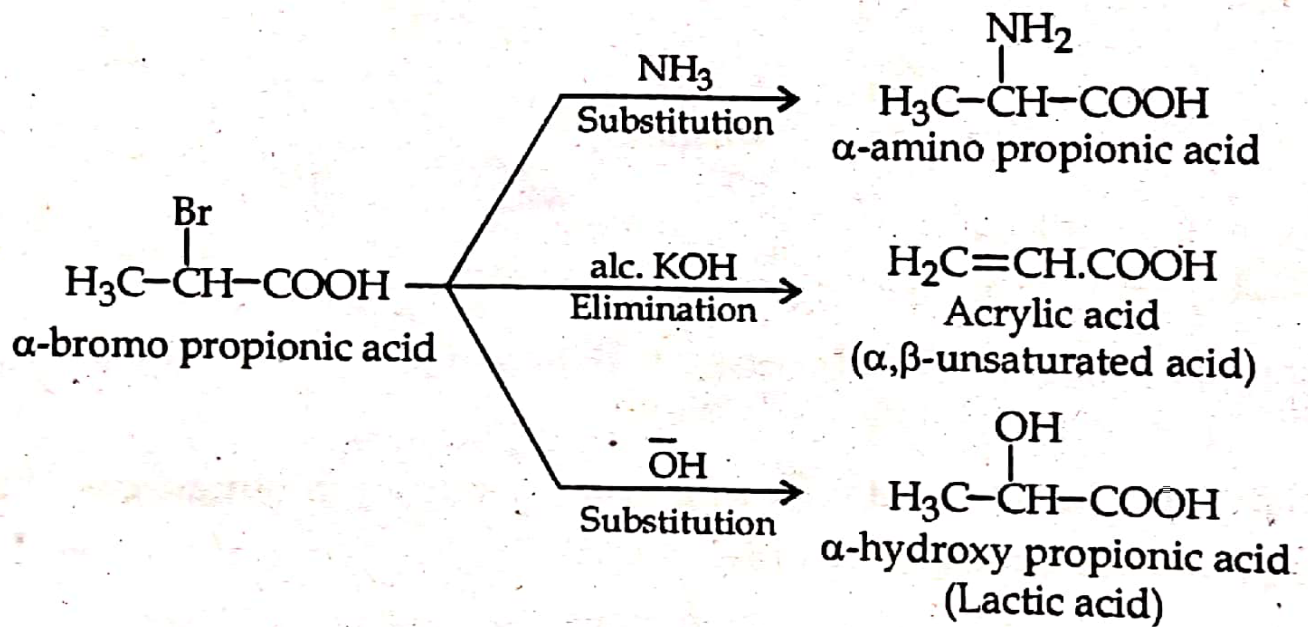




8. **HVZ reaction (Hell Volhard Zeilinski):** When carboxylic acid is treated with chlorine or bromine in the presence of red phosphorous, α-halo acid is formed. Thjis reaction is shown by only those acids which have α-hydrogen.

$$CH_3COOH + Cl_2 \xrightarrow{\text{Red P}} ClCH_2COOH \xrightarrow{Cl_2} Cl_2CHCOOH \xrightarrow{Cl_2} CCl_3COOH$$

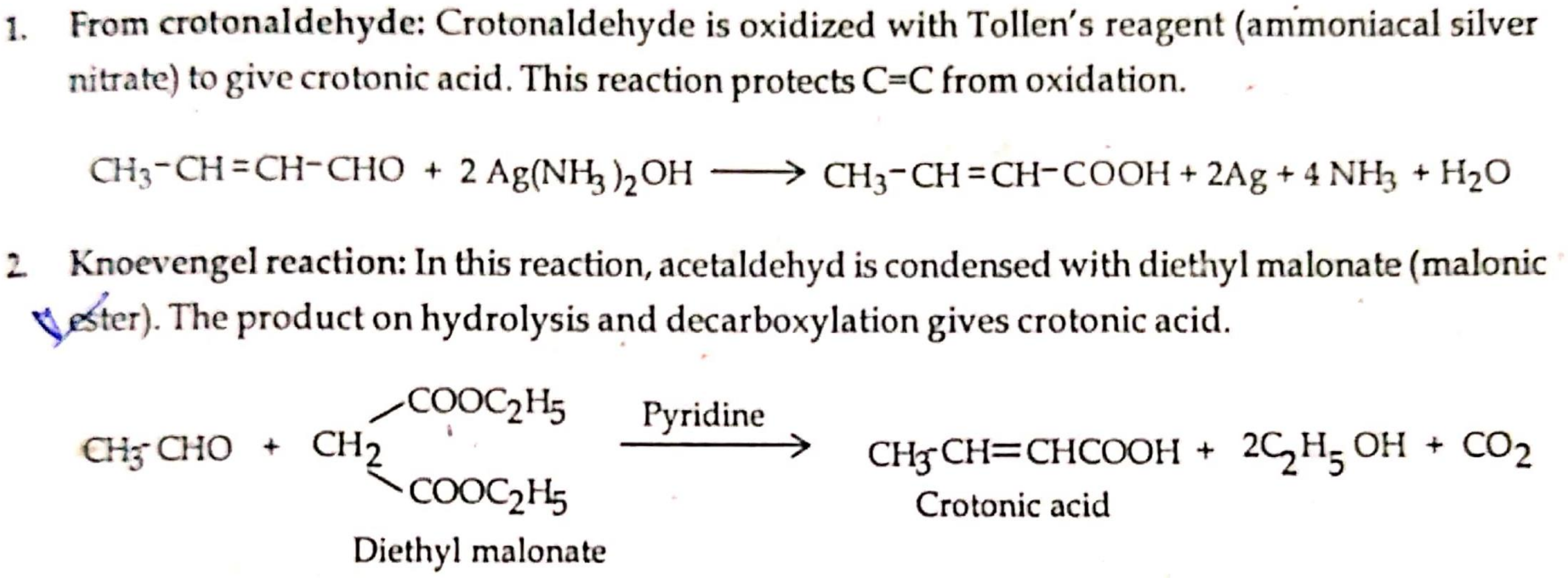
This reaction has great synthetic importance because α-halo acid can be converted into a large number of compounds as shown below.



Crotonic acid: $CH_3CH=CHCO_2H$

Crotonic acid is a short-chain unsaturated carboxylic acid, described by the formula $CH_3CH=CHCO_2H$. It is called crotonic acid because it was erroneously thought to be a saponification product of croton oil.

- Preparations



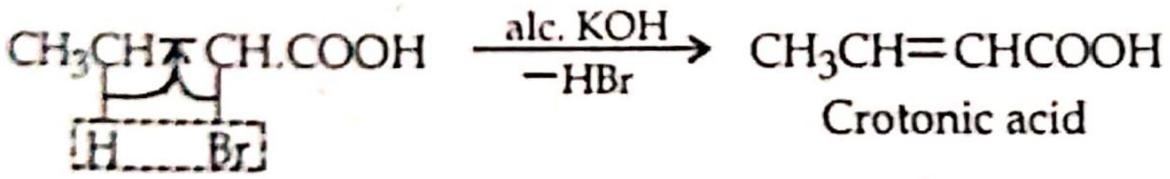
1. **From crotonaldehyde:** Crotonaldehyde is oxidized with Tollen's reagent (ammoniacal silver nitrate) to give crotonic acid. This reaction protects C=C from oxidation.

$$CH_3-CH=CH-CHO + 2\,Ag(NH_3)_2OH \longrightarrow CH_3-CH=CH-COOH + 2Ag + 4\,NH_3 + H_2O$$

2. **Knoevengel reaction:** In this reaction, acetaldehyd is condensed with diethyl malonate (malonic ester). The product on hydrolysis and decarboxylation gives crotonic acid.

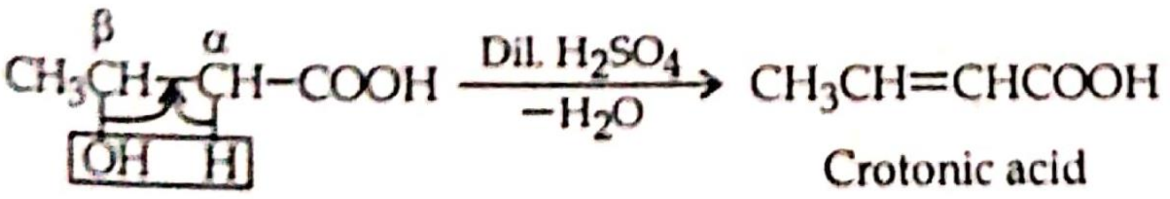
$$CH_3-CHO + \underset{\text{Diethyl malonate}}{CH_2\left\langle\begin{matrix}COOC_2H_5\\COOC_2H_5\end{matrix}\right.} \xrightarrow{\text{Pyridine}} \underset{\text{Crotonic acid}}{CH_3-CH=CHCOOH} + 2C_2H_5OH + CO_2$$

3. **From α-halo butyric acid:** When α - bromo or α - chloro butyric acid is heated with ethanolic KOH, undergoes elimination reaction to give crotonic acid.



$$\underset{\boxed{H\quad Br}}{CH_3CH-CH.COOH} \xrightarrow[-HBr]{alc.\ KOH} \underset{\text{Crotonic acid}}{CH_3CH=CHCOOH}$$

4. **From β-hydroxy butyric acid:** β - hydroxy butyric acid when heated with dil. H_2SO_4, or anhydrous zinc chloride, lose water molecule to form crotonic acid.



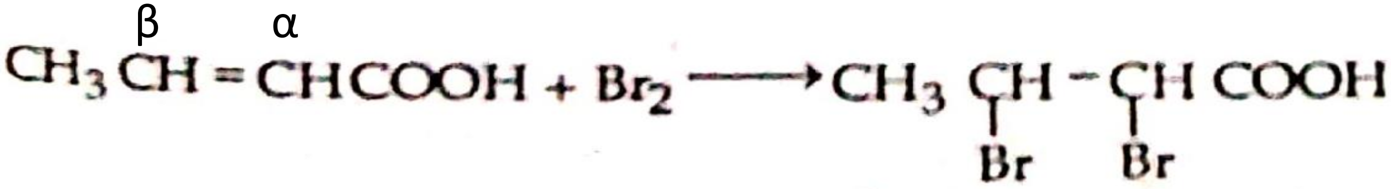
$$\underset{\boxed{OH\quad H}}{CH_3\overset{\beta}{C}H-\overset{\alpha}{C}H-COOH} \xrightarrow[-H_2O]{Dil.\ H_2SO_4} \underset{\text{Crotonic acid}}{CH_3CH=CHCOOH}$$

β- hydroxy butyric acid

Chemical reactions

1. Addition Reaction:

When treated with chlorine or bromine, it forms α, β-dihalobutyric acid

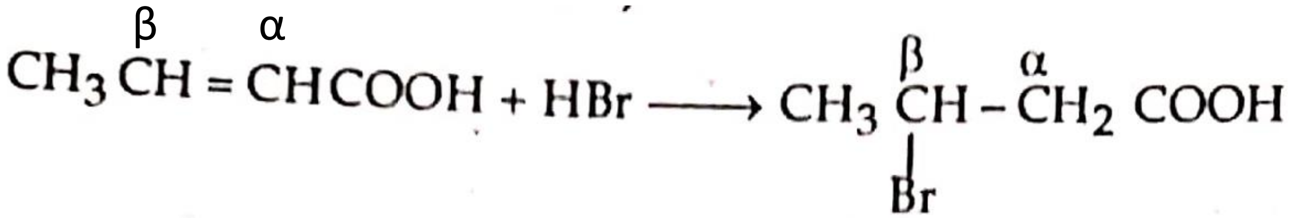


$$\overset{\beta}{CH_3CH}=\overset{\alpha}{CH}COOH + Br_2 \longrightarrow CH_3\underset{Br}{\underset{|}{CH}}-\underset{Br}{\underset{|}{CH}}COOH$$

α,β-dibromo butyric acid

2. Addition of halogen acids:

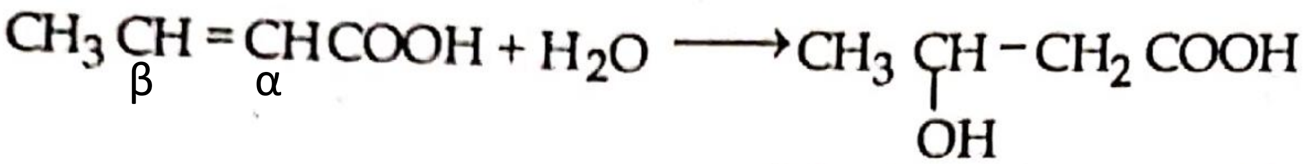
α, β-unsaturated acid add on halogen acid forming β-halo butyric acid (3-halobutanoic acid)



$$CH_3\overset{\beta}{CH}=\overset{\alpha}{CH}COOH + HBr \longrightarrow CH_3\underset{Br}{\underset{|}{\overset{\beta}{CH}}}-\overset{\alpha}{CH_2}COOH$$

β-bromo butyric acid

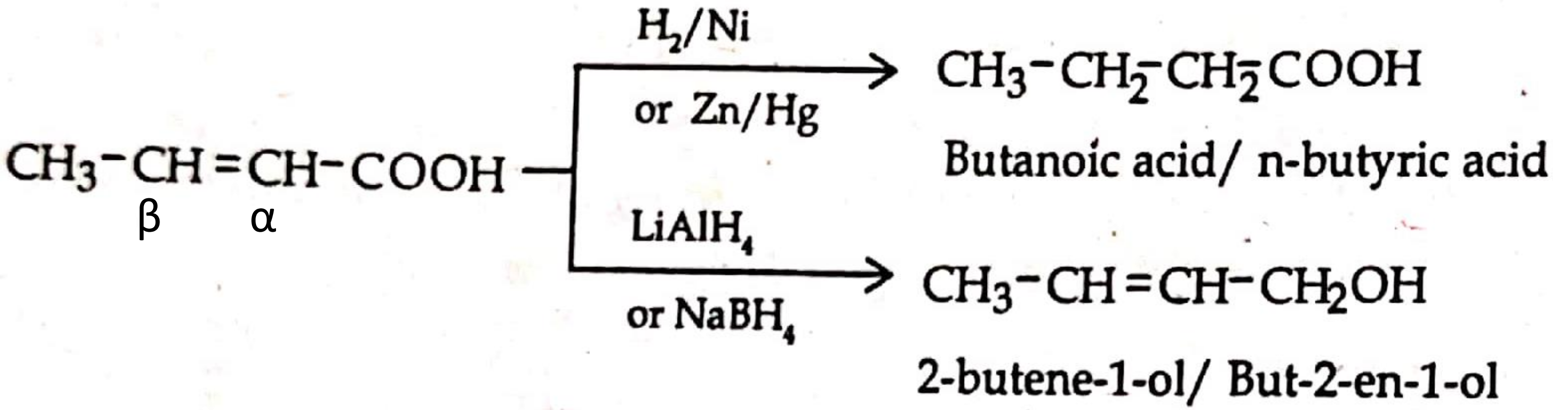
3. **Hydrolysis**: Crotonic acid adds a water molecule forming β-hydroxybutyric acid (3-hydroxy butanoic acid)



$$CH_3\underset{\beta}{CH}=\underset{\alpha}{CH}COOH + H_2O \longrightarrow CH_3\underset{OH}{\underset{|}{CH}}-CH_2COOH$$

β-hydroxy butyric acid

4. **Reduction:** Crotonic acid when reduced with H_2/Ni or zinc amalgam gives butanoic acid. If reducing agent is $LiAlH_4$ or $NaBH_4$, unsaturated alcohol is formed.



$$CH_3-\underset{\beta}{CH}=\underset{\alpha}{CH}-COOH \xrightarrow[\text{or } Zn/Hg]{H_2/Ni} CH_3-CH_2-CH_2-COOH$$

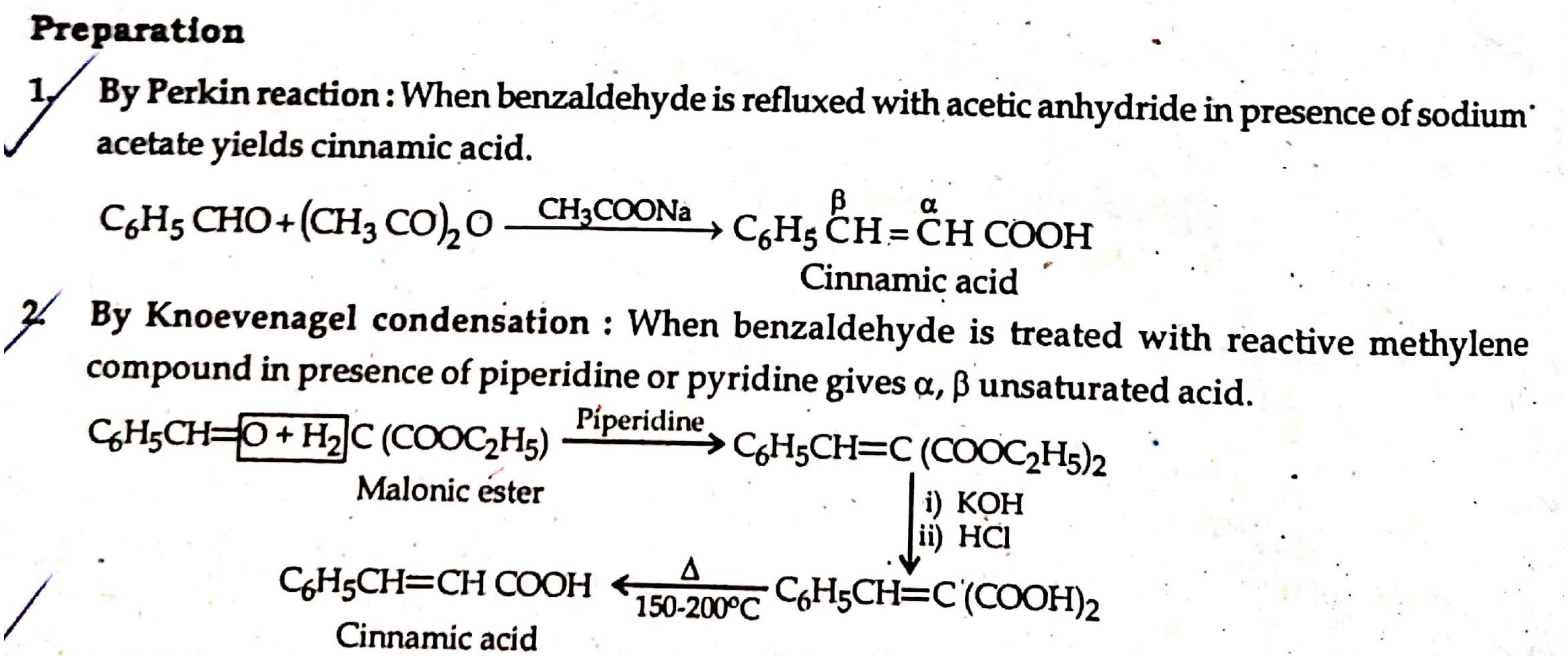
Butanoic acid/ n-butyric acid

$$CH_3-\underset{\beta}{CH}=\underset{\alpha}{CH}-COOH \xrightarrow[\text{or } NaBH_4]{LiAlH_4} CH_3-CH=CH-CH_2OH$$

2-butene-1-ol/ But-2-en-1-ol

Cinnamic acid : $C_6H_5CH{=}CHCOOH$

Cinnamic acid is an organic compound with the formula $C_6H_5CH{=}CHCOOH$. It is a white crystalline compound that is slightly soluble in water, and freely soluble in many organic solvents. Classified as an unsaturated carboxylic acid,



Preparation

1. **By Perkin reaction :** When benzaldehyde is refluxed with acetic anhydride in presence of sodium acetate yields cinnamic acid.

$$C_6H_5\,CHO + (CH_3\,CO)_2O \xrightarrow{CH_3COONa} C_6H_5\,\overset{\beta}{C}H = \overset{\alpha}{C}H\;COOH$$

Cinnamic acid

2. **By Knoevenagel condensation :** When benzaldehyde is treated with reactive methylene compound in presence of piperidine or pyridine gives α, β unsaturated acid.

$$C_6H_5CH{=}\boxed{O + H_2}C\,(COOC_2H_5) \xrightarrow{\text{Piperidine}} C_6H_5CH{=}C\,(COOC_2H_5)_2$$

Malonic ester

$$C_6H_5CH{=}C\,(COOC_2H_5)_2 \xrightarrow{\text{i) KOH, ii) HCl}} C_6H_5CH{=}C\,(COOH)_2$$

$$C_6H_5CH{=}CH\;COOH \xleftarrow[150\text{-}200^\circ C]{\Delta} C_6H_5CH{=}C\,(COOH)_2$$

Cinnamic acid

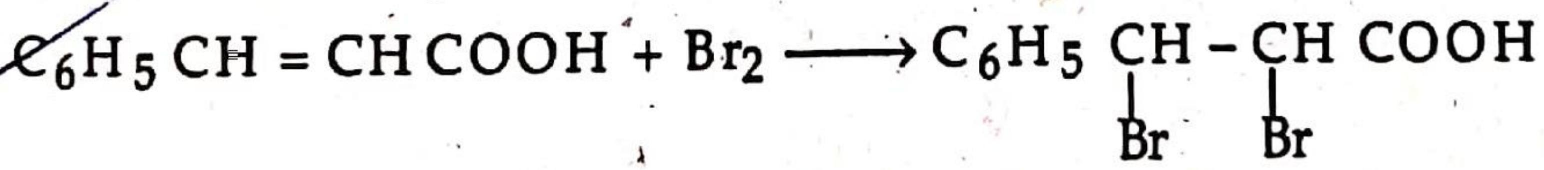
Chemical Reactions :

1. **Esterification :** Cinnamic acid when treated with alcohol is presence of mineral acid forms ester.

$$C_6H_5CH{=}CHCOOH + C_2H_5OH \xrightarrow[H^+]{Esterifi^{n.}} C_6H_5CH{=}CHCOOC_2H_5 + H_2O$$

Cinnamic acid Ethyl cinnamate

2. **Addition of halogens :** When halogens add to cinnamic acid forms dihalo derivative.



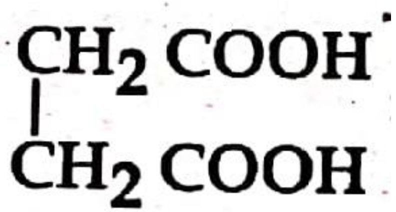
$$C_6H_5CH = CHCOOH + Br_2 \longrightarrow C_6H_5\underset{\displaystyle Br}{\underset{|}{C}H}-\underset{\displaystyle Br}{\underset{|}{C}H}\,COOH$$

Dibromo derivative
(Dibromo cinnamic acid)

3. **Addition of halogens acid :** β - halo acids are formed by the addition of hydrogen halides.

$$C_6H_5\overset{\beta}{C}H{=}\overset{\alpha}{C}H\,COOH + HX \longrightarrow C_6H_5\overset{\overset{\displaystyle X}{|}}{\overset{\beta}{C}}H-\overset{\alpha}{C}H_2\,COOH$$

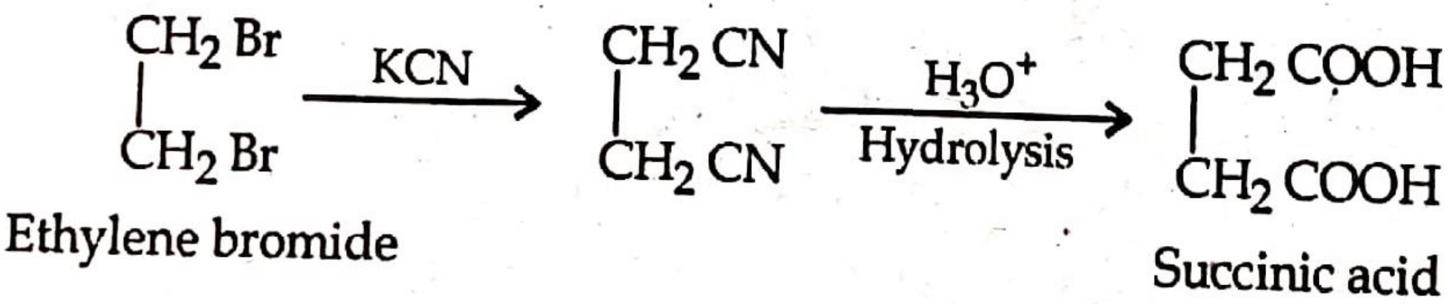
Succinic Acid :



$$\begin{array}{l} CH_2\,COOH \\ | \\ CH_2\,COOH \end{array}$$

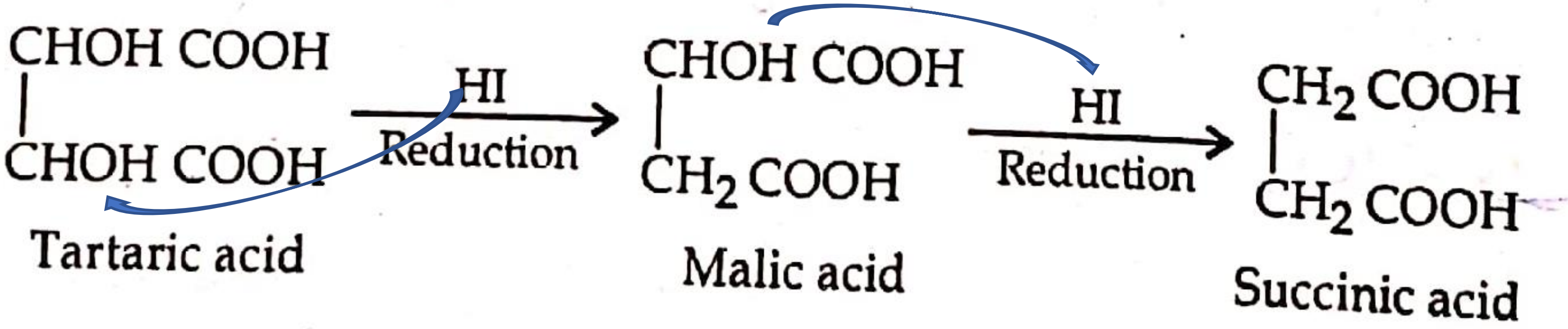
Preparation

1. **From ethylene bromide :** Ethylene bromide on treatment with KCN forms cyanides which on hydrolysis gives succinic acid.



$$\begin{array}{l} CH_2\,Br \\ | \\ CH_2\,Br \end{array} \xrightarrow{KCN} \begin{array}{l} CH_2\,CN \\ | \\ CH_2\,CN \end{array} \xrightarrow[\text{Hydrolysis}]{H_3O^+} \begin{array}{l} CH_2\,COOH \\ | \\ CH_2\,COOH \end{array}$$

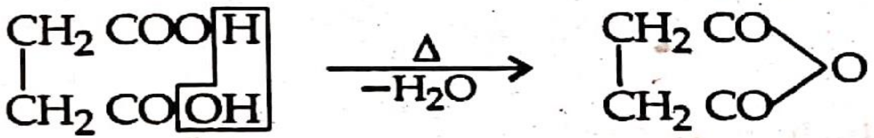
2. **From tartaric acid and malic acid :** With hydroiodic acid, tartaric acid is first reduced to malic acid and then to succinic acid.



$$\begin{array}{l} CHOH\ COOH \\ | \\ CHOH\ COOH \end{array} \xrightarrow[\text{Reduction}]{HI} \begin{array}{l} CHOH\ COOH \\ | \\ CH_2\,COOH \end{array} \xrightarrow[\text{Reduction}]{HI} \begin{array}{l} CH_2\,COOH \\ | \\ CH_2\,COOH \end{array}$$

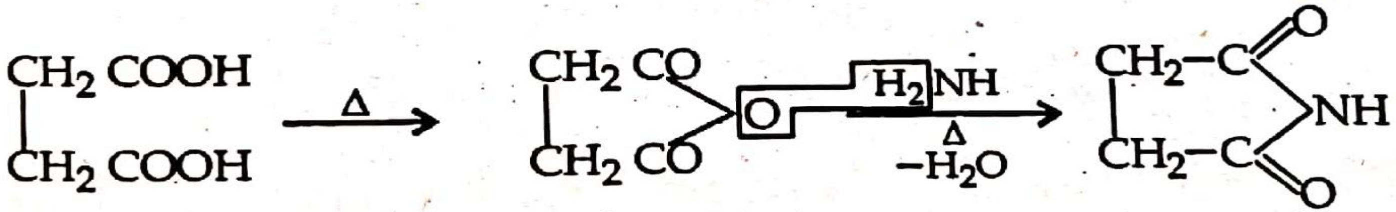
Chemical Reactions :

1. **Action of Heat :** When succinic acid is heated, lose water molecule to form succinic anhydride.



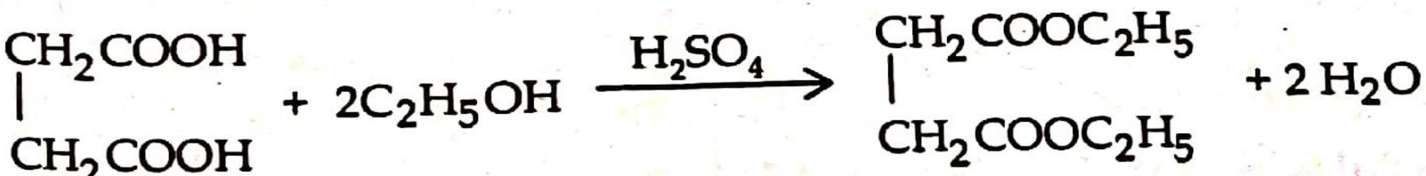
Succinic acid Succinic anhydride

2. **Action of Ammonia:** When heated with ammonia, if first lose water molecule and then reacts with ammonia to form succinimide.



Succinic acid Succinic anhydride Succinimide

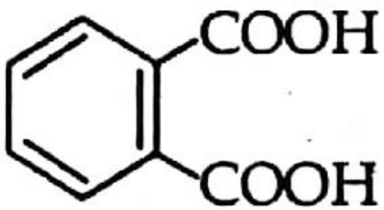
3. **Esterification:** Succinic acid when heateed with alcohol in the presence of conc. sulphuric acid, undergoes esterification.



$$\begin{matrix} CH_2COOH \\ | \\ CH_2COOH \end{matrix} + 2C_2H_5OH \xrightarrow{H_2SO_4} \begin{matrix} CH_2COOC_2H_5 \\ | \\ CH_2COOC_2H_5 \end{matrix} + 2\,H_2O$$

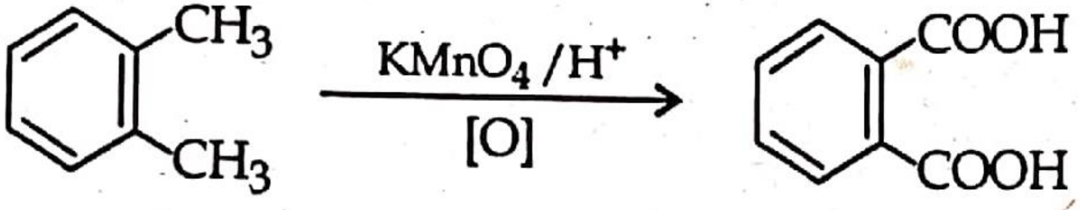
Succinic acid Diethyl succinate

Phthalic Acid:



Preparation

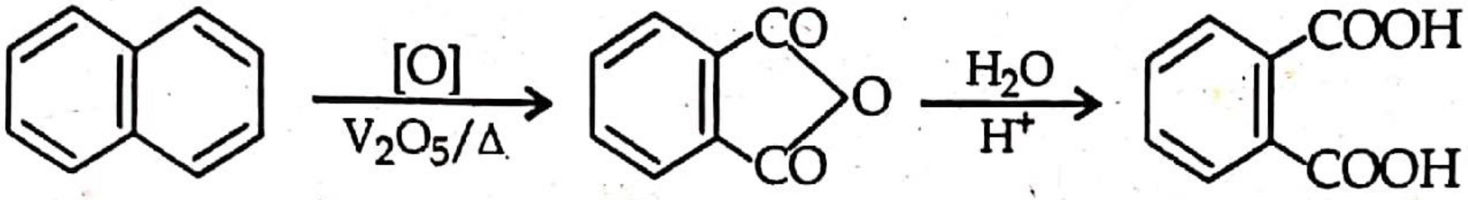
1. **From *o*–xylene:** *o*–xylene on oxidation with acidified $KMnO_4$ gives phthalic acid.



o - xylene

Phthalic acid

2. **From naphthalene:** Naphthalene on strong heating with vanadium pentoxide gives phthalic anhydride which on acid hydrolysis gives phthalic acid.



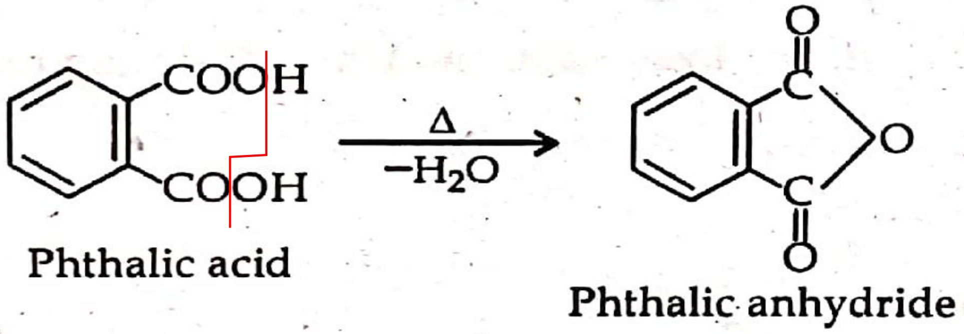
Naphthalene

Phthalic anhydride

Phthalic acid

Chemical Reaction :

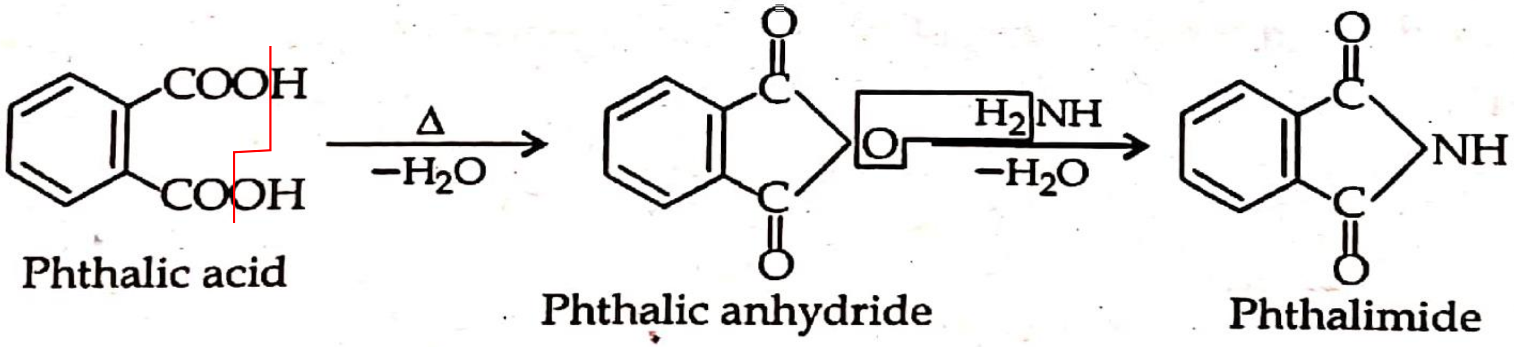
1. **Action of Heat :** When heated alone it forms phthalic anhydride.



Phthalic acid

Phthalic anhydride

2. **With NH_3 :** ***Formation of phthalimide :*** When heated with ammonia, if first lose water molecule and then reacts with ammonia to form phthalimide.

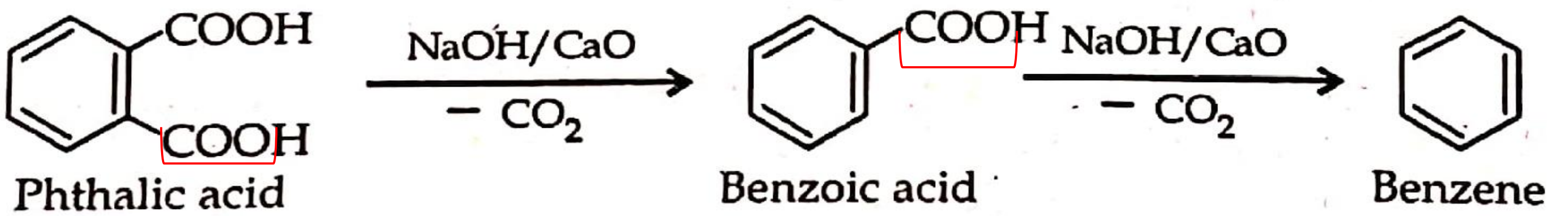


Phthalic acid

Phthalic anhydride

Phthalimide

3. **With Sodalime :** When heated with sodalime, it decarboxylates to benzene.



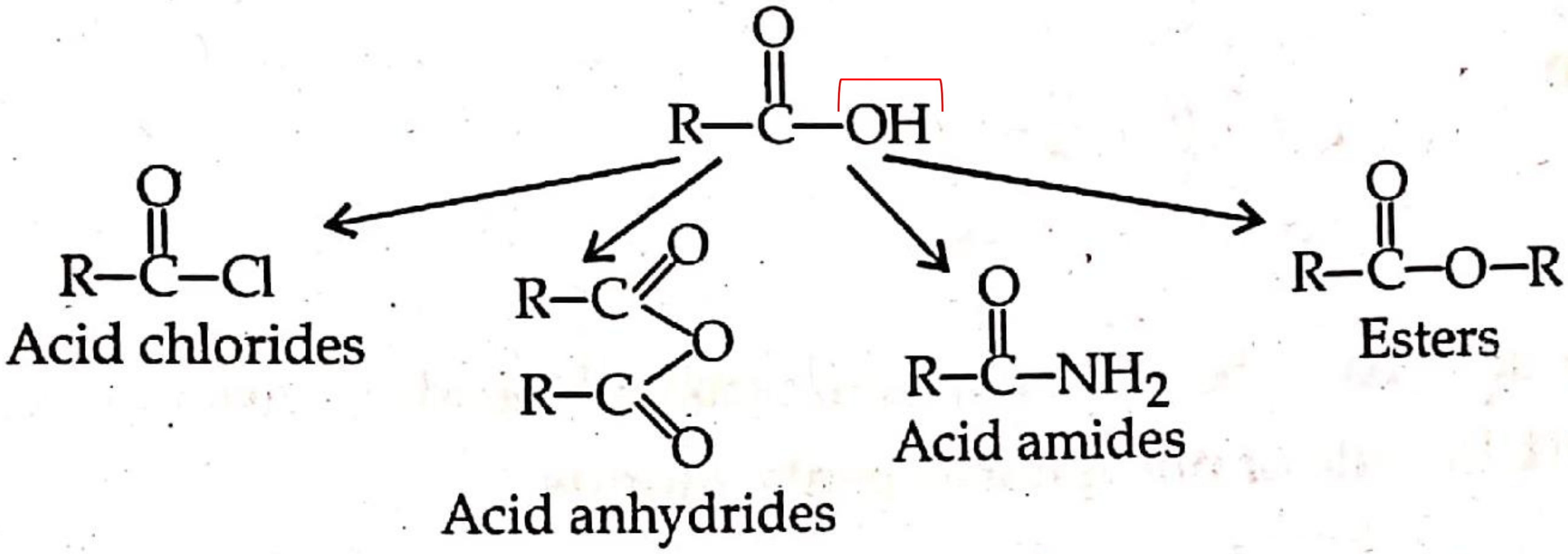
Phthalic acid

Benzoic acid

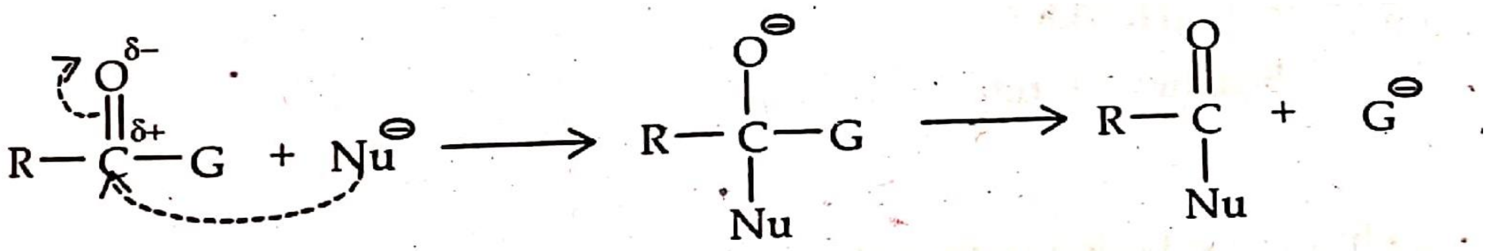
Benzene

B. Carboxylic Acid Derivatives:

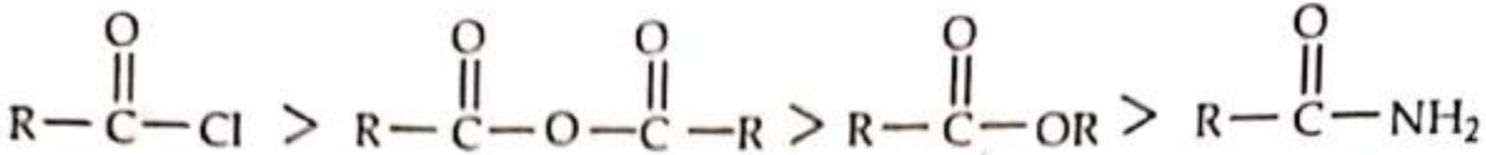
Certain organic compounds are derived from carboxylic acids by the replacement of –OH of the –COOH group by other atoms or groups of atoms as shown below. They car be considered as carboxylic acid derivatives.



Relative stability and reactivity of acid derivatives:



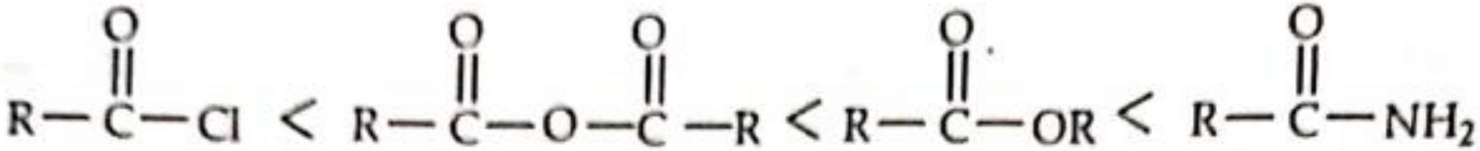
Hence, the order of reactivity of acid derivatives is-



$$R-\overset{O}{\overset{\|}{C}}-Cl > R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R > R-\overset{O}{\overset{\|}{C}}-OR > R-\overset{O}{\overset{\|}{C}}-NH_2$$

Acid chloride Anhydride Ester Amide

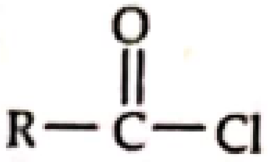
As the stability is opposite to the reactivity, the stability follows the order-



$$R-\overset{O}{\overset{\|}{C}}-Cl < R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R < R-\overset{O}{\overset{\|}{C}}-OR < R-\overset{O}{\overset{\|}{C}}-NH_2$$

Acid chloride Anhydride Ester Amide

Acid Chloride:



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl$$

Preparations

1. From carboxylic acid: It can be prepared from carboxylic acids by reaction with thionyl chloride, or phosphorus trichloride or phosphorus pentachloride.

$$RCOOH \xrightarrow[PCl_3 \text{ or } PCl_5]{SOCl_2 \text{ or}} RCOCl$$

$$CH_3COOH \xrightarrow[PCl_3 \text{ or } PCl_5]{SOCl_2} CH_3\ CO\ Cl$$

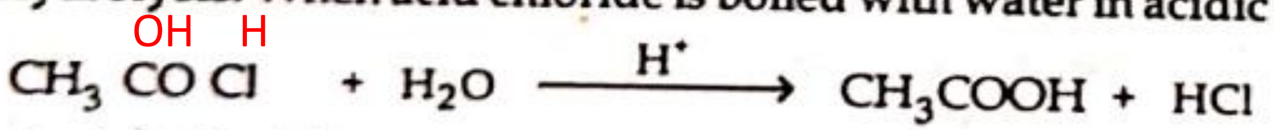
Acetic acid — Acetyl chloride

$$C_6H_5COOH \xrightarrow[PCl_3 \text{ or } PCl_5]{SOCl_2} C_6H_5\ COCl$$

Benzoic acid — Benzoyl chloride

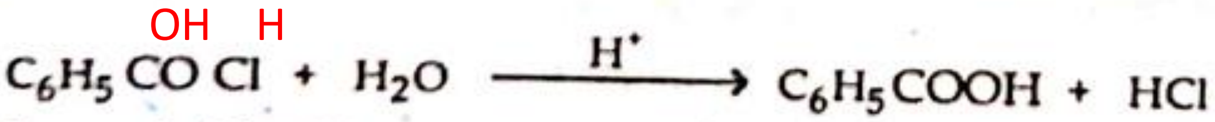
Chemical Reactions:

1. **Hydrolysis:** When acid chloride is boiled with water in acidic medium, it gives carboxylic acid.



$$CH_3\overset{OH}{CO}\overset{H}{Cl} + H_2O \xrightarrow{H^+} CH_3COOH + HCl$$

Acetyl chloride — Acetic acid



$$C_6H_5\overset{OH}{CO}\overset{H}{Cl} + H_2O \xrightarrow{H^+} C_6H_5COOH + HCl$$

Benzoyl chloride — Benzoic acid

2. **Ammonolysis:** When treated with ammonia, acid chloride gives amide

$$CH_3COCl + 2NH_3 \longrightarrow CH_3CONH_2 + NH_4Cl$$

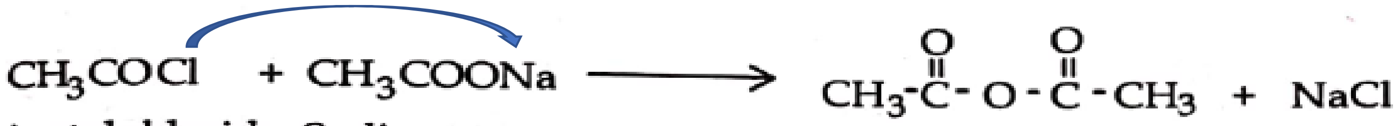
Acetyl chloride — Acetamide

3. **Alcoholysis:** When acid chloride is boiled with alcohol, it gives ester.

$$CH_3COCl + C_2H_5OH \longrightarrow CH_3COOC_2H_5 + HCl$$

Acetyl chloride — Ethyl acetate

4. **Formation of anhydride:** When acid chloride is treated with sodium salt of carboxylic acid, it gives anhydride.



$CH_3COCl + CH_3COONa \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CH_3 + NaCl$

Acetyl chloride Sodium acetate Acetic anhydride

5. **Reduction with $LiAlH_4$:** On reduction with $LiAlH_4$, acid chloride gives alcohol.

$CH_3\ \overset{H_2}{C}\overset{H}{O}\ \overset{H}{Cl} + 4[H] \xrightarrow{LiAlH_4} CH_3CH_2OH + HCl$

Acetyl chloride Ethanol

$C_6H_5\overset{H_2}{C}\overset{H}{O}\ \overset{H}{Cl} + 4[H] \xrightarrow{LiAlH_4} C_6H_5CH_2OH + HCl$

Benzoyl chloride Benzyl alcohol

6. **Rosenmund reduction:** When acid chloride is reduced with hydrogen gas in the presence of $Pd/BaSO_4$ catalyst, aldehyde is formed. This reaction is an example of catalytic poisoning (Refer '*Catalysis*' in Semester-I). Pd acts as catalyst while $BaSO_4$ is used as catalytic poison to avoid further reduction to alcohol.

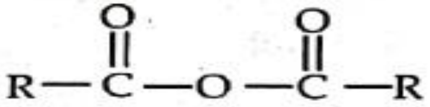
$CH_3C\overset{H}{O}\overset{H}{Cl} + H_2 \xrightarrow{Pd/BaSO_4} CH_3CHO + HCl$

Acetyl chloride Acetaldehyde

$C_6H_5C\overset{H}{O}\overset{H}{Cl} + H_2 \xrightarrow{Pd/BaSO_4} C_6H_5CHO + HCl$

Benzoyl chloride Benzaldehyde

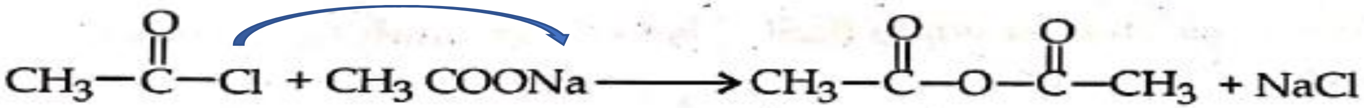
Acid anhydride



$$R-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R$$

Preparation

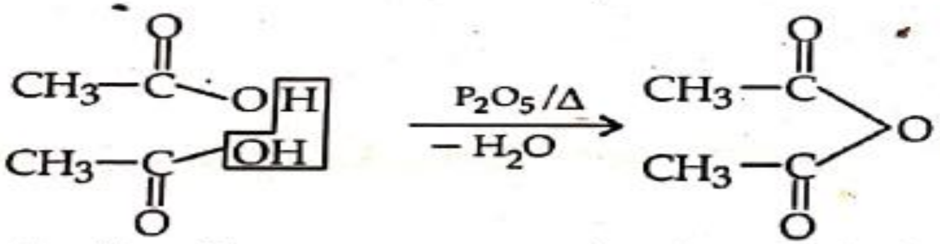
1. **From Acid chlorides :** Acid anhydrides are prepared by reaction between acid chlorides and carboxylic acids or its salt. For example,



$$CH_3-\overset{\overset{O}{\|}}{C}-Cl + CH_3COONa \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CH_3 + NaCl$$

Acetic anhydride

2. ✓ **From carboxylic acid:** When carboxylic acid is heated with dehydrating agent, acid anhydride is formed.



Acetic acid

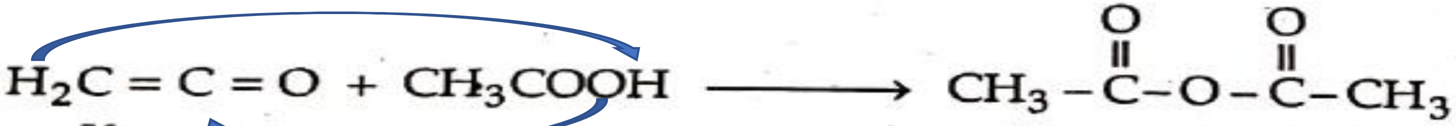
Acetic anhydride

3. **From acetone:** Acetone is strongly heated with triphenyl phosphorous oxide to form ketene. This is treated with acetic acid to give anhydride.

$$CH_3COCH_3 \xrightarrow[700^\circ - 750^\circ C]{\text{Pyrolysis}} H_2C=C=O + CH_4\uparrow$$

Ketene

✓

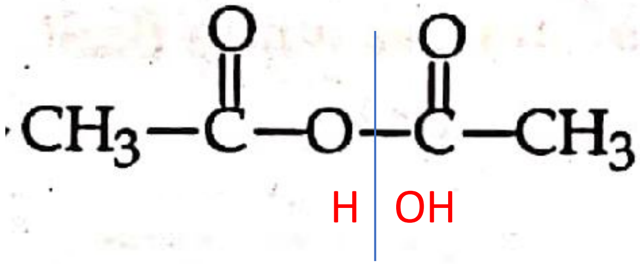


$$H_2C=C=O + CH_3COOH \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CH_3$$

Ketene

Acetic anhydride

Chemical Reactions:



$CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3$

1. **Acid hydrolysis:** It gives acetic acid on boiling with dilute acid.

   $(CH_3CO)_2O + H_2O \xrightarrow{H^+} 2\,CH_3COOH$

   Acetic anhydride — Acetic acid

2. **Base hydrolysis:** It gives acetate salt.

   $(CH_3CO)_2O + 2NaOH \longrightarrow 2\,CH_3COONa + H_2O$

   Acetic anhydride — Sodium acetate

3. **Ammonolysis:** When acetic anhydride is heated with ammonia, acetamide is formed.

   $(CH_3CO)_2O + 2NH_3 \xrightarrow{\Delta} CH_3CONH_2 + H_2O$

   Acetic anhydride — Acetamide

4. **With alcohol:** When acetic anhdride is is heated with alcohol, ester is formed.

   $(CH_3CO)_2O + 2C_2H_5OH \longrightarrow 2\,CH_3COOC_2H_5 + H_2O$

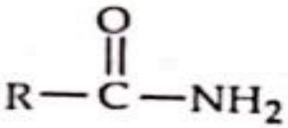
   Acetic anhydride — Ethyl acetate

5. **With HCl:** When acetic anhydride is heated with HCl, acetyl chloride and acetic acid are formed.

   $(CH_3CO)_2O + HCl \longrightarrow CH_3COOH + CH_3COCl$

   Acetic anhydride — Acetic acid — Acetyl chloride

Acid amide



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2$$

Preparation

1. **By ammonolysis:** Carboxylic acid, acid chloride or acid anhydride is treated with ammonia to give amide.

✓ $$\underset{\text{Acetic acid}}{CH_3COOH} + NH_3 \longrightarrow \underset{\text{Ammonium acetate}}{CH_3COO\,NH_4} \xrightarrow{\Delta} \underset{\text{Acetamide}}{CH_3\ CO\,NH_2} + H_2O$$

$$\underset{\text{Benzoic acid}}{C_6H_5COOH} + NH_3 \longrightarrow \underset{\text{Ammonium benzoate}}{C_6H_5COO\,NH_4} \xrightarrow{\Delta} \underset{\text{Benzamide}}{C_6H_5CO\,NH_2} + H_2O$$

✓ $$\underset{\text{Acetyl chloride}}{CH_3\ CO\,Cl} + 2NH_3 \longrightarrow \underset{\text{Acetamide}}{CH_3COONH_2} + NH_4Cl$$

$$\underset{\text{Benzoyl chloride}}{C_6H_5\ CO\,Cl} + 2NH_3 \longrightarrow \underset{\text{Benzamide}}{C_6H_5COONH_2} + NH_4Cl$$

✓ $$\underset{\text{Acetic anhydride}}{(CH_3CO)_2O} + 2NH_3 \xrightarrow{\Delta} \underset{\text{Acetamide}}{2\,CH_3CONH_2} + H_2O$$

Chemical Reactions:

1. **Hydrolysis :** They are easily hydrolysed by heating with dilute acid or alkali. For example,

OH H

$$\underset{\text{Acetamide}}{CH_3CONH_2} + H_2O \xrightarrow{H^+} \underset{\text{Acetic acid}}{CH_3COOH}$$

OH H

$$\underset{\text{Benzamide}}{C_6H_5CONH_2} + H_2O \xrightarrow{H^+} \underset{\text{Benzoic acid}}{C_6H_5COOH}$$

$$\underset{\text{Acetamide}}{CH_3CONH_2} + NaOH \longrightarrow \underset{\text{Acetic acid}}{CH_3COONa + NH_3}$$

$$\underset{\text{Benzamide}}{C_6H_5CONH_2} + NaOH \longrightarrow \underset{\text{Benzoic acid}}{C_6H_5COONa + NH_3}$$

2. **Reduction :** Amides can be easily reduced either catalytically or by $LiAlH_4$ to primary amines.

H_2 H_2

$$\underset{\text{Acetamide}}{CH_3CONH_2} + 4\,[H] \xrightarrow{LiAlH_4} \underset{\text{Ethayl amine}}{CH_3CH_2NH_2}$$

3. **Dehydration :** On heating with phosphorus pentoxide, amides lose a molecule of water to form cyanides.

$$\underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow[\Delta]{P_2O_5} \underset{\text{Methyl cyanide/ Acetonitrile}}{CH_3{-}C{\equiv}N} + H_2O$$

Amphoteric nature of amides

Amides are very feeble bases. This is due to the fact that the lone pair of electrons on nitrogen atom is involved in resonance with carbonyl group. The resonating structures of amide can be shown as:

(I) (II)

Thus, electron pair of nitrogen is not easily available for protonation. Consequently, the basic character is considerably decreased. However, under suitable conditions amides can also exhibit a feeble acidic character. The amphoteric character of amides is illustrated by the following reactions:

1. **Basic character:** In accordance with resonating structure I shown above, it is evident that nitrogen atom of amide molecule has a lone pair of electrons. Therefore, it can act as a base. For example, acetamide (as base) reacts with hydrochloric acid (an acid) to form a salt.

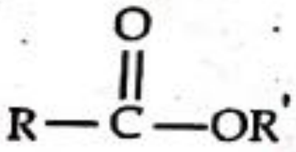
$$CH_3CONH_2 + HCl \longrightarrow CH_3CONH_3Cl$$

2. **Acidic character:** In accordance with resonating structure II shown above, it is clear that the development of positive character on nitrogen atom facilitates the release of proton. Thus, amide can act as acid. For example, acetamide (as acid) reacts with mercuric oxide (a base) to form mercury salt and water.

$$2CH_3CONH_2 + HgO \longrightarrow (CH_3CONH)_2Hg + H_2O$$

Similarly, acetamide reacts with metallic sodium to form sodium salt and hydrogen.

Esters



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OR'$$

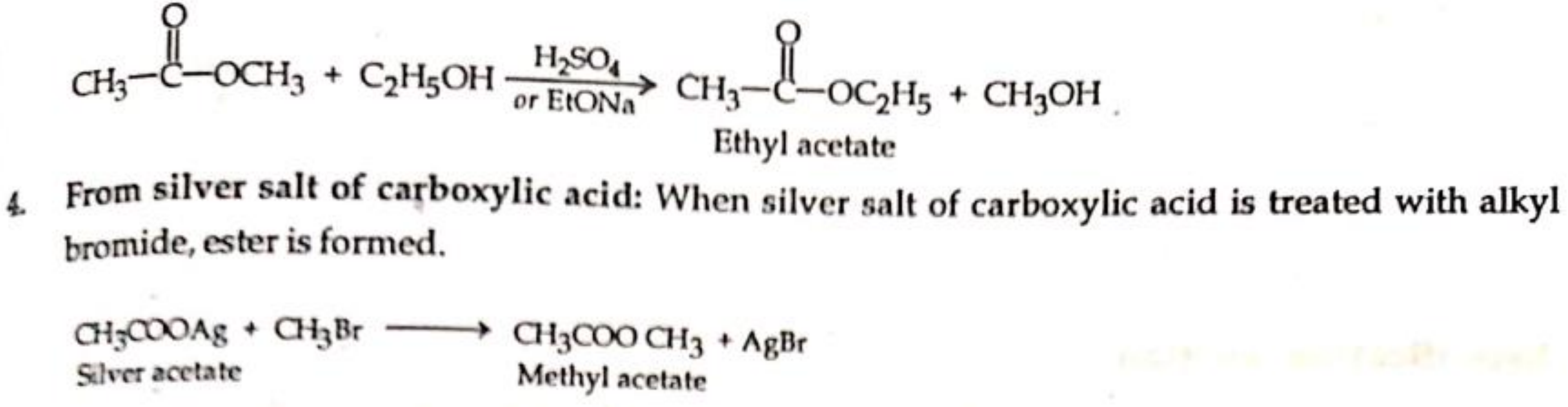
An ester is the product of condensation reaction between a carboxylic acid and an alcohol. The reaction is known as *esterification reaction*. The fragrance of fruits, flowers and essential oils is largely due to esters.

Preparation

1. **From carboxylic acids, acid chlorides or acid anhydride:** Refer previous sections.
2. **From diazomethane :** Methyl esters are prepared by the action of diazomethane on carboxylic acids.

$$\underset{\text{Acetic acid}}{CH_3COOH} + CH_2N_2 \longrightarrow \underset{\text{Methyl acetate}}{CH_3COOCH_3} + N_2$$

3. Transesterification: Reaction of esters with alcohols to give a new ester is known as transesterification. It is catalyzed by acid or a base



$$CH_3-\overset{O}{\overset{\|}{C}}-OCH_3 + C_2H_5OH \xrightarrow[\text{or EtONa}]{H_2SO_4} CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5 + CH_3OH$$

Ethyl acetate

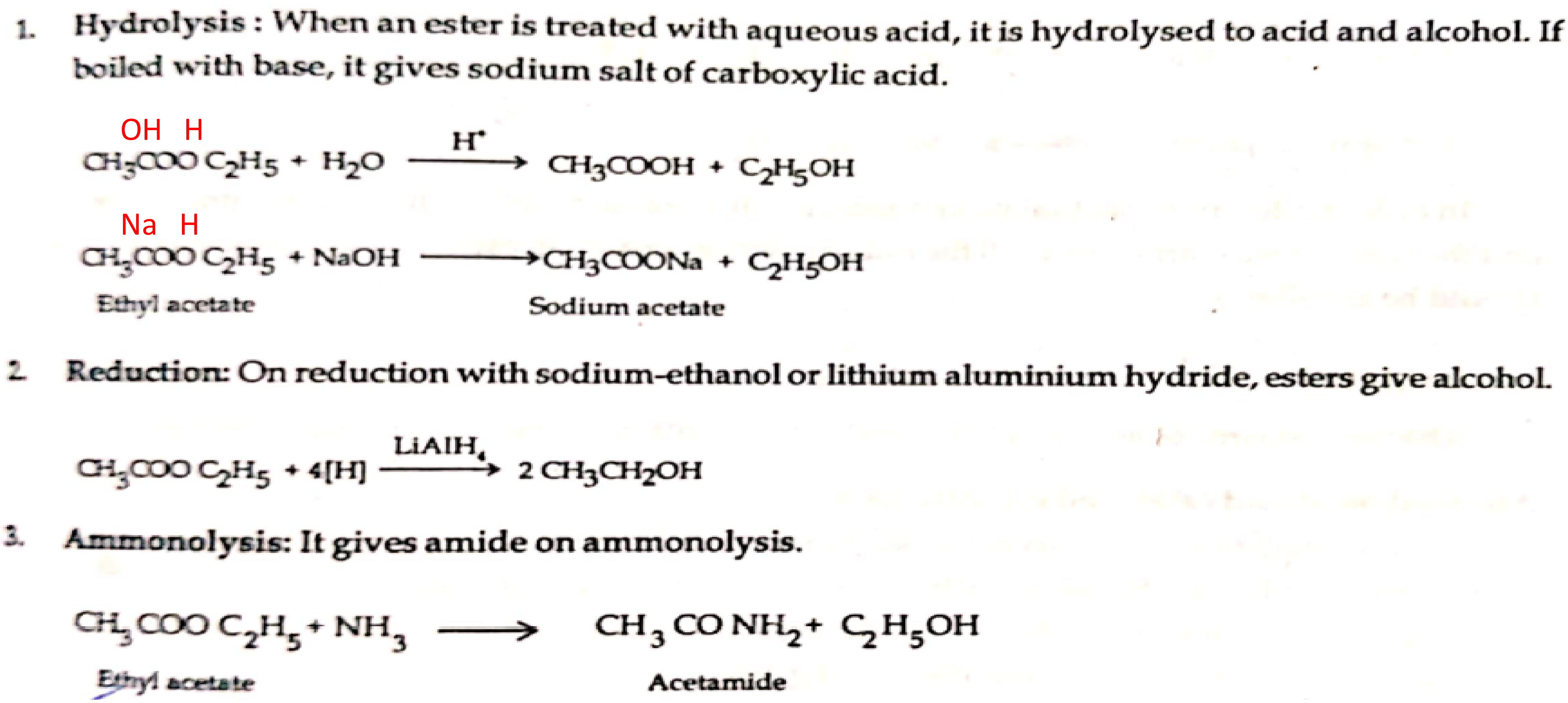
4. **From silver salt of carboxylic acid: When silver salt of carboxylic acid is treated with alkyl** bromide, ester is formed.

$$CH_3COOAg + CH_3Br \longrightarrow CH_3COOCH_3 + AgBr$$

Silver acetate

Methyl acetate

Chemical reactions:



1. **Hydrolysis :** When an ester is treated with aqueous acid, it is hydrolysed to acid and alcohol. If boiled with base, it gives sodium salt of carboxylic acid.

OH H

$$CH_3COO\,C_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

Na H

$$CH_3COO\,C_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$$

Ethyl acetate Sodium acetate

2. **Reduction:** On reduction with sodium-ethanol or lithium aluminium hydride, esters give alcohol.

$$CH_3COO\,C_2H_5 + 4[H] \xrightarrow{LiAlH_4} 2\,CH_3CH_2OH$$

3. **Ammonolysis:** It gives amide on ammonolysis.

$$CH_3COO\,C_2H_5 + NH_3 \longrightarrow CH_3CONH_2 + C_2H_5OH$$

Ethyl acetate Acetamide

Esterification reaction

The reaction of acid and alcohol to form ester is called as esterification reaction. During esterification, loss of water molecule can take place in two ways-

$$\text{R-COO}\boxed{\text{H + HO}}\text{R}' \longrightarrow \text{RCOOR}' + H_2O \quad \text{OR}$$

$$\text{R-CO}\boxed{\text{OH + H}}\text{OR}' \longrightarrow \text{RCOOR}' + H_2O$$

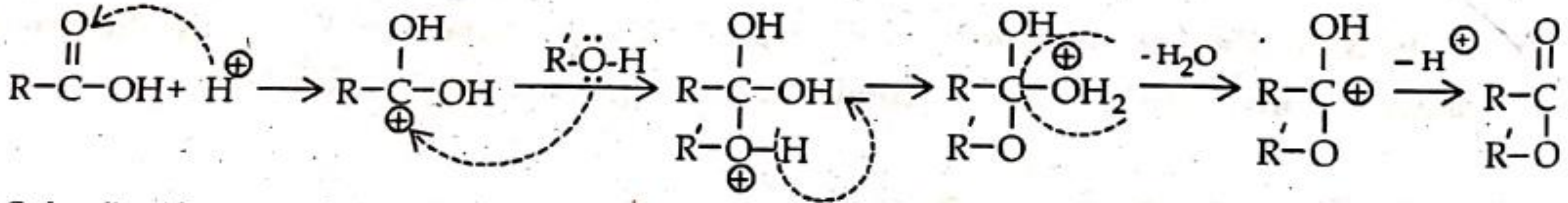
In order to determine actual mechanism, alcohol was labelled with radioisotopic oxygen (^{18}O) and the reaction was carried out. All the radioactivity appeared in ester. Hence, the actual mechanism should be as follows-

$$\text{R-CO}\boxed{\text{OH + H}}\overset{18}{\text{O}}\text{R}' \longrightarrow \text{RCO}\overset{18}{\text{O}}\text{R}' + H_2O$$

The mechanisms of acid and base catalyzed esterification have been discussed below.

Mechanism of acid catalyzed esterification

1. Proton attacks carbonyl oxygen of acid to form carbonium ion.
2. Alcohol molecule attacks on carbonium ion forming oxonium ion.
3. Transfer of proton takes place from one oxygen to other.
4. The product loses water molecule forming ester.

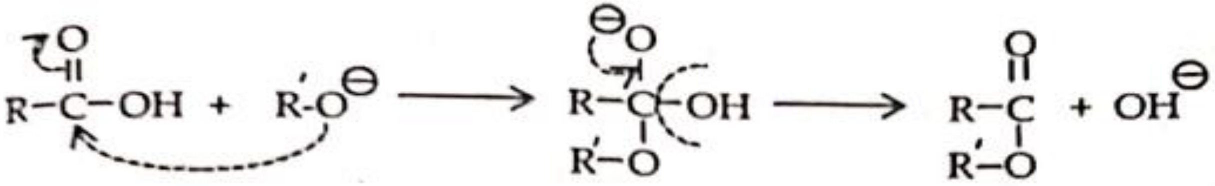


Carboxylic acid Carbonium ion Oxonium ion Carbonium ion Ester

Mechanism of base catalyzed esterification

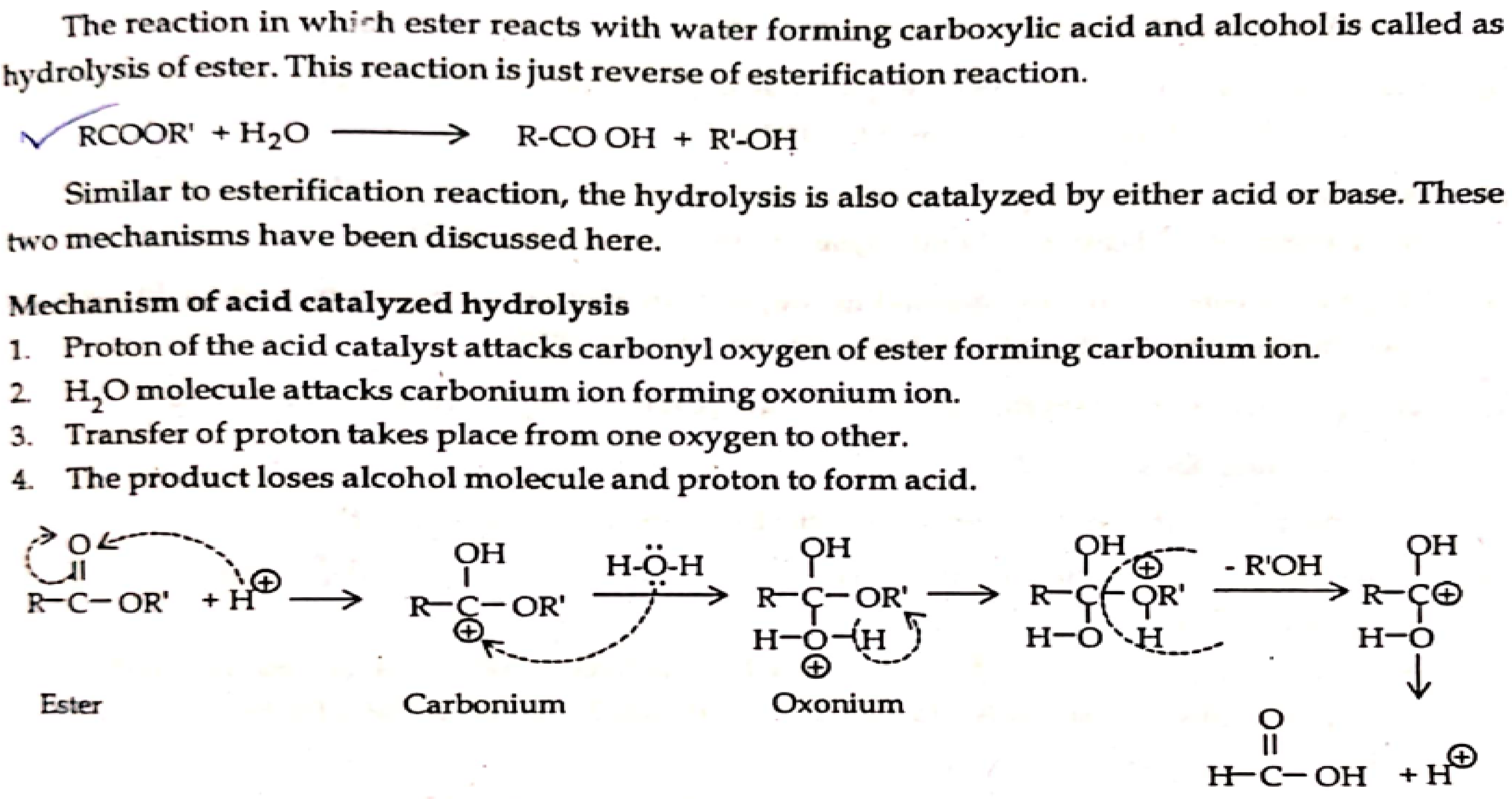
1. Base takes out proton from alcohol forming alkoxide ion.
2. Alkoxide ion attacks on carbonyl carbon of acid.
3. The product loses hydroxide ion forming ester.

$$R'\text{-}O\text{-}H + OH^{\ominus} \longrightarrow R'\text{-}O^{\ominus} + H_2O$$



Carboxylic acid Ester

Hydrolysis of esters:



The reaction in which ester reacts with water forming carboxylic acid and alcohol is called as hydrolysis of ester. This reaction is just reverse of esterification reaction.

$$RCOOR' + H_2O \longrightarrow R\text{-}CO\,OH + R'\text{-}OH$$

Similar to esterification reaction, the hydrolysis is also catalyzed by either acid or base. These two mechanisms have been discussed here.

Mechanism of acid catalyzed hydrolysis

1. Proton of the acid catalyst attacks carbonyl oxygen of ester forming carbonium ion.
2. H_2O molecule attacks carbonium ion forming oxonium ion.
3. Transfer of proton takes place from one oxygen to other.
4. The product loses alcohol molecule and proton to form acid.

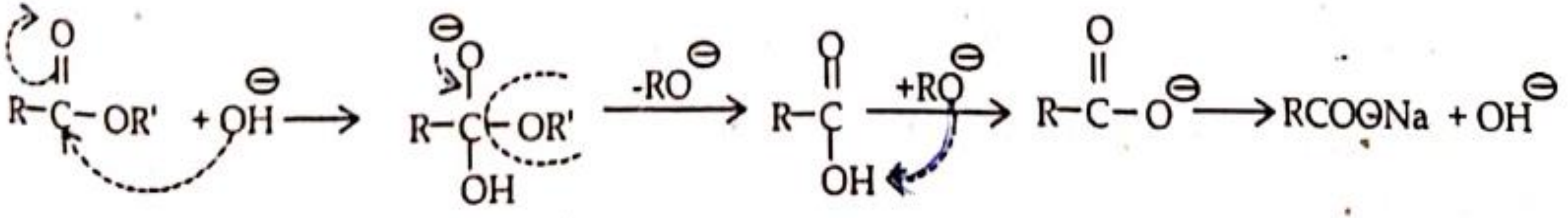
Ester

Carbonium

Oxonium

Mechanism of base catalyzed hydrolysis

1. OH^- from the base attacks carbonyl carbon of ester forming an intermediate.
2. It loses alkoxide ion forming carboxylic acid.
3. This alkoxide ion is highly unstable and so it takes up proton from carboxylic acid forming more stable carboxylate ion.
4. Carboxylate ion takes up cation from the base forming a salt.



Thank you &
Best of Luck