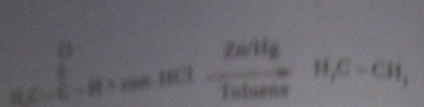
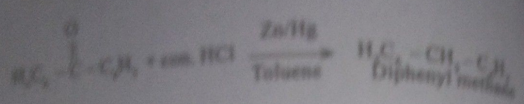
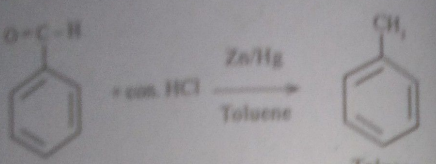


$$H_3C-\overset{O}{\overset{\|}{C}}-H + \text{con. HCl} \xrightarrow[\text{Toluene}]{Zn/Hg} H_3C-CH_3$$



$$H_5C_6-\overset{O}{\overset{\|}{C}}-C_6H_5 + \text{con. HCl} \xrightarrow[\text{Toluene}]{Zn/Hg} H_5C_6-CH_2-C_6H_5$$

Diphenyl metha



Toluene

University questions

1. Discuss the mechanism of Kolbe's reaction.
2. Write the equation of Rimer Tiemann reactions.
3. Write short notes on the following mechanism.
   i. Gattermann   ii. Lederer - Manasse   iii. Hoube Hoes
4. How will prepare cresols?
5. Discuss the properties of p - amino phenols.
6. How will classified phenols.
7. Mention the preparation and properties of α – and β – napthol
8. Define Epoxides.
9. What synthetic uses of Epoxides?
10. Write short notes on crown ethers.
11. Write the mechanism of 2,4, di nitro phenyl hydrosizne
12. Write the mechanism reduction of carbonyl group by using LiAl

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Unit - III

Carboxylic acids and Esters

Carboxylic acid

3.1 Unsaturated acids

Most of the unsaturated acids are known by their common names. Their IUPAC names are obtained by selecting the longest carbon chain containing the double bond and the carboxyl group, and naming the acid as Alkenoic acid. The position of the double bond with respect to the carboxyl group is indicated by a number.

$CH_2=CH-COOH$
Propenoic acid
(Acrylic acid)

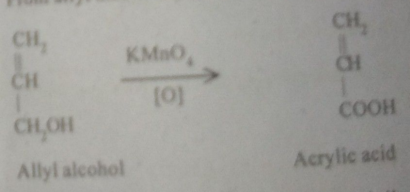
$\overset{4}{C}H_3\overset{3}{C}H=\overset{2}{C}H-\overset{1}{C}OOH$
2 - Butenoic acid
(Crotonic acid)

Acrylic acid ($CH_2=CH-COOH$)

Preparation :

Acrylic acid is obtained.

From allyl alcohol by the following steps :



$$\begin{matrix} CH_2 \\ \| \\ CH \\ | \\ CH_2OH \end{matrix} \xrightarrow[{[O]}]{KMnO_4} \begin{matrix} CH_2 \\ \| \\ CH \\ | \\ COOH \end{matrix}$$

Allyl alcohol   Acrylic acid

2. By oxidation of acrolein with ammoniacal silver nitrate.

$$CH_2=CH-CHO + Ag_2O \longrightarrow CH_2=CH-COOH + 2Ag$$

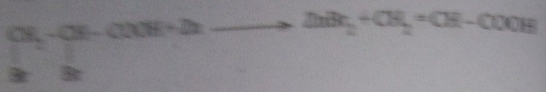
Acrolein   Acrylic acid

3. β– hydroxypropionic acid is heated with base.

$$HO-CH_2-CH_2-COOH \xrightarrow{\Delta} CH_2=CH-COOH + H_2O$$

β– hydroxypropionic acid   Acrylic acid

4. α, β – di bromo propionic acid is heated with zinc.



$$\underset{Br}{CH_2} - \underset{Br}{CH} - COOH + Zn \longrightarrow ZnBr_2 + CH_2 = CH - COOH$$

5. By carbonylationof acetylene inthe presence of water and nickel carbonyl catalyst.

$$\underset{\text{Acetylene}}{HC \equiv CH + CO + H_2O} \xrightarrow{Ni(CO)_4} \underset{\text{Acrylic acid}}{CH_2 = CH - COOH}$$

6. Hydrolysis of vinyl cyanide

$$CH_2 = CH - CN + 2H_2O \xrightarrow{H^+} CH_2 = CH - COOH + NH_3$$

Properties :

Physical :

1. Acrylic acid is a colourless pungent - smelling liquid
2. Boiling point 141°C.
3. It is misible with water, alcohol and ether.

Chemical :

Acrylic acid behaves both as an alkene and a carboxylic acid.

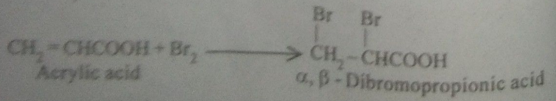
A. Reactions of the double bond

1. Reduction Acrylic acid undergoes reduction with sodium and ethanol to give propionic acid.

$$\underset{\text{Acrylic acid}}{CH_2 = CHCOOH + 2[H]} \xrightarrow[C_2H_5OH]{Na} \underset{\text{Propionic acid}}{CH_3CH_2COOH}$$

2. *Addition of Halogens :*

Acrylic acid reacts with Cl_2 or Br_2 to form addition products.



$$\underset{\text{Acrylic acid}}{CH_2 = CHCOOH + Br_2} \longrightarrow \underset{\alpha,\,\beta\text{ - Dibromopropionic acid}}{\overset{Br}{CH_2} - \overset{Br}{CHCOOH}}$$

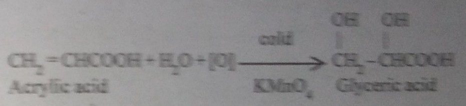
3. *Addition of Halogen acids :*

Acrylic acid reacts with dilute HCl solution to give β – Bromopropionic acid

$$\underset{\text{Acrylic acid}}{CH_2 = CHCOOH + HBr} \longrightarrow \underset{\beta\text{ - Bromopropionic acid}}{BrCH_2CH_2COOH}$$

4. *Reaction with Dil. $KMnO_4$:*

Acrylic acid reacts with dilute cold $KMnO_4$ solution to give glyceric acid.



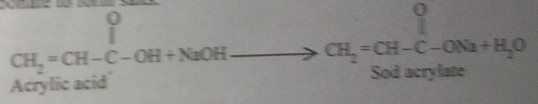
$$\underset{\text{Acrylic acid}}{CH_2 = CHCOOH + H_2O + [O]} \xrightarrow[KMnO_4]{cold} \underset{\text{Glyceric acid}}{\overset{OH}{CH_2} - \overset{OH}{CHCOOH}}$$

5. *Polymerization :*

On standing, acrylic acid slowly polymrizes to a glassy solid.

B. Reactions of – COOH group

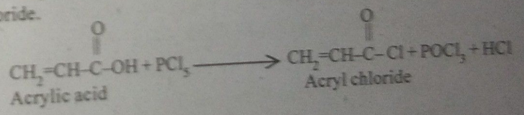
6. *Salt formation :* Acrylic acid reacts with sodium hydroxide or sodium carbonate to form salts.



$$\underset{\text{Acrylic acid}}{CH_2 = CH - \overset{O}{\overset{\|}{C}} - OH + NaOH} \longrightarrow \underset{\text{Sod acrylate}}{CH_2 = CH - \overset{O}{\overset{\|}{C}} - ONa + H_2O}$$

7. *Reaction with PCl_5*

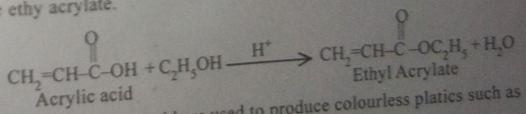
Acrylic acid reacts with phosphorus pentachloride to give acryl chloride.



$$\underset{\text{Acrylic acid}}{CH_2{=}CH{-}\overset{O}{\overset{\|}{C}}{-}OH + PCl_5} \longrightarrow \underset{\text{Acryl chloride}}{CH_2{=}CH{-}\overset{O}{\overset{\|}{C}}{-}Cl + POCl_3 + HCl}$$

8. *Esterification :*

Acrylic acid reacts with ethanol int he presence of acid catalyst to give ethy acrylate.



$$\underset{\text{Acrylic acid}}{CH_2{=}CH{-}\overset{O}{\overset{\|}{C}}{-}OH} + C_2H_5OH \xrightarrow{H^+} \underset{\text{Ethyl Acrylate}}{CH_2{=}CH{-}\overset{O}{\overset{\|}{C}}{-}OC_2H_5 + H_2O}$$

Esters of acrylic acid are used to produce colourless platics such as lucite and plexiglass.

CROTONIC ACID

Trans - 2 - Butenoic acid $CH_3CH = CHCOOH$

Preparation

1. By the oxidation of crotonaldehyde with ammoniacal silver nitrate.

$$\underset{\text{Crotonaldehyde}}{CH_3CH{=}CHCHO} + Ag_2O \longrightarrow \underset{\text{Crotonic acid}}{CH_3CH = CHCOOH} + 2Ag$$

2. β- Hydroxy butric acid is heated with base.

$$CH_3-CH(OH)-CH_2-COOH \longrightarrow CH_3-CH{=}CH-COOH + H_2O$$

3. By heating acetaldehyde and diethyl malonate in the presence of pyridine (Knoevenagl reaction) followed by the hydrolysis and decarboxylation.

$$\underset{\text{Acetalydehyde}}{CH_3CH = O} + \underset{\text{Diethyl malonate}}{H_2C(COOC_2H_5)_2} \xrightarrow[\Delta\,(-H_2O)]{\text{Pyridine}} CH_3CH = C(COOC_2H_5)_2$$

$$\xrightarrow[\Delta]{\text{aq. KOH}} CH_3CH = C(COOK)_2 \xrightarrow[(-CO_2)]{H^+ / \Delta} \underset{\text{Crotonic acid}}{CH_3CH = CHCOOH}$$

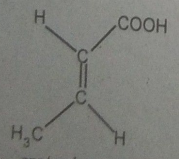
Properties :

1. Crotonic acid is a colourless solid mp 72°C.
2. Like acrylic acid, it gives reactions of an alkene and a carboxylic acid.
3. It undergoes bromination with N - bromosuccinimide to form γ - bromocrotonic acid, $BrCH_2CH\ CHCOOH$.

Structures :

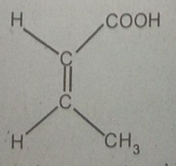
It is a geometrical isomerism. It has two form

1. cis form



crotonic acid
freezing point 345K

2. trans form



iso crotonic acid
freezing point 289K

OLEIC ACID, $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$

Oleic acid occurs as triolein (glyceryl ester) in oils and fats. It is a colourless oil (m.p. 280K) Insoluble in water but soluble in alcohol and ether. Catalytic reduction of oleic acid gives stearic acid. Sodium or potassium salts of the acid are used as soaps. A few other reactions are

i. Oxidation

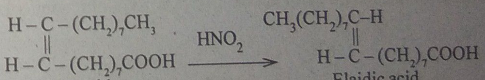
With acid permanganate it gives nonionic acid and azelaic acid.

$$\underset{\text{Oleic acid}}{C_{17}H_{33}COOH} \xrightarrow[KMnO_4]{C_2H_5ONa} \underset{\text{Nonanoic acid}}{CH_3(CH_2)_7COOH} + \underset{\text{Azelaic acid}}{HOOC(CH_2)_7COOH}$$

This experiment indicates the position of the double bond which is further confirmed by ozonolysis when $OHC\ (CH_2)_7CH_3$ and $OHC(CH_2)_7CO_2H$ are obtained.

2. Action of nitrous acid

Action of nitrous acid. When treated with nitrous acid, oleic acid changes into its geometrical isomer elaidic acid. (trans - form - m.p. 324K).



$$\begin{array}{c} H-C-(CH_2)_7CH_3 \\ \| \\ H-C-(CH_2)_7COOH \end{array} \xrightarrow{HNO_2} \begin{array}{c} CH_3(CH_2)_7C-H \\ \| \\ H-C-(CH_2)_7COOH \end{array}$$

Oleic acid
(cis - form)

Elaidic acid
(trans - form)

CINNAMIC ACID, $C_6H_5CH = CHCOOH$

Cinnamic acid is 3 - phenylpropenoic acid.

Preparation :

Cinnamic acid is obtained.

1. Claisen condensation

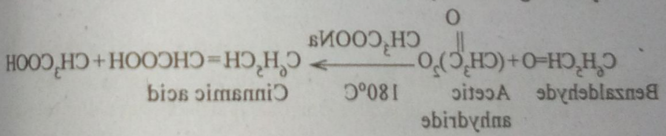
By treatment of benzaldehyde with ethyl acetate in the presence of sodijm ethoxide followed by acid - hydrolysis of the resulting ester.

$$\underset{\text{Benzaldehyde}}{C_6H_5CH = O} + \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} \xrightarrow[-H_2O]{C_2H_5ONa} \underset{\text{Ester}}{C_6H_5CH = CHCOOC_2H_5}$$

$$\xrightarrow{H_2O} \underset{\text{Cinnamic acid}}{C_6H_5CH = CHCOOH}$$

2. Perkin's reaction

By heating benzaldehyde with acetic anhydride at 180°C.



$$\underset{\text{Benzaldehyde}}{C_6H_5CH{=}O} + \underset{\text{Acetic anhydride}}{(CH_3\overset{\overset{O}{\|}}{C})_2O} \xrightarrow[180^oC]{CH_3COONa} \underset{\text{Cinnamic acid}}{C_6H_5CH{=}CHCOOH} + CH_3COOH$$

3. Knoevenagels's reaction

By heating benzaldehyde with malonic acid in alcoholic ammonia solution.

$$C_6H_5CH{=}O + \underset{\text{Malonic acid}}{CH_2(COOH)_2} \xrightarrow[\Delta]{NH_3} \underset{\text{Cinnamic acid}}{C_6H_5CH = CHCOOH} + CO_2 + H_2O$$

Properties :

1. Cinnamic acid is a crystalline solid, mp 133°C.
2. It is sparingly soluble in water.
3. It behaves as an α, β - unsaturated acid and a benzene derivative.

---

1. Cinnamic acid reacts with sodium hydroxide to form sodium cinnamate.

$$\underset{\text{Cinnamic acid}}{C_6H_5CH = CHCOOH} + NaOH \longrightarrow \underset{\text{Sod. Cinnamate}}{C_6H_5CH = CHCOOC_2H_5} + H_2O$$

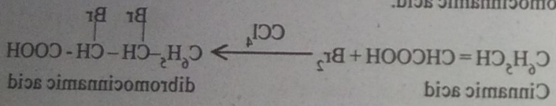
2. Cinnamic acid reacts with ethyl alcohol in the presence of an acid catalyst to give ethyl cinnamate.

$$\underset{\text{Cinnamic acid}}{C_6H_5CH = CHCOOH} + C_2H_5OH \xrightarrow{H^+} \underset{\text{Ethyl cinnamate}}{C_6H_5CH{=}CHCOOC_2H_5} + H_2O$$

3. Cinnamic acid reacts with PCl_5 or $SOCl_2$ to form cinnamoyl chloride.

$$\underset{\text{Cinnamic acid}}{C_6H_5CH = CHCOOH} \xrightarrow{PCl_5} \underset{\text{cinnamoyl chloride}}{C_6H_5CH = CHCOCl} + POCl_3 + HCl$$

4. Cinnamic acid reacts with bromine in carbon tetrachloride to give dibromocinnamic acid.



$$\underset{\text{Cinnamic acid}}{C_6H_5CH = CHCOOH} + Br_2 \xrightarrow{CCl_4} \underset{\text{dibromocinnamic acid}}{C_6H_5\text{-}\overset{\overset{Br}{|}}{C}H - \overset{\overset{Br}{|}}{C}H - COOH}$$

5. Cinnamic acid undergoes reduction with sodium amalgam and water to give 3 - phenylpropanoic acid.

$$\underset{\text{Cinnamic acid}}{C_6H_5CH = CHCOOH} + 2[H] \xrightarrow[H_2O]{Na \backslash Hg} \underset{\text{3 - phenylpropanoic acid.}}{C_6H_5CH_2CH_2COOH}$$

It undergoes reduction with lithium aluminium hydride to form 3-phenyl - 2- propenol

$$\underset{\text{Cinnamic acid}}{C_6H_5CH = CHCOOH} + [H] \xrightarrow{LiAlH_4} \underset{\text{3 - phenyl - 2 - propenol}}{C_6H_5CH = CHCH_2OH}$$

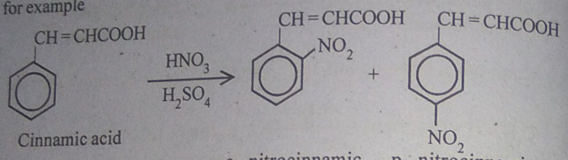
6. Cinnamic acid undergoes oxidation with hot acidic $KMnO_4$ to give benzoic acid.

$$\underset{\text{Cinnamic acid}}{C_6H_5CH = CHCOOH} + [O] \xrightarrow[\Delta]{KMnO_4} \underset{\text{Benzoic acid}}{C_6H_5COOH}$$

7. Cinnamic acid undergoes decarboxylation with soda - lime to yield styrene.

$$\underset{\text{Cinnamic acid}}{C_6H_5CH{=}CHCOOH} + NaOH \xrightarrow[\Delta]{CaO} \underset{\text{Styrene}}{C_6H_5CH{=}CH_2} + Na_2CO_3 + H_2O$$

8. It undergoes electrophilic substitution reactions to form o - p - isomers for example



Cinnamic acid

o - nitrocinnamic acid

p - nitrocinnamic acid

3.2. Hydroxy acids

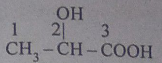
The carboxylic acids in which one or more hydrogen atoms of the hydrocarbon group have been replaced by atom or groups such as OH, X (haligen) of NH_2, are referred to as substituted acids. They are designated as hydroxy acids, halo acids or amino acids depending on the subsitutent present, For example,

$HO-CH_2-COOH$	$Br-CH_2-COOH$	H_2N-CH_2-COOH
Hydroxyacetic acid	Bromoacetic acid	Aminoacetic acid

Some of the hydroxy acids are very common naturally occurring sustances and are usually referred to by common names. The halo acids, on the other hand, are mostly synthetic and are assigned IUPAC names. The position of the hydroxy and halogen substitutents on the carbon chain are indicated by Greek letters or by number

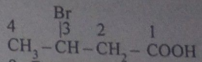
$$\begin{array}{cccccc} \varepsilon & \delta & \gamma & \beta & \alpha & \\ 6 & 5 & 4 & 3 & 2 & 1 \\ C- & C- & C- & C- & C- & COOH \end{array}$$

For example



$$\overset{1}{CH_3}-\overset{\overset{OH}{|}}{\overset{2}{C}H}-\overset{3}{COOH}$$

α - Hydroxpropionic acid
2- hydroxypropanoic acid



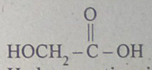
$$\overset{4}{CH_3}-\overset{\overset{Br}{|}}{\overset{3}{C}H}-\overset{2}{CH_2}-\overset{1}{COOH}$$

β - Bromobutyric acid
3 - Bromobutanoic acid

Here we will disucss the hydroxy acdis and the halo acids only, while the amino acids will be taken up along with proteins.

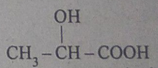
Hydroxy acids

They are the derivatives of carboxylic acids in whcih one or more hydrogen atoms of the hydrocarbon group are replaced by as many – OH groups. They are referred to as α, β, γ, δ etc., hydroxy acids according as the OH is bonded to α, β, γ or δ carbon of the cahin. Some of the important hydroxy acids are ;



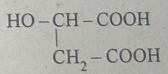
$$HOCH_2-\overset{\overset{O}{\|}}{C}-OH$$

Hydroxyacetic acid
(Glycollic acid)



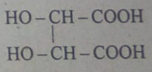
$$CH_3-\overset{\overset{OH}{|}}{CH}-COOH$$

α - Hydroxpropionic acid
(Lactic acid)



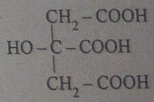
$$\begin{array}{l} HO-CH-COOH \\ \quad\;\;\; | \\ \quad\;\; CH_2-COOH \end{array}$$

Malic acid



$$\begin{array}{l} HO-CH-COOH \\ \quad\;\;\; | \\ HO-CH-COOH \end{array}$$

Tartaric acid



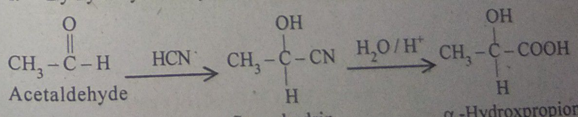
$$\begin{array}{l} \quad\;\; CH_2-COOH \\ \quad\;\;\; | \\ HO-C-COOH \\ \quad\;\;\; | \\ \quad\;\; CH_2-COOH \end{array}$$

Citric acid

Methods of preparation

For α – hydroxy acids

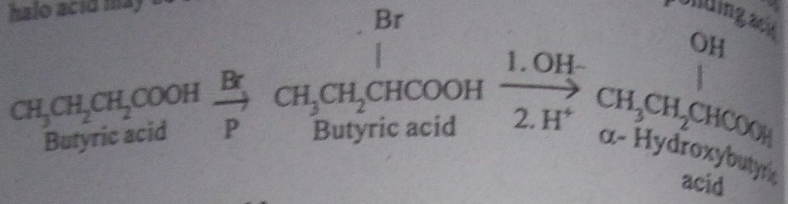
1. By hydrolysis of cyanohydrins derived from aldehydes or ketones.



$$\underset{\text{Acetaldehyde}}{CH_3-\overset{\overset{O}{\|}}{C}-H} \xrightarrow{HCN} \underset{\text{Cyanohydrin}}{CH_3-\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}}-CN} \xrightarrow{H_2O/H^+} CH_3-\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}}-COOH$$

α -Hydroxpropionic acid
(Lactic acid)

2. By hydrolysis of halo acids with dilute aqueous alkali. The desi halo acid may be obtained by HVZ reaction from the corresponding aci



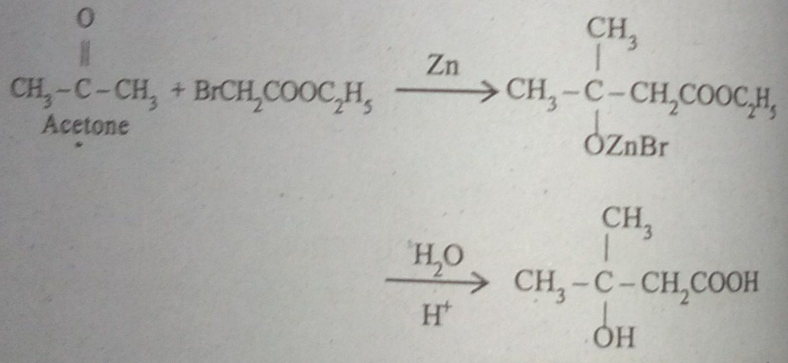
$$\underset{\text{Butyric acid}}{CH_3CH_2CH_2COOH} \xrightarrow[P]{Br} \underset{\text{Butyric acid}}{CH_3CH_2\overset{\overset{Br}{|}}{C}HCOOH} \xrightarrow[2.\ H^+]{1.\ OH^-} \underset{\alpha\text{- Hydroxybutyric acid}}{CH_3CH_2\overset{\overset{OH}{|}}{C}HCOOH}$$

For β – hydroxy acids

3. By reduction of β - keto acids or esters with $LiAlH_4$ in the presenc of pyridine.

$$\underset{\substack{\text{Ethyl acetoacetate}\\ (\alpha,\beta\text{ - keto ester})}}{CH_3COCH_2COOC_2H_5} \xrightarrow[\text{Pyridine}]{LiAlH_4} CH_3CH(OH)CH_2COOC_2H_5 \xrightarrow[H^+]{H_2O} \underset{\beta\text{ - Hydroxybutyric acid}}{CH_3CH(OH)CH_2COOH}$$

4. By reformatsky reaction e.g.,



$$\underset{\text{Acetone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3} + BrCH_2COOC_2H_5 \xrightarrow{Zn} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{OZnBr}{|}}{C}}-CH_2COOC_2H_5 \xrightarrow[H^+]{H_2O} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-CH_2COOH$$

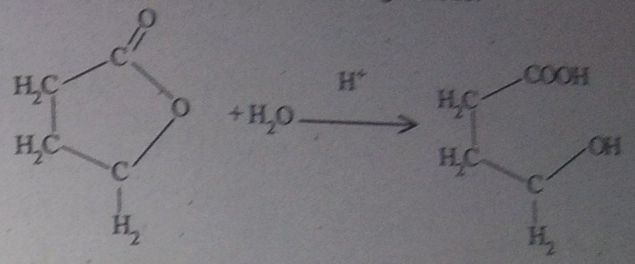
3 - Hydroxy - 3 - methyl butanoic acid

5. By careful oxidation of an aldol with Tollen's reagent (ammoniacol $AgNO_3$).

$$\underset{\text{Acetaldehyde aldol}}{CH_3CH(OH)CH_2CHO} \xrightarrow{[O]} \underset{\beta\text{ – Hydroxybutyric acid}}{CH_3CH(OH)CH_2COOH}$$

For γ, δ and longer hydroxy acids

6. By hydrolysis of the corresponding lactone.



Physical properties

1. The hydroxy acids are colourless crystalline solids or syrupy liquids.
2. Their melting and boiling points are much higher than those of the parent unsubstituted acids.
3. They are more soluble in water than either the parent carboxylic acid or the alcohol, since both the functional groups (OG and COOH) in them can form hydrogen bonds with water. They are less soluble in alcohol and ether.
4. They are stronger acids than the corresponding unsubstituted acids owing tot he electron with drawing effect of the OH group. For example, hydroxyacetic acid ($Ka = 14.76 \times 10^{-5}$) is considerably stronger acids than acetic acid ($Ka = 1.8 \times 10^{-5}$).

Chemical properties

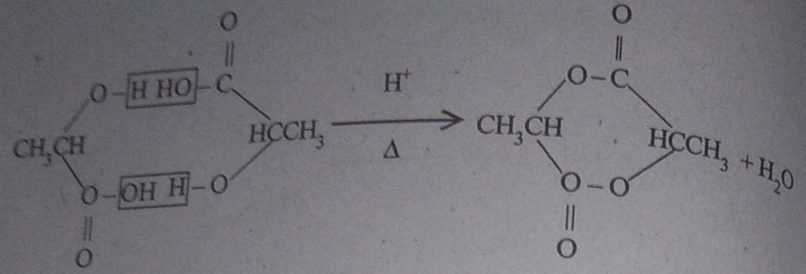
The hydroxy acids have a carboxylic group and an alcoholic OH group in the same molecule. They give characteristic reactions of both these functions. The action of heat on hydroxy aicds is of special interest.

Action of Heat on hydroxy acids

Hydroxy acids when heated in presence of a little mineral aicd (HCl or H_2SO_4) yield a variety of products depending onthe distance between OH and COOH groups.

1. ***Alpha - Hydroxy acids :***

α – hydroxy acids form an intermolecular cyclic diester called a lactide. They do so by reaction between OH of one molecule with COOH group of the second molecule.



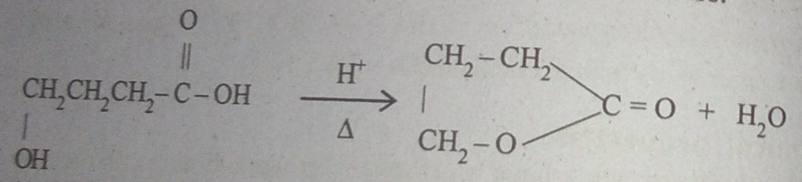
2. ***Beta - hydroxy acids :***

β – Hydroxy acids dehydrate by splitting out OH and H from adjacent carbon atoms, forming unsaturated acids.

$$\underset{\beta\text{ - Hydroxybutyric acid}}{CH_3\overset{OH}{\overset{|}{C}}H-\overset{H}{\overset{|}{C}}HCOOH} \xrightarrow[\Delta]{H^+} \underset{\text{Crotonic acid}}{CH_3CH=CH-COOH} + H_2O$$

3. ***Gamma and Delta hydroxy acids :***

γ – and δ– hydroxy acids form internal esters known as lactones. The COOH at one end of the molecule reacts with OH on the other, to form give and six membered cyclic esters i.e., γ – and δ – lactones.

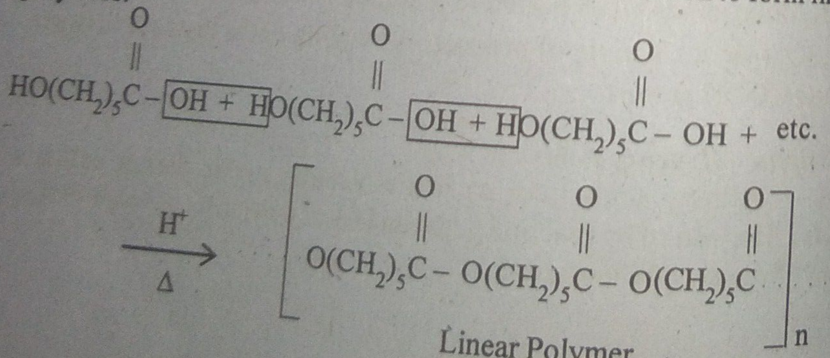


β - Hydroxybutyric acid

γ - lactone

4. ***Epsilonand Longer Hydroxy acids :***

ε – hydroxy acids undergo intermolecular esterification to form linear polymers.



$$HO(CH_2)_5\overset{O}{\overset{\|}{C}}-\boxed{OH + H}O(CH_2)_5\overset{O}{\overset{\|}{C}}-\boxed{OH + H}O(CH_2)_5\overset{O}{\overset{\|}{C}}-OH + \text{etc.}$$

$$\xrightarrow[\Delta]{H^+} \left[O(CH_2)_5\overset{O}{\overset{\|}{C}}-O(CH_2)_5\overset{O}{\overset{\|}{C}}-O(CH_2)_5\overset{O}{\overset{\|}{C}}\right]_n$$

Linear Polymer

3.3. Dicarboxylic acids

1. **Oxalic acid** : $\begin{array}{c} COOH \\ | \\ COOH \end{array}$

Preparation :

1. ***From glycol :***

Ethylene glycol on oxidation with acid potassium dichromate gives oxalic acid.

$$\begin{array}{c} CH_2OH \\ | \\ CH_2OH \end{array} \xrightarrow[K_2Cr_2O_7/H_2SO_4]{[O]} \begin{array}{c} COOH \\ | \\ COOH \end{array}$$

2. ***From cyanogen :***

When cyanogen is hydrolysed with dil. HCl oxalic acid is formed.

$$\begin{array}{c} CN \\ | \\ CN \end{array} + 4H_2O + 2HCl \xrightarrow{\Delta} \begin{array}{c} COOH \\ | \\ COOH \end{array} + 2NH_4Cl$$

3. In presence of dry ice at 300°C sodium on heating forms oxalic acids.

$$\underset{\text{Dry ice}}{2CO_2} + 2Na \xrightarrow{H^+} \begin{array}{c} COOH \\ | \\ COOH \end{array}$$

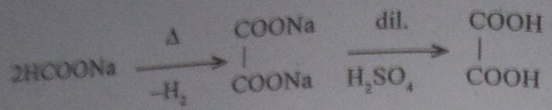
4. ***Synthesis :***

From ethylene oxalic acid is synthesised as follows.

$$\begin{array}{c} CH_2 \\ \| \\ CH_2 \end{array} \xrightarrow{Cl_2} \begin{array}{c} CH_2Cl \\ | \\ CH_2Cl \end{array} \xrightarrow{KOH} \begin{array}{c} CH_2OH \\ | \\ CH_2OH \end{array} \xrightarrow{\Delta} \begin{array}{c} COOH \\ | \\ COOH \end{array}$$

5. ***Manufacture :***

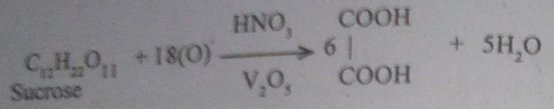
Sodium formate on heating at 360°C forms sodium salt which on treatment with dil H_2SO_4 gives oxalic acids.



$$2HCOONa \xrightarrow[-H_2]{\Delta} \begin{array}{c} COONa \\ | \\ COONa \end{array} \xrightarrow[H_2SO_4]{dil.} \begin{array}{c} COOH \\ | \\ COOH \end{array}$$

6. ***Laboratary preparation :***

Sucrose on heating with concentrated HNO_3 in presences of V_2O_5 catalyst gives oxalic acid

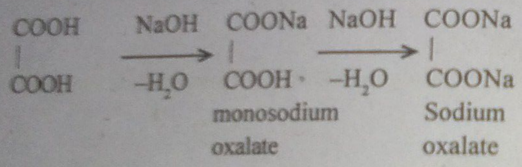


$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + 18(O) \xrightarrow[V_2O_5]{HNO_3} 6 \begin{array}{c} COOH \\ | \\ COOH \end{array} + 5H_2O$$

Properties :

1. ***Salt formation :***

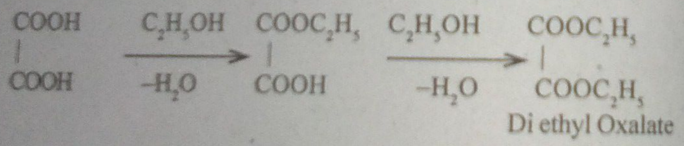
Oxalic acid reacts with alkalic forming two types of salts.



$$\begin{array}{c} COOH \\ | \\ COOH \end{array} \xrightarrow[-H_2O]{NaOH} \underset{\begin{array}{c}\text{monosodium}\\ \text{oxalate}\end{array}}{\begin{array}{c} COONa \\ | \\ COOH \end{array}} \xrightarrow[-H_2O]{NaOH} \underset{\begin{array}{c}\text{Sodium}\\ \text{oxalate}\end{array}}{\begin{array}{c} COONa \\ | \\ COONa \end{array}}$$

2. ***Formation of ester :***

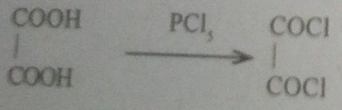
Oxalic acid reacts with alcohol giving two types of esters.



$$\begin{array}{c} COOH \\ | \\ COOH \end{array} \xrightarrow[-H_2O]{C_2H_5OH} \begin{array}{c} COOC_2H_5 \\ | \\ COOH \end{array} \xrightarrow[-H_2O]{C_2H_5OH} \underset{\text{Di ethyl Oxalate}}{\begin{array}{c} COOC_2H_5 \\ | \\ COOC_2H_5 \end{array}}$$

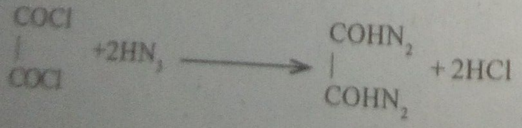
3. ***From PCl_5 :***

Oxalic acid reacts with excess of PCl_5 giving oxalyl chloride.



$$\begin{array}{c} COOH \\ | \\ COOH \end{array} \xrightarrow{PCl_5} \begin{array}{c} COCl \\ | \\ COCl \end{array}$$

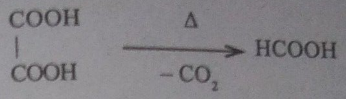
Oxalyl chloride reacts with ammonia giving oxamide.



$$\begin{array}{c} COCl \\ | \\ COCl \end{array} + 2HN_3 \longrightarrow \begin{array}{c} COHN_2 \\ | \\ COHN_2 \end{array} + 2HCl$$

4. ***Action of heat :***

Oxalic acid on heating about its melting point gives formic acid.



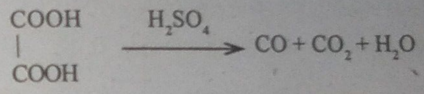
$$\begin{array}{c} COOH \\ | \\ COOH \end{array} \xrightarrow[-CO_2]{\Delta} HCOOH$$

5. ***With glycerol :***

When oxalic acid is heated with glycerol at 110°C gives **formic acid.** While **allyl alcohol** is formed at 260°C.

6. ***With Con. H_2SO_4 :***

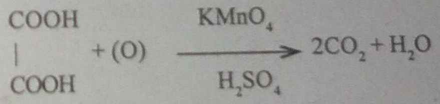
When oxalic acid is heated at 90°C it decomposes to give CO and CO_2.



$$\begin{array}{c} COOH \\ | \\ COOH \end{array} \xrightarrow{H_2SO_4} CO + CO_2 + H_2O$$

7. ***With $KMnO_4$:***

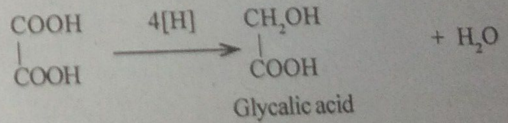
Oxalic acid on treating with acid potassium permaganate gives CO_2 and water.



$$\begin{array}{c} COOH \\ | \\ COOH \end{array} + (O) \xrightarrow[H_2SO_4]{KMnO_4} 2CO_2 + H_2O$$

8. ***Reduction :***

When oxalic acid is reduced with nascent hydrogen gives glycalic acid.



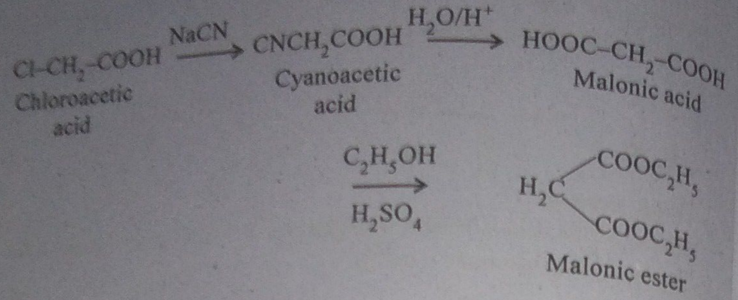
$$\begin{array}{c} COOH \\ | \\ COOH \end{array} \xrightarrow{4[H]} \underset{\text{Glycalic acid}}{\begin{array}{c} CH_2OH \\ | \\ COOH \end{array}} + H_2O$$

2. Malonic acid

This acid occurs as calcium salt in sugar beet.

Preparaion :

Malonic acid is prepared from chloroacetic acid by treating with aqueous sodium cyanide to give cyanoacetic acid and subsequent hydrolysis with dilute hydrochloric acid.



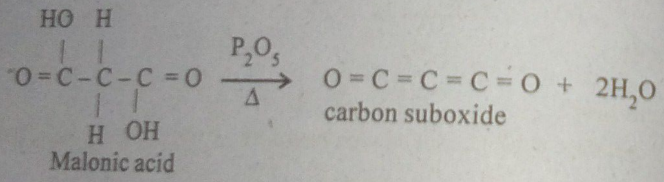
Properties :

1. Malonic acid is a white cystaline solid, mp 135°C.
2. It is soluble in water and ethanol, but sparingly in ether.
3. It gives all the usual reactions of a dicarboxylic acid.

$$\underset{\text{Malonic acid}}{HCOOH-CH_2-COOH} \xrightarrow{150^\circ C} \underset{\text{Acetic acid}}{CH_3COOH} + CO_2$$

2. *Action with P_2O_5 :*

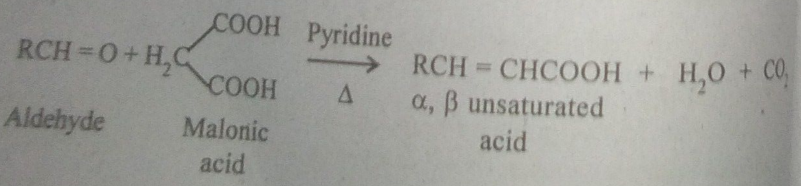
On heating with P_2O_5, malonic acid gives carbon suboxide.



$$\underset{\text{Malonic acid}}{O=\overset{\overset{HO}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{OH}{|}}{C}}-C=O} \xrightarrow[\Delta]{P_2O_5} \underset{\text{carbon suboxide}}{O=C=C=C=O} + 2H_2O$$

4. **Unsaturated acids :**

When with Aldehydes when pyridine solution of malonic acid and an aldehyde is heated, α, β unsaturated acid is produced.



Uses :

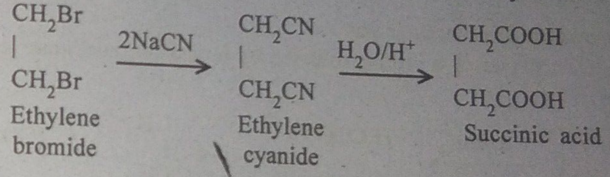
It diethyl ester is a valuable synthetic reagent for the preparation of a variety of carboxylic acids.

3. Succinic acid (HOOCCH₂.CH₂COOH)

Succinic acid was first obtained as a result of distillation of amber and hence its name (Latin, succinum = amber). It is also produced during the alcoholic fermentation of sugar.

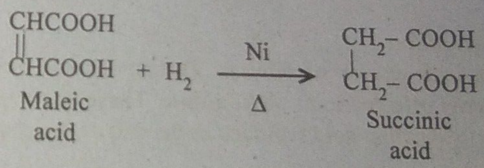
Preparaion :

1. Succinic acid is prepared from ethylene bromide by treating with sodium cyanide and subsequent hydrolysis of ethylene cyanide.



$$\underset{\text{Ethylene bromide}}{\begin{array}{c}CH_2Br\\|\\CH_2Br\end{array}} \xrightarrow{2NaCN} \underset{\text{Ethylene cyanide}}{\begin{array}{c}CH_2CN\\|\\CH_2CN\end{array}} \xrightarrow{H_2O/H^+} \underset{\text{Succinic acid}}{\begin{array}{c}CH_2COOH\\|\\CH_2COOH\end{array}}$$

2. It is obtained industrially by catalytic reduction of maleic acid.



$$\underset{\text{Maleic acid}}{\begin{array}{c}CHCOOH\\||\\CHCOOH\end{array}} + H_2 \xrightarrow[\Delta]{Ni} \underset{\text{Succinic acid}}{\begin{array}{c}CH_2-COOH\\|\\CH_2-COOH\end{array}}$$

Succinic acid can also be synthesised with the help of malonic acid.

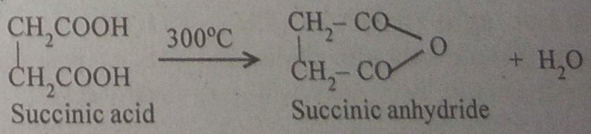
Properties :

Succinic acid forms white monoclinic prisms, mp 188°C. It is soluble in ethyl alcohol and ether, but moderately soluble in water.

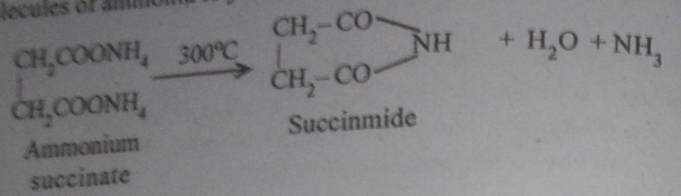
Succinic acid gives all the normal reactions of a dicarboxylic acid.

1. *Action of heat:*

On heating to 300°C, it loses at molecule of water to form succinic anhydride.



2. ***Reaction with Ammonia :***
With ammonia it forms ammonium succinate which upon heating loses a molecules of ammonia to yield succinimide.



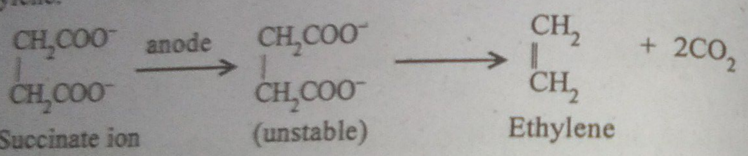
$$CH_2COONH_4 / CH_2COONH_4 \xrightarrow{300^{\circ}C} \text{Succinimide} + H_2O + NH_3$$

Ammonium succinate

Succinmide

When succinimide is treated with an alkaline solution of Br_2 at 0°C, it forms N - bromosuccinimide (NBS) which is a valuable reagent for allylic bromination.

3. ***Electrolysis of potassium salt :***
The electrolysis of a strong solution of potassium succinate gives ethylene.



$$\begin{matrix} CH_2COO^- \\ | \\ CH_2COO^- \end{matrix} \xrightarrow{\text{anode}} \begin{matrix} CH_2COO^{\cdot} \\ | \\ CH_2COO^{\cdot} \end{matrix} \longrightarrow \begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + 2CO_2$$

Succinate ion (unstable) Ethylene

4. ***Action with glycol :***
When heated with excess of ethyene glycol, succnic acid forms polyesters commonly referred to as alkyl esters. These esters are acidic ain character due to succinic acid residues at the end of the chain.

$$HOOC-(CH_2)_2-COOH+HOCH_2CH_2OH+HOOC-(CH_2)_2-COOH+.....$$
$$\longrightarrow HOOC-(CH_2)_2-CO[-O-(CH_2)_2-O-CO-(CH_2)_2-CO-]OH$$

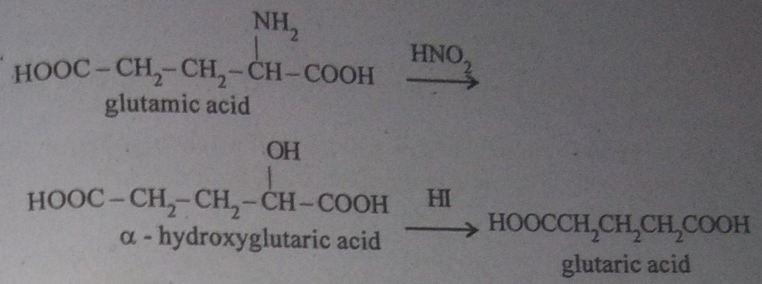
Polyester

Uses :

1. In the manufacture of lacquers and dyes.
2. In volumetric analysis as a standard substance for acid - base titrations.
3. Succinic acid is used for the manufacture of polyester resins.

4. Glutaric acid (HOOC – $(CH_2)_3$–COOH)

Glutaric acid is treated with nitrous acid gives α - hydroxy glutaric acid again treated with hydro iodic acid gives glutaric acid.



$$HOOC-CH_2-CH_2-\overset{NH_2}{\overset{|}{C}H}-COOH \xrightarrow{HNO_2}$$

glutamic acid

$$HOOC-CH_2-CH_2-\overset{OH}{\overset{|}{C}H}-COOH \xrightarrow{HI} HOOCCH_2CH_2CH_2COOH$$

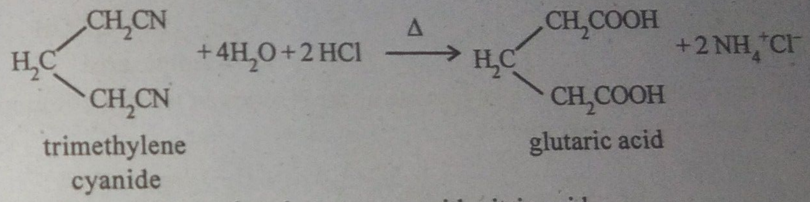
α - hydroxyglutaric acid

glutaric acid

Preparaion :

Synthetic methods

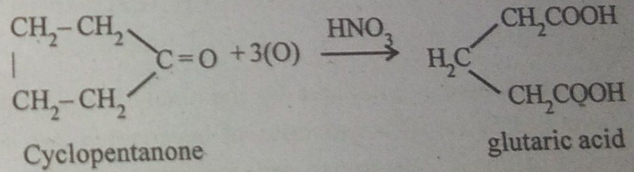
1. On hydrolysis of trimethylene cyanide with hydrochloric acid gives glutaric acid.



trimethylene cyanide

glutaric acid

2. By oxidation of cyclopentanone with nitric acid.

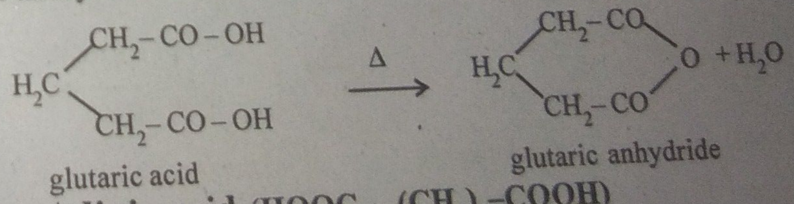


Cyclopentanone

glutaric acid

Properties :

Glutaric acid is a crystalline solid, mp 98°. Like succinic acid, this acid also loses a molecule of water when heated alone, or with acetic anhydride or thionyl chloride.



glutaric acid

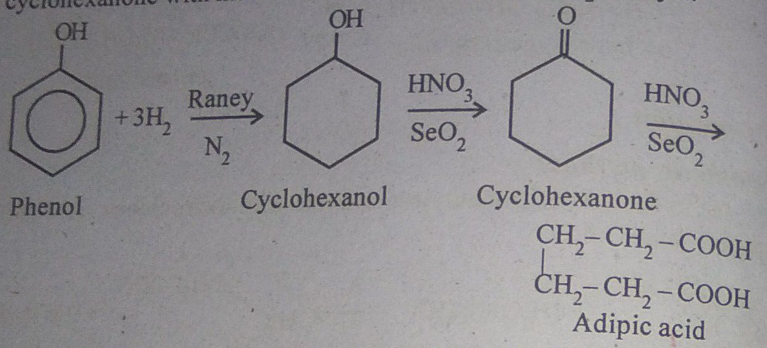
glutaric anhydride

4. Adipic acid (HOOC – $(CH_2)_4$–COOH)

This acid got its name from teh fact that it was first obtained by the oxidation of fats.

Preparaion :

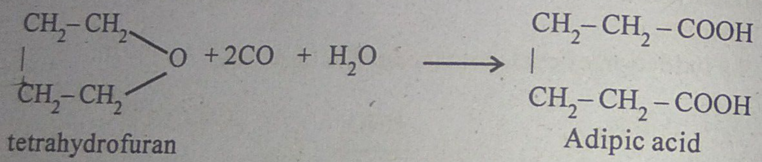
1. It can be perpared by the reaction of monosodiomalonic ester with ethylene bromide.
2. It is obtained commercially by the oxidation of phenol, or cyclohexanone with nitric acid in the presence of SeO_2 catalyst.



Phenol Cyclohexanol Cyclohexanone

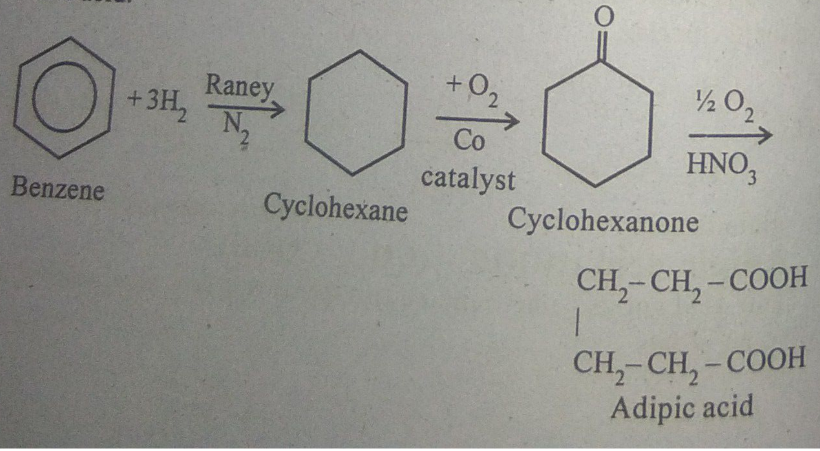
CH_2-CH_2-COOH
CH_2-CH_2-COOH
Adipic acid

3. It is also prepared on a large scale by the reaction of tetrahydrofuran with carbon monoxide and water.



tetrahydrofuran + 2CO + H_2O ⟶ Adipic acid

4. Now a days adipic acid is produced by the catalytic oxidation of cyclohexane (obtained by catalytic reduction of benzene) in two steps. In thefirst step cyclohexane is converted to cyclohexaone by air - oxidation inteh presence of cobalt catalyst at 100°C under a pressure of 150. In the second step the cyclohexanone is oxidised to adipic acid with the help of nitric acid.

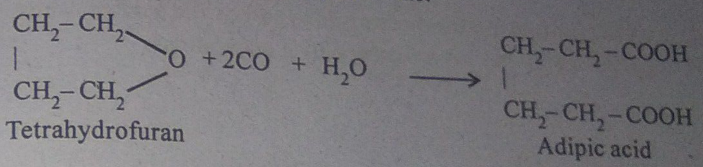


Benzene Cyclohexane Cyclohexanone

CH_2-CH_2-COOH
CH_2-CH_2-COOH
Adipic acid

Properties :

Adipic acid is a crystalline solid, mp 150°c. When heated in presenc of $Ba(OH)_2$, it is converted cyclopentanone.

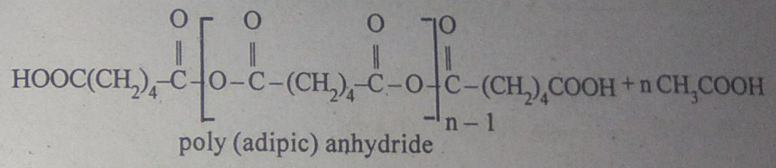


Tetrahydrofuran + 2CO + H_2O ⟶ Adipic acid

Upon heating with acetic anhydride, it gives imea polymeric anhydride.

$$(n+1)\,HOOC(CH_2)_4COOH + n(CH_2CO)_3O \xrightarrow{\Delta}$$

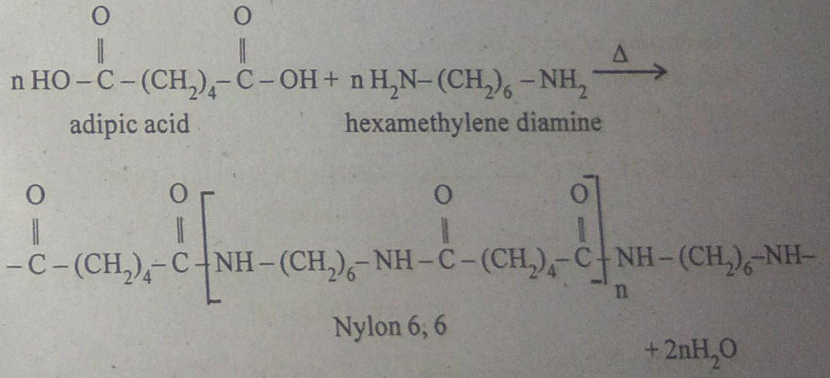
adipic acid acetic anhydride



$$HOOC(CH_2)_4-\overset{O}{\overset{\|}{C}}\left[O-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-O\right]_{n-1}\overset{O}{\overset{\|}{C}}-(CH_2)_4COOH + n\,CH_3COOH$$

poly (adipic) anhydride

Adipic acid undergo condensation polymerisation with 1, 6 - diaminohexane (hexamethylenediamine) to give a polyamide, Nylon 6, 6. It is one of the most popular of the in synthetic fibres and is so named because in each repeating unit its molecule contain six carbons in the amine fragment and six in the acid fragment.



$$n\,HO-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-OH + n\,H_2N-(CH_2)_6-NH_2 \xrightarrow{\Delta}$$

adipic acid hexamethylene diamine

$$-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}\left[NH-(CH_2)_6-NH-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}\right]_n NH-(CH_2)_6-NH-$$

Nylon 6, 6

$+2nH_2O$

3.4. Mechanism of conversion of acids

Acid derivatives are the derivatives of carboxylic acids in which the OH of COOH group has been replaced by a other atoms.

Examples :

$$\text{RCOOH} \xrightarrow[+X]{-OH} \text{RCOX (Acyl halides } X = Cl, Br, I)$$

$$\text{RCOOH} \xrightarrow[+NH_2]{-OH} \text{RCONH}_2 \text{ (Acid amide)}$$

$$\text{RCOOH} \xrightarrow[+OR']{-OH} \text{RCOOR' (Ester)}$$

$$\text{RCOOH} \xrightarrow[+COOR]{-OH} \text{RCOCOOR' (Acid anhydride)}$$

Method's of Preparation :

1. ***Preparation of acyl chloride :***

Acid chlorides are perpared by the action of phosphorus trichloride PCl_3 or PCl_5 or $SOCl_2$ on a carboxylic acid.

$$3CH_3COOH + PCl_3 \longrightarrow \underset{\text{acyl chloride}}{3CH_3COCl} + H_3PO_3$$

$$CH_3CH_2COOH + PCl_5 \longrightarrow \underset{\text{propionyl chloride}}{CH_3CH_2COCl} + HCl + POCl_3$$

$$C_6H_5COOH + SOCl_2 \longrightarrow \underset{\text{benzyl chloride}}{C_6H_5COCl} + HCl + SO_2$$

2. ***Preparation of acetic anhydride :***

a. Carboxylic acids undergo intermolecular anhydride formation in the presence of a strong dehydrating agent like phosphorus pentoxide.

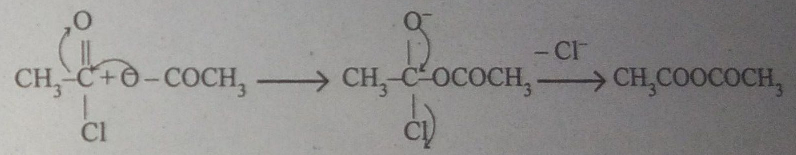
$$2RCOOH \xrightarrow{P_2O_5} RCOOCOR + H_2O$$

b. Acetic anhydride is prepared conveninetly in the laboratory by distilling a mixture of anhydrous sodium acetate and acetyl chloride.

$$CH_3COCl + NaOCOCH_3 \longrightarrow CH_3COCOOCH_3 + NaCl$$

Mechanism :

$$CH_3COONa \longrightarrow Na^+ + CH_3COO^-$$



$$CH_3-\overset{\overset{O}{\|}}{\underset{\underset{Cl}{|}}{C}} + \bar{O}-COCH_3 \longrightarrow CH_3-\overset{\overset{O^-}{|}}{\underset{\underset{Cl}{|}}{C}}-OCOCH_3 \xrightarrow{-Cl^-} CH_3COOCOCH_3$$

3. ***Preparation of acid amides :***

a. The simple amides can be prepared by heating the ammonium salt of the corresponding acid at 170° – 230°. The ammonium salt degydrates to form the amide.

$$CH_3COONH_4 \xrightarrow{\Delta} CH_3CONH_2 + H_2O$$

Alternatively, ammonium salt of the relavent carboxylic acid can be heated in an inert solvent to get the amide.

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

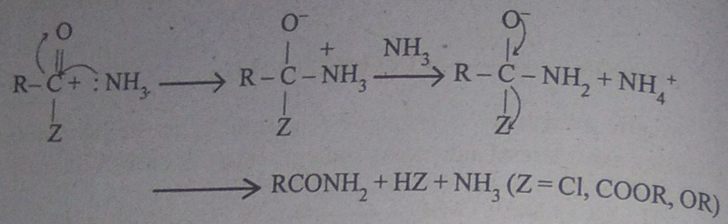
$$C_6H_5COCl + 2NH_3 \longrightarrow C_6H_5CONH_2 + NH_4Cl$$

This is reaction is called Schotten Baumann reaction.

c. Esters are reacted with concentration solution of ammonia to form amide.

$CH_3COOC_2H_5 + NH_3 \longrightarrow CH_3CONH_2 + C_2H_5OH$

Mechanism :



d. Acid amides are obtained by the controlled or partial hydrolysis of alkyl nitriles.

$CH_3CN + H_2O \longrightarrow CH_3CONH_2$

$C_6H_5CN + H_2O \longrightarrow C_6H_5CONH_2$

Hydrolysis of acid derivative into acid :

1. Hydrolysis of acid halides.

$CH_3COCl + H_2O \longrightarrow CH_3COOH + HCl$

$C_6H_5COCl + H_2O \longrightarrow C_6H_5COOH + HCl$

2. Acetic anhydride react with water slowly to produce the corresponding acids.

$(CH_3CO)_2O + H_2O \longrightarrow 2CH_3COOH$

$(C_6H_5CO)_2O + H_2O \longrightarrow 2C_6H_5COOH$

3. Acid amide react with water slowly to produce the corresponding acids.

$CH_3CONH_2 + H_2O \longrightarrow CH_3COOH + NH_3$

$C_6H_5CONH_2 + H_2O \longrightarrow C_6H_5COOH + NH_3$

4. Hydrolysis of esters.

$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$

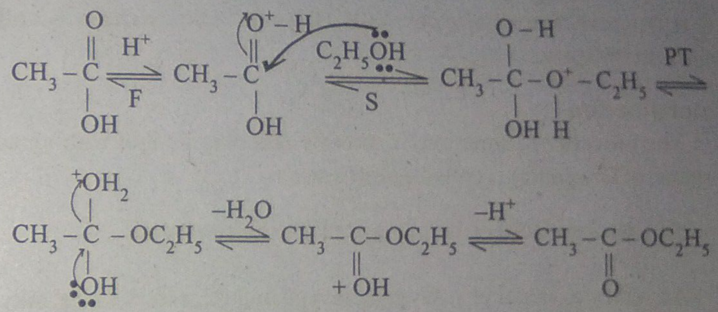
$C_6H_5COOC_2H_5 + NaOH \longrightarrow C_6H_5COONa + C_2H_5OH$

Esterification :

The process of formation of ester by reacting alcohol with an acid (organic of inorganic) is called esterification.

Mechanism:

Esterification is a reversible reaction.



F = Fast, S = Slow, PT = Proton transfer

Alcohol react with acyl chloride to form ester.

$C_2H_5OH + ClCOCH_3 \longrightarrow CH_3COOC_2H_5 + HCl$

This is called acylation.

$C_2H_5OH + ClCOC_6H_5 \longrightarrow C_6H_5COOC_2H_5 + HCl$

benzyl chloride — ethyl benzonate

This is called benzoylation.

Trans esterification

When an ester gests refluxed with an alcohol (other than the one used in its preparation) preferably in the presence of a small quantity of acid or sodium alkoxide as catalyst, the orginal alcohol residue in the ester gets replaced by the new alcohol. this ester interchanges, which is actually alcoholysis (splitting by alcohol) of an ester, is called transesterification.

$$\underset{\text{n butyl acetone}}{CH_3COOC_4H_9} + C_2H_5OH \xrightarrow{C_2H_5ONa} \underset{\text{ethyl acetate}}{CH_3COOC_2H_5} + C_4H_9OH$$

It is generally used for preparaing the ester of a higher alcohol (C_4H_9OH)from that of a lower (C_2H_5OH) one. This reaction is called transesterification.

Esterification :

The process of formation of ester by reacting alcohol with an acid (organic of inorganic) is called esterification.

This reaction acid or base are used for the catalysted.

Ac refers to the acyl - oxygen clevage and AL refers to the alkyl - oxygen cleavage, and numbers 1 and 2 refer to unimolecular and bimolecular reactions.

1. Acid catalysed unimolecular acyl - oxygen fission. ($A_{AC}{}^1$)
2. Acid catalysed bimolecular acyl - oxygen fission. ($A_{AC}{}^2$)
3. Acid catalysed unimolecular alkyl - oxygen fission. ($A_{AL}{}^1$)
4. Acid catalysed bimolecular alkyl - oxygen fission. ($A_{AL}{}^2$)
5. Base catalysed unimolecular acyl - oxygen fission. ($B_{AC}{}^1$).
6. Base catalysed bimolecular acyl - oxygen fission ($B_{AC}{}^2$).
7. Base catalysed unimolecular alkyl - oxygen fission ($B_{AL}{}^1$)
8. Base catalysed bimolecular alkyl - oxygen fission ($B_{AL}{}^2$).

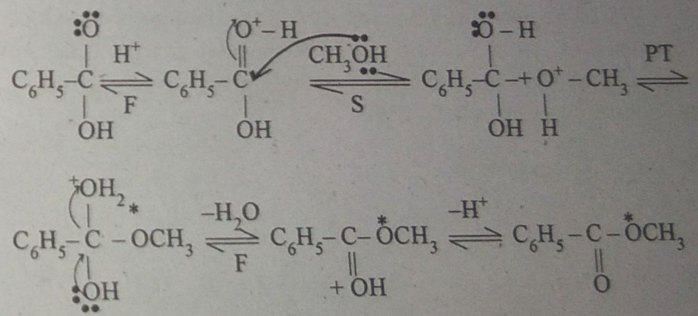
Of these the three esterification mechanisms observed are $A_{AC}{}^1$, $A_{AC}{}^2$, $A_{AL}{}^1$.

Effect of Substitutents structural and stericfactors :

1. $A_{AC}{}^2$ Mechanism :

The study of the mechanism of this type of hydrolysis and esterification has been made on the basis of the principle of microscopic reversibility. It means tha "*If a given sequence of steps consitute the favoured mechanism of the forward reaction and if these sequences are reversed that they constitute the favoured mechanism of the reverse reaction*".

Roberts et al carried out esterification of methyl alcohol with benzoic acid wherein the oxygen atom of –OH of COOH group is replaced by O^{18}. They found that the water formed during the esterification of an acid with methanol gave water having O^{18}. This is only possible when there occurs acyl - oxygen fission during esterification, therefore according to the principle of microscopic reversibility similar fission must occur during hydrolysis also.

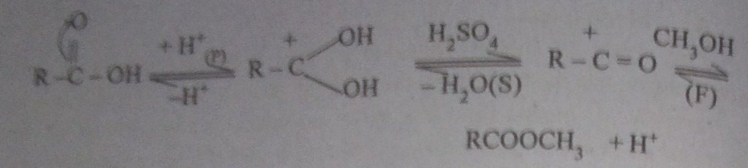


F = Fast, S = Slow, PT = Proton transfer

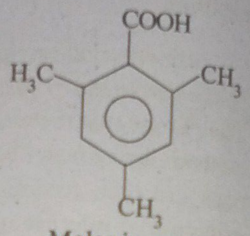
This step involves a change in hybridisation of the carbon atom of the carboxyl group from sp^2 to sp^3 state and because of this steric retardation will be expected to increase as the size or branching of the alkyl group of the acid part (or acyl part) increases.

$CH_3COOH > CH_3CH_2COOH > (CH_3)_2CHCOOH > (CH_3)_3CCOOH < (C_6H_5)_3C\,COOH$

2. $A_{AC}{}^{1}$ **Mechanism :**



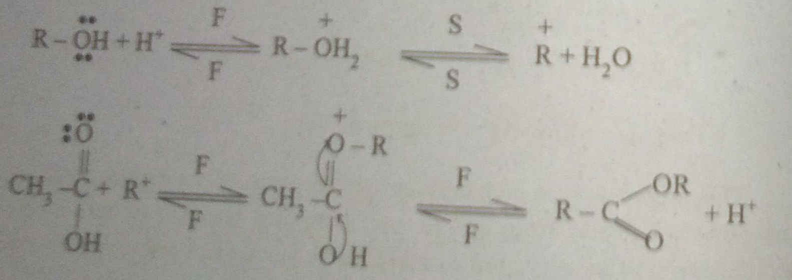
This type of esterification and hydrolysis has be found only in some special cases. Newman (1941) reported that mesitoic acid (2, 4, 6 - trimethyl benzoic acid) does not undergo esterification under ordinary condition, but when dissolved in concentrated sulphuric acid and the mixture poured00 into cold methanol, the corresponding methyl ester is readily obtained.



Malonic ester

The formation of acylium ion (2, 6 -) gets facilitated both by steric hindrance, as also by stabilisation of the positive charge because of the presence of electron donating (methyl) group by contributing the resonance structures of the type.

3. $A_{AL}{}^{1}$ **Mechanism :**



This mechanism involved in 3° alchol only. Because the inter mediate of carbonium ion more stable. This stability is reason for the +I effect of three alkyl group of 3° alchol.

Hydrolysis :

Hydrolysis of acid chloride.

$$\underset{\text{acetyl chloride}}{CH_3COCl} \xrightarrow{H_2O} \underset{\text{acetic acid}}{CH_3COOH} + HCl$$

$$\underset{\text{benzyl chloride}}{C_6H_5COCl} \xrightarrow[\text{dil. NaOH}]{H_2O\text{ (or)}} \underset{\text{benzoic acid}}{C_6H_5COOH} + HCl$$

Acetic anhydride slowly hydrolysis by water. But fastly hydrolysis by base.

$$\underset{\text{acetic anhydride}}{(CH_3CO)_2O} + H_2O \longrightarrow \underset{\text{acetic acid}}{2CH_3COOH}$$

$$\underset{\text{benzyl anhydride}}{(C_6H_5CO)_2O} + H_2O \longrightarrow \underset{\text{benzonic acid}}{2C_6H_5COOH}$$

Acidamide slowly hydrolysis by water. But fastly hydrolysis by base.

$$\underset{\text{acetamide}}{CH_3CONH_2} \xrightarrow[\text{base}]{H_2O} \underset{\text{acetic acid}}{CH_3COOH} + NH_3$$

$$\underset{\text{benzoamide}}{C_6H_5CONH_2} \xrightarrow{\text{acid (or) base}} \underset{\text{benzonic acid}}{C_6H_5COOH}$$

Esters are hydrolysis by acid and base. Ester gives alcohol and acid or its salt. Eg.,

$$\underset{\text{ethyl acetate}}{CH_3COOC_2H_5} \xrightarrow[H^+]{H_2O} \underset{\text{acetic acid}}{CH_3COOH} + \underset{\text{ethanol}}{C_2H_5OH}$$

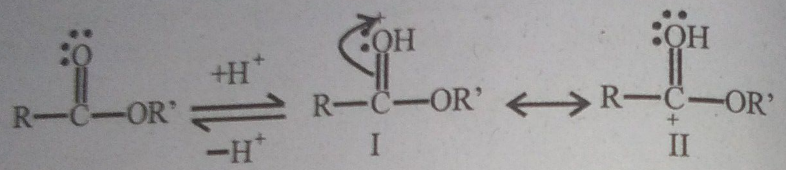
$$CH_3COOC_2H_5 + NaOH \xrightarrow{[H_2O]} \underset{\text{sodium acetatate}}{CH_3COONa} + C_2H_5OH$$

Mechanism :

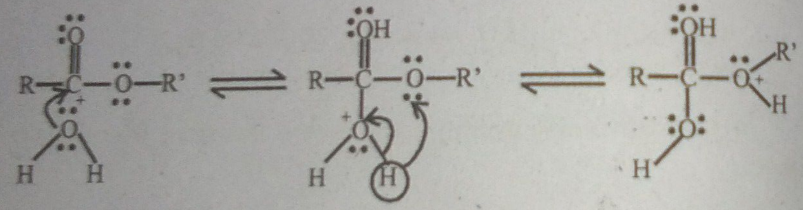
1. ***Acid hydrolysis :***

It is a reversible reaction. The reaction involved three steps.

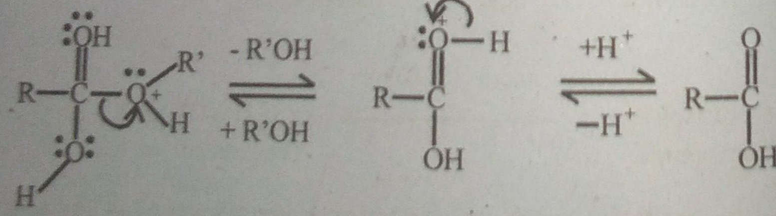
i Hydrogen attack carbonyl oxygen. To obtained I and II structure.



ii. Water molecule involved reaction.



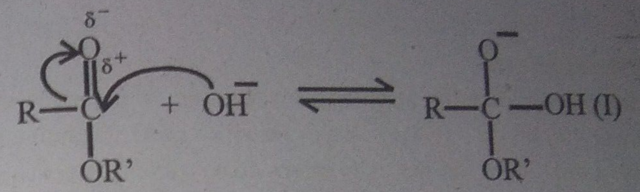
iii. Acid obtained removed from R'OH.



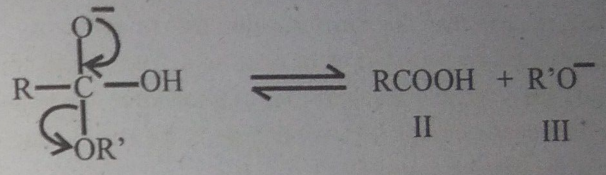
2. ***Base hydrolysis :***

Mechanism involved in three steps.

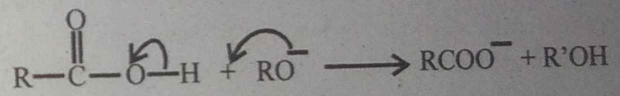
i Hydroxyl ion attack carbonyl oxygen. To obtained I structure.



ii. I gives structure II and III.



iii. Proton transfer



Sponification :

During alkaline hydrolysis of an ester, sodium or potassium salt of the acid is formed. As alkali salts of the higher fatty acids are soaps, alkaline hydrolysis of an ester is called saponification.

$CH_2OCOC_{17}H_{35}$
$CHOCOC_{17}H_{35}$ + $\underset{\text{Base}}{3NaOH}$ $\longrightarrow$
$CH_2OCOC_{17}H_{35}$

fat (or) oil

triglyceride

CH_2OH
$CHOH$ + $\underset{\text{Soap}}{3C_{17}H_{35}COONa}$
CH_2OH
glycerol

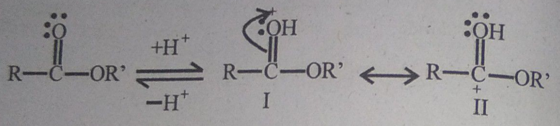
$$CH_3COOC_2H_5 + NaOH \xrightarrow{[H_2O]} \underset{\text{sodium acetatate}}{CH_3COONa} + C_2H_5OH$$

Mechanism :

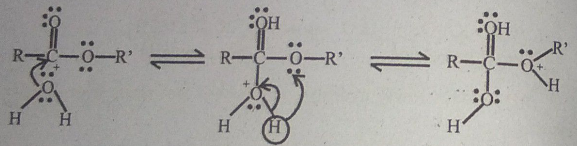
*I. **Acid hydrolysis :***

It is a reversible reaction. The reaction involved three steps.

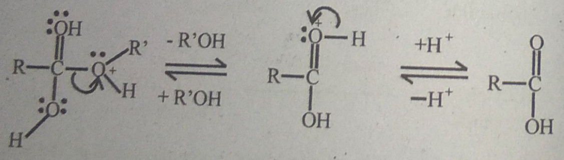
i. Hydrogen attack carbonyl oxygen. To obtained I and II structure.



ii. Water molecule involved reaction.



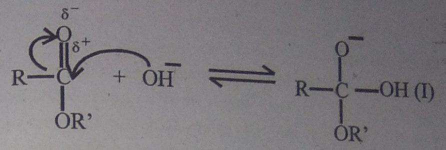
iii. Acid obtained removed from R'OH.



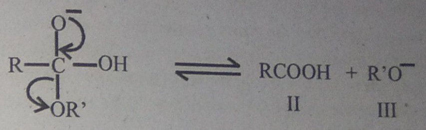
*2. **Base hydrolysis :***

Mechanism involved in three steps.

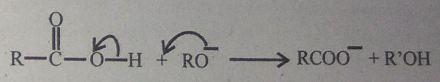
i. Hydroxyl ion attack carbonyl oxygen. To obtained I structure.



ii. I gives structure II and III.



iii. Proton transfer



Sponification :

During alkaline hydrolysis of an ester, sodium or potassium salt of the acid is formed. As alkali salts of the higher fatty acids are soaps, alkaline hydrolysis of an ester is called saponification.

$CH_2OCOC_{17}H_{35}$
$CHOCOC_{17}H_{35}$ + $\underset{\text{Base}}{3NaOH}$ ⟶
$CH_2OCOC_{17}H_{35}$
fat (or) oil
triglyceride

CH_2OH
$CHOH$ + $\underset{\text{Soap}}{3C_{17}H_{35}COONa}$
CH_2OH
glycerol

3.4. Tautomerism

This is a type of isomerism in which the isomers are inter - convertible under normal conditions. (tauto - same : meros - part), A tautomeric substance is a mixture of two mutually inter - convertible isomers called ***tautomers***. If one from is to be changed to another a definite amount of energy must be supplied to take away from the substance. If this amount of energy is very small then the transformation will be quite easy. This will result in an equilibrium mixture of the tautomers. Since the tautomeric change is rapid and reversible, the separation of the mixture into tautomers is difficult, Tautomeric change is possible only in the liquid state or in solution or in the gaseous state.

Tautomeric change results from the shifting of an atom or group from one part of a molecule to another. In majority of cases the shifted atom is hydrogen in the ionic from (proton). Such tautomerism is referred to as prototropy. In some other types there is migration of anions like OH^- or Cl^-. This is called ***anionotropy***. This is a less common type.

Types of Tautomerism :

Various compounds that exhibit tautomerism can be classified as follows :

- i. Open - system of tautomerism or Ionotropy
- ii. Ring - chain tautomerism
- iii. Valence tautomerism

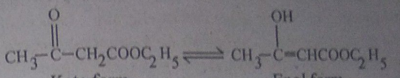
i. Open System of Tautomerism or Ionotropy :

In this type of tautomerism, both tautomers are open chain substances. This can be further sub - divided into two groups.

a. Cationotropy :

Tautomerism is referred to as cationotropy when atoms or groups of atoms shifts as cations. A large majority of cases of cationotropy, however is prototropy wherein protons are involved.

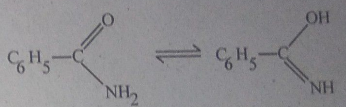
i. For example prototropy in case of **keto - enol tautomerism**.



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2COOC_2H_5 \rightleftharpoons CH_3-\overset{\overset{OH}{|}}{C}=CHCOOC_2H_5$$

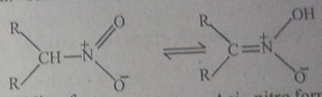
Keto form　　　Enol form

ii. Another type of prototropy involves the **amido - imido tautomerism** of the amides of carboxylic acids.



Amido form　　　Imido form

iii. Primary and secondary nitroparaffins are also found to exist mainly as nitro compounds in equilibrium with small proportions of aci - isomerism. This is called **nitro - aci nitro tautomerisms.**



Nitro form　　　Aci - nitro form

b. Anionotropy :

Tautomerism is referred to as anionotropy when atoms or groups of atoms shift as anions. For example anionotropy in following ;

$$CH_3-CH=CH-CH_2Cl \rightleftharpoons CH_3-CHCl-CH=CH_2$$

Crotyl chloride　　　Methylvinyl carbinyl chloride

2. Ring - chain Tautomerism :

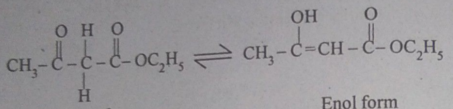
In this type of tautomerism, one form is cyclic and other is acyclic (open - chain). The two forms of this type differ in the position of either a proton or anionic atom or group. This type of tautomerism is found in carbohydrates.

3. Valence tautomerism :

In this type of tautomerism the two tautomers differ only in the redistribution of the valencies.

Keto - Enol Tautomerism

When a methylene group is attached to two carbonyl groups, the hydrogen atom migrates to one or other carbonyl group. Thus enol form arises. This type of tautomerism is called the ***keto - enol tautomerism.*** In this tautomerism a hydrogen atom migrates from a carbon atom to oxygen atom. The keto - enol tautomerism in acetoacetic ester is shown below.



$CH_3-\overset{O}{\overset{\|}{C}}-\underset{H}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-OC_2H_5 \rightleftharpoons CH_3-\overset{OH}{\overset{|}{C}}=CH-\overset{O}{\overset{\|}{C}}-OC_2H_5$

Keto form

Enol form

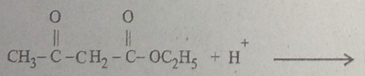
Keto enol tautomerism of acetoacetic esters

Acetoacetic ester behaves as though it is an enol and also a ketone in its reactions. We say this is due to tautomerism. Thus if a compound behaves as a ketone and as an enol we can conclude that there is tautomerism. Since there is an equilibrium during testing the compound would behave as though it consists of enol or keto form only.

Acid and base catalysed mechanism :

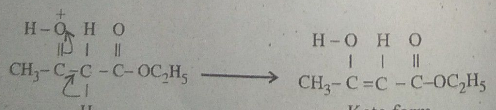
The keto - enol tautomerism of acctoacetic ester is catalysed both by acids and bases.

1. *Acid catalysed mechanism*



$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OC_2H_5 + \overset{+}{H} \longrightarrow$

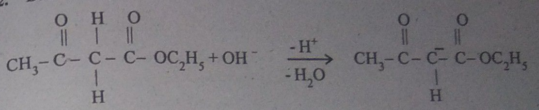
Keto form



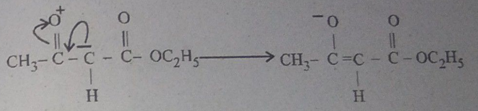
$CH_3-\overset{H-\overset{+}{O}}{\overset{\|}{C}}-\underset{H}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-OC_2H_5 \longrightarrow CH_3-\overset{H-O}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-OC_2H_5$

Keto form

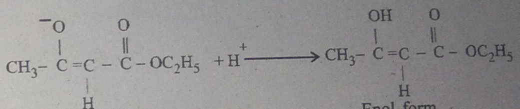
2. *Base catalysed mechanism*



$CH_3-\overset{O}{\overset{\|}{C}}-\underset{H}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-OC_2H_5 + OH^- \xrightarrow[-H_2O]{-H^+} CH_3-\overset{O}{\overset{\|}{C}}-\underset{H}{\overset{-}{C}}-\overset{O}{\overset{\|}{C}}-OC_2H_5$



$CH_3-\overset{\overset{+}{O}}{\overset{\|}{C}}-\underset{H}{C}-\overset{O}{\overset{\|}{C}}-OC_2H_5 \longrightarrow CH_3-\overset{^-O}{\overset{|}{C}}=\underset{H}{C}-\overset{O}{\overset{\|}{C}}-OC_2H_5$

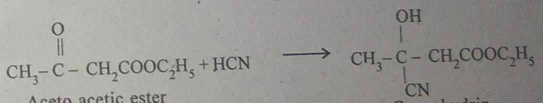


$CH_3-\overset{^-O}{\overset{|}{C}}=\underset{H}{C}-\overset{O}{\overset{\|}{C}}-OC_2H_5 + \overset{+}{H} \longrightarrow CH_3-\overset{OH}{\overset{|}{C}}=\underset{H}{C}-\overset{O}{\overset{\|}{C}}-OC_2H_5$

Enol form

Reactions in favour of keto form

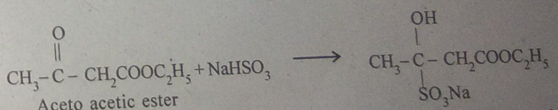
1. ***Addition reactions :***
   It gives additions compounds with HCN and $NaHSO_3$.



$CH_3-\overset{O}{\overset{\|}{C}}-CH_2COOC_2H_5 + HCN \longrightarrow CH_3-\underset{CN}{\overset{OH}{C}}-CH_2COOC_2H_5$

Aceto acetic ester

Cyanohydrin



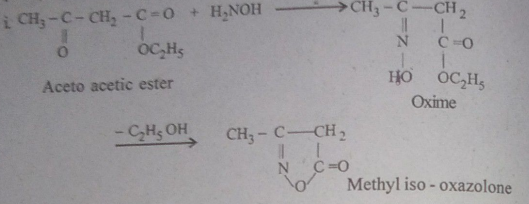
$CH_3-\overset{O}{\overset{\|}{C}}-CH_2COOC_2H_5 + NaHSO_3 \longrightarrow CH_3-\underset{SO_3Na}{\overset{OH}{C}}-CH_2COOC_2H_5$

Aceto acetic ester

Bisulphite compound

2. *Condensation reaction :*

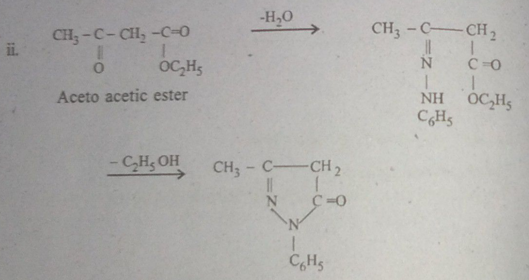
It gives condensation product with hydroxylamine and phenylhydrazine.



Aceto acetic ester

Oxime

Methyl iso - oxazolone

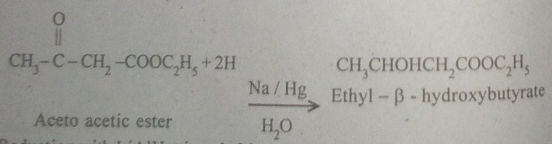


Aceto acetic ester

3, Methyl - 1 - phenyl pyrazolone

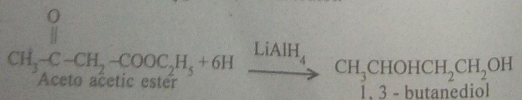
3. Reduction :

Acetoacetic ester on reduction with sodium amalgam gives ethyl β – hydroxybutyrate.



$$\underset{\text{Aceto acetic ester}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_2-COOC_2H_5} + 2H \xrightarrow[H_2O]{Na/Hg} \underset{\text{Ethyl}-\beta-\text{hydroxybutyrate}}{CH_3CHOHCH_2COOC_2H_5}$$

Reduction with $LiAlH_4$ gives 1, 3 butanediol.



$$\underset{\text{Aceto acetic ester}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_2-COOC_2H_5} + 6H \xrightarrow{LiAlH_4} \underset{\text{1, 3 - butanediol}}{CH_3CHOHCH_2CH_2OH}$$

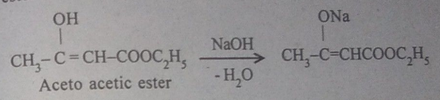
4. *Ketonic hydrolysis :*

As we have seen earlier ketonic hydrolysis yields ketones.

Reactions in favour of enol form

1. *Formation of sodium salt :*

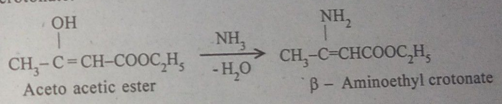
The hydrogen of the hydroxy group of the enol form of acetoacetic ester is weakly acidic. Hence it reacts with alkalies to give salts.



$$\underset{\text{Aceto acetic ester}}{CH_3-\overset{\overset{OH}{|}}{C}=CH-COOC_2H_5} \xrightarrow[-H_2O]{NaOH} CH_3-\overset{\overset{ONa}{|}}{C}=CHCOOC_2H_5$$

2. *With ammonia :*

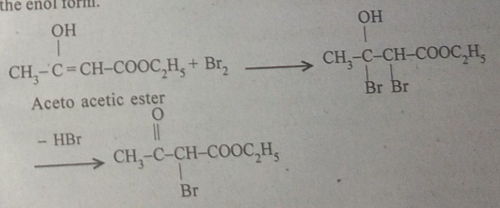
Acetoacetic ester reacts with ammonia to form β – aminoethyl crotonate.



$$\underset{\text{Aceto acetic ester}}{CH_3-\overset{\overset{OH}{|}}{C}=CH-COOC_2H_5} \xrightarrow[-H_2O]{NH_3} \underset{\beta-\text{Aminoethyl crotonate}}{CH_3-\overset{\overset{NH_2}{|}}{C}=CHCOOC_2H_5}$$

3. *With bromine :*

It decolourises bromine water. Bromine adds to the double bond of the enol form.

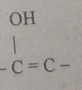


$$\underset{\text{Aceto acetic ester}}{CH_3-\overset{\overset{OH}{|}}{C}=CH-COOC_2H_5} + Br_2 \longrightarrow CH_3-\underset{\underset{Br}{|}}{\overset{\overset{OH}{|}}{C}}-\underset{\underset{Br}{|}}{CH}-COOC_2H_5$$

$$\xrightarrow{-HBr} CH_3-\overset{\overset{O}{\|}}{C}-\underset{\underset{Br}{|}}{CH}-COOC_2H_5$$

4. *With ferric chloride*

Acetoacetic ester gives violet colour with ferric chloride. This colour reaction is a characteristics reaction of phenol and enolic compounds with

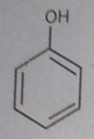


the group $-\overset{\overset{OH}{|}}{C}=C-$

5. ***With benzene diazonium chloride***

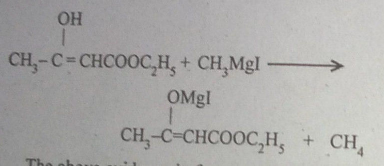
It couples with benzene diazonium chloride as phenol.

Reaction (4) and (5) indicate that aceto aceticester resembles phenol. In phenol also there is enol structure.



6. ***With Grignard reagent :***

The enol form of acetoacetic ester reacts with Grignard reagent.



$$CH_3-\overset{\overset{\displaystyle OH}{|}}{C}=CHCOOC_2H_5 + CH_3MgI \longrightarrow CH_3-\overset{\overset{\displaystyle OMgI}{|}}{C}=CHCOOC_2H_5 + CH_4$$

The above evidence in favour of keto form and enol form show that acetoacetic ester is in two tautomeric forms.

Separation of keto and enol forms (Knorr)

Separated of keto form :

A solution of acetoacetic ester in petroleum ether is cooled to −78°C. A colourless crystalline solid separates. It does not give violet colour with ferric chloride and it does not decolourise bromine solution. Therefore it is the keto form.

Separated of enol form :

A suspension of the sodium salt of acetoacetic ester in petroleum ether is taken. HCl gas is passed through it. Sodium chloride present in the mixture is separated by filtration. The filtrate contains the enolic form. It gives intense violet colour with ferric chloride and decolourises bromine solution.

The keto form or the enol form if allowed to stand for some time gives the tautomeric mixture only.

Estimation of keto and enol forms :

Now it is well established that acetoacetic ester exists in keto and enol forms and equilibrium exists between these two forms under ordinary conditions. The exact composition of each form can be determined by physical as also by chemical methods. However, one should select such a method that should not disturb the equilibrium of the mixture during estimation. Because of this reason, physical methods are preferred.

Physical methods :

The various methods are as given below :

i. ***By measurement of refractive index.*** In this method first of all, the refractive index of the ordinary ester is determined. Then, its value is compared with the values of the different mixtures of the keto and enol forms of known composition. Knorr used this method and found that the equilibrium mixture of acetoacetic ester contains 7.7% of the enol form and 92.3% of the keto form.

ii. ***By measurement of electrical conducitivity.*** In this method when we use one form which is an electrolyte and measure its electrical conductivity which may be employed to determine its percentage in the mixture.

iii. ***By N.M.R. and infrared spectroscopy.*** These techniques have been used successfully for determining the equilibrium composition of tautomers.

iv. ***By optical rotation measurement.*** This method has been used successfully to determine the quantity of the two tautomeric forms in any equilibrium mixture.

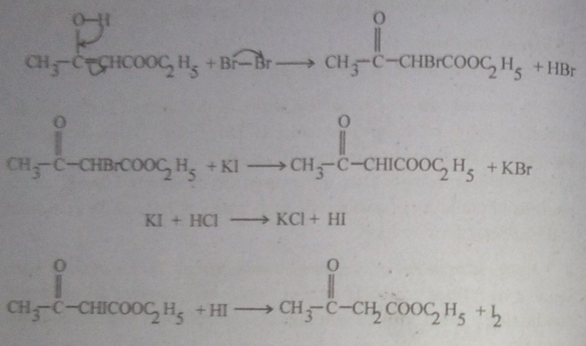
Chemical methods :

The various methods are as follows :

i. ***Kurt Meyer method.***

This method is based upon the observation that the enol form of acetoacetic ester, but not its keto form, reacts rapidly with bromine, forming bromo ketones.

The process consists in treating weighted sample of ester with the excess of standard ethanolic solution of bromine. The excess of bromine, that may disturb the equilibrium, is removed by the addition of β - naphthol. After acidifying this reaction mixture with hydrochloric acid, potassium iodide is added to it when the α - bromo - ketone is reduced by the hydrogen iodide, liberating iodine. This is then titrated with sodium thiosulphate. Each molecule of iodine so produced corresponds to molecule of enol form in the original sample.



$$CH_3-\overset{\overset{O-H}{|}}{C}=CHCOOC_2H_5 + Br-Br \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-CHBrCOOC_2H_5 + HBr$$

$$CH_3-\overset{\overset{O}{\|}}{C}-CHBrCOOC_2H_5 + KI \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-CHICOOC_2H_5 + KBr$$

$$KI + HCl \longrightarrow KCl + HI$$

$$CH_3-\overset{\overset{O}{\|}}{C}-CHICOOC_2H_5 + HI \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-CH_2COOC_2H_5 + I_2$$

The main drawback of this method is that final reduction is very slow.

ii. ***Flow method.***

In this method, the solution of the keto - enol mixture and an acidified bromide - bromate solution are simultaneously mixed and diluted in a mixing chamber and then the mixture is made to flow fast a platinum electrode. Then, the relative quantities of the two solutions are adjusted so that the potential measured at the platinum electrode shows a sharp rise that correspond to the end point in the titration of the enol form by the bromine. This method gives good results of enol contents as low as 10^{-5} percent.

iii. ***Ozonide method :***

When a tautomeric mixture is treated with ozone, the enol form forms ozonide. This is decomposed with water and the products are characterized and estimated.

University Questions

1. How will you prepare cinnamic acids? Mention the properties.
2. How will you prepare crotonic acids? Mention the properties.
3. Discuss the preparation and properties of malic and citric acids.
4. Write short notes on trans esterification.
5. Discuss the structural and steric factors of hydrolysis of ester.
6. Define tautomerism.
7. Write short notes on keto - enol and amido - imido tautomerism.
8. Explain the characteristic reactions of active methylene group.