



**CLASSROOM STUDY
PACKAGE**

CHEMISTRY

**CARBOXYLIC ACIDS
AND THEIR DERIVATIVES**

JEE EXPERT

CARBOXYLIC ACIDS AND THEIR DERIVATIVES

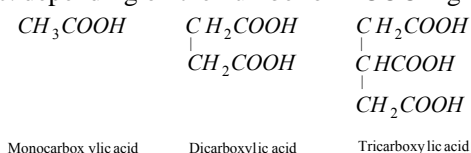
CARBOXYLIC ACIDS

Carboxylic acids are the compounds containing the carboxyl functional group $\left(\begin{array}{c} -C-OH \\ || \\ O \end{array} \right)$

The carboxyl group is made up of carbonyl ($>C=O$) and hydroxyl ($-OH$) group.

Classification:

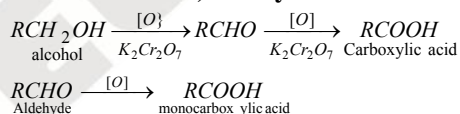
- (1) Carboxylic acids are classified as monocarboxylic acids, dicarboxylic acids, tricarboxylic acids etc. depending on the number of $-COOH$ groups present in the molecule.



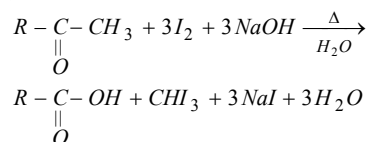
- (2) Monocarboxylic acids of aliphatic series are commonly known as fatty acids such as palmitic acid ($C_{15}H_{31}COOH$) and stearic acid ($C_{17}H_{35}COOH$).
- (3) The general formula for monocarboxylic acids is $C_nH_{2n+1}COOH$ or $C_nH_{2n}O_2$. Where n = number of carbon atoms.
- (4) The carboxylic acids may be aliphatic or aromatic depending upon whether $-COOH$ group is attached to aliphatic alkyl chain or aryl group respectively.

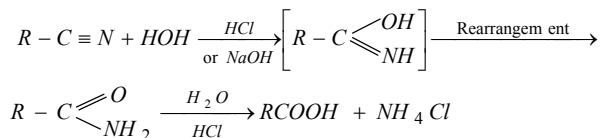
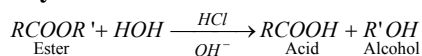
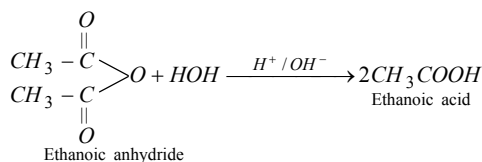
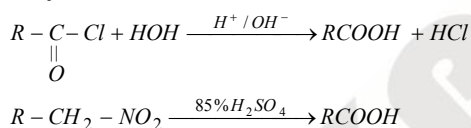
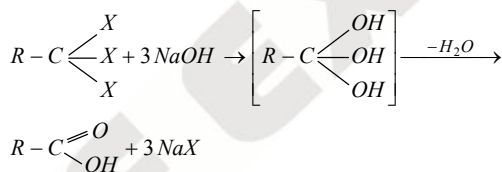
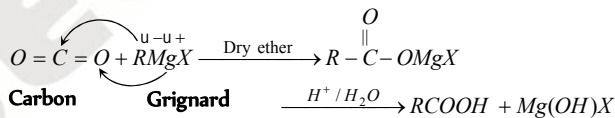
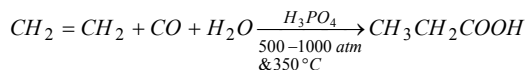
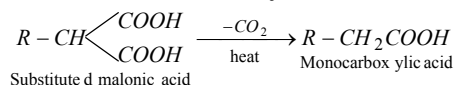
Methods of preparation of monocarboxylic acid

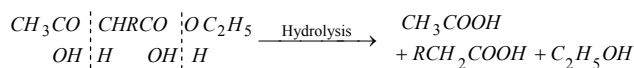
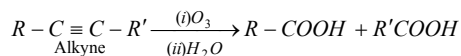
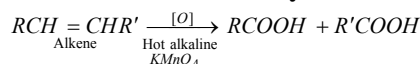
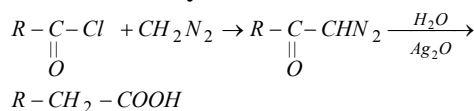
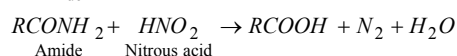
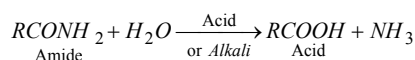
- (1) **By oxidation of alcohols, aldehydes and ketones**



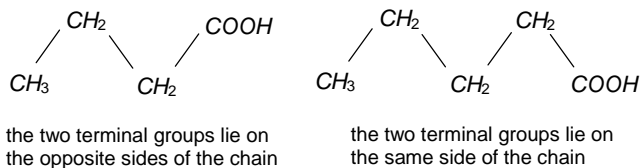
- ☐ Aldehyde can be oxidized to carboxylic acid with mild oxidising agents such as ammoniacal silver nitrate solution $[Ag_2O \text{ or } Ag(NH_3)_2^+ OH^-]$
- ☐ Methanoic acid can not be prepared by oxidation method.
- ☐ Ketones can be oxidized under drastic conditions using strong oxidising agent like $K_2Cr_2O_7$.
- ☐ Methyl ketones can also be converted to carboxylic acid through the haloform reaction.



(2) **By Hydrolysis of nitriles, ester, anhydrides and acid chloride**(i) **Hydrolysis of nitriles**(ii) **Hydrolysis of Esters**(iii) **Hydrolysis of Anhydrides**(iv) **Hydrolysis of acid chloride and nitro alkane**(v) **Hydrolysis of Trihalogen :**(3) **From Grignard Reagent**(4) **From Alkene or Hydro-carboxy-addition (koch reaction)**(5) **Special methods**(i) **Carboxylation of sodium alkoxide**(ii) **Action of heat on dicarboxylic acid**

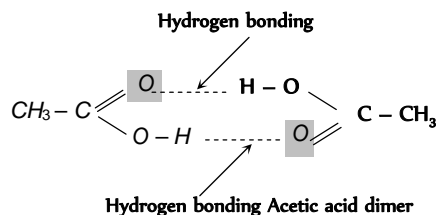
(iii) **From acetoacetic ester**(iv) **Oxidation of alkene and alkyne**(v) **The Arndt-Eistert synthesis**(vi) **From acid amides****Physical properties of monocarboxylic acids:**

- (1) **Physical state :** The first three members (upto 3 carbon atoms) are colourless, pungent smelling liquids. The next six members are oily liquids having unpleasant smell. The higher members are colourless and odourless waxy solids.
- (2) **Solubility :** The lower members of the aliphatic carboxylic acid family (upto C₄) are highly soluble in water. The solubility decreases with the increase in the size of the alkyl group. All carboxylic acids are soluble in alcohol, ether and benzene etc.
 - ❑ The solubility of lower members of carboxylic acids is due to the formation of hydrogen bonds between the –COOH group and water molecules.
 - ❑ Acetic acid exists in the solution in dimer form due to intermolecular hydrogen bonding. The observed molecular mass of acetic acid is 120 instead of 60.
- (3) **Melting point**
 - (i) The melting points of carboxylic acids do not vary smoothly from one member to another.
 - (ii) The melting point of the acids having even number of carbon atoms are higher than those containing an odd number immediately above and below them.
 - (iii) The acids with even number of carbon atoms have the –COOH group and the terminal –CH₃ group on the opposite side of the carbon chain.
 - (iv) In the case of odd numbers, the two groups lie on the same side of the chain.



When the terminal groups lie on the opposite sides the molecules fit into each other more closely. More effective packing of the molecule in the lattice. Therefore, results into higher melting point.

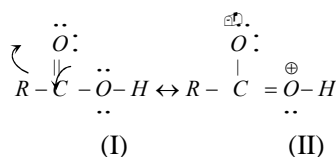
- (4) **Boiling point** : Boiling point of carboxylic acids increase regularly with increase of molecular mass. Boiling points of carboxylic acids are higher than those of alcohols of same molecular mass. This is due to intermolecular hydrogen bonding between two acid molecules.



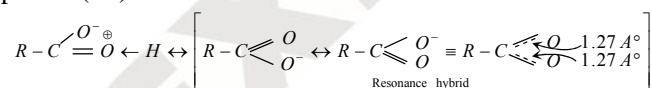
Acidic nature of monocarboxylic acids:

(1) Cause of acidic nature

(i) A molecule of carboxylic acid can be represented as a resonance hybrid of the following structures.



(ii) Due to electron deficiency on oxygen atom of the hydroxyl group (Structure II), there is a displacement of electron pair of O-H bond toward the oxygen atom. This facilitates the release of hydrogen as proton (H^+).



(iii) The resulting carboxylate ion is also stabilized by resonance (As negative charge is dispersed on both the oxygen atoms). This enhances the stability of carboxylate anion and makes it a weaker base or strong acid.

(2) Effect of substituent on acidic nature

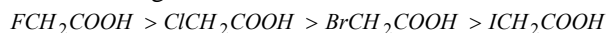
(i) An electron withdrawing substituent ($-I$ effect) stabilizes the anion by dispersing the negative charge and therefore increases the acidity.



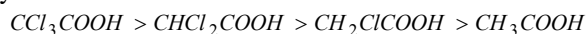
(ii) An electron releasing substituent ($+I$ effect) stabilizes negative charge on the anion resulting in the decrease of stability and thus decreases the acidity of acid.

Electron withdrawing nature of halogen : $\text{F} > \text{Cl} > \text{Br} > \text{I}$

Thus, the acidic strength decreases in the order :

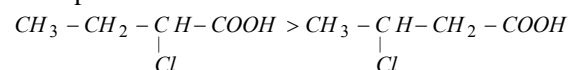


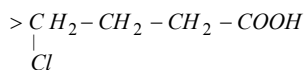
similarly :



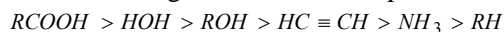
(iii) Inductive effect is stronger at α -position than β -position similarly at β -position it is more stronger than at γ -position

Example:



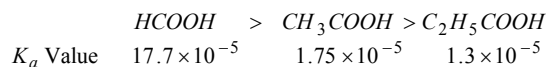


(iv) Relative acid strength in different compounds



☐ Greater the value of K_a or lesser the value of pK_a stronger is the acid, i.e. $pK_a = -\log K_a$

☐ Acidic nature (K_a) \propto 1/molecular weight



☐ The formic acid is strongest of all fatty acids.

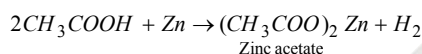
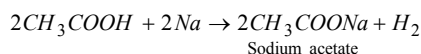
☐ Acetic acid is less weak acid than sulphuric acid due to less degree of ionisation.

Chemical properties of monocarboxylic acids:

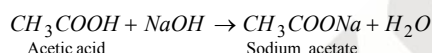
(1) Reaction involving removal of proton from –OH group

(i) **Action with blue litmus** : All carboxylic acids turn blue litmus red.

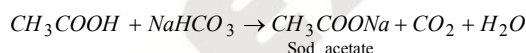
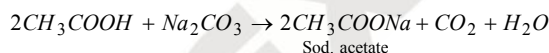
(ii) **Reaction with metals**



(iii) **Action with alkalies**



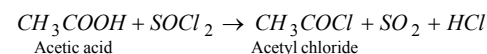
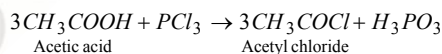
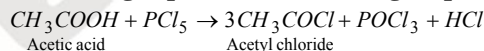
(iv) **Action with carbonates and bicarbonates**



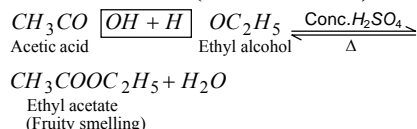
☐ Reaction of carboxylic acid with aqueous sodium carbonates solution produces brisk effervescence. However most phenols do not produce effervescence. Therefore, this reaction may be used to distinguish between carboxylic acids and phenols.

(2) Reaction involving replacement of –OH group

(i) Formation of acid chloride



(ii) **Formation of esters (Esterification)**

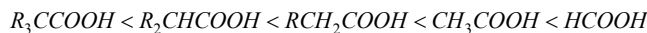


(a) The reaction is shifted to the right by using excess of alcohol or removal of water by distillation.

(b) The reactivity of alcohol towards esterification.

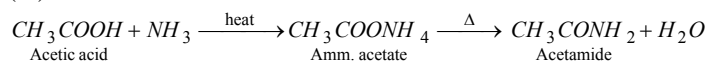
tert-alcohol < sec-alcohol < pri-alcohol < methyl alcohol

(c) The acidic strength of carboxylic acid plays only a minor role.

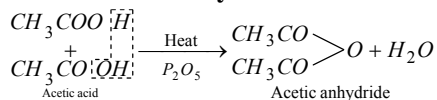


When **methanol** is taken in place of **ethanol**, then reaction is called **trans esterification**.

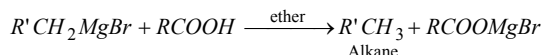
(iv) **Formation of amides**



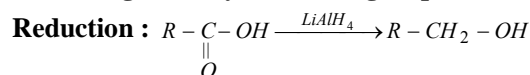
(v) **Formation of acid anhydrides**



(vi) **Reaction with organo-metallic reagents**

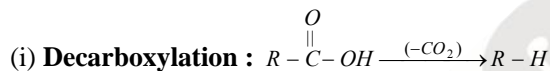


(3) **Reaction involving carbonyl (>C = O) group:**

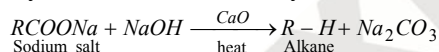


Carboxylic acid are difficult to reduce either by catalytic hydrogenation or $\text{Na}/\text{C}_2\text{H}_5\text{OH}$

(4) **Reaction involving attack of carboxylic group (–COOH)**



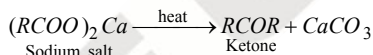
When anhydrous alkali salt of fatty acid is heated with sodalime then :



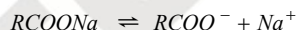
□ When sodium formate is heated with sodalime H_2 is evolved. (Exception)



(ii) **Heating of calcium salts**

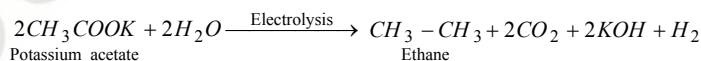


(iii) **Electrolysis : (Kolbe's synthesis)**

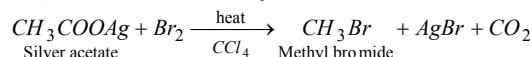


At anode $2\text{RCOO}^- \rightarrow R - R + 2\text{CO}_2 + 2e^-$

At cathode $2\text{Na}^+ + 2e^- \rightarrow 2\text{Na} \xrightarrow{2\text{H}_2\text{O}} 2\text{NaOH} + \text{H}_2$

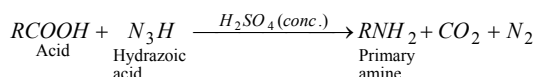


(iv) **Formation of Alkyl halide (Hunsdiecker's reaction)**



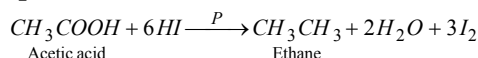
□ In Hunsdiecker reaction, one carbon atom less alkyl halide is formed from acid salt.

(v) **Formation of amines (Schmidt reaction)**



In Schmidt reaction, one carbon less product is formed.

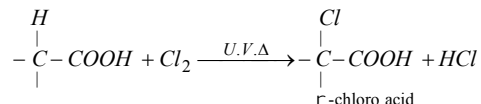
(vi) **Complete reduction**



In the above reaction, the –COOH group is reduced to a CH_3 group.

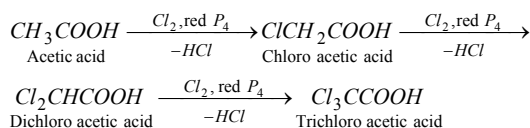
(5) Reaction involving hydrogen of α -carbon**Halogenation:**

(i) In presence of U.V. light

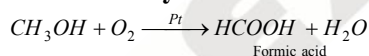


(ii) In presence of Red P and diffused light [Hell Volhard-zelinsky reaction]

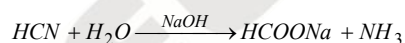
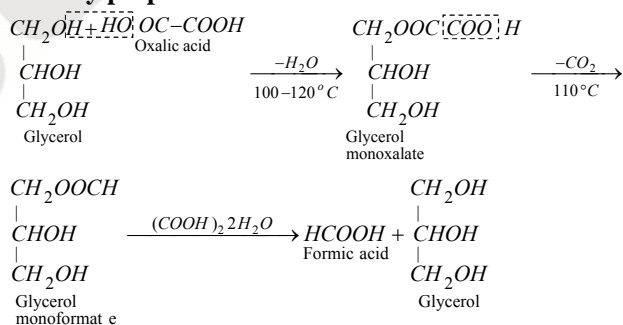
Carboxylic acid having an α -hydrogen react with Cl_2 or Br_2 in the presence of a small amount of red phosphorus to give chloro acetic acid. The reaction is known as **Hell Volhard-zelinsky reaction**.

**Individual members of monocarboxylic acids:****Formic Acid or Methanoic acid (HCOOH)**

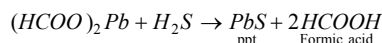
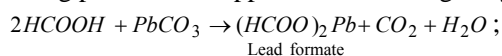
Formic acid is the first member of monocarboxylic acids series. It occurs in the sting of bees, wasps, red ants, stinging nettles. and fruits. In traces it is present in perspiration, urine, blood and in caterpillar's.

(1) **Methods of preparation**(i) **Oxidation of methyl alcohol or formaldehyde**

(ii) **Hydrolysis of hydrocyanic acid** : Formic acid is formed by the hydrolysis of HCN with acids or alkalis.

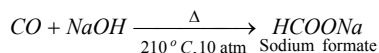
(iii) **Laboratory preparation**

The following procedure is applied for obtaining anhydrous formic acid.

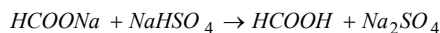


(iv) **Industrial preparation** : Formic acid is prepared on industrial scale by heating sodium

hydroxide with carbon monoxide at 210°C under a pressure of about 10 atmospheres.



Sodium formate thus formed is distilled with sodium hydrogen sulphate, when anhydrous formic acid distils over.



(2) **Physical properties**

- (i) It is a colourless pungent smelling liquid.
- (ii) It melts at 8.4°C and boils at 100.5°C.
- (iii) It is miscible with water, alcohol and ether. It forms azeotropic mixture with water.
- (iv) It is strongly corrosive and causes blisters on skin.
- (v) It exists in aqueous solution as a dimer involving hydrogen bonding.

(3) **Uses :** Formic acid is used.

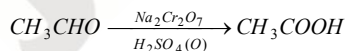
- (i) In the laboratory for preparation of carbon monoxide.
- (ii) In the preservation of fruits.
- (iii) In textile dyeing and finishing.
- (iv) In leather tanning.
- (v) As coagulating agent for rubber latex.
- (vi) As an antiseptic and in the treatment of gout.
- (vii) In the manufacture of plastics, water proofing compounds.
- (viii) In electroplating to give proper deposit of metals.
- (ix) In the preparation of nickel formate which is used as a catalyst in the hydrogenation of oils.
- (x) As a reducing agent.
- (xi) In the manufacture of oxalic acid.

Acetic Acid (Ethanoic Acid) (CH₃COOH)

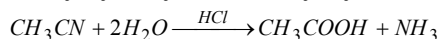
Acetic acid is the oldest known fatty acid. It is the chief constituent of vinegar and hence its name (Latin acetum = vinegar)

(1) **Preparation**

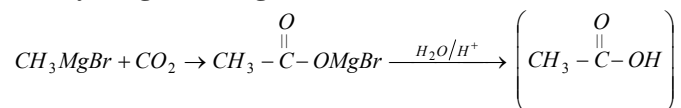
(i) **By oxidation of acetaldehyde (Laboratory-preparation)**



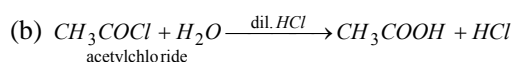
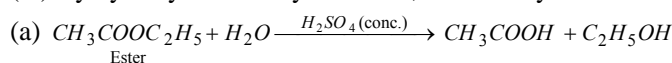
(ii) **By hydrolysis of methyl cyanide with acid**

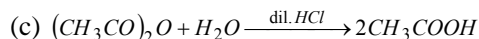


(iii) **By Grignard reagent**

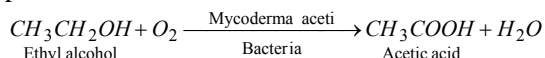


(iv) **By hydrolysis of acetyl chloride, acetic anhydride or acetamide and ester**



**(v) Manufacture of acetic acid:**

(a) From ethyl alcohol (Quick vinegar process) : Vinegar is 6-10% aqueous solution of acetic acid. It is obtained by fermentation of liquors containing 12 to 15% ethyl alcohol. Fermentation is done by Bacterium *Mycoderma aceti* in presence of air at 30-35°C. The process is termed **acetous fermentation**.

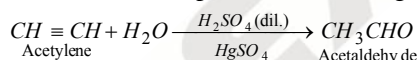


It is a slow process and takes about 8 to 10 days for completion.

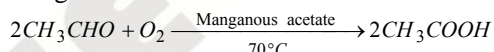
In this process, the following precautions are necessary:

- The concentration of the ethyl alcohol should not be more than 15%, otherwise the bacteria becomes inactive.
 - The supply of air should be regulated. With less air the oxidation takes place only upto acetaldehyde stage while with excess of air, the acid is oxidised to CO₂ and water.
 - The flow of alcohol is so regulated that temperature does not exceed 35°C, which is the optimum temperature for bacterial growth.
- Acetic acid can be obtained from vinegar with the help of lime. The calcium acetate crystallised from the solution is distilled with concentrated sulphuric acid when pure acetic acid distils over.

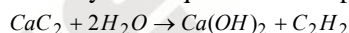
(b) From acetylene : Acetylene is first converted into acetaldehyde by passing through 40% sulphuric acid at 60°C in presence of 1% HgSO₄ (catalyst).



The acetaldehyde is oxidised to acetic acid by passing a mixture of acetaldehyde vapour and air over manganous acetate at 70°C.

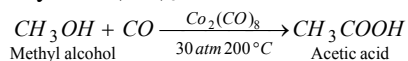


□ Acetylene required for this purpose is obtained by action of water on calcium carbide.



The yield is very good and the strength of acid prepared is 97%. The method is also quite cheap.

(c) By the action of CO on methyl alcohol : Methyl alcohol and carbon monoxide react together under a pressure of 30 atmospheres and 200°C in presence of a catalyst cobalt octacarbonyl, Co₂(CO)₈ to form acetic acid.

**(2) Physical properties**

(i) At ordinary temperature, acetic acid is a colourless, corrosive liquid with a sharp pungent odour of vinegar. It has a sour taste.

(ii) Below 16.5°C, it solidifies as an icy mass, hence it is named glacial acetic acid.

(iii) It boils at 118°C. The high boiling point of acetic acid in comparison to alkanes, alkyl halides or alcohols of nearly same molecular masses is due to more stronger hydrogen

bonding between acid molecules. This also explains dimer formation of acetic acid in vapour state.

(iv) It is miscible with water, alcohol and ether in all proportions.

(v) It is good solvent for phosphorus, sulphur, iodine and many organic compounds.

(3) **Uses :** It is used,

(i) As a solvent and a laboratory reagent.

(ii) As vinegar for table purpose and for manufacturing pickles.

(iii) In coagulation of rubber latex.

(iv) For making various organic compounds such as acetone, acetic anhydride, acetyl chloride, acetamide and esters.

(v) For making various useful metallic acetates, such as:

(a) Basic copper acetate which is used for making green paints.

(b) Al, Fe and Cr acetates which are used as mordants in dyeing.

(c) Lead tetra-acetate which is a good oxidising agent.

(d) Basic lead acetate which is used in the manufacture of white lead.

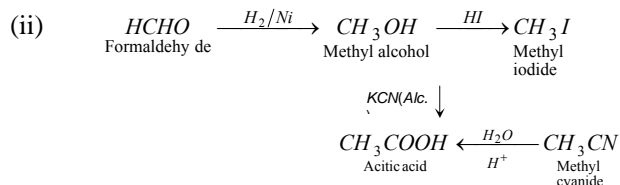
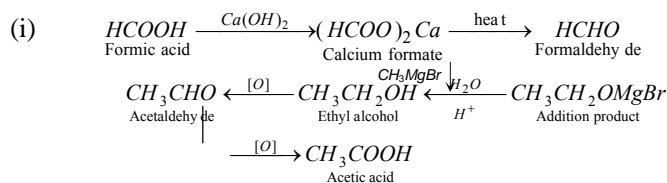
(e) Aluminium acetate which is used in the manufacture of water-proof fabrics.

(f) Alkali acetates which are used as diuretics.

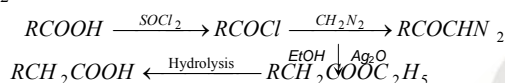
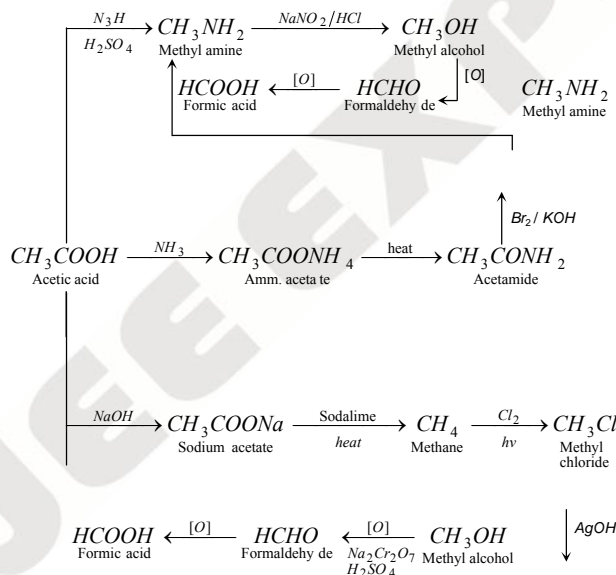
Table : 28.1 Comparison of Formic Acid and Acetic Acid:

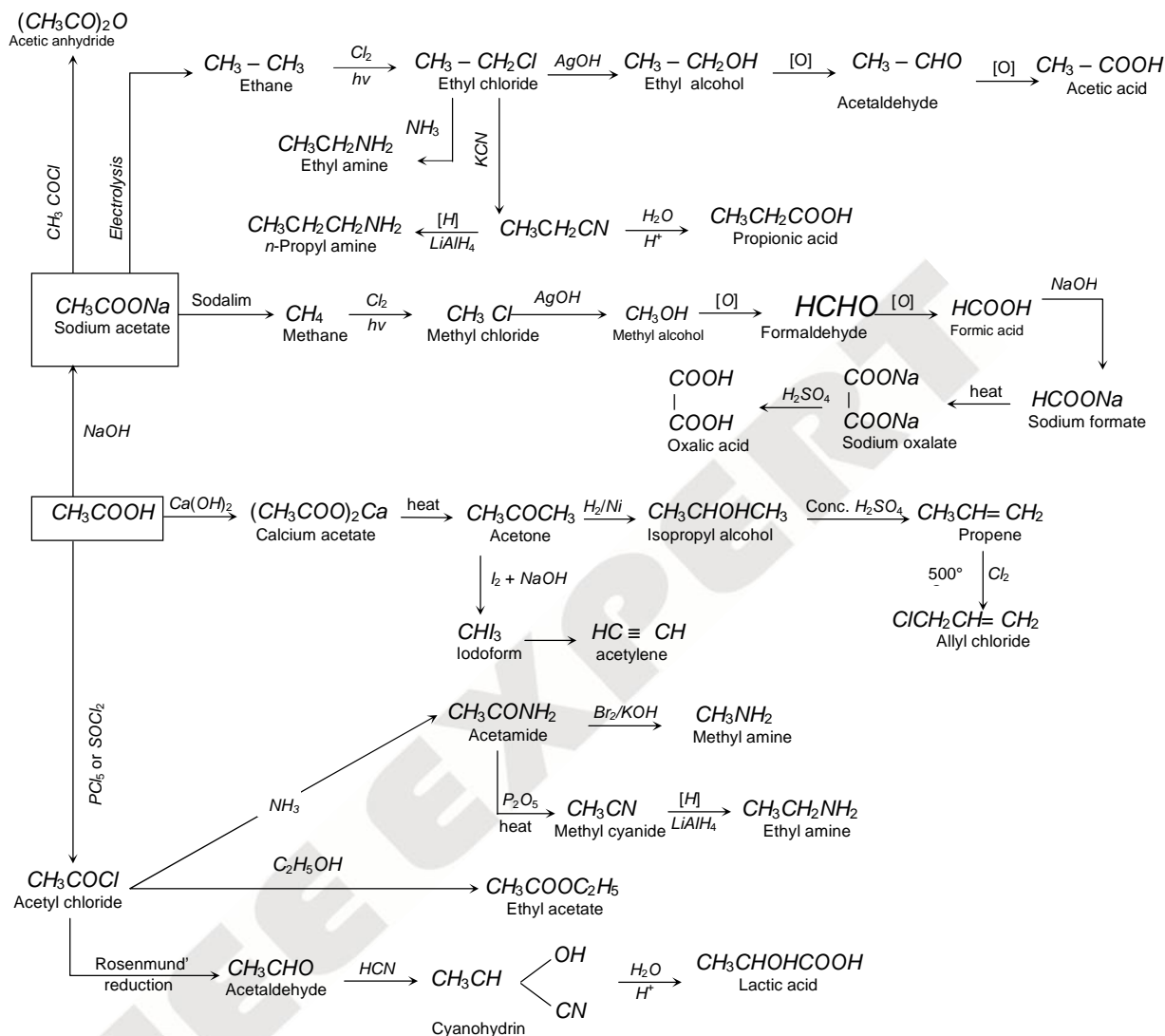
Property	Formic acid	Acetic acid
1. Acidic nature, (i) With electro-positive metals	Forms salts, Hydrogen is evolved. $HCOOH + Na \rightarrow HCOONa + \frac{1}{2}H_2$	Forms salts. Hydrogen is evolved. $CH_3COOH + Na \rightarrow CH_3COONa + \frac{1}{2}H_2$
(ii) With bases	Forms salts. $HCOOH + NaOH \rightarrow HCOONa + H_2O$	Forms salts. $CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$
(iii) With carbonates and bicarbonates	Forms salts. Carbon dioxide is evolved. $HCOOH + NaHCO_3 \rightarrow HCOONa + H_2O + CO_2$	Forms salts. Carbon dioxide is evolved. $CH_3COOH + NaHCO_3 \rightarrow$ $CH_3COONa + H_2O + CO_2$
2. Ester formation	Forms esters when treated with alcohols. $HCOOH + C_2H_5OH \rightarrow HCOOC_2H_5 + H_2O$	Forms esters when treated with alcohols. $CH_3COOH + C_2H_5OH \xrightarrow{H_2SO_4 (conc.)}$ $CH_3COOC_2H_5 + H_2O$
3. Reaction with PCl_5	Forms formyl chloride which decomposes into CO and HCl. $HCOOH + PCl_5 \rightarrow HCOCl(HCl + CO) + POCl_3 + HCl$	Forms acetyl chloride which is a stable compound. $CH_3COOH + PCl_5 \rightarrow$ $CH_3COCl + POCl_3 + HCl$
4. Heating of ammonium salt	Forms formamide. $HCOONH_4 \rightarrow HCONH_2 + H_2O$	Forms acetamide. $CH_3COONH_4 \rightarrow CH_3CONH_2 + H_2O$
5. Heating alone	it decomposes into CO_2 and H_2 $HCOOH \rightarrow CO_2 + H_2$	Unaffected

6. Heating with conc. H_2SO_4	Decomposed into CO and H_2O $HCOOH \xrightarrow[H_2SO_4]{Conc.} CO + H_2O$	Unaffected
7. Reaction with Cl_2 in presence of red P	Unaffected	Forms mono, di or trichloro acetic acids.
8. Action of heat on salts, (i) Calcium salt	Forms formaldehyde. $(HCOO)_2Ca \rightarrow HCHO + CaCO_3$	Forms acetone. $(CH_3COO)_2Ca \rightarrow CH_3COCH_3 + CaCO_3$
(ii) Sodium salt	Forms sodium oxalate. $2HCOONa \xrightarrow{heat} \begin{matrix} COONa \\ \\ COONa \end{matrix} + H_2$	Unaffected.
(iii) Sodium salt with soda-lime	Forms sodium carbonate and H_2 . $HCOONa + NaOH \xrightarrow{CaO} Na_2CO_3 + H_2$	Forms sodium carbonate and methane. $CH_3COONa + NaOH \xrightarrow{CaO} CH_4 + Na_2CO_3$
9. Electrolysis of sodium or potassium salt	It evolves hydrogen.	It forms ethane.
10. On heating with P_2O_5	Unaffected	Forms acetic anhydride. $2CH_3COOH \xrightarrow{P_2O_5} (CH_3CO)_2O + H_2O$
11. Reducing nature, (i) Tollen's reagent	Gives silver mirror or black precipitate. $HCOOH + Ag_2O \rightarrow 2Ag + CO_2 + H_2O$	Unaffected.
(ii) Fehling's solution	Gives red precipitate $HCOOH + 2CuO \rightarrow Cu_2O + CO_2 + H_2O$	Unaffected.
(iii) Mercuric chloride	Forms a white ppt. which changes to greyish black. $HgCl_2 \rightarrow Hg_2Cl_2 \rightarrow 2Hg$	Unaffected.
(iv) Acidified $KMnO_4$	Decolourises	Unaffected.
12. Acid (neutral solution) + $NaHSO_3$ + Sodium nitroprusside.	Greenish blue colour.	Unaffected.
13. Acid (neutral solution) + neutral ferric chloride	Red colour which changes to brown ppt. on heating.	Wine red colour.

Interconversions:(1) **Ascent of series :** Conversion of formic acid into acetic acid.

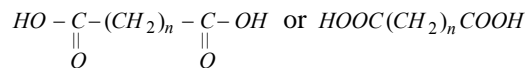
Arndt-Eistert homologation : This is a convenient method of converting an acid, RCOOH to RCH₂COOH.

(2) **Descent of series :** Conversion of acetic acid into formic acid.

Conversion of Acetic acid into other organic compound:**Dicarboxylic acids:**

The acids containing two carboxylic groups are called dicarboxylic acids.

The saturated dicarboxylic acid are represented by the general formula $\text{C}_n\text{H}_{2n}(\text{COOH})_2$ where $n = 0, 1, 2, 3$ etc.



According to IUPAC system, the suffix-dioic acid is added to the name of parent alkane, i.e. Alkane dioic acid.

Table : 28.2

<u>Formula</u>	<u>Common name</u>	<u>IUPAC name</u>
HOOC ^{COOH} COOH	Oxalic acid	Ethanedioic acid
HOOCCH ₂ COOH	Malonic acid	1-3 Propanedioic acid
HOOCCH ₂ CH ₂ COOH	Succinic acid	1,4-Butanedioic acid
HOOC(CH ₂) ₃ COOH	Glutaric acid	1,5-Pentanedioic acid
HOOC(CH ₂) ₄ COOH	Adipic acid	1,6-Hexanedioic acid

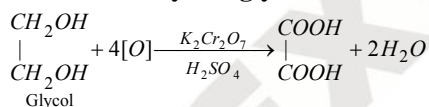
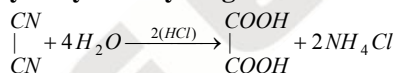
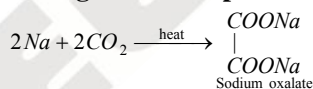
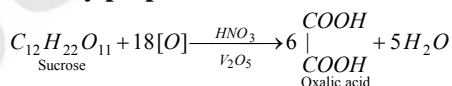
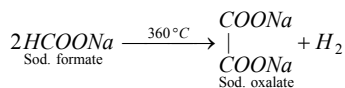
Oxalic Acid or Ethanedioic Acid :

Oxalic acid is first member of dicarboxylic series.

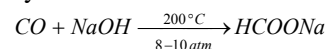
It occurs as potassium hydrogen oxalate in the wood sorrel, rhubarb and other plants of oxalis group and as calcium oxalate in plants of rumex family.

It is found in the form of calcium oxalate in stony deposits in kidneys and bladder in human body.

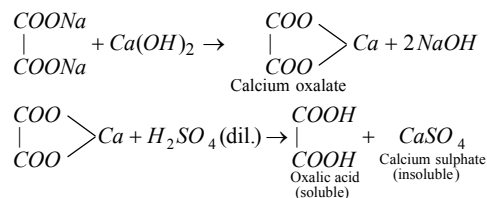
Oxalic acid present in tomatoes.

(1) Methods of Preparation :**(i) By oxidation of ethylene glycol with acidified potassium dichromate****(ii) By hydrolysis of cyanogen with conc. hydrochloric acid :****(iii) By heating sodium or potassium in a current of carbon dioxide at 360°C****(iv) Laboratory preparation****(v) Industrial method**

Sodium formate is obtained by passing carbon monoxide over fine powdered of sodium hydroxide.



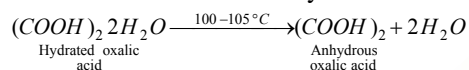
The sodium oxalate thus formed is dissolved in water and calcium hydroxide is added. The precipitate of calcium oxalate is formed which is separated by filtration. It is decomposed with calculated quantity of dilute sulphuric acid.

(2) **Physical Properties**

- (i) It is a colourless crystalline solid. It consists of two molecules of water as water of crystallisation.
- (ii) The hydrated form has the melting point 101.5°C while the anhydrous form melts at 190°C .
- (iii) It is soluble in water and alcohol but insoluble in ether.
- (iv) It is poisonous in nature. It affects the central nervous system.

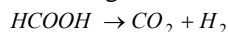
(3) **Chemical Properties**

- (i) **Action of heat** : It becomes anhydrous.

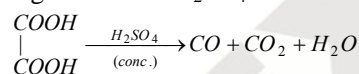


- (a) At 200°C , $(\text{COOH})_2 \longrightarrow \text{HCOOH} + \text{CO}_2$
- Formic acid

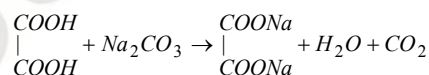
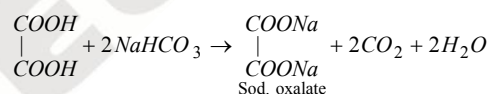
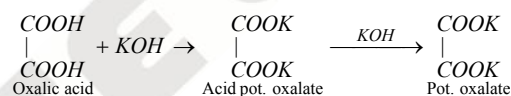
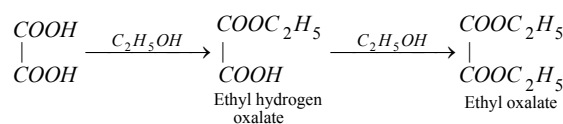
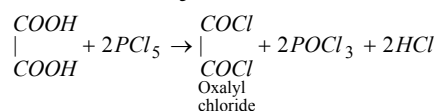
On further heating, formic acid also decomposes.

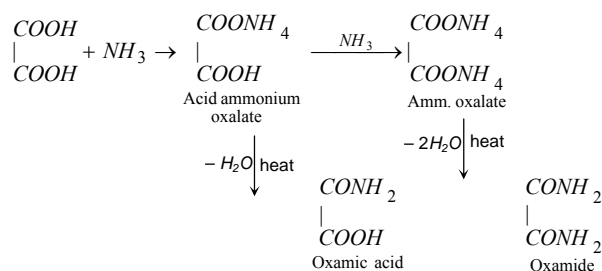
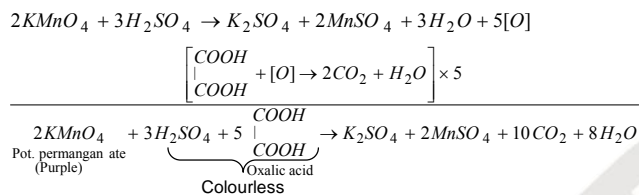


- (b) Heating with conc. H_2SO_4

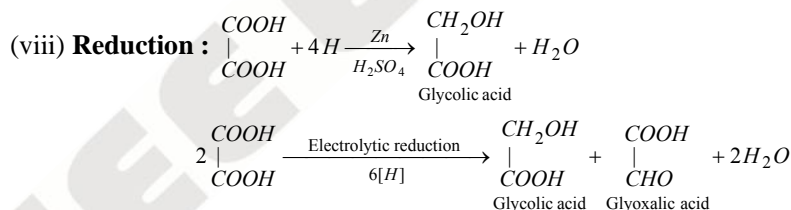
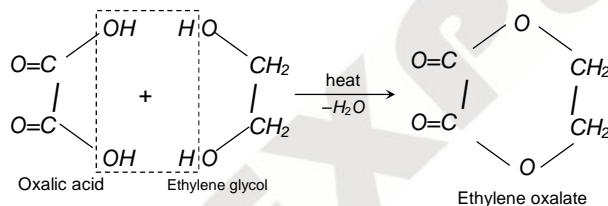
(ii) **Acidic nature**

Salt formation

(iii) **Esterification**(iv) **Reaction with PCl_5 :**

(v) **Reaction with ammonia**(vi) **Oxidation** : When oxalic acid is warmed with acidified KMnO_4 .

□ Oxalic acid decolourises the acidic KMnO_4 solution.

(vii) **Reaction with ethylene glycol**

(ix) **Reaction with Glycerol** : At $100^\circ - 110^\circ\text{C}$, formic acid is formed. At 260° , allyl alcohol is formed.

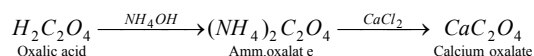
(4) **Uses** : Oxalic acid (Polyprotic acid) is used,

- (i) In the manufacture of carbon monoxide, formic acid and allyl alcohol.
- (ii) As a laboratory reagent and as a standard substance in volumetric analysis.
- (iii) In the form of antimony salt as a mordant in dyeing and calico printing.
- (iv) In the manufacture of inks.
- (v) For removing ink stains and rust stains and for bleaching straw, wood and leather.
- (vi) In the form of ferrous potassium oxalate as developer in photography.

(5) **Analytical test**

- (i) The aqueous solution turns blue litmus red.
- (ii) The aqueous solution evolves effervescences with NaHCO_3 .

(iii) The neutral solution gives a white precipitate with calcium chloride solution. It is insoluble in acetic acid.



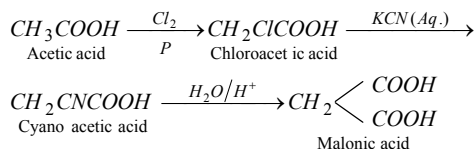
(iv) Oxalic acid decolourises hot potassium permanganate solution having dilute sulphuric acid.

(v) With hot conc. H_2SO_4 , it evolves carbon monoxide which burns with blue flame.

Malonic Acid or Propane-1,3-Dioic Acid $CH_2 \begin{matrix} \swarrow COOH \\ \searrow COOH \end{matrix}$ or $CH_2(COOH)_2$ or $(C_3H_4O_4)$

The acid occurs as calcium salt in sugar beet. It was so named because it was first obtained from malic acid (hydroxy succinic acid) by oxidation.

(1) **Methods of Preparation :** From acetic acid



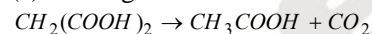
(2) **Physical Properties**

- (i) It is a white crystalline solid.
- (ii) It's melting point is $135^\circ C$.
- (iii) It is soluble in water and alcohol but sparingly soluble in ether.

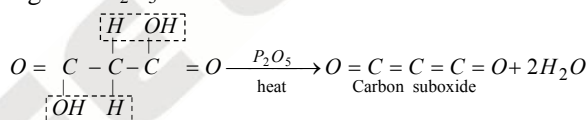
(3) **Chemical Properties**

(i) **Action of heat**

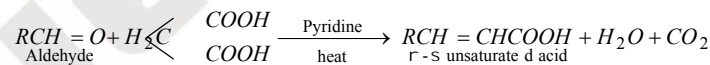
(a) Heating at $150^\circ C$:



(b) Heating with P_2O_5 :

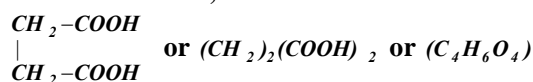


(ii) **Reaction with aldehyde :** With aldehydes, α - β unsaturated acids are formed.



(4) **Uses :** Its diethyl ester (malonic ester) is a valuable synthetic reagent for preparation of a variety of carboxylic acids.

Succinic Acid or Butane-1,4-Dioic Acid :

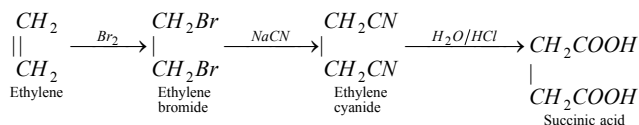


It was first obtained by the distillation of yellow fossil, resin, amber and hence its name (Latin, Succinum = amber).

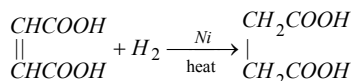
It is also formed in small amount during the fermentation of sugar.

(1) Methods of Preparation

(i) From ethylene

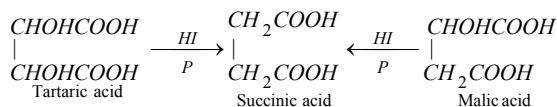


(ii) From maleic acid [catalytic reduction]



□ This is an industrial method.

(iii) Reduction of tartaric acid or malic acid

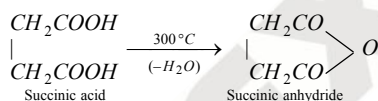


(2) Physical properties

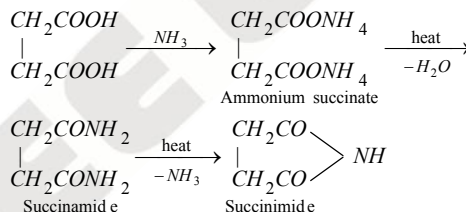
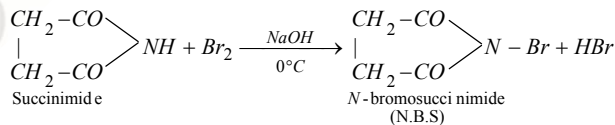
(i) It is a white crystalline solid. It melts at 188°C

(ii) It is less soluble in water. It is comparatively more soluble in alcohol.

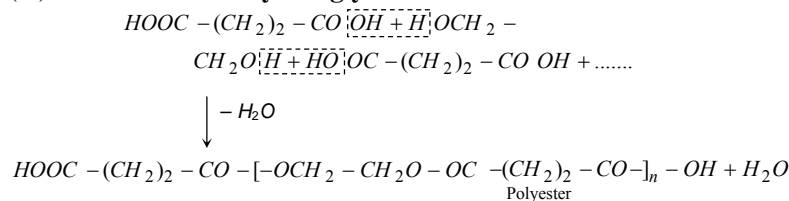
(3) **Chemical Properties :** Succinic acid gives the usual reactions of dicarboxylic acid, some important reactions are :

(i) Action of heat : At 300°C 

(ii) With ammonia

(iii) Reaction with Br_2 

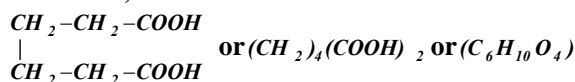
(iv) Reaction with ethylene glycol



When sodium or potassium salt in aqueous solution is electrolysed, ethylene is obtained at anode.

- (4) **Uses :** It finds use in volumetric analysis, medicine and in the manufacture of dyes, perfumes and polyester resins.

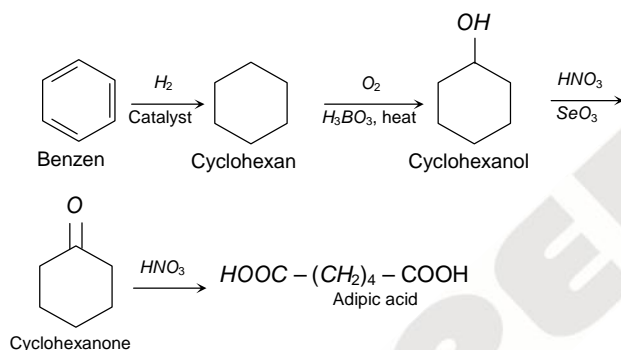
Adipic Acid or Hexane-1,6 –Dioic Acid:



It was first obtained by the oxidation of fats (Latin, adeps = fat.)

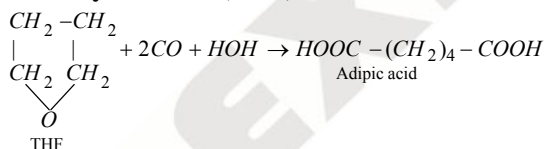
(1) **Methods of Preparation**

(i) **From benzene (In industries)**



☐ It is an industrial method.

(ii) **From tetrahydrofuran (THF)**



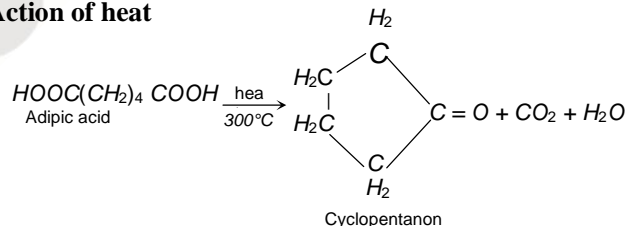
(2) **Physical Properties**

- (i) It is a white crystalline solid. Its melting point is 150°C .
- (ii) It is fairly soluble in alcohol and ether but less soluble in water.

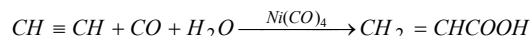
(3) **Chemical Properties**

It shows all the general reaction of dicarboxylic acids.

(i) **Action of heat**



Industrial method : This is a new method of its manufacture.

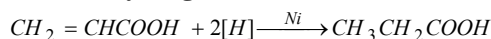


(2) **Physical Properties**

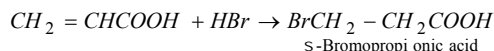
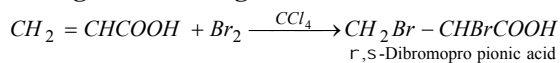
- ☐ It is colourless pungent smelling liquid. Its boiling point is 141°C.
- ☐ It is miscible with water, alcohol and ether.
- ☐ It shows properties of an alkene as well as of an acid.

(3) **Chemical Properties**

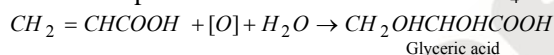
(i) **With nascent hydrogen (Na and C₂H₅OH)**



(ii) **With halogens and halogen acids :** Markownikoff's rule is not followed.

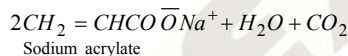
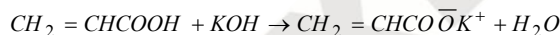


(iii) **Oxidation :** In presence of dilute alkaline KMnO₄.

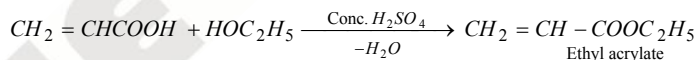


- ☐ On vigorous oxidation, oxalic acid is formed.

(iv) **Salt formation**



(v) **Ester formation**



(vi) **With PCl₅** $CH_2 = CHCOOH + PCl_5 \rightarrow CH_2 = CH - COCl$

Acryl chloride

(4) **Uses :** Its ester are used for making plastics such as Lucite and plexiglass.

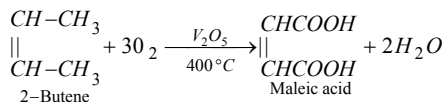
Unsaturated dicarboxylic acids:

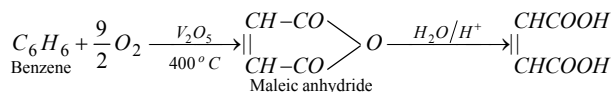
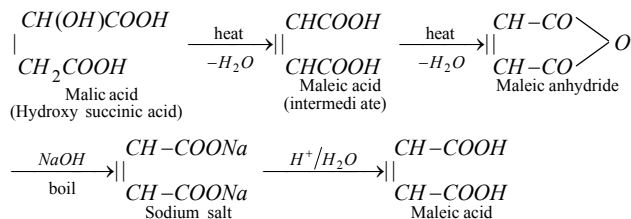
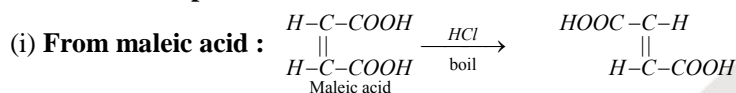
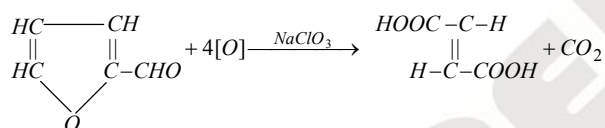
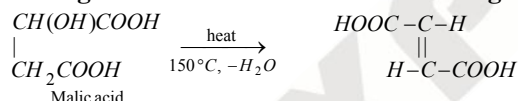
The molecular formula of the simplest unsaturated dicarboxylic acid is $HOOC.CH = CH.COOH$. This formula, however represents two chemical compounds, maleic acid and fumaric acid, which are geometrical isomers.



(1) **Methods of Preparation of Maleic Acid**

(i) **By catalytic oxidation of 2-butene or benzene**



**(ii) From malic acid :****(2) Methods of Preparation of Fumaric Acid****(ii) By oxidation of furfural with sodium chlorate****(iii) By heating malic acid at about 150°C for long time****(iv) By heating bromosuccinic acid with alcoholic potash :** By heating bromosuccinic acid with alcoholic potash.**(3) Physical Properties**

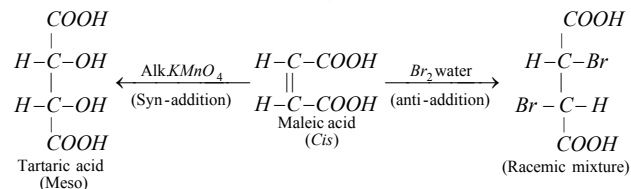
- (i) Both are colourless crystalline solids. Both are soluble in water.
 (ii) The melting point of maleic acid (130.5°C) is lower than the melting point of fumaric acid (287°C).

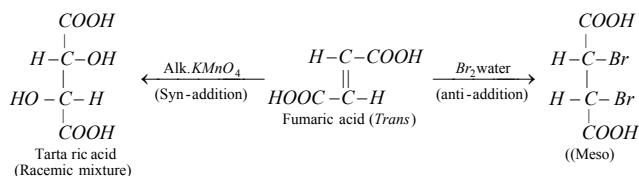
(4) Chemical Properties

Chemically, both the acids give the reactions of alkenes and dibasic acids except that the maleic acid on heating forms an anhydride while fumaric acid does not give anhydride.



Both form succinic acid on reduction with sodium amalgam. They undergo addition reactions with bromine, hydrobromic acid, water, etc. and form salts, esters and acid chlorides as usual. With alkaline KMnO_4 solution, they get oxidised to tartaric acid.



**Higher fatty acids:**

Palmitic, stearic and oleic acids are found in natural fats and oils as glyceryl esters.

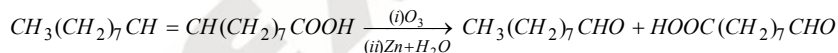
They have derived their names from the natural source from which they are prepared by hydrolysis with alkali.

Table : 28.3

Name of acids	Source	Molecular formula
Palmitic acid	Palm oil	$\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$
Stearic acid	Stear (meaning tallow)	$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$
Oleic acid	Olive oil.	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$

Palmitic and stearic acids are waxy colourless solids with melting points 64°C and 72°C , respectively. They are insoluble in water but soluble in ethanol and ether. They find use in the manufacture of soaps and candles. Soaps contain sodium or potassium salts of these higher fatty acids.

Oleic acid has low melting point, i.e., 16°C . It is insoluble in water but soluble in alcohol and ether. Besides the reactions of acids, it also gives reactions of alkenes. Two aldehydes are formed on ozonolysis.



It is used for making soaps, lubricants and detergents.

- (1) **Difference between oils and fats :** Oils and fats belong to the same chemical group, yet they are different in their physical state.

(i) Oils are liquids at ordinary temperature (below 20°C) while fats are semi solids or solids (their melting points are more than 20°C). A substance may be classed as fat in one season and oil in another season or the same glyceride may be solid at a hill station and liquid in plains. Thus, this distinction is not well founded as the physical state depends on climate and weather.

(ii) The difference in oils and fats is actually dependent on the nature of monocarboxylic acid present in the glyceride. Oils contain large proportion of the glycerides of lower carboxylic acids, (e.g., butyric acid, caprylic acid and caproic acid) and unsaturated fatty acids, (e.g., oleic, linoleic and linolenic acids) while fats contain a large proportion of glycerides of higher saturated carboxylic acids, (e.g., palmitic, stearic acids).

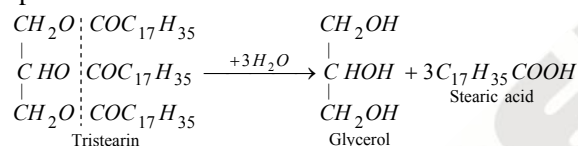
Lard (fat of hogs) is a solid fat and its composition in terms of fatty acids produced on hydrolysis is approximately 32% palmitic acid, 18% stearic acid, 45% oleic acid and 5% linolenic acid. Olive oil on the other hand, contains 84% oleic acid, 4% linoleic acid, 9% palmitic acid and 3% stearic acid.

(2) **Physical Properties of oils and Fats**

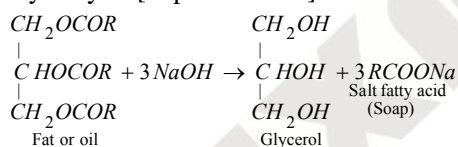
- (i) Fats are solids, whereas oils are liquids.
- (ii) They are insoluble in water but soluble in ether, chloroform and benzene.
- (iii) They have less specific gravity than water and consequently float on the surface when mixed with it.
- (iv) Pure fats and oils are colourless, odourless and tasteless but natural fats and oils possess a characteristic odour due to presence of other substances.
- (v) They have specific melting points, specific gravity and refractive index hence they can be identified by these oil constants.
- (vi) Animal fats contain cholesterol, an unsaturated alcohol, whereas vegetable fats contains phytosterol.

(3) **Chemical Properties :** They give reactions of carbon-carbon double bonds and ester groups.(i) **Hydrolysis**

(a) By superheated steam

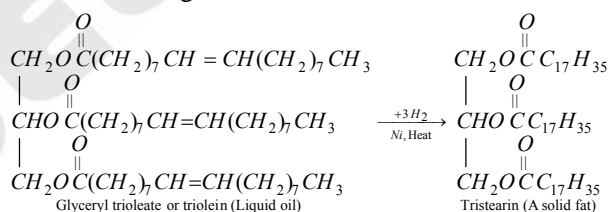
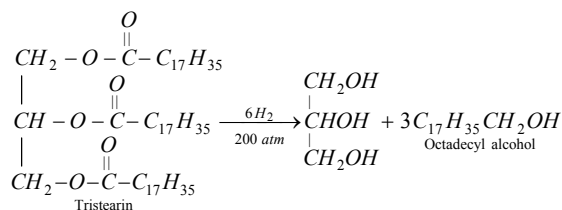


(b) Base hydrolysis [Saponification]



(c) Enzyme hydrolysis : Enzyme like lipase, when added to an emulsion of fat in water, hydrolyses it into acid and glycerol in about two or three days.

(ii) **Hydrogenation :** In the presence of finely divided nickel, at low pressure the hydrogenation process is called hardening of oils.

(iii) **Hydrogenolysis [Reduction to alcohol]**

(iv) **Drying** : Certain oils, containing glycerides of unsaturated fatty acids having two or three double bonds have the tendency of slowly absorbing oxygen from atmosphere and undergoing polymerisation to form hard transparent coating. This process is known as drying and such oils are called drying oils. Unsaturated oils such as linseed oil are, therefore, used as medium of paints and varnishes.

(v) **Rancidification** : On long storage in contact with air and moisture, oils and fats develop unpleasant smell. The process is known as rancidification. It is believed that rancidification occurs due to hydrolysis-oxidation.

(4) **Analysis of oils and fats :**

(i) **Acid value** : It indicates the amount of free acid present in the oil or fat. It is defined as the number of milligrams of KOH required to neutralize the free acid present in one gram of the oil or fat. It is determined by dissolving a weighed amount of oil or fat in alcohol and titrating it against a standard solution of KOH using phenolphthalein as an indicator.

(ii) **Saponification value** : It is a measure of fatty acids present as esters in oils and fats. It is defined as the number of milligrams of KOH required to saponify one gram of the oil or fat or number of milligrams of KOH required to neutralize the free acids resulting from the hydrolysis of one gram of an oil or fat. It is determined by refluxing a Saponification number of fat or oil

$$= \frac{168,000}{M}, \quad \text{Where } M = \text{molecular mass}$$

(iii) **Iodine value** : Iodine value of a fat or oil is a measure of its degree of unsaturation. It is defined as the number of grams of iodine taken up by 100 grams of fat or oil for saturation. For a saturated acid glyceride, the iodine value is zero. Thus, the iodine value for a fat is low whereas for oil, it is high. As iodine does not react readily, in actual practice, iodine monochloride is used. Iodine monochloride is known as Wij's reagent.

(iv) **Reichert-Meissl value, (R/M value)** : It indicates the amount of steam volatile fatty acids present in the oil or fat. It is defined as the number of millilitres of 0.1 N KOH solution required to neutralize the distillate of 5 grams of hydrolysed fat. It is determined by hydrolysing a known weighed amount (5 grams) of the fat with alkali solution and the mixture is acidified with dilute sulphuric acid and steam distilled. The distillate is cooled, filtered and titrated against 0.1 N KOH.

(5) **Uses**

(i) Many oils and fats are used as food material.

(ii) Oils and fats are used for the manufacture of glycerol, fatty acids, soaps, candles, vegetable ghee, margarine, hair oils, etc.

(iii) Oils like linseed oil, tung oil, etc., are used for the manufacture of paints, varnish, etc.

(iv) Castor oil is used as purgative and codliver oil as a source of vitamins A and D. Almond oil is used in pharmacy. Olive oil is also used as medicine.

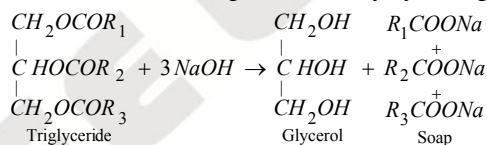
(v) Oils are also used as lubricants and illuminants.

Table : 28.4 Difference between vegetable oils and Mineral oils :

Property	Vegetable oils	Minerals oils
1. Composition	These are triesters of glycerol with higher fatty acids.	These are hydrocarbons (saturated). Kerosene oil– Alkanes from C ₁₂ to C ₁₆ .
2. Source	Seeds root and fruits of plants.	These occur inside earth in the form of petroleum.
3. Hydrolysis	Undergo hydrolysis with alkali. Form soap and glycerol.	No hydrolysis occurs.
4. On adding NaOH and phenolphthalein	Decolourisation of pink colour occurs.	No effect.
5. Burning	Burns slowly	Burn very readily.
6. Hydrogenation	Hydrogenation occurs in presence of nickel catalyst. Solid glycerides (fats) are formed.	No hydrogenation occurs.

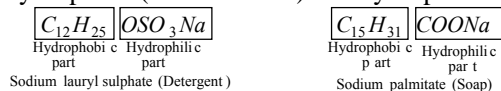
- (6) **Soaps :** Soaps are the metallic salts of higher fatty acids such as palmitic, stearic, oleic, etc. The sodium and potassium salts are the common soaps which are soluble in water and used for cleansing purposes. Soaps of other metals such as calcium, magnesium, zinc, chromium, lead, etc., are insoluble in water. These are not used for cleansing purposes but for other purposes (lubricants, driers, adhesives, etc.)

Ordinary soaps (sodium and potassium) are the products of hydrolysis of oils and fats with sodium hydroxide or potassium hydroxide. The oils and fats are mixed glycerides and thus soaps are mixtures of salts of saturated and unsaturated long chain carboxylic acids containing 12 to 18 carbon atoms. This process always yields glycerol as a byproduct.



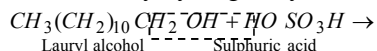
There are three methods for manufacture of soaps :

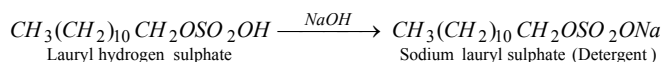
- The cold process
 - The hot process
 - Modern process
- (7) **Synthetic Detergents :** The synthetic detergents or **Syndets** are substitutes of soaps. They have cleansing power as good or better than ordinary soaps. Like soap, they contain both hydrophilic (water soluble) and hydrophobic (oil-soluble) parts in the molecule.



Some of the detergents used these days are given below:

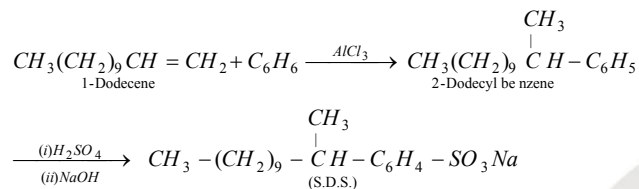
- (i) **Sodium alkyl sulphates :** These are sodium salts of sulphuric acid esters of long chain aliphatic alcohols containing usually 10 to 15 carbon atoms. The alcohols are obtained from oils or fats by hydrogenolysis.





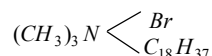
The other examples are sodium cetyl sulphate, $\text{C}_{16}\text{H}_{33}\text{OSO}_2\text{ONa}$ and sodium stearyl sulphate, $\text{CH}_3(\text{CH}_2)_{16}\text{CH}_2\text{OSO}_2\text{ONa}$. Unlike ordinary soaps, they do not produce OH^- ions on hydrolysis and thus can be safely used for woollen garments.

(ii) **Sodium alkyl benzene sulphonates** : Sodium p-dodecyl benzene sulphonate (S.D.S.) acts as a good detergent. It is most widely used since 1975.

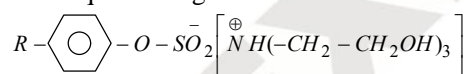


These long chain alkyl benzene sulphonate (L.A.S.) are most widely used syndets.

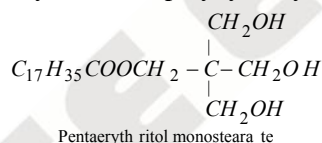
(iii) **Quaternary ammonium salts** : Quaternary ammonium salts with long chain alkyl group have been used as detergents, e.g., trimethyl stearyl ammonium bromide.



(iv) Sulphonates with triethanol ammonium ion in place of sodium serve as highly soluble materials for liquid detergents.



(v) Partially esterified polyhydroxy compounds also acts as detergents.

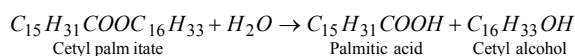


Detergents are superior cleansing agents due to following properties.

- (i) These can be used both in soft and hard waters as the calcium and magnesium ions present in hard water form soluble salts with detergents. Ordinary soap cannot be used in hard water.
- (ii) The aqueous solution of detergents are neutral. Hence these can be used for washing all types of fabrics without any damage. The solution of ordinary soap is alkaline and thus cannot be used to wash delicate fabrics.

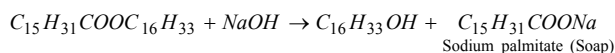
- (8) **Waxes** : Waxes are the esters of higher fatty acids with higher monohydric alcohols. The acids and alcohols commonly found in waxes are palmitic, cerotic acid ($\text{C}_{25}\text{H}_{51}\text{COOH}$), melissic acid ($\text{C}_{30}\text{H}_{61}\text{COOH}$) and cetyl alcohol ($\text{C}_{16}\text{H}_{33}\text{OH}$), ceryl alcohol ($\text{C}_{26}\text{H}_{53}\text{OH}$), myricyl alcohol ($\text{C}_{30}\text{H}_{61}\text{OH}$), etc.

Waxes are insoluble in water but are readily soluble in benzene, petroleum, carbon disulphide etc. Waxes on hydrolysis with water yields higher fatty acids and higher monohydric alcohols.



When hydrolysis is carried with caustic alkalies, soap and higher monohydric alcohols are

formed.



The common waxes are:

- (i) **Bees wax**, Myricyl palmitate, $C_{15}H_{31}COOC_{30}H_{61}$
- (ii) **Spermaceti wax**, Cetyl palmitate, $C_{15}H_{31}COOC_{16}H_{33}$
- (iii) **Carnauba wax**, Myricyl cerotate, $C_{25}H_{51}COOC_{30}H_{61}$

Waxes are used in the manufacture of candles, polishes, inks, water proof coating and cosmetic preparations.

Waxes obtained from plants and animals are different than **paraffin wax** which is a petroleum product and a mixture of higher hydrocarbons (20 to 30 carbon atoms). So paraffin wax is not an ester.

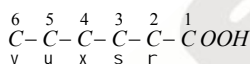
Candles are prepared by mixing paraffin wax (90%) with higher fatty acids like stearic and palmitic. The fatty acids are added to paraffin wax as to give strength to candles. The mixture is melted and poured into metal tubes containing stretched threads. On cooling candles are obtained.

Substituted carboxylic acids:

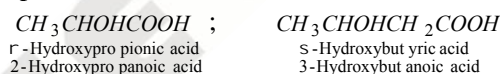
The compounds formed by the replacement of one or more hydrogen atoms of the hydrocarbon chain part of the carboxylic acids by atoms or groups such as X (halogen), OH or NH_2 , are referred to as substituted acids. For example,



The position of the substituents on the carbon chain are indicated by Greek letters or numbers.



For example,



Lactic Acid or α -hydroxy propionic acid or 2-hydroxy propanoic acid

It is the main constituent of sour milk. It is manufactured by fermentation of molasses by the micro-organism (*Bacterium acidilactici*-sour milk) in presence of $CaCO_3$.

(1) Method of Preparation

From acetaldehyde :

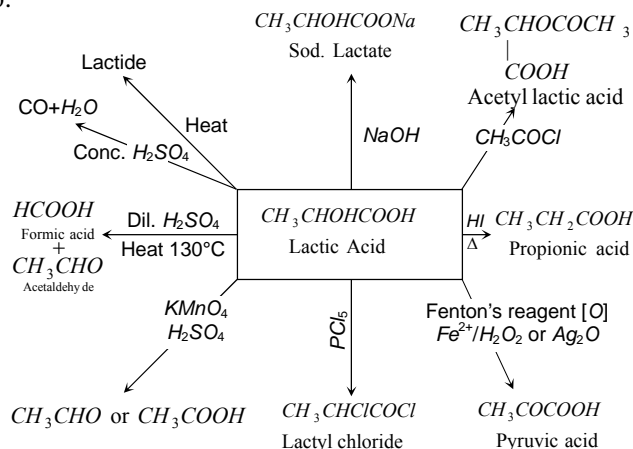


(2) Physical Properties

It is a colourless syrupy liquid having a sour taste and smell.

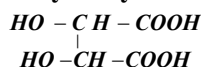
It is hygroscopic and very soluble in water. It is optically active and exists in three distinct forms.

- (3) **Chemical Properties :** It gives reactions of secondary alcoholic group and a carboxylic group.



- (4) **Uses :** It is used in medicine as calcium and iron lactates, as mordant in dyeing, as acidulant in beverages and **candies**, as a solvent (ethyl and butyl lactates) for cellulose nitrate.

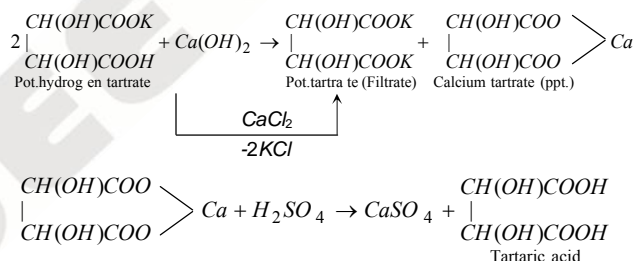
Tartaric Acid. Or α, α' -Dihydroxy succinic acid or 2,3-Dihydroxy-Butane-1,4-Dioic acid



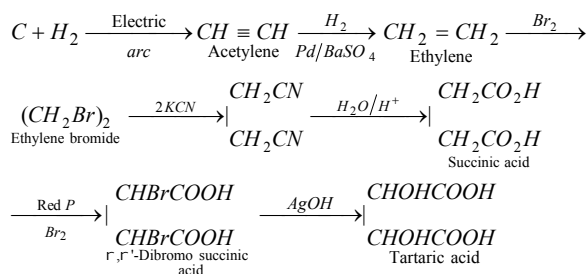
It is found as free or potassium salt in grapes, tamarind, and berries.

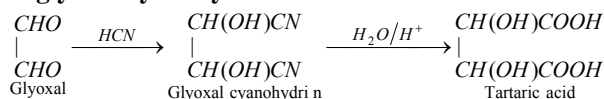
(1) Methods of Preparation

(i) **Argol** which separates as a crust during fermentation of grape juice is impure potassium hydrogen tartrate. Argol is boiled with limewater. Calcium tartrate is precipitated which is filtered. The solution contains potassium tartrate which is also precipitated by addition of CaCl_2 . The calcium salt is then decomposed with calculated quantity of dilute H_2SO_4 . The precipitate (CaSO_4) is filtered and the filtrate on concentration gives the crystals of tartaric acid.

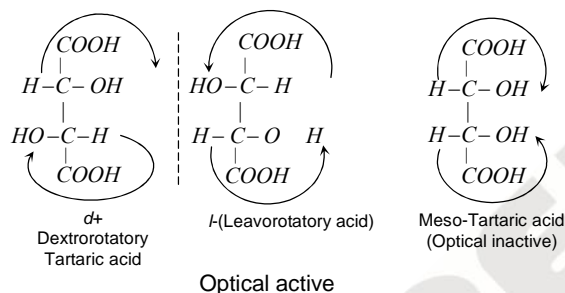


(ii) Synthetic method

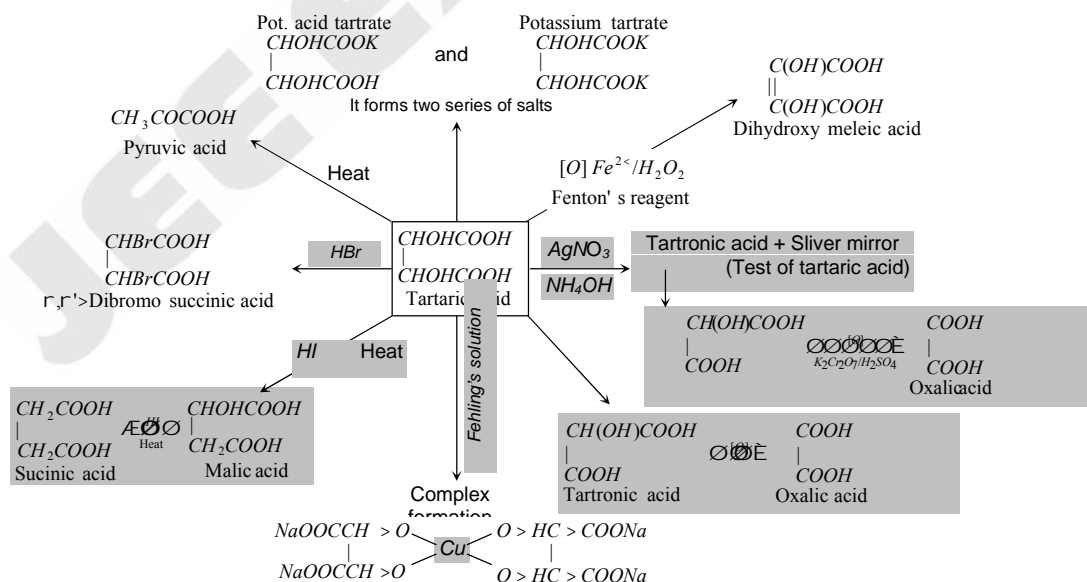


(iii) **From glyoxal cyanohydrin :**

- (2) **Physical Properties :** It is a colourless crystalline compound. It is soluble in water and alcohol but insoluble in ether. It contains two asymmetric carbon atoms and thus shows optical isomerism (four forms). Natural tartaric acid is the dextro variety. It contains two secondary alcoholic groups and two carboxylic groups.

Optical Isomerism in tartaric acid

- (i) d + Tartaric acid-Dextro-rotatory
 (ii) l –Tartaric acid-Leavorotatory
 (iii) Meso tartaric acid-optically inactive due to internal compensation.

(3) **Chemical Properties**

- (4) **Uses :** It is used in carbonated beverages and effervescent tablets, in making baking powder (cream of tartar) and mordant in dyeing (potassium hydrogen tartrate), in preparing Fehling's solution (sodium potassium tartrate–Rochelle salt), in medicine as emetic, dyeing and calico-printing (tartar emetic-potassium antimonyl tartrate) and silver mirroring.

(5) **Tests**

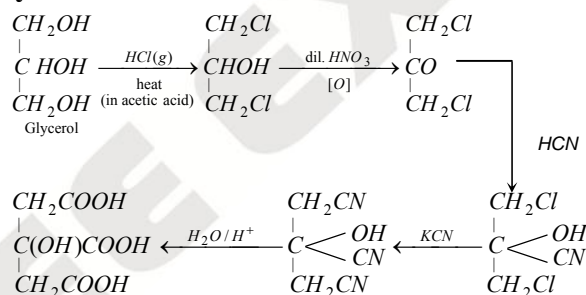
- (i) When heated strongly, tartaric acid chars readily giving a smell of burnt sugar to produce free carbon and pyruvic acid.
- (ii) **With AgNO_3** : A neutral solution of tartaric acid gives a white ppt. which is soluble in ammonia. A silver mirror is obtained on warming the ammonical silver nitrate solution (Tollen's reagent).
- (iii) **With Fenton's reagent** : (H_2O_2 containing a little of ferrous salt) and caustic soda, It gives a violet colour.
- (iv) **With Resorcinol and conc. H_2SO_4** : It gives blue colour.

Citric Acid Or 2-Hydroxypropane Or 1,2,3-Tri Carboxylic Acid Or S-Hydroxy Tricarballic Acid

It occurs in the juice of citrus fruits such as lemon, galgal, orange, lime, etc. Lemon juice contains 6-10% of citric acid.

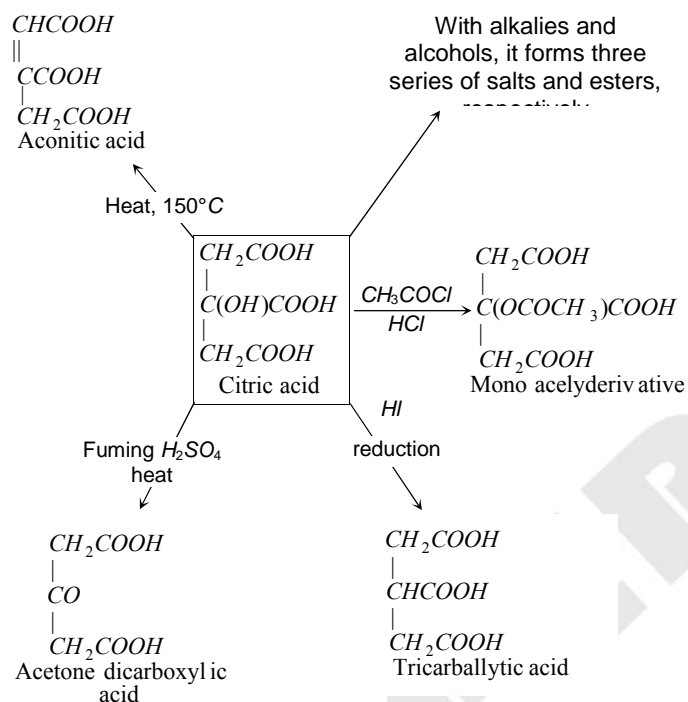
(1) **Methods of Preparation**

- (i) **By Fermentation** : Citric acid is obtained by carrying fermentation of dilute solution of molasses with micro-organism, *Aspergillus niger*, at $26-28^\circ\text{C}$ for 7 to 10 days. The resulting solution is neutralised with $\text{Ca}(\text{OH})_2$ to form insoluble precipitate, calcium citrate. It is decomposed by dilute H_2SO_4 . The CaSO_4 is filtered off and the solution is concentrated under vacuum to get crystals of citric acid.
- (ii) **By Lemon juice** : It is also obtained from lemon juice. The juice is boiled to coagulate proteins. From clear solution, citric acid is obtained as calcium salt with $\text{Ca}(\text{OH})_2$.

(iii) **By synthetic method**

- (2) **Physical Properties** : It is a colourless crystalline compound. It possesses one water molecule as water of crystallisation. It is soluble in water and alcohol but less soluble in ether. It is not optically active compound. It is nontoxic in nature. It behaves as an alcohol and tribasic acid.

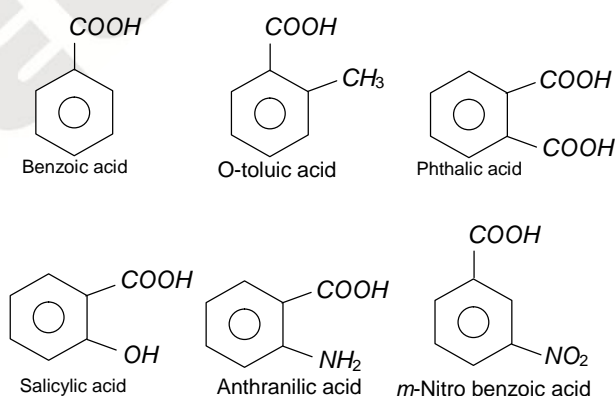
(3) Chemical properties



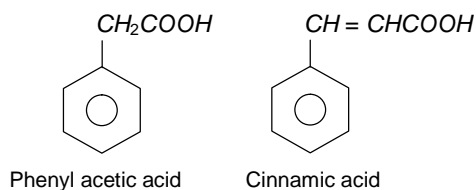
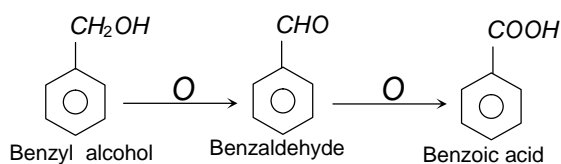
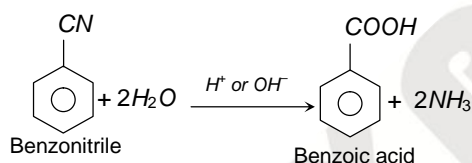
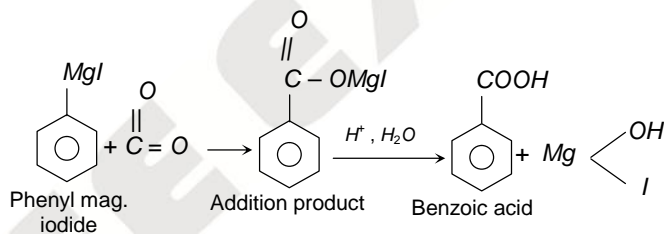
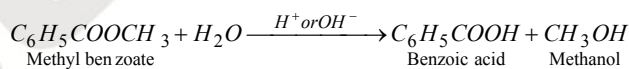
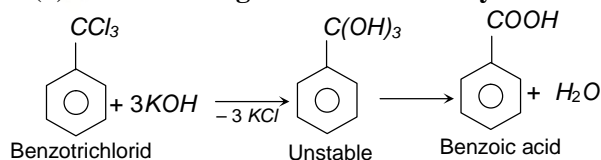
- (4) **Uses** : It finds use in making lemonades, as acidulant in food and soft drinks and makes the lemon sour, as mordant in dyeing and calico printing. Ferric ammonium citrate, magnesium citrate (as an antacid and laxative), sodium or potassium citrate are used in medicine. Ferric ammonium citrate finds use in making blue prints.

Aromatic Carboxylic Acids:

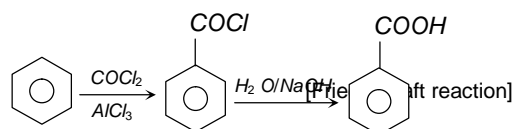
Aromatic acid contain one or more carboxyl group (COOH) attached directly to aromatic nucleus.

Examples

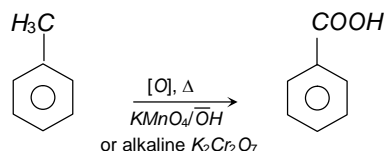
Aromatic acid containing- COOH group in the side chain, they are considered as aryl substituted aliphatic acid.

Examples**Benzoic Acid:****(1) Methods of Preparation****(i) From oxidation of Benzyl alcohol [Laboratory method]****(ii) From hydrolysis of nitriles or cyanides****(iii) From Grignard reagent****(iv) By hydrolysis of esters****(v) From trihalogen derivatives of hydrocarbons**

(vi) From benzene

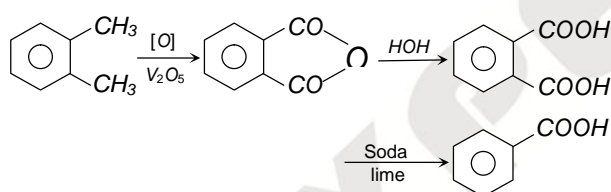


(vii) From Toluene

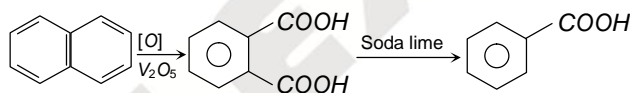


□ Chromic trioxide in glacial acetic acid or Co-Mn acetate can also be taken in place of alkaline KMnO_4 .

(viii) From o-xylene [Industrial method]



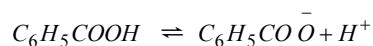
(ix) From naphthalene [Industrial method]



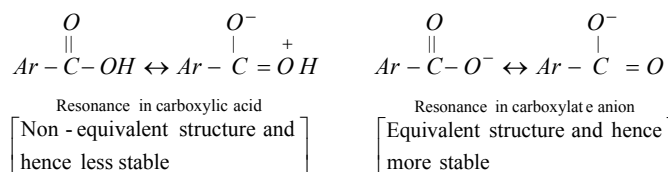
(2) Physical Properties

- (i) It is a white crystalline solid.
- (ii) It has m.p. 394 K.
- (iii) It is sparingly soluble in cold water but fairly soluble in hot water, alcohol and ether.
- (iv) It has a faint aromatic odour and readily sublimes and is volatile in steam.

(3) Acidity of Aromatic Carboxylic Acid : Aromatic acid dissociates to give a carboxylate anion and proton.



Since the carboxylate anion (ArCOO^-) is resonance stabilised to a greater extent than the carboxylic acid (ArCOOH).



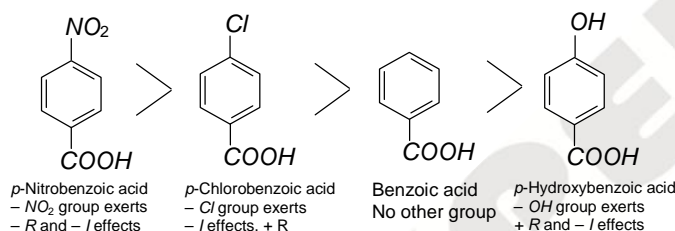
Effect of Substituents on Acidity : The overall influence of a substituent on acidity of substituted benzoic acids is due to two factors.

(i) **Inductive effect :** If the substituent exerts $-I$ effect, it increases the acidity of carboxylic acids, while if it exerts $+I$ effect it decreases the acidity. Inductive effect affects all positions, i.e., o-, m- and p-.

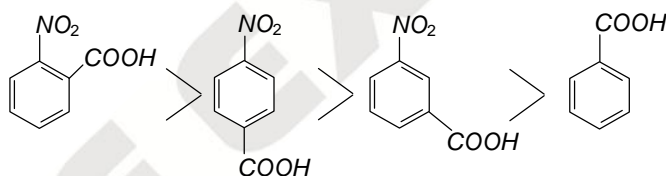
(ii) **Resonance effect :** Like inductive effect, if the resonance producing group exerts minus effect i.e., if it withdraws electrons, it increases the strength of the benzoic acid. Similarly, if the group causes +R effect it decreases the acidity of benzoic acid. However, remember that resonance effect affects only o- and p- positions. Thus if resonance producing group is present in the m-position it will not exert its effect.

In case resonance and inductive effects both operate in the molecule, resonance effect being stronger overpowers the inductive effect.

Thus on the above basis, the following order of acidity can be explained.

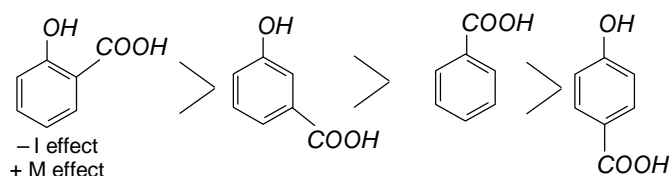


Similarly :



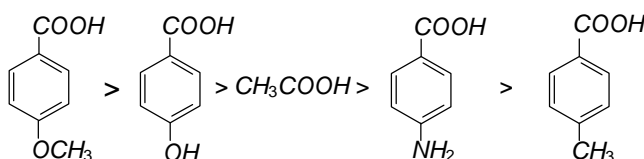
Acidity is only due to electron withdrawing inductive effect of the $-\text{NO}_2$ group (resonance does not affect the m-position) while in the p-isomer acidity is due to electron withdrawing inductive as well as resonance effect.

The acidity of the three isomers of hydroxybenzoic acids follows the following order.



Resonance effect cannot operate and hence only the acid-strengthening $-I$ effect takes part with the result m-hydroxybenzoic acid is stronger acid than benzoic acid. Like other substituted benzoic acid.

Acidic character among benzoic acids having different electron releasing group.



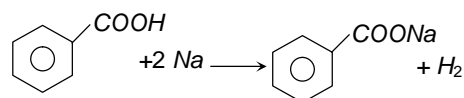
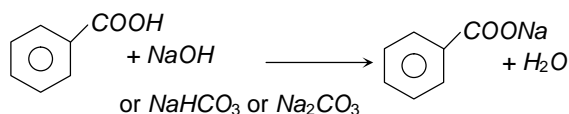
(4) **Chemical Properties :**

(i) Reactions of carboxylic group

(ii) Reactions of aromatic ring

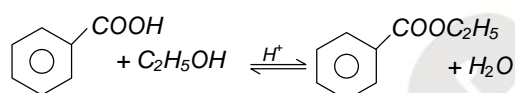
(i) **Reactions of Carboxylic Group**

(a) Reaction with metals

(b) Reaction with Alkalies Or NaHCO_3 Or Na_2CO_3 :

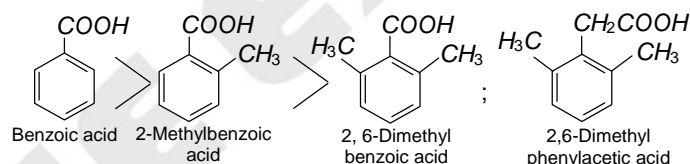
(c) Formation of Esters :

Aromatic acid (benzoic acid) having no group in its ortho positions can be readily esterified with alcohol in presence of a mineral acid.



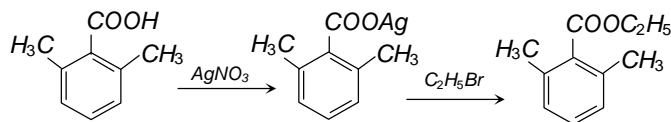
In presence of ortho substituent the rate of esterification is greatly decreased due to steric effect.

The esterification of the various benzoic acids :



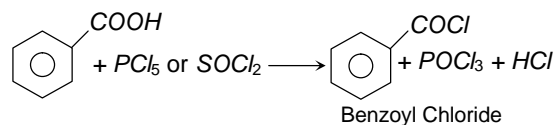
The substituted phenylacetic acid is easily esterified because $-\text{COOH}$ group is separated from benzene ring by $-\text{CH}_2-$ part.

The ortho-substituted benzoic acids can be easily esterified by treating the silver salt of the acid with alkyl halides, i.e.,

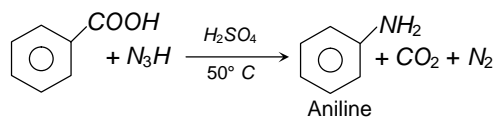


This is due to the fact that in such cases the attack of the alkyl group of the alkyl halides is on the oxygen atom of the $-\text{COOH}$ group but not on the sterically hindered carbon atom.

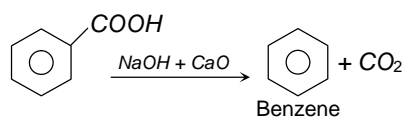
(d) Formation of acid chloride



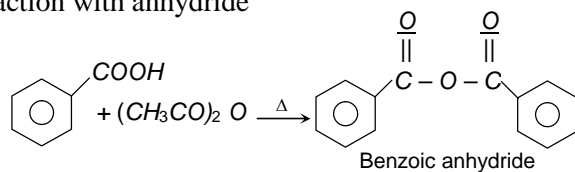
(e) Reaction with N_3H [Schmidt reaction]



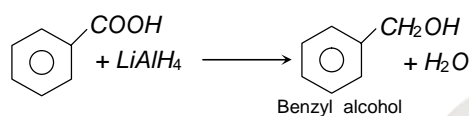
(f) Reaction with sodalime



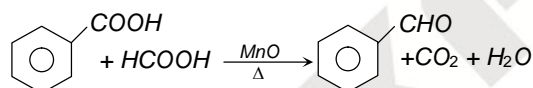
(g) Reaction with anhydride



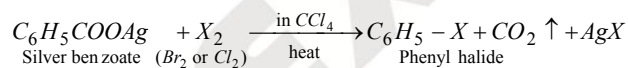
(h) Reduction



(i) Decarboxylation

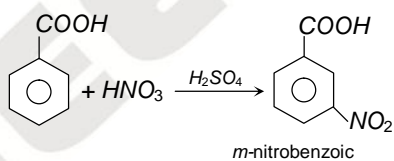


(j) Hunsdiecker reaction :

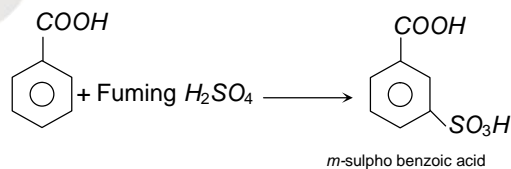


(ii) Reactions of Aromatic Ring

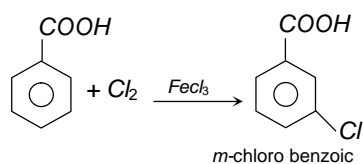
(a) Nitration



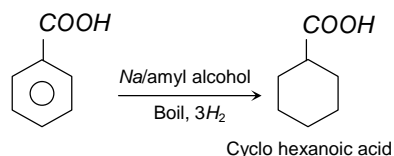
(b) Sulphonation



(c) Chlorination



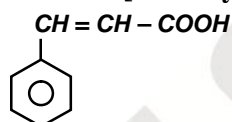
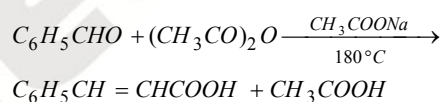
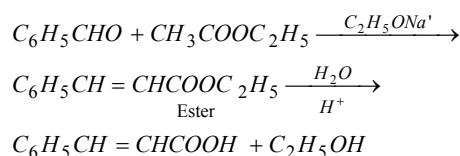
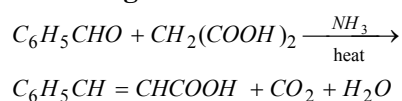
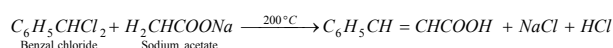
(d) Reduction

(5) **Uses :** Benzoic acid is used,

- (i) in medicine in the form of its salts especially as urinary antiseptic.
- (ii) As sodium benzoate for preservation of food such as fruit juices, tomato ketchup, pickles etc.
- (iii) In the preparation of aniline blue.
- (iv) In treatment of skin diseases like eczema.

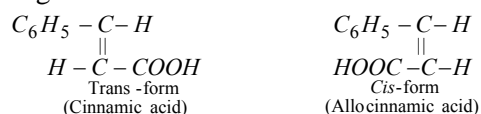
(6) **General Tests**

- (i) Benzoic acid dissolves in hot water but separates out in the form of white shining flakes on cooling.
- (ii) It evolves CO_2 with sodium bicarbonate, i.e., it gives effervescence with sodium carbonate.
- (iii) Neutral ferric chloride gives a buff coloured precipitate.
- (iv) When warmed with ethyl alcohol and a little conc. H_2SO_4 , a fragrant odour of ethyl benzoate is obtained.
- (v) When heated strongly with soda lime, benzene vapours are evolved which are inflammable.

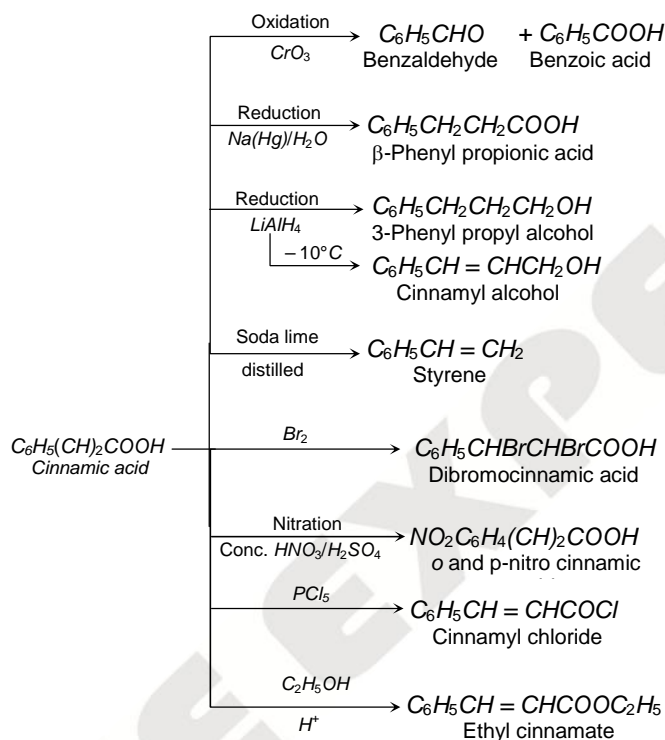
Cinnamic Acid [S-Phenyl acrylic acid](1) **Methods of Preparation**(i) **By Perkin's reaction**(ii) **By Claisen condensation**(iii) **By Knoevenagel reaction**(iv) **Industrial method**

(2) **Physical Properties**

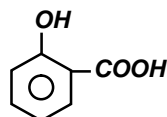
- (i) It is a white crystalline solid and its melting point 133°C .
- (ii) It is sparingly soluble in water.
- (iii) It exhibits geometrical isomerism.



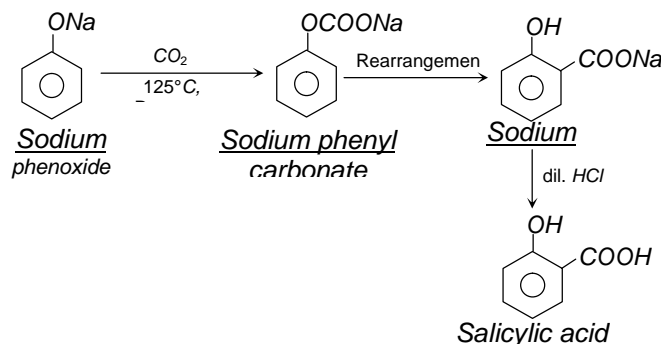
Cinnamic acid (stable form) occurs in nature both free and as esters in balsams and resins.

(3) **Chemical properties**

Salicylic acid [O-Hydroxy benzoic acid];

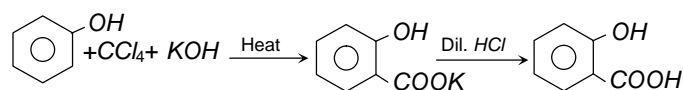


Salicylic acid is present in many essential oils in the form of esters. Oil of winter green is a methyl ester of salicylic acid.

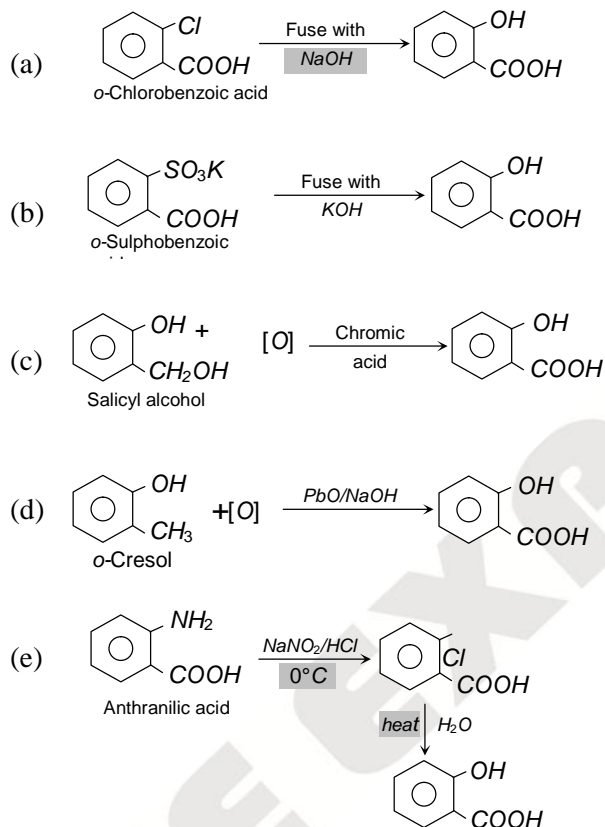
(1) **Methods of preparation**(i) **Kolbe Schmidt reaction**

It is a commercial method. The reaction yields both o- and p- isomers. Salicylic acid is more volatile and separated by steam distillation.

(ii) **Reimer-Tiemann reaction**

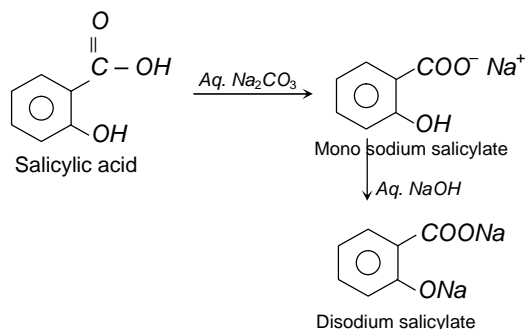
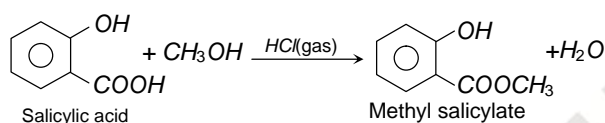


(iii) **From benzene derivatives**

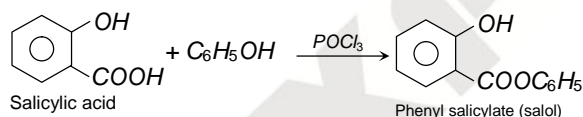


(2) **Physical properties**

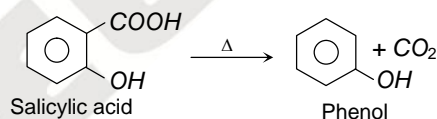
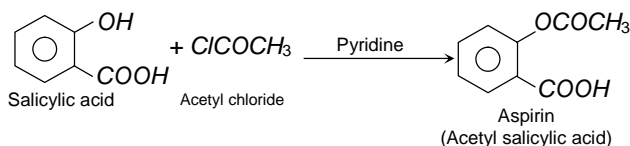
- (i) It is a colourless needle shaped crystalline compound.
- (ii) Its m.p. is 156°C.
- (iii) It is sparingly soluble in cold water but readily soluble in hot water, alcohol, ether and chloroform.
- (iv) It is steam volatile.
- (v) It is poisonous in nature. However, its derivative used in medicine internally and externally as antipyretic and antiseptic.

(3) **Chemical properties**(i) **Reaction with Na_2CO_3 , NaHCO_3 or NaOH** (ii) **Reaction with alcohols or phenols**

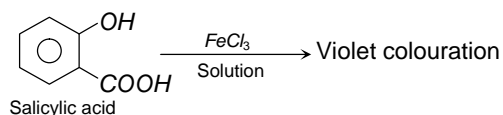
Methyl salicylate is an oily liquid (oil of winter green) with pleasant material. It is also used in medicine in the treatment of rheumatic pain and as a remedy for aches, sprains and bruises. It is used in perfumery and as a flavouring. It is used for making of iodox.

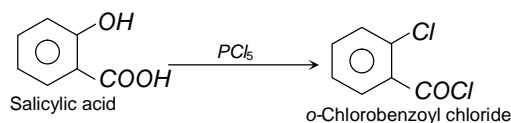


Salol is a white solid m.pt. 43°C . It is a good internal antiseptic. It is used in making of toothpastes. Salol absorbs ultraviolet light and its main use now is sun-screening agent and stabiliser of plastics.

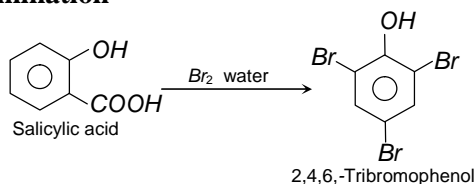
(iii) **Decarboxylation**(iv) **Acetylation**

□ Aspirin is a white solid, melting point 135°C . It is used as antipyretic and pain killer (analgesic action).

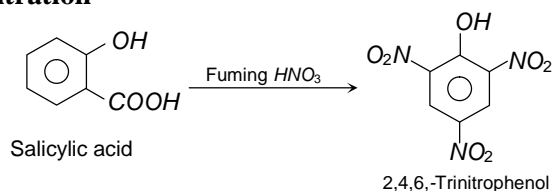
(v) **Reaction with ferric chloride solution**

(vi) Reaction with PCl_5 

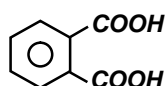
(vii) Bromination



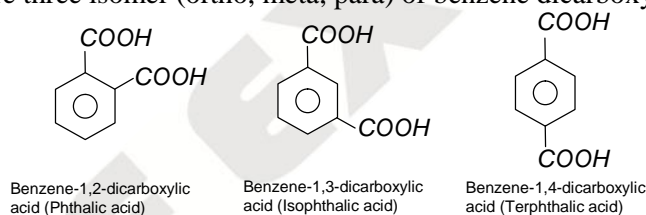
(viii) Nitration



Phthalic acid [1,2,-Benzene dicarboxylic acid]

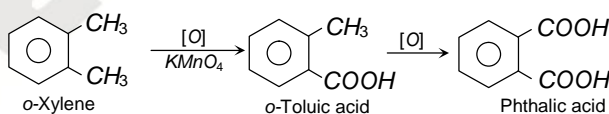


There are three isomer (ortho, meta, para) of benzene dicarboxylic acid.

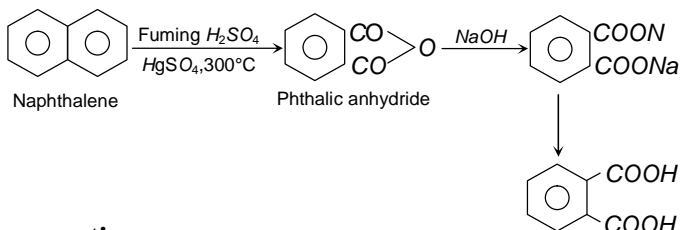


(1) Methods of preparation

(i) By the oxidation of o-xylene :



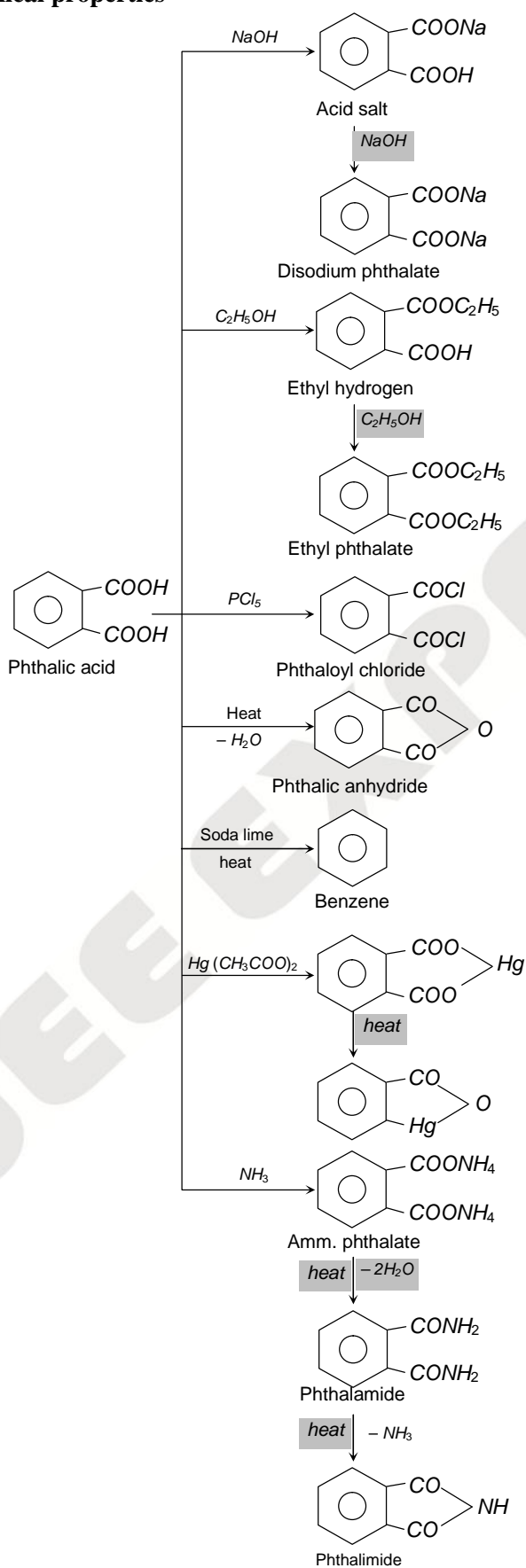
(ii) From naphthalene (Industrial method) : It is known as aerial oxidation.



(2) Physical properties

- (i) It is colourless crystalline compound.
- (ii) Its melting point is not sharp ($195\text{--}213^\circ\text{C}$).
- (iii) It is sparingly soluble in cold water but soluble in hot water, alcohol, ether, benzene etc.

(3) Chemical properties



- (4) **Uses :** It is used in the manufacture of plastics, dyes and other compounds such as phthalic anhydride, phthalimide, anthraquinone and fluorescein etc.

Acid derivatives

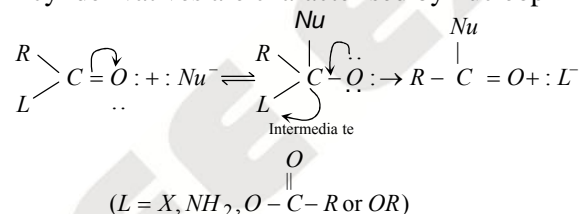
The compounds which are obtained by replacing the $-OH$ of the carboxylic group by other atoms or groups such as X^- , $-NH_2$, $-OR$ and $O-\overset{\overset{O}{\parallel}}{C}-R$ are known as acid derivatives.

- $R-\overset{\overset{O}{\parallel}}{C}-$ group is common to all the derivatives and is known as acyl group and these derivatives are termed as acyl compound.
- The important derivatives are given below :

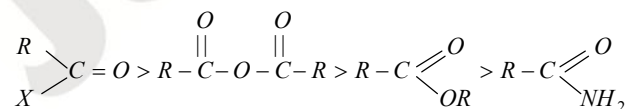
Group replacing $-OH$	Name	Structure
$(X = F, Cl, Br, I)$	Acyl halide	$R-\overset{\overset{O}{\parallel}}{C}-X$
$-NH_2$	Amide	$R-\overset{\overset{O}{\parallel}}{C}-NH_2$
$-OR'$	ester	$R-\overset{\overset{O}{\parallel}}{C}-OR'$ (R' may be R)
$-OOCR$	anhydride	$R-\overset{\overset{O}{\parallel}}{C}-O-\overset{\overset{O}{\parallel}}{C}-R$

Reactivity

Acyl derivatives are characterised by nucleophilic substitution reactions.



The relative reactivities of various acyl compounds have been found to be in the following order:



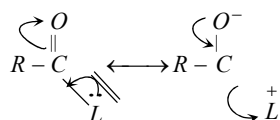
Out of acid halides, the acid chlorides are more important ones.

The overall order of reactivity can be accounted for in terms of the following three factors:

- (i) Basicity of the leaving group (ii) Resonance effects and (iii) Inductive effects.

(i) **Basicity of the leaving group :** Weaker bases are good leaving groups. Hence, the acyl derivatives with weaker bases as leaving groups are more reactive. Chloride ion is the weakest base while $-NH_2$ is the strongest base. Thus, acyl chlorides are most reactive and amides are least reactive.

(ii) **Resonance effect :** The leaving group in each case has an atom with lone pair of electrons adjacent to the carbonyl group. The compound exists, therefore, as a resonance hybrid.



This makes the molecule more stable. The greater the stabilization, the smaller is the reactivity of the acyl compound.

However, acyl chlorides are least affected by resonance. Due to lower stabilization, the acid chlorides are more reactive as the loss of $-Cl$ is easier. Greater stabilization is achieved by resonance in esters and amides and thus, they are less reactive.

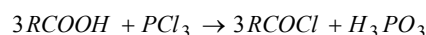
(iii) **Inductive effect** : Higher the $-I$ effect, more reactive is the acyl compound. Inductive effect of oxygen in ester is greater than nitrogen in amide, hence ester is more reactive than an amide.



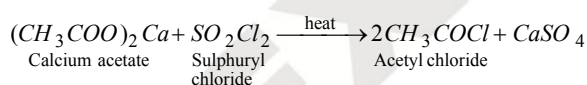
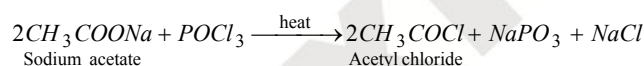
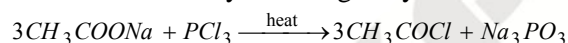
where R may be alkyl or aryl group.

(1) Methods of Preparation

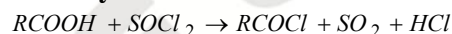
(i) **From carboxylic acid** : $RCOOH + PCl_5 \rightarrow RCOCl + POCl_3 + HCl$



(ii) **Industrial method** : By distilling anhydrous sodium acetate



(iii) **With thionyl chloride** :



This is the best method because SO_2 and HCl are gases and easily escape leaving behind acyl chloride.

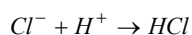
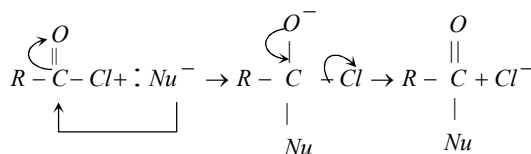
(2) **Physical properties** : The lower acyl chloride are mobile, colourless liquid while the higher members are coloured solids.

Acyl chloride have very pungent, irritating order and are strong lachrymators (tears gases)

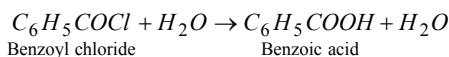
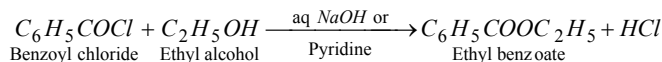
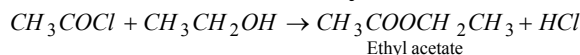
They fume in air due to the formation of hydrochloric acid by hydrolysis.

They are readily soluble in most of the organic solvent. Acyl chloride don't form intermolecular hydrogen bonding. Therefore, their boiling points are lower than those of their parent acids.

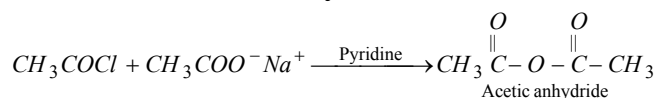
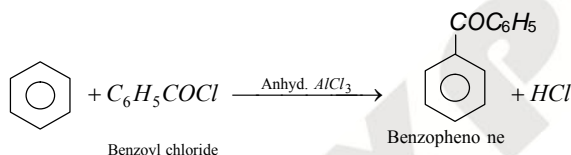
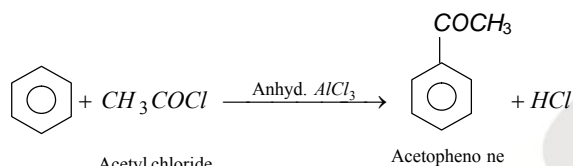
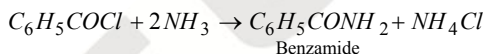
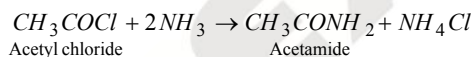
(3) Chemical properties



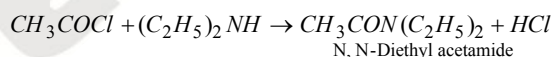
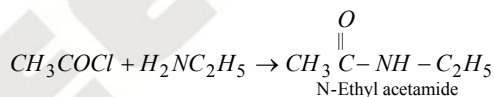
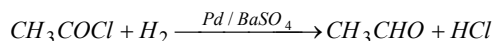
(i) **Hydrolysis** : $CH_3COCl + HOH \rightarrow CH_3COOH + HCl$
 Acetyl chloride Acetic acid

(ii) **Reaction with alcohols (alcoholysis)**

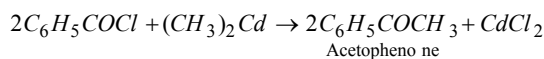
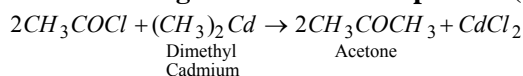
This reaction is called **Schotten Baumann reaction**.

(iii) **Reaction with salts of carboxylic acid**(iv) **Reaction with benzene (acylation)** : This reaction is called friedel craft reaction.(v) **Reaction with ammonia or amines :**

However, acyl chlorides react with amines to form substituted amides.

(vi) **Reduction** : $CH_3COCl \xrightarrow[\text{NaBH}_4]{\text{LiAlH}_4 \text{ or}} CH_3CH_2OH$
Ethanol (Primary alcohol)

This reaction is called **Rosenmund reaction**.

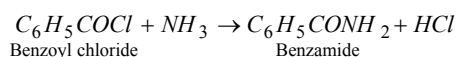
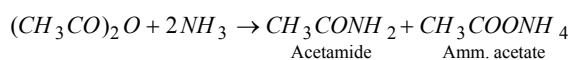
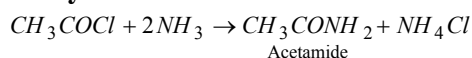
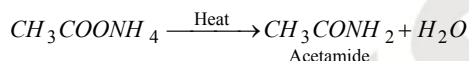
(vii) **Reaction with organocadmium compounds (formation of ketones)**

(4) **Uses**

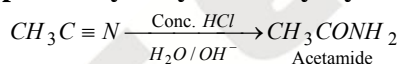
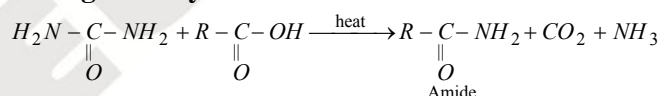
- (i) As an acetylating agent.
- (ii) In the estimation and determination of number of hydroxyl and amino groups.
- (iii) In the preparation of acetaldehyde, acetic anhydride, acetamide, acetanilide, aspirin, acetophenone etc.



where, $R = -CH_3, -CH_2CH_3, -C_6H_5$

(1) **Methods of preparation**(i) **Ammonolysis of acid derivatives**(ii) **From ammonium salts of carboxylic acids (Laboratory Method)**

□ Ammonium acetate is always heated in presence of glacial acetic acid to avoid the side product (CH_3COOH).

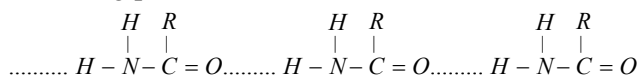
(iii) **By partial hydrolysis of alkyl cyanide :**(iv) **By heating carboxylic acid and urea**(2) **Physical properties**

(i) **Physical state :** Formamide is a liquid while all other amides are solids.

(ii) **Boiling points :** Amides have high boiling points than the corresponding acids.

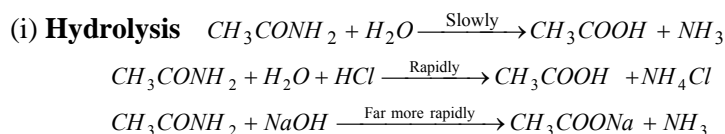
Acetamide	Boiling points 494 K
Acetic Acid	Boiling points 391 K
Benzamide	Boiling points 563 K
Benzoic acid	Boiling points 522 K

The higher boiling points of amides is because of intermolecular hydrogen bonding

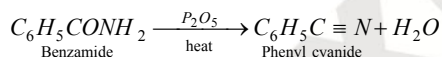
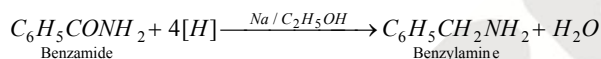
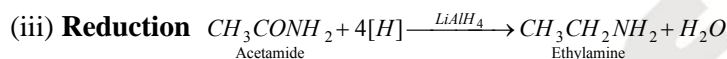
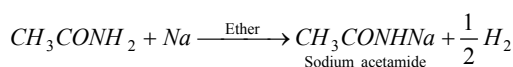
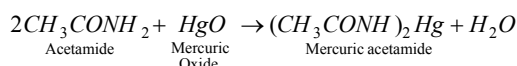
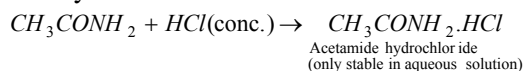
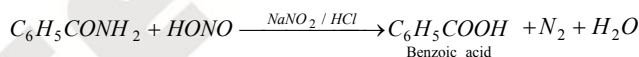
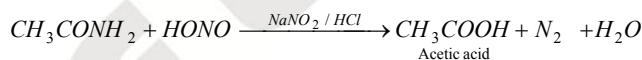


(iii) **Solubility :** The lower members of amide family are soluble in water due to the formation of hydrogen bonds with water.

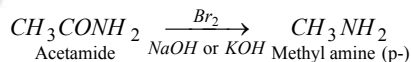
(3) Chemical properties

(ii) **Amphoteric nature (Salt formation)**

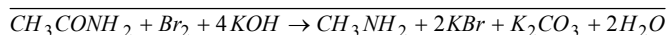
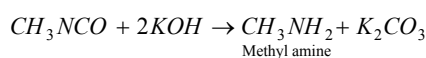
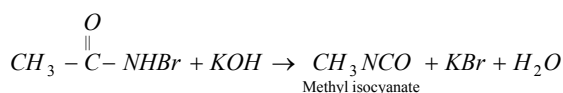
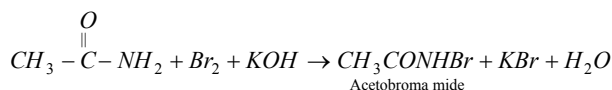
It shows feebly acidic as well as basic nature.

(v) **Reaction with nitrous acid**

(vi) **Hofmann bromamide reaction or Hofmann degradation** : This is an important reaction for reducing a carbon atom from a compound, i.e., $-CONH_2$ is changed to $-NH_2$ group.

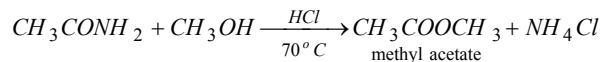


This reaction occurs in three steps:

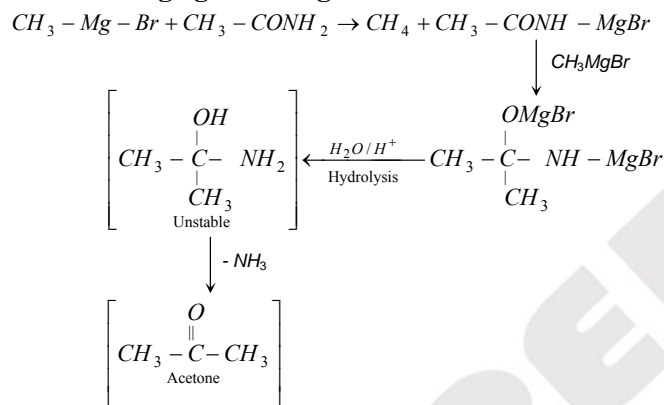


- ❑ In this reaction a number of intermediates have been isolated; N-bromamides, $RCONHBr$; salts of these bromamides $[RCONBr^-] K^+$; Isocyanates, $RNCO$.
- ❑ Nitrene rearranges to form isocyanate.

(vii) **Action with alcohol :**



(viii) **Reaction with grignard reagent**



(4) **Uses**

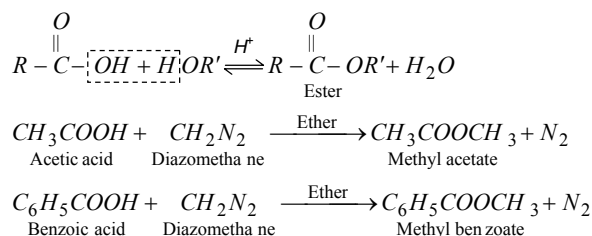
- (i) In organic synthesis. The compounds like methyl cyanide, Methylamine and ethylamine can be prepared.
 - (ii) In leather tanning and paper industry.
 - (iii) As a wetting agent and as soldering flux.
- Amides such as dimethyl formamide (DMF), dimethyl acetamide (DMA) are used as solvents for organic and inorganic compounds.

Esters, $R-\overset{\overset{O}{||}}{C}-OR$

These are the most important class of acid derivatives and are widely distributed in nature in plants, fruits and flowers.

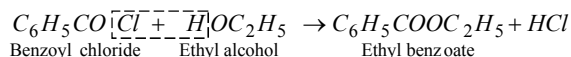
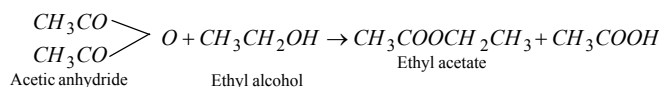
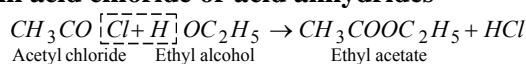
(1) **Methods of preparation**

(i) **From carboxylic acid [Esterification] : Laboratory method.**

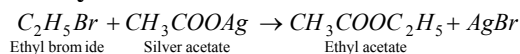


- ❑ With diazomethane is the best method.

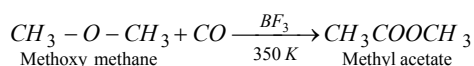
(ii) From acid chloride or acid anhydrides



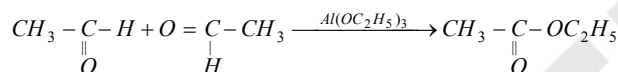
(iii) From alkyl halide :



(iv) From ether :



(v) From Tischenko reaction :



(2) Physical properties

(i) **Physical state and smell :** Esters are colourless liquids (or solids) with characteristic fruity smell. Flavours of some of the esters are listed below :

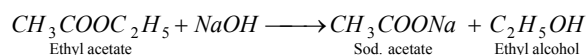
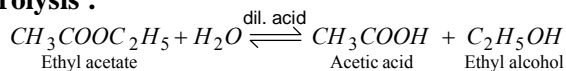
Ester	Flavour	Ester	Flavour
Amyl acetate	Banana	Isobutyl formate	Raspberry
Benzyl acetate	Jasmine	Ethyl butyrate	Pineapple
Amyl butyrate	Apricot	Octyl acetate	Orange

(ii) **Solubility :** They are sparingly soluble in water but readily soluble in organic solvents such as alcohol, ether etc.

(iii) **Boiling points :** Their boiling points are lower than the corresponding acids because of the absence of hydrogen bonding. i.e., ethyl acetate = 77.5°C.

(3) Chemical properties:

(i) Hydrolysis :

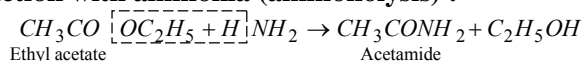


Hydrolysis of ester by alkalies (NaOH) is known as saponification and leads to the formation of soaps

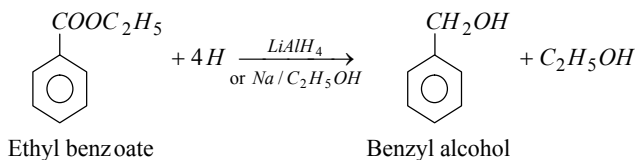
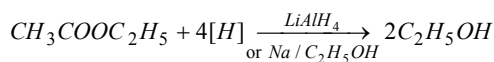
☐ This reaction (saponification) is irreversible because a resonance stabilized carboxylate (acetate) ion is formed.

☐ The acid hydrolysis of esters is reversible.

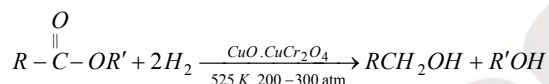
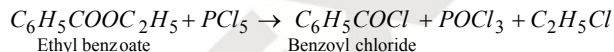
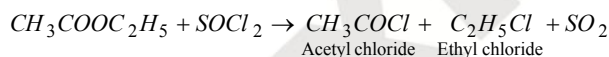
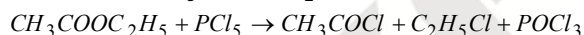
(ii) Reaction with ammonia (ammonolysis) :



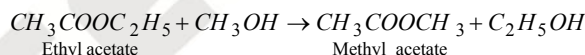
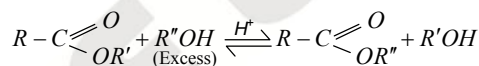
(iii) Reduction



- ❑ Reduction in presence of $\text{Na} / \text{C}_2\text{H}_5\text{OH}$ is known as Bouveault Blanc reduction.
- ❑ The catalytic hydrogenation of ester is not easy and requires high temperature and pressure. The catalyst most commonly used is a mixture of oxides known as copper chromate ($\text{CuO} \cdot \text{CuCr}_2\text{O}_4$).

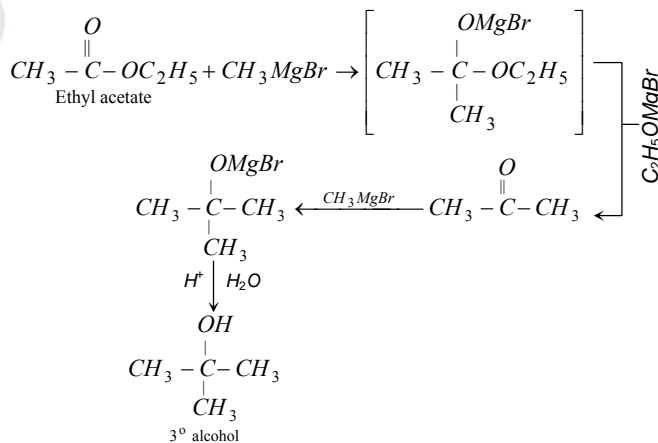
(iv) Reaction with PCl_5 or SOCl_2 

(v) Reaction with alcohols : On refluxing ester undergoes exchange of alcohols residues.

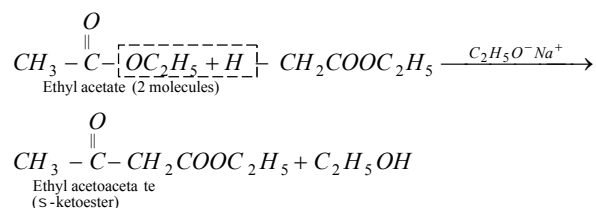


- ❑ This reaction is known as alcoholysis or trans esterification.

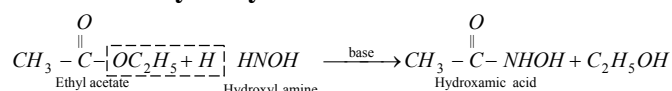
(vi) Reaction with Grignard reagents



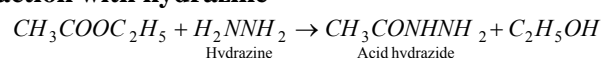
(vii) Claisen condensation



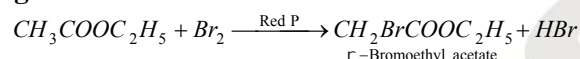
(viii) Reaction with hydroxyl amine



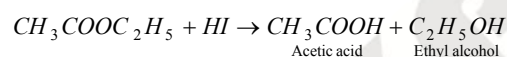
(ix) Reaction with hydrazine



(x) Halogenation



(xi) Reaction with HI

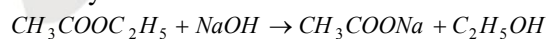


(4) Uses

- (i) As a solvent for oils, fats, cellulose, resins etc.
- (ii) In making artificial flavours and essences.
- (iii) In the preparation of ethyl acetoacetate.

(5) General Tests

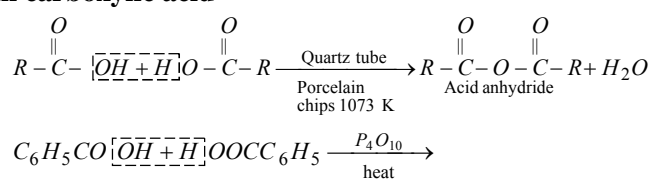
- (i) It has sweet smell
- (ii) It is neutral towards litmus
- (iii) A pink colour is developed when one or two drops of phenolphthalein are added to dilute sodium hydroxide solution. The pink colour is discharged when shaken or warmed with ethyl acetate.
- (iv) Ethyl acetate on hydrolysis with caustic soda solution forms two compounds, sodium acetate and ethyl alcohol.

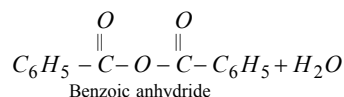
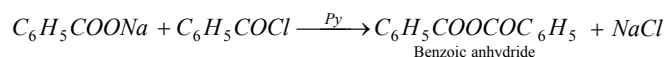
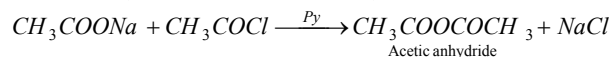
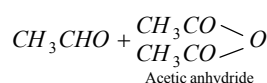
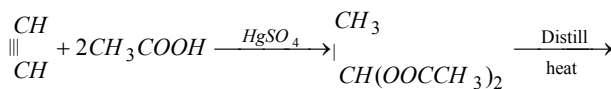
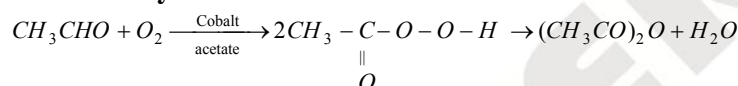


Acid Anhydride $\begin{array}{c} \text{CH}_3\text{CO} \\ \text{CH}_3\text{CO} \end{array} > \text{O} \text{ or } (\text{CH}_3\text{CO})_2\text{O}$

(1) Method of preparation

(i) From carboxylic acid

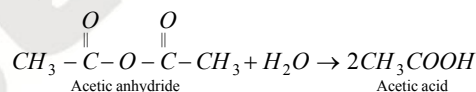
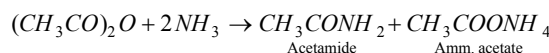
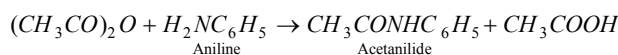
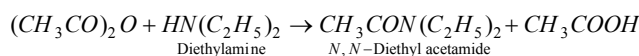
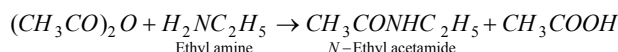
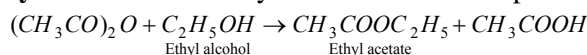


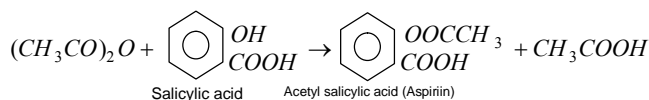
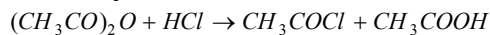
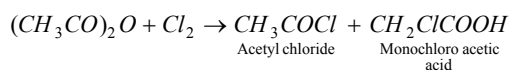
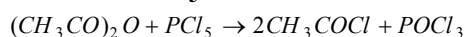
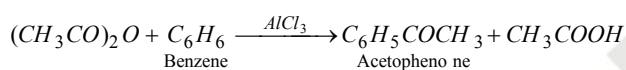
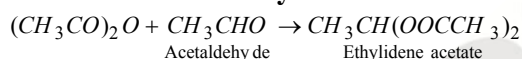
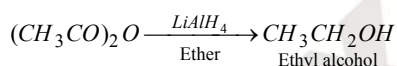
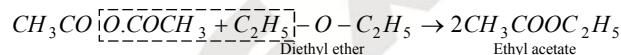
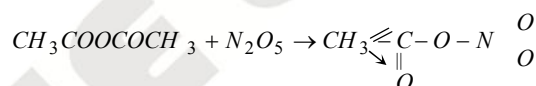
(ii) **From carboxylic acid salt and acyl chloride [Laboratory method]**(iii) **From acetylene**(iv) **From acetaldehyde :**(2) **Physical properties**

(i) **Physical state :** Lower aliphatic anhydrides are colourless liquids with sharp irritating smell. The higher members of the family as well as the aromatic acid anhydrides are solids in nature.

(ii) **Solubility :** They are generally insoluble in water but are soluble in the organic solvents such as ether, acetone, alcohol, etc.

(iii) **Boiling points :** The boiling points of acid anhydrides are higher than those of carboxylic acids because of the greater molecular size.

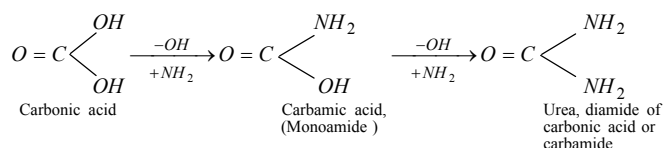
(3) **Chemical Properties**(i) **Hydrolysis :**(ii) **Action with ammonia**(iii) **Acetylation :** Acetic anhydride react with compound having active hydrogen.

**(iv) Action of dry HCl****(v) Reaction with chlorine****(vi) Reaction with PCl_5** **(vii) Friedel craft's reaction****(viii) Reaction with acetaldehyde****(ix) Reduction****(x) Action with ether :****(xi) Action with N_2O_5** **(4) Uses : Acetic anhydride is used**

- (i) as an acetylating agent.
- (ii) For the detection and estimation of hydroxyl and amino group.
- (iii) in the manufacture of cellulose acetate, aspirin, phenacetin, acetamide, acetophenone, etc.

Urea or Carbamide $O=C \begin{matrix} \nearrow NH_2 \\ \searrow NH_2 \end{matrix}$

Urea may be considered as diamide of an unstable and dibasic carbonic acid from which both the hydroxyl groups have been replaced by $-NH_2$ groups.

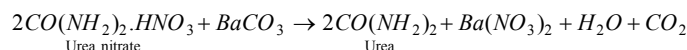


- ❑ First time isolated from urine in 1773 by Roulle and hence the name urea was given.
- ❑ It was the first organic compound synthesised in the laboratory from inorganic material (by heating a mixture of ammonium sulphate and potassium cyanate) by Wohler in 1828.

- ❑ This preparation gave a death blow to Vital force theory.
- ❑ It is the final decomposition product of protein's metabolism in man and mammals and is excreted along with urine.
- ❑ Adults excrete about 30 grams of urea per day in the urine.

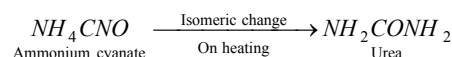
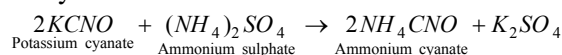
(1) **Method of preparation :**

(i) **From urine :** Urine is treated with conc. nitric acid where crystals of urea nitrate $CO(NH_2)_2 \cdot HNO_3$ are obtained.



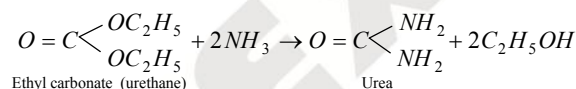
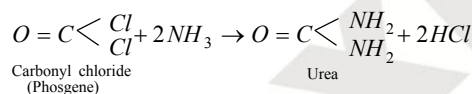
(ii) **Laboratory preparation**

(a) **Wohler synthesis**



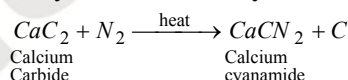
❑ The solid residue is extracted with alcohol and the extract evaporated when the crystals of urea are obtained. It can be recrystallised from water.

(b) **From phosgene or alkyl carbonate**



(iii) **Industrial method**

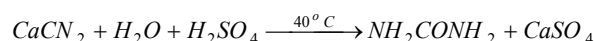
(a) **By partial hydrolysis of calcium cyanide**



The cyanamide is treated with dilute sulphuric acid at $40^\circ C$ where partial hydrolysis occurs with the formation of urea.



or



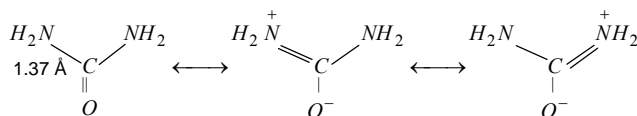
(b) **From carbon dioxide and ammonia**



(2) **Physical properties :**

Urea is a colourless, odourless crystalline solid. It melts at $132^\circ C$. It is very soluble in water, less soluble in alcohol but insoluble in ether, chloroform and benzene.

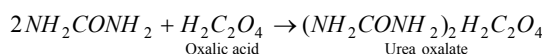
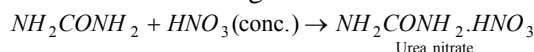
Crystal structure: In solid urea, both nitrogen atoms are identical.



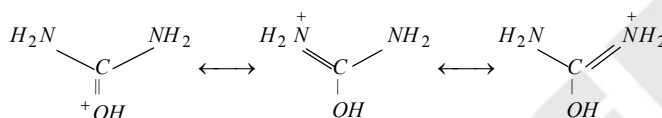
This indicates that C – N bond in urea has some double bond character.

(3) Chemical Properties

(i) **Basic nature (Salt formation):** It behaves as a weak monoacid base ($K_b = 1.5 \times 10^{-14}$). It forms salt with strong acid.

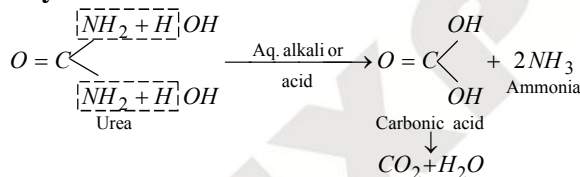


Urea is a stronger base than ordinary amide. It is due to the resonance stabilization of cation, the negatively charged oxygen atom is capable of coordination with one proton.

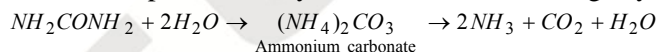


□ An aqueous solution of urea is neutral.

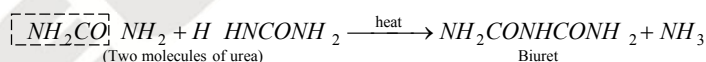
(ii) Hydrolysis



An enzyme, urease, present in soyabean and soil also brings hydrolysis.

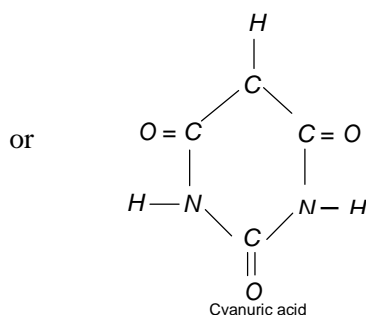
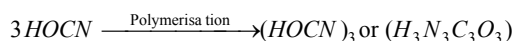
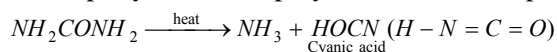


(iii) Action of heat

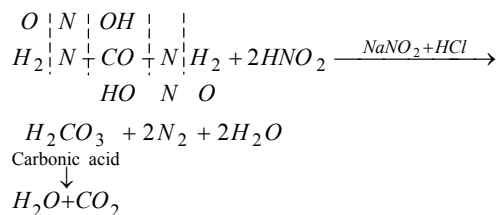


Urea is identified by the test known as biuret test. The biuret residue is dissolved in water and made alkaline with a few drops of NaOH. When a drop of copper sulphate solution is added to the alkaline solution of biuret, a violet colouration is produced.

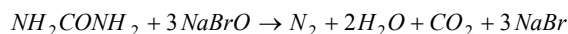
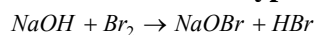
when heated rapidly at 170°C , polymerisation takes place:



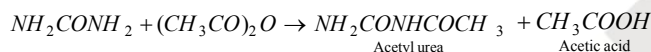
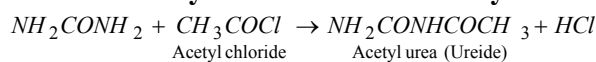
(iv) Reaction with nitrous acid



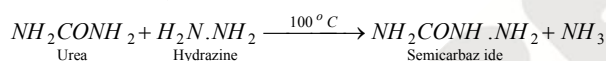
(v) Reaction with alkaline hypohalides



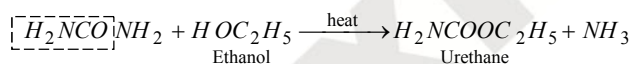
(vi) Reaction with acetyl chloride or acetic anhydrides



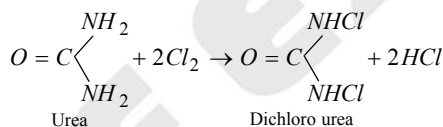
(vii) Reaction with hydrazine



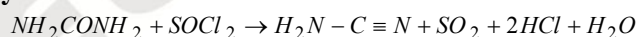
(viii) Reaction with ethanol



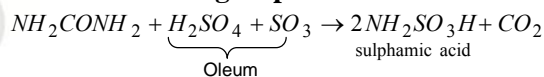
(ix) Reaction with chlorine water



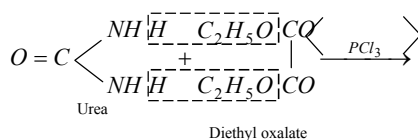
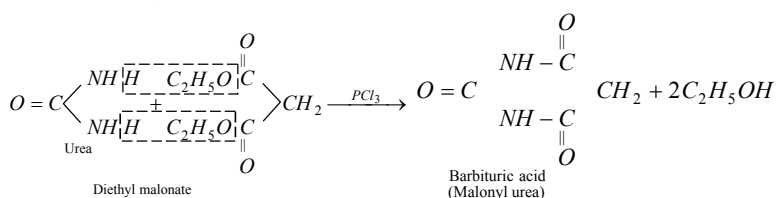
(x) Dehydration

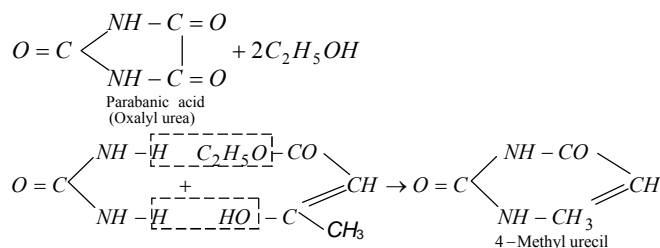
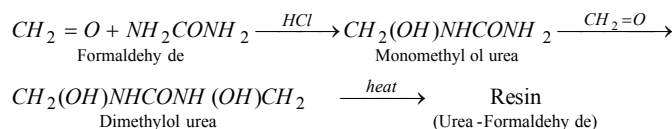


(xi) Reaction with fuming sulphuric acid



(xii) Formation of cyclic ureides



(xiii) **Reaction with formaldehyde**(4) **Uses**

- Mainly as a nitrogen fertilizer. It has 46.4% nitrogen.
- In the manufacture of formaldehyde-urea plastic and semicarbazide.
- As animal feed.
- For making barbiturates and other drugs.
- As a stabilizer for nitrocellulose explosives.

(5) **General Tests**

- When heated with sodium hydroxide, ammonia is evolved.
- When heated gently, it forms biuret which gives violet colouration with sodium hydroxide and a drop of copper sulphate solution.
- Its aqueous solution with concentrated nitric acid gives a white precipitate.
- On adding sodium nitrite solution and dil. HCl (i.e., HNO_2) to urea solution, nitrogen gas is evolved and gives effervescence due to carbon dioxide.

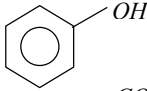
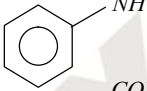
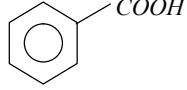
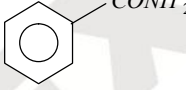
Tips & Tricks

➤	Oxidation of 1° alcohols and aldehyde cannot be carried out with alkaline $\text{K}_2\text{Cr}_2\text{O}_7$ since under these condition K_2CrO_4 is formed which does not act as an oxidising agent.
➤	During oxidation of alkyl benzenes with alkaline KMnO_4 or acidified $\text{K}_2\text{Cr}_2\text{O}_7$, the aromatic nucleus remain intact but each side chain oxidised to $-\text{COOH}$ group irrespective of its length. The ease of oxidation of alkyl benzenes follows the order. Toluene > Ethyl benzene > Isopropyl benzene. Tert butyl benzene however does not undergo oxidation to give benzoic acid since it does not have any benzylic H-atom.
➤	Carboxylic acids are stronger acids than phenols since carboxylate ion is better stabilized by resonance than phenoxide ion.
➤	The melting points of carboxylic acids show oscillation or alternation effect, i.e. melting point of an acid containing even number of carbon atom is higher than the next lower or higher homologue containing odd number of carbon atom, due to greater symmetry and close packing of molecules in the crystal lattice.

➤	Carboxylic acid do not give the characteristic reaction of the carbonyl group. The reason being that due to resonance, the double bond character of the C = O bond in carboxylic acid is greatly reduced as compared to that in aldehyde and ketone.
➤	The boiling point of acid derivatives follow the order. $RCONH_2 > (RCO)_2O > RCOOH > RCOOR' > RCOCl$.
➤	The boiling point of acid chloride and ester are lower than those of their parent acid due to absence of H-bonding in their molecule.
➤	The boiling points of acid anhydrides are higher than those of the acids from which they are derived because of stronger Vander Waal's forces of attraction owing to the larger size of their molecules.
➤	The melting points and boiling points of acid amide are much higher than those of the acids from which they are derived due to strong intermolecular H-bonding even though their molecular masses are almost identical.
➤	Aromatic acid chlorides are less reactive than aliphatic acid chlorides primarily due to greater electron donating effect of the benzene ring over alkyl group which tends to reduce the electron deficiency of aromatic acyl carbon.
➤	Phthalimide and succinimide on treatment with Br_2 -KOH undergo Hofmann bromamide reaction to form anthranilic acid and β -aminopropionic acid respectively.
➤	Urea acts as a monoacidic base.
➤	Malonic acid on heating with P_2O_5 gives carbon suboxide (C_3O_2).
➤	Tamarind contain tartaric acid which does not exist in nature.
➤	Baking powder is a mixture of sodium bicarbonate and cream of tartar i.e. acid potassium hydrogen sulphate.
➤	Smell of ammonia in public urinals is due to hydrolysis of urea present in urine by the enzyme urease present in atmosphere.
➤	Tartar emetic (i.e. potassium antimony D(+) tartrate is used to cause nausea and vomiting during treatment of poisoning.
➤	Magnesium citrate is used as an antacid.
➤	Succinic acid was prepared by the distillation of amber.
➤	Malic acid is found in apples, grapes etc.

EXERCISE - I

General Introduction of Carboxylic Acids and Their Derivatives

- Identify the wrong statement from the following
 - Salicylic acid's a monobasic acid
 - Methyl salicylate is an ester
 - Salicylic acid gives violet colour with neutral ferric chloride as well as brisk effervescence with sodium bicarbonate
 - Methyl salicylate does not occur in natural oils
- Which of the following is optically active
 - Ethylene glycol
 - Oxalic acid
 - Glycerol
 - Tartaric acid
- Palmitic acid is
 - $C_{16}H_{31}COOH$
 - $C_{17}H_{35}COOH$
 - $C_{15}H_{31}COOH$
 - $C_{17}H_{31}COOH$
- Which one among the following represents an amide
 - 
 - 
 - 
 - 
- The name of the compound having the structure $ClCH_2CH_2COOH$ is
 - 3-chloropropanoic acid
 - 2-chloropropanoic acid
 - 2-chloroethanoic acid
 - Chlorosuccinic acid
- Fats and oils are mixture of
 - Glycerides and saturated fatty acids
 - Glycerides and unsaturated fatty acids
 - Glycerides of saturated and unsaturated fatty acids
 - Only saturated and unsaturated fatty acids
- Which one is not a glyceride
 - Fat
 - Oil
 - Phospholipid
 - Soaps
- $(RCO)_2NH$ is
 - Primary amine
 - Secondary amine
 - Secondary amide
 - Tertiary amide
- Which of the following is the formula of tartaremetic
 - $\begin{array}{c} CH(OH)COOH \\ | \\ CH(OH)COOK \end{array}$
 - $\begin{array}{c} CH(OH)COONa \\ | \\ CH(OH)COO(SbO) \end{array}$
 - $\begin{array}{c} CH(OH)COOK \\ | \\ CH(OH)COOK \end{array}$
 - $\begin{array}{c} CH(OH)COOK \\ | \\ CH(OH)COONa \end{array}$

10. Which compound is known as oil of winter green
(a) Phenyl benzoate (b) Phenyl salicylate
(c) Phenyl acetate (d) Methyl salicylate
11. Which of the following structure of carboxylic acid accounts for the acidic nature
(a) $R - C \begin{smallmatrix} \nearrow O \\ \searrow OH \end{smallmatrix}$ (b) $R - C^+ \begin{smallmatrix} \nearrow OH \\ \searrow OH \end{smallmatrix}$
(c) $R - C \begin{smallmatrix} \nearrow O \\ \searrow H \end{smallmatrix}$ (d) None of these
12. Acetoacetic ester behaves as
(a) An unsaturated hydroxy compound (b) A keto compound
(c) Both of these ways (d) None of these
13. The general formula $(RCO)_2O$ represents
(a) An ester (b) A ketone (c) An ether (d) An acid anhydride
14. A tribasic acid is
(a) Oxalic acid (b) Tartaric acid (c) Lactic acid (d) Citric acid
15. Amphiphilic molecules are normally associated with
(a) Isoprene based polymers
(b) Soaps and detergents
(c) Nitrogen based fertilizers e.g. urea
(d) Pain relieving medicines such as aspirin
16. Wax are long chain compounds belonging to the class
(a) Acids (b) Alcohols (c) Esters (d) Ethers
17. Glycine may be classed as all of the following except
(a) A base (b) An acid
(c) A zwitter ion (d) Optically active acid
18. Which of the following is not a fatty acid
(a) Stearic acid (b) Palmitic acid
(c) Oleic acid (d) Phenyl acetic acid
19. Vinegar obtained from canesugar contains
(a) Citric acid (b) Lactic acid (c) Acetic acid (d) Palmitic acid
20. The general formula for monocarboxylic acids is
(a) C_nH_nCOOH (b) $C_nH_{2n+1}COOH$ (c) $C_nH_{2n-1}COOH$ (d) $C_nH_{2n}O_2$
21. Number of oxygen atoms in an acetamide molecule is
(a) 1 (b) 2 (c) 3 (d) 4

22. Urea is
(a) Monoacidic base (b) Diacidic base (c) Neutral (d) Amphoteric
23. Fats and oils are
(a) Acids (b) Alcohols (c) Esters (d) Hydrocarbons
24. The general formulas $C_nH_{2n}O_2$ could be for open chain
(a) Diketones (b) Carboxylic acids (c) Diols (d) Dialdehydes
25. $\begin{array}{c} O \\ || \\ H-C-Cl \end{array}$ is called
(a) Acetyl chloride (b) Formyl chloride
(c) Chlorethane (d) Oxochloromethane
26. Urea
(a) Is an amide of carbonic acid
(b) It is diamide of carbonic acid
(c) Gives carbonic acid on hydrolysis
(d) Resembles carbonic acid
27. Which of the following acids is isomeric with phthalic acid
(a) Succinic acid (b) Salicylic acid
(c) 1, 4-benzene dicarboxylic acid (d) Methyl benzoic
28. The ester among the following is
(a) Calcium lactate (b) Ammonium acetate
(c) Sodium acetate (d) None of these
29. Sodium or potassium salts of higher fatty acids are called
(a) Soaps (b) Terpenes (c) Sugars (d) Alkaloids
30. Formamide is
(a) $HCONH_2$ (b) CH_3CONH_2 (c) $HCOONH_4$ (d) $(HCHO + NH_3)$
31. Oleic, stearic and palmitic acids are
(a) Nucleic acids (b) Amino acids (c) Fatty acids (d) None of these
32. Which one is called ethanoic acid
(a) $HCOOH$ (b) CH_3COOH
(c) CH_3CH_2COOH (d) $CH_3CH_2CH_2COOH$
33. Vinegar is
(a) $HCHO$ (b) $HCOOH$ (c) CH_3CHO (d) CH_3COOH
34. Which of these do not contain $-COOH$ group
(a) Aspirin (b) Benzoic acid (c) Picric acid (d) Salicylic acid

35. Vinegar obtained from sugarcane has
 (a) CH_3COOH (b) $HCOOH$ (c) C_6H_5COOH (d) CH_3CH_2COOH
36. Carbolic acid is
 (a) C_6H_5CHO (b) C_6H_6 (c) C_6H_5COOH (d) C_6H_5OH
37. The most acidic of the following is
 (a) $ClCH_2COOH$ (b) C_6H_5COOH (c) CD_3COOH (d) CH_3CH_2COOH
38. Which is most reactive of the following
 (a) Ethyl acetate (b) Acetic anhydride (c) Acetamide (d) Acetyl chloride

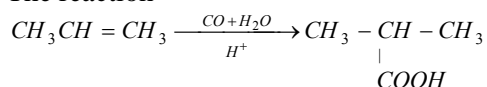
EXERCISE - II

Preparation of Carboxylic Acids and Their Derivatives

1. Hydrolysis of $CH_3CH_2NO_2$ with 85% H_2SO_4 gives
 (a) CH_3CH_2OH (b) C_2H_6 (c) $CH_3CH = NOH$ (d) CH_3COOH
2. When formic acid reacts with PCl_5 it forms
 (a) Formyl chloride (b) Acetyl chloride
 (c) Methyl chloride (d) Propionyl chloride
3. Laboratory method for the preparation of acetyl chloride is
 (a) $CH_3COOH + SOCl_2 \rightarrow CH_3COCl$ (b) $CH_3COOH + PCl_3 \rightarrow CH_3COCl$
 (c) $CH_3COONa + PCl_3 \rightarrow CH_3COCl$ (d) All of these
4. Tischenko reaction yields ester in the presence of catalyst which is
 (a) $LiAlH_4$ (b) *N*-bromosuccinamide
 (c) $Al(OC_2H_5)_3$ (d) $Zn - Hg / HCl$
5. Acetic acid is obtained when
 (a) Methyl alcohol is oxidised with potassium permanganate
 (b) Calcium acetate is distilled in the presence of calcium formate
 (c) Acetaldehyde is oxidised with potassium dichromate and sulphuric acid
 (d) Glycerol is heated with sulphuric acid
6. Acetic acid is manufactured by the fermentation of
 (a) Ethanol (b) Methanol (c) Ethanal (d) Methanal
7. $CO + NaOH \rightarrow$
 (a) $HCOONa$ (b) $C_2H_2O_4$ (c) $HCOOH$ (d) CH_3COOH

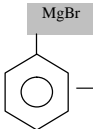
8. Carboxylic acids react with diazomethane to form
 (a) Amine (b) Alcohol (c) Ester (d) Amide
9. $C_2H_2 \xrightarrow[H_2SO_4]{HgOH\ 1\%} A \xrightarrow{[O]} B$, B is
 (a) An acid (b) An aldehyde (c) A ketone (d) Ethanol
10. Reimer-Tiemann reaction involves a
 (a) Carbonium ion intermediate (b) Carbene intermediate
 (c) Carbanion intermediate (d) Free radical intermediate
11. The product D of the reaction
 $CH_3Cl \xrightarrow{KCN} (A) \xrightarrow{H_2O} (B) \xrightarrow{NH_3} (C) \xrightarrow{\Delta} (D)$ is
 (a) $CH_3CH_2NH_2$ (b) CH_3CN (c) $HCONH_2$ (d) CH_3CONH_2
12. Which of the following on hydrolysis forms acetic acid
 (a) CH_3CN (b) CH_3OH (c) C_2H_5OH (d) $C_2H_5NH_2$
13. When benzyl alcohol is oxidised with $KMnO_4$, the product obtained is
 (a) Benzaldehyde (b) Benzoic acid (c) CO_2 and H_2O (d) None of these
14. Which of the following gives benzoic acid on oxidation
 (a) Chlorophenol (b) Chlorotoluene (c) Chlorobenzene (d) Benzyl chloride
15. $(CH_3)_2CO \xrightarrow[(HCl)]{NaCN} A \xrightarrow[\Delta]{H_3O^+} B$ In the above sequence of reactions A and B are
 (a) $(CH_3)_2C(OH)CN$, $(CH_3)_2C(OH)COOH$
 (b) $(CH_3)_2C(OH)CN$, $(CH_3)_2C(OH)_2$
 (c) $(CH_3)_2C(OH)CN$, $(CH_3)_2CHCOOH$
 (d) $(CH_3)_2C(OH)CN$, $(CH_3)_2C=O$
16. Two moles of acetic acid are heated with P_2O_5 . The product formed is
 (a) 2 moles of ethyl alcohol (b) Formic anhydride
 (c) Acetic anhydride (d) 2 moles of methyl cyanide
17. Formic acid is obtained when
 (a) Calcium acetate is heated with conc. H_2SO_4
 (b) Calcium formate is heated with calcium acetate
 (c) Glycerol is heated with oxalic acid at $110^\circ C$
 (d) Acetaldehyde is oxidised with $K_2Cr_2O_7$ and H_2SO_4
18. Acetyl chloride cannot be obtained by treating acetic acid with
 (a) $CHCl_3$ (b) $SOCl_2$ (c) PCl_3 (d) PCl_5
19. o -xylene when oxidised in presence of V_2O_5 the product is
 (a) Benzoic acid (b) Phenyl acetic acid (c) Phthalic acid (d) Acetic acid

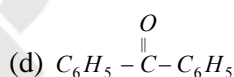
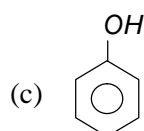
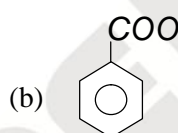
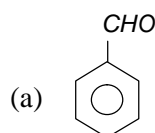
20. The reaction



is known as

- (a) Wurtz reactions (b) Koch reaction
(c) Clemenson's reduction (d) Kolbe's reaction
21. By aerial oxidation, which one of the following gives phthalic acid
(a) Naphthalene (b) Benzene (c) Mesitylene (d) Toluene

22.  In the reaction, product *P* is



23. Glacial acetic is obtained by

- (a) Distilling vinegar
(b) Crystallizing separating and melting acetic acid
(c) Treating vinegar with dehydrating agent
(d) Chemically separating acetic acid
24. In esterification, OH^- ion for making H_2O comes from
(a) Acid (b) Alcohol (c) Ketone (d) Carbohydrate
25. Heating a mixture of ethyl alcohol and acetic acid in presence of conc. H_2SO_4 produces a fruity smelling compound. This reaction is called
(a) Neutralisation (b) Ester hydrolysis
(c) Esterification (d) Williamson's synthesis
26. Product formed by heating a mixture of ammonium chloride and potassium cyanate is
(a) N_2O (b) NH_3 (c) CH_3NH_2 (d) H_2NCONH_2
27. Rearrangement of an oxime to an amide in the presence of strong acid is called
(a) Curtius rearrangement (b) Fries rearrangement
(c) Beckmann rearrangement (d) Sandmeyer reaction
28. Which reagent will bring about the conversion of carboxylic acids into esters
(a) $\text{C}_2\text{H}_5\text{OH}$ (b) Dry $\text{HCl} + \text{C}_2\text{H}_5\text{OH}$ (c) LiAlH_4 (d) $\text{Al}(\text{OC}_2\text{H}_5)_3$

29. The acid formed when propyl magnesium bromide is treated with carbon dioxide is
(a) C_3H_7COOH (b) C_2H_5COOH
(c) Both (a) and (b) (d) None of the above
30. CO_2 on reaction with ethyl magnesium bromide gives
(a) Ethane (b) Propanoic acid
(c) Acetic acid (d) None of these
31. Acetic anhydride is obtained from acetyl chloride by the reaction of
(a) P_2O_5 (b) H_2SO_4 (c) CH_3COONa (d) CH_3COOH
32. Hydrolysis of acetamide produces
(a) Acetic acid (b) Acetaldehyde (c) Methylamine (d) Formic acid
33. Ethyl acetate is obtained when methyl magnesium iodide reacts with
(a) Ethyl formate (b) Ethyl chloroformate (c) Acetyl chloride (d) Carbon dioxide
34. Sodium acetate reacts with acetyl chloride to form
(a) Acetic acid (b) Acetone (c) Acetic anhydride (d) Sodium formate
35. Ammonium acetate reacts with acetic acid at $110^\circ C$ to form
(a) Acetamide (b) Formamide (c) Ammonium cyanate (d) Urea
36. Tischenko reaction is used for preparation of
(a) Ether (b) Ester (c) Amide (d) Acid anhydride
37. The silver salt of a fatty acid on refluxing with an alkyl halide gives an
(a) Acid (b) Ester (c) Ether (d) Amine
38. Which reaction is used for the preparation of α -Bromoacetic acid ?
(a) Kolbe's Reaction (b) Reimer-Tiemann Reaction
(c) Hell volhard Zelinsky Reaction (d) Perkin's Reaction
39. Tertiary alcohols (3°) having atleast four carbon atoms upon drastic oxidation yield carboxylic acid with
(a) One carbon atom less (b) Two carbon atoms less
(c) Three carbon atom less (d) All the above three options are correct
40. When succinic acid is heated, product formed is
(a) Succinic anhydride (b) Acetic acid
(c) CO_2 and methane (d) Propionic acid
41. In the reaction, $C_6H_5OH \xrightarrow{NaOH} (A) \xrightarrow[140^\circ C, (4-7 \text{ atm})]{CO_2} (B) \xrightarrow{HCl} (C)$, the compound (C) is
(a) Benzoic acid (b) Salicylaldehyde
(c) Chlorobenzene (d) Salicylic acid

42. When an acyl chloride is heated with Na salt of a carboxylic acid, the product is
 (a) An ester (b) An anhydride (c) An alkene (d) An aldehyde
43. The compound X , in the reaction, is

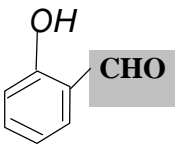
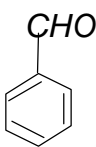

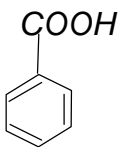
$$X \xrightarrow{CH_3MgI} Y \xrightarrow{\text{hydrolysis}} Mg(OH)I + CH_3COOH$$

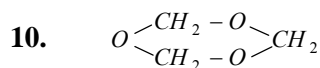
 (a) CH_3CHO (b) CO_2 (c) $(CH_3)_2CO$ (d) $HCHO$
44. $CH_3CONH_2 \xrightarrow{NaNO_2 / HCl} X$
 (a) CH_3COOH (b) $CH_3CO \overset{+}{N} H_3 Cl^-$ (c) CH_3NH_2 (d) CH_3CHO
45. Primary aldehyde on oxidation gives
 (a) Esters (b) Carboxylic acid (c) Ketones (d) Alcohols
46. Toluene is oxidised to benzoic acid by
 (a) $KMnO_4$ (b) $K_2Cr_2O_7$ (c) H_2SO_4 (d) Both (a) and (b)
47.
$$MeO-\text{C}_6\text{H}_4-CHO + (X) \xrightarrow[H_3O^+]{CH_3COONa} \text{C}_6\text{H}_4-CH=CHCOOH$$

 The compound (X) is
 (a) CH_3COOH (b) $BrCH_2COOH$ (c) $(CH_3CO)_2O$ (d) $CHO > COOH$
48. Salicylic acid is prepared from phenol by
 (a) Reimer Tiemann reaction (b) Kolbe's reaction
 (c) Kolbe-electrolysis reaction (d) None of these
49. Acetic acid will be obtained on oxidation of
 (a) Ethanol (b) Propanal (c) Methanal (d) Glyoxal

EXERCISE -III

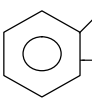
Properties of Carboxylic Acids and Their Derivatives

- Which of the following acids has the smallest dissociation constant
 (a) $\text{CH}_3\text{CHFCOOH}$ (b) $\text{FCH}_2\text{CH}_2\text{COOH}$ (c) $\text{BrCH}_2\text{CH}_2\text{COOH}$ (d) $\text{CH}_3\text{CHBrCOOH}$
- What is obtained, when propene is treated with *N*-bromo succinimide
 (a) $\text{CH}_3 - \underset{\text{Br}}{\text{C}} = \text{CH}_2$ (b) $\text{BrCH}_2 - \text{CH} = \text{CH}_2$
 (c) $\text{BrCH}_2 - \text{CH} = \text{CHBr}$ (d) $\text{BrCH}_2 - \underset{\text{Br}}{\text{CH}} - \text{CH}_2\text{Br}$
- What will be the product, when carboxy phenol, obtained by Reimer Tiemann's process, is deoxidised with *Zn* powder
 (a)  (b)  (c)  (d) 
- The vapour of a carboxylic acid *HA* when passed over MnO_2 at 573 K yields propanone. The acid *HA* is
 (a) Methanoic acid (b) Ethanoic acid (c) Propanoic acid (d) Butanoic acid
- Which acid is strongest or Which is most acidic
 (a) $\text{Cl}_2\text{CH.COOH}$ (b) ClCH_2COOH (c) CH_3COOH (d) $\text{Cl}_3\text{C.COOH}$
- Ethyl acetate at room temperature is a
 (a) Solid (b) Liquid (c) Gas (d) Solution
- Urea is a better fertilizer than ammonium sulphate because
 (a) It has greater percentage of nitrogen
 (b) It is more soluble
 (c) It is weakly basic
 (d) It does not produce acidity in soil
- The reaction of acetamide with water is an example of
 (a) Alcoholysis (b) Hydrolysis (c) Ammonolysis (d) Saponification
- The acid which reduces Fehling solution is
 (a) Methanoic acid (b) Ethanoic acid (c) Butanoic acid (d) Propanoic acid

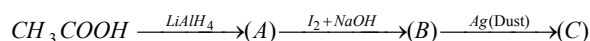


The above shown polymer is obtained when a carbon compound is allowed to stand. It is a white solid. The polymer is

- (a) Trioxane (b) Formose (c) Paraformaldehyde (d) Metaldehyde
11. What will happen if $LiAlH_4$ is added to an ester
 (a) Two units of alcohol are obtained
 (b) One unit of alcohol and one unit of acid is obtained
 (c) Two units of acids are obtained
 (d) None of these
12. When anisole is heated with HI , the product is
 (a) Phenyl iodide and methyl iodide (b) Phenol and methanol
 (c) Phenyl iodide and methanol (d) Methyl iodide and phenol
13. When CH_3COOH reacts with $CH_3 - Mg - X$
 (a) CH_3COX is formed (b) Hydrocarbon is formed
 (c) Acetone is formed (d) Alcohol is formed
14. Which class of compounds shows H -bonding even more than in alcohols
 (a) Phenols (b) Carboxylic acids (c) Ethers (d) Aldehydes
15. When propanamide reacts with Br_2 and $NaOH$ then which of the following compound is formed
 (a) Ethyl alcohol (b) Propyl alcohol (c) Propyl amine (d) Ethylamine
16. Hydrolysis of an ester gives a carboxylic acid which on Kolbe's electrolysis yields ethane. The ester is
 (a) Ethyl methanoate (b) Methyl ethanoate (c) Propylamine (d) Ethylamine
17. On prolonged heating of ammonium cyanate or urea, we get
 (a) N_2 (b) CO_2
 (c) Biurette (d) Ammonium carbonate
18. In the Gabriel's phthalimide synthesis, phthalimide is treated first with
 (a) C_2H_5I / KOH (b) Ethanolic Na
 (c) Ethanol and H_2SO_4 (d) Ether and $LiAlH_4$
19. Which of the following is the strongest acid
 (a) CH_3COOH (b) $BrCH_2COOH$ (c) $ClCH_2COOH$ (d) FCH_2COOH
20. Which of the following reduces Tollen's reagent
 (a) Acetic acid (b) Citric acid (c) Oxalic acid (d) Formic acid

21. Oxalic acid may be distinguished from tartaric acid by
 (a) Sodium bicarbonate solution
 (b) Ammonical silver nitrate solution
 (c) Litmus paper
 (d) Phenolphthalein
22. The reaction of $HCOOH$ with conc. H_2SO_4 gives
 (a) CO_2 (b) CO (c) Oxalic acid (d) Acetic acid
23. Sulphonation of benzoic acid produces mainly
 (a) *o*-sulphobenzoic acid (b) *m*-sulphobenzoic acid
 (c) *p*-sulphobenzoic acid (d) *o*- and *p*-sulphobenzoic acid
24. Which one is strongest acid
 (a) CH_2FCOOH (b) $CH_2ClCOOH$ (c) $CHCl_2COOH$ (d) CHF_2COOH
25. Which does not give silver mirror with ammoniacal $AgNO_3$
 (a) $HCHO$ (b) CH_3CHO (c) CH_3COOH (d) $HCOOH$
26. $2CH_3COOH \xrightarrow[300^\circ C]{MnO} A$, product 'A' in the reaction is
 (a) CH_3CH_2CHO (b) CH_3-CH_2-OH
 (c) CH_3COCH_3 (d) $CH_3-\overset{\overset{O}{\parallel}}{C}-O-\overset{\overset{O}{\parallel}}{C}-CH_3$
27. Acetic acid is weak acid than sulphuric acid because
 (a) It decompose on increasing temperature (b) It has less degree of ionisation
 (c) It has $-COOH$ group (d) None of these
28. In CH_3COOH and $HCOOH$, $HCOOH$ will be
 (a) Less acidic (b) Equally acidic (c) More acidic (d) None
29. Acetic anhydride reacts with excess of ammonia to form
 (a) $2CH_3COONH_4$ (b) $2CH_3CONH_2$
 (c) $CH_3CONH_2 + CH_3COONH_4$ (d) $2CH_3COOH$
30. In the following sequence of reactions, what is D

 $\xrightarrow{SOCl_2} A \xrightarrow{NaN_3} C \xrightarrow{\text{Heat}} D$
 (a) Primary amine (b) An amide
 (c) Phenyl isocyanate (d) A chain lengthened hydrocarbon
31. Hydrolytic reaction of fats with caustic soda is known as
 (a) Esterification (b) Saponification (c) Acetylation (d) Carboxylation

32. In the reaction



the final product (C) is

- (a) C_2H_5I (b) C_2H_5OH (c) C_2H_2 (d) CH_3COCH_3

33. Reaction of ethyl formate with excess of CH_3MgI followed by hydrolysis gives

- (a) *n*-propyl alcohol (b) Ethanal
(c) Propanal (d) Isopropyl alcohol

34. Of the following four reactions, formic and acetic acids differ in which respect

- (a) Replacement of hydrogen by sodium (b) Formation of ester with alcohol
(c) Reduction of Fehling solution (d) Blue litmus reaction

35. Formaldehyde and formic acid can be distinguished using

- (a) Tollen's reagent (b) Fehling solution
(c) Ferric chloride (d) Sodium bicarbonate

36. Ester and acetamide are distinguished by

- (a) Hydrolysis with strong acids or alkali (b) Derivatives of fatty acids
(c) Both (a) and (b) (d) None of these

37. Acetic acid exists as a dimer in benzene solution. This is due to

- (a) Condensation (b) Presence of $-COOH$ group
(c) Presence of π - hydrogen (d) Hydrogen bonding

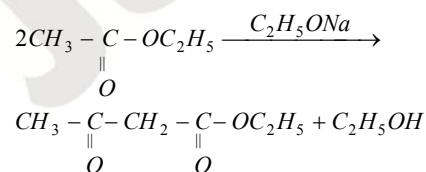
38. Which of the following compounds will react with $NaHCO_3$ solution to give sodium salt and carbon dioxide

- (a) Phenol (b) *n*-hexanol (c) Acetic acid (d) Both (a) and (b)

39. Acetic acid dissolved in benzene shows a molecular mass of

- (a) 30 (b) 60 (c) 120 (d) 240

40. The reaction



is called

- (a) Etard reaction (b) Perkin's reaction
(c) Claisen condensation (d) Claisen Schmidt reaction

41. Which is the strongest acid ? (pK_a value is given in the bracket)

- (a) $HCOOH$ (3.77) (b) C_6H_5COOH (4.22)
(c) CH_3COOH (4.71) (d) CH_3CH_2COOH (4.88)

42. In the presence of iodine catalyst, chlorine reacts with acetic acid to form
- (a) $\text{CH}_3-\overset{\overset{\text{O}}{\parallel}}{\text{C}}-\text{Cl}$ (b) $\text{CH}_2\text{Cl}-\overset{\overset{\text{O}}{\parallel}}{\text{C}}-\text{OH}$ (c) $\text{CH}_3-\overset{\overset{\text{Cl}}{\mid}}{\underset{\underset{\text{Cl}}{\mid}}{\text{C}}}-\text{OH}$ (d) $\text{CH}_3-\overset{\overset{\text{O}}{\parallel}}{\text{C}}-\text{O}-\text{Cl}$
43. The acid showing salt-like character in aqueous solution is
- (a) Acetic acid (b) Benzoic acid
(c) Formic acid (d) α -amino acetic acid
44. $\text{CH}_3\text{COOH} \xrightarrow[\text{P}_2\text{O}_5]{\Delta} \text{X}$. Identify X
- (a) CH_3COCH_3 (b) CH_3CHO (c) $(\text{CH}_3\text{CO})_2\text{O}$ (d) CH_4
45. Formic acid
- (a) Is immiscible with water
(b) Reduces the ammonical silver nitrate
(c) Is a weak acid nearly three and a half times weaker than acetic acid
(d) Is prepared by heating potassium hydroxide
46. Given below are some statements concerning formic acid, which of them is true
- (a) It is a weaker acid than acetic acid
(b) It is a reducing agent
(c) When its calcium salt is heated, it forms a ketone
(d) It is an oxidising agent
47. Which decolourises the colour of acidic KMnO_4
- (a) CH_3COOH (b) $\text{CH}_3\text{CH}_2\text{COOH}$ (c) $\text{COOH} \cdot \text{COOH}$ (d) $\text{CH}_3\text{COOC}_2\text{H}_5$
48. A colourless water soluble organic liquid decomposes sodium carbonate and liberates carbon dioxide. It produces black precipitate with Tollen's reagent. The liquid is
- (a) Acetaldehyde (b) Acetic acid (c) Formaldehyde (d) Formic acid
49. The end product B in the sequence of reactions
- $$\text{R}-\text{X} \xrightarrow{\text{CN}^-} \text{A} \xrightarrow{\text{NaOH}} \text{B}$$
- (a) An alkane (b) A carboxylic acid
(c) Sodium salt of carboxylic acid (d) A ketone
50. $\text{CH}_3\text{CH}_2\text{COOH} \xrightarrow{\text{Cl}_2/\text{Fe}} \text{X} \xrightarrow[\text{KO}_4]{\text{Alcoholic}} \text{Y}$
- Compound Y is
- (a) $\text{CH}_3\text{CH}_2\text{OH}$ (b) $\text{CH}_3\text{CH}_2\text{CN}$ (c) $\text{CH}_2=\text{CHCOOH}$ (d) $\text{CH}_3\text{CHClCOOH}$
51. In the precipitation of soap, which can be used instead of NaCl
- (a) Na (b) CH_3COONa (c) Na_2SO_4 (d) Sodium silicate

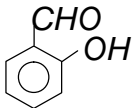
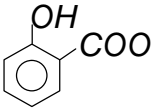
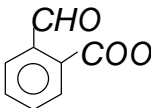
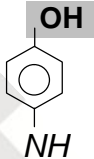
52. Which of the following can possibly be used as analgesic without causing addiction and moon modification
 (a) Morphine (b) *N*-acetyl-para-aminophenol
 (c) Drazepom (d) Tetrahydrocannabinol
53. Which of the following esters cannot undergo Claisen self condensation
 (a) $CH_3 - CH_2 - CH_2 - CH_2 - COOC_2H_5$ (b) $C_6H_5COOC_2H_5$
 (c) $C_6H_5CH_2COOC_2H_5$ (d) $C_6H_{11}CH_2COOC_2H_5$
54. When acetic acid is dissolved in benzene its molecular mass
 (a) Decreases (b) Increases
 (c) Either increases or decreases (d) Suffers no change
55. Benzoic acid has higher molecular weight in benzene and less in water because
 (a) Water has lower freezing point and higher boiling point than benzene
 (b) It dissociates to a greater extent in benzene than in water
 (c) It associates in water and dissociates in benzene
 (d) It dissociates in water and associates in benzene
56. What is the main reason for the fact that carboxylic acids can undergo ionization
 (a) Absence of α - hydrogen
 (b) Resonance stabilisation of the carboxylate ion
 (c) High reactivity of α - hydrogen
 (d) Hydrogen bonding
57. Which of the following compounds will evolve hydrogen on treatment with metal
 (a) C_2H_5OH (b) CH_3COOH (c) (a) and (b) both (d) None of these
58. When urea is heated, it forms biurette, alkaline solution of which forms with $CuSO_4$ solution
 (a) Violet colour (b) Red colour (c) Green colour (d) Black colour
59. Which of the following would be expected to be most highly ionised in water
 (a) $CH_2ClCH_2CH_2COOH$ (b) $CH_3CHCl.CH_2.COOH$
 (c) $CH_3.CH_2.CCl_2.COOH$ (d) $CH_3.CH_2.CHCl.COOH$
60. Alkaline hydrolysis of esters is known as
 (a) Saponification (b) Hydration (c) Esterification (d) Alkalisation
61. Which of the following undergoes hydrolysis when dissolved in water
 (a) CH_3COONa (b) CH_3CONH_2 (c) Both (a) and (b) (d) $C_6H_5CH_3$
62. Name the end product in the following series of reactions

$$CH_3COOH \xrightarrow{NH_3} A \xrightarrow[P_2O_5]{\Delta} B$$

 (a) CH_4 (b) CH_3OH
 (c) Acetonitrile (d) Ammonium acetate

63. Reduction of carboxylic acids gives
 (a) Alcohol with hydrogen in presence of palladium
 (b) Alcohol with $LiAlH_4$
 (c) Aldehyde with $LiAlH_4$
 (d) Alcohol with $2HI(P)$
64. Which of the following substances when boiled with caustic soda solution will evolve ammonia
 (a) Ethylamine (b) Aniline (c) Acetamide (d) Acetoxime
65. $CH_2 = CH - (CH_2)_5 COOH \xrightarrow[HBr]{\text{Peroxide}} Z$
 where Z is
 (a) $CH_3 - \underset{\substack{| \\ Br}}{CH} - (CH_2)_5 COOH$ (b) $BrCH_2 - (CH_2)_6 COOH$
 (c) $CH_2 = CH - (CH_2)_5 - CH_2OH$ (d) C_6H_5COOH
66. $HCOOH$ shows all tests of aldehyde because
 (a) It has one aldehyde group (b) It is member of aldehyde
 (c) All acids show tests of aldehyde (d) Does not show any test
67. Which one of the following orders of acid strength is correct
 (a) $RCOOH > HC \equiv CH > HOH > ROH$ (b) $RCOOH > ROH > HOH > HC \equiv CH$
 (c) $RCOOH > HOH > ROH > HC \equiv CH$ (d) $RCOOH > HOH > HC \equiv CH > ROH$
68. The order of decreasing rate of reaction with ammonia is
 (a) Anhydrides, esters, ethers (b) Anhydrides, ethers, esters
 (c) Ethers, anhydrides, esters (d) Esters, ethers, anhydrides
69. Oxidation of toluene with CrO_3 in the presence of $(CH_3CO)O_2$ gives a product 'A' which on treatment with aqueous $NaOH$ produces
 (a) C_6H_5CHO (b) $(C_6H_5CO)_2O$
 (c) C_6H_5COONa (d) 2, 4-diacetyl toluene
70. $CH_3COOCH_3 + \text{excess } PhMgBr$
 $\rightarrow \text{product} \xrightarrow{H^+} X$
 The product X is
 (a) 1, 1-diphenylethanol (b) 1, 1-diphenylmethanol
 (c) Methyl phenylethanol (d) Methyl phenylketone
71. Which of the following is most acidic
 (a) Formic acid (b) Chloroacetic acid (c) Propionic acid (d) Acetic acid
72. Urea on slow heating gives
 (a) $NH_2CON.HNO_2$ (b) $NH_2CONHCONH_2$ (c) $HCNO$ (d) $NH_2CONH_2.HNO_3$

73. The principal organic product formed in the following reaction is

$$CH_2 = CH(CH_2)_8 COOH + HBr \xrightarrow{\text{peroxide}}$$
 (a) $CH_3CHBr(CH_2)_8 COOH$ (b) $CH_2 = CH(CH_2)_8 COBr$
 (c) $CH_2BrCH_2(CH_2)_8 COOH$ (d) $CH_2 = CH(CH_2)_7 CHBrCOOH$
74. Which one of the following compound gives aspirin on reacting with acetic anhydride in presence of H_2SO_4
- (a)  (b)  (c)  (d) 
75. An acyl halide is formed when PCl_5 reacts with an
 (a) Acid (b) Alcohol (c) Amide (d) Ester
76. Which one of the following orders is wrong with respect to the property indicated
 (a) Formic acid > acetic acid > propanoic acid (acid strength)
 (b) Fluoroacetic acid > chloroacetic acid > bromoacetic acid (acid strength)
 (c) Benzoic acid > phenol > cyclohexanol (acid strength)
 (d) Aniline > cyclohexylamine > benzamide (basic strength)
77. A fruity smell is produced by the reaction of C_2H_5OH with
 (a) PCl_5 (b) CH_3COCH_3 (c) CH_3COOH (d) None of these
78. Which of the following orders of relative strengths of acids is correct
 (a) $FCH_2COOH > ClCH_2COOH > BrCH_2COOH$
 (b) $ClCH_2COOH > BrCH_2COOH > FCH_2COOH$
 (c) $BrCH_2COOH > ClCH_2COOH > FCH_2COOH$
 (d) $ClCH_2COOH > FCH_2COOH > BrCH_2COOH$
79. When acetamide is treated with $NaOBr$, the product formed is
 (a) CH_3CN (b) $CH_3CH_2NH_2$ (c) CH_3NH_2 (d) None of the above
80. The fatty acid which shows reducing property is
 (a) Acetic acid (b) Ethanoic Acid (c) Oxalic acid (d) Formic acid
81. The reagent that can be used to distinguish between methanoic acid and ethanoic acid is
 (a) Ammoniacal silver nitrate solution (b) Neutral ferric Chloride solution
 (c) Sodium carbonate solution (d) Phenolphthalein
82. Hydrolysis of an ester gives acid A and alcohol B. A reduces Fehling solution and oxidation of B gives A. The ester is
 (a) Methyl formate (b) Ethyl formate (c) Methyl acetate (d) Ethyl acetate

83. Order of reactivity is

- (a) $R-\overset{\overset{O}{\parallel}}{C}-X > RCONH_2 > RCOOCOR > RCOOR$ (b) $RCOX > RCOOCOR > RCOOR > RCONH_2$
 (c) $RCOOR > RCONH_2 > RCOX > RCOOCOR$ (d) $RCOOCOR > RCOOR > RCOX > RCONH_2$

84. Right order of acidic strength is

- (a) $CH_2ClCOOH > HCOOH > C_2H_5COOH > CH_3COOH$
 (b) $CH_2ClCOOH > HCOOH > CH_3COOH > C_2H_5COOH$
 (c) $C_2H_5COOH > CH_3COOH > HCOOH > CH_2ClCOOH$
 (d) $HCOOH > CH_2ClCOOH > CH_3COOH > C_2H_5COOH$

85. Saponification of ethyl benzoate with caustic soda as alkali gives

- (a) Benzyl alcohol and ethanoic acid
 (b) Sodium benzoate and ethanol
 (c) Benzoic acid and sodium ethoxide
 (d) Phenol and ethanoic acid
 (e) Sodium benzoate and ethanoic acid

86. Lactic acid on oxidation by alkaline potassium permanganate gives

- (a) Tartaric acid (b) Pyruvic acid (c) Cinnamic acid (d) Propionic acid

87. $RCOOH \longrightarrow RCH_2OH$

This mode of reduction of an acid to alcohol can be affected only by

- (a) Zn / HCl
 (b) Na -alcohol
 (c) Aluminium isopropoxide and isopropyl alcohol
 (d) $LiAlH_4$

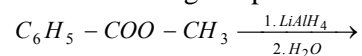
88. Which one of the following compounds forms a red coloured solution on treatment with neutral $FeCl_3$ solution

- (a) CH_3COCH_3 (b) CH_3OCH_3 (c) CH_3CH_2OH (d) CH_3COOH

89. Urea can be tested by

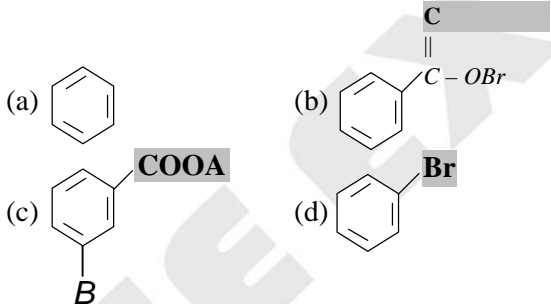
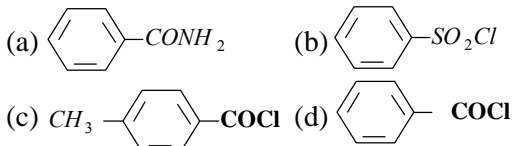
- (a) Benedict test (b) Mullicken test (c) Ninhydrin (d) Biuret test

90. What are the organic products formed in the following reaction



- (a) C_6H_5-COOH and CH_4 (b) $C_6H_5-CH_2-OH$ and CH_4
 (c) $C_6H_5-CH_3$ and CH_3-OH (d) $C_6H_5-CH_2-OH$ and CH_3-OH

91. Reaction between an acid and alcohol will give
(a) Higher C containing acid (b) Secondary alcohol
(c) Alkane (d) Ester
92. Benzoic acid gives benzene on being heated with X and phenol gives benzene on being heated with Y. Therefore X and Y are respectively
(a) Sodalime and copper (b) Zn dust and NaOH
(c) Zn dust and sodalime (d) Sodalime and zinc dust
93. The product obtained when acetic acid is treated with phosphorus trichloride is
(a) $CH_3COOPCl_3$ (b) CH_3COOCl (c) CH_3COCl (d) $ClCH_2COOH$
94. Acetyl chloride is reduced with $LiAlH_4$ the product formed is
(a) Methyl alcohol (b) Ethyl alcohol (c) Acetaldehyde (d) Acetone
95. In the preparation of an ester, the commonly used dehydrating agent is
(a) Phosphorus pentoxide (b) Anhydrous calcium carbide
(c) Anhydrous aluminium chloride (d) Concentrated sulphuric acid
96. In the esterification reaction of alcohols
(a) OH^- is replaced by C_6H_5OH (b) H^+ is replaced by sodium metal
(c) OH^- is replaced by chlorine (d) OH^- is replaced by CH_3COO^- group
97. Lower carboxylic acids are soluble in water due to
(a) Low molecular weight (b) Hydrogen bonding
(c) Dissociation into ions (d) Easy hydrolysis
98. Acetamide reacts with P_2O_5 (phosphorus pentaoxide) to give
(a) Methyl cyanide (b) Methyl cyanate (c) Ethyl cyanide (d) Ethyl isocyanate
99. The reaction
 $CH_3COOH + Cl_2 \xrightarrow{P} ClCH_2COOH + HCl$ is called
(a) Hell-Volhard-Zelinsky reaction (b) Birch reaction
(c) Rosenmund reaction (d) Hunsdiecker reaction
100. An aqueous solution of urea
(a) Is neutral (b) Is acidic
(c) Is basic (d) Can act as an acid and a base
101. Nitration of benzoic acid gives
(a) 3-nitrobenzoic acid (b) 2-nitrobenzoic acid
(c) 2, 3-dinitrobenzoic acid (d) 2, 4-dinitrobenzoic acid
102. The reagent used for converting ethanoic acid to ethanol is
(a) $LiAlH_4$ (b) $KMnO_4$ (c) PCl_3 (d) $K_2Cr_2O_7 / H^+$

103. Which one of the following has the maximum acid strength
 (a) *o*-nitrobenzoic acid (b) *m*-nitrobenzoic acid
 (c) *p*-nitrobenzoic acid (d) *p*-nitrophenol
104. When benzoic acid is treated with PCl_5 at $100^\circ C$, it gives
 (a) Benzoyl chloride (b) *o*-chlorobenzoic acid
 (c) *p*-chlorobenzoic acid (d) Benzyl chloride
105. Oxalic acid on being heated upto $90^\circ C$ with conc. H_2SO_4 forms
 (a) $HCOOH + CO_2$ (b) $CO_2 + H_2O$ (c) $CO_2 + CO + H_2O$ (d) $HCOOH + CO$
106. Benzoic acid is less acidic than salicylic acid because of
 (a) Hydrogen bond (b) Inductive effect (c) Resonance (d) All of these
 (e) None of these
107. Lactic acid on heating with conc. H_2SO_4 gives
 (a) Acetic acid (b) Propionic acid (c) Acrylic acid (d) Formic acid
108. Acetamide is
 (a) Acidic (b) Basic (c) Neutral (d) Amphoteric
109. Silver benzoate reacts with bromine to form

110. Acetic anhydride reacts with diethyl ether in presence of anhydrous $AlCl_3$ to form
 (a) Ethyl acetate (b) Methyl propionate (c) Methyl acetate (d) Propionic acid
111. Treatment of benzoic acid with $Cl_2 / FeCl_3$ will give
 (a) *p*-chlorobenzoic acid (b) *o*-chlorobenzoic acid
 (c) 2, 4-dichlorobenzoic acid (d) *m*-chlorobenzoic acid
112. Hinsberg's reagent is


113. Which of the following is the correct order of increasing strengths of carboxylic acids

- (a) $CH_2FCOOH < CH_3COOH$
 $< CH_2ClCOOH < CCl_3COOH$
 (b) $CH_3COOH < CH_2ClCOOH$
 $< CH_2FCOOH < CCl_3COOH$
 (c) $CH_2ClCOOH < CH_2FCOOH$
 $< CCl_3COOH < CH_3COOH$
 (d) $CCl_3COOH < CH_2ClCOOH$
 $< CH_2FCOOH < CH_3COOH$

114. The weakest acid among the following is

- (a) CH_3COOH (b) $Cl_2CHCOOH$ (c) $ClCH_2COOH$ (d) Cl_3CCOOH

115. Consider the acidity of the carboxylic acids

- (a) $PhCOOH$ (b) $o-NO_2C_6H_4COOH$
 (c) $p-NO_2C_6H_4COOH$ (d) $m-NO_2C_6H_4COOH$

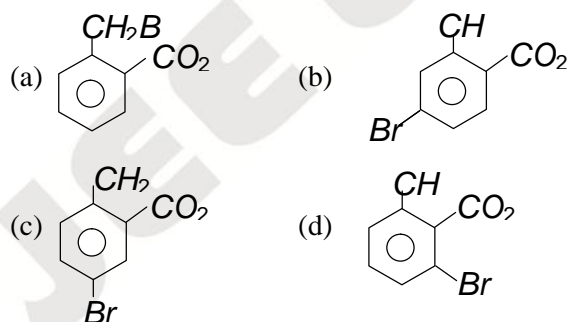
Which of the following order is correct?

- (a) $b > d > a > c$ (b) $b > d > c > a$ (c) $a > b > c > d$ (d) $b > c > d > a$

116. On mixing ethyl acetate with aqueous sodium chloride, the composition of the resultant solution is

- (a) $CH_3COCl + C_2H_5OH + NaOH$ (b) $CH_3COONa + C_2H_5OH$
 (c) $CH_3COOC_2H_5 + NaCl$ (d) $CH_3Cl + C_2H_5COONa$

117. *o*-Toluic acid on reaction with $Br_2 + Fe$, gives



118. The reaction of an ester $RCOOR'$ with an alcohol $R''OH$ in the presence of an acid gives

- (a) $RCOOH$ (b) $R'COOH$ (c) $R''COOR$ (d) $RCOOR''$ (e) $R'COOR''$

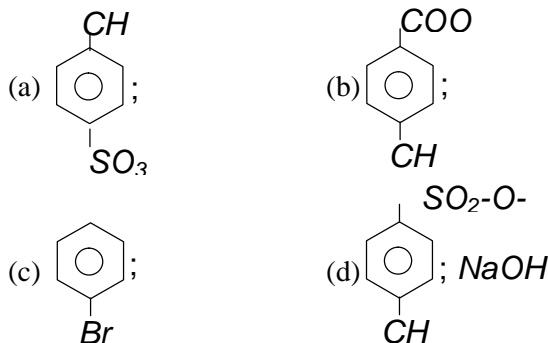
119. $RCOOH$ on treatment with PCl_5 and KCN , is subjected to hydrolysis followed by Clemmensen's reduction, the product obtained is

- (a) $RCH_2 - COCl$ (b) $RCH_2 - COOH$
 (c) $RCOCN$ (d) RCN
 (e) $R - OH$

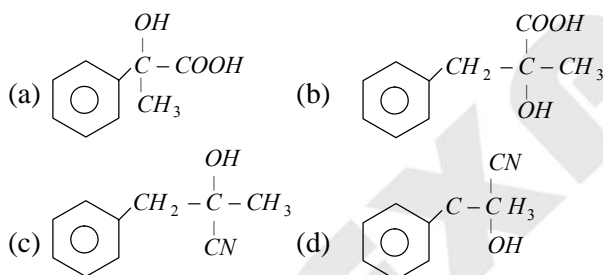
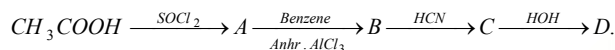
120. The reagent which does not give acid chloride on treating with a carboxylic acid is
 (a) PCl_5 (b) Cl_2 (c) $SOCl_2$ (d) PCl_3
121. An organic compound is boiled with alcoholic potash. The product is cooled and acidified with HCl . A white solid separates out. The starting compound may be
 (a) Ethyl benzoate (b) Ethyl formate (c) Ethyl acetate (d) Methyl acetate
122. The OH group of an alcohol or the $-COOH$ group of a carboxylic acid can be replaced by $-Cl$ using
 (a) Chlorine (b) Hydrochloric acid
 (c) Phosphorus pentachloride (d) Hypochlorous acid
123. Which of the following is most acidic
 (a) Picric acid (b) p -nitrophenol
 (c) m -nitrophenol (d) o - p dinitrophenol
124. Benedict's solution is not reduced by
 (a) Formaldehyde (b) Acetaldehyde (c) Glucose (d) Acetic anhydride
125. CH_3COOH is reacted with $CH \equiv CH$ in presence of Hg^{++} , the product is
 (a) $CH_3(OOCCH_3)$
 $\quad \quad \quad |$
 $\quad \quad \quad CH_2(OOCH_3)$ (b) CH_3
 $\quad \quad \quad |$
 $\quad \quad \quad CH_2-(OOC-CH_3)$ (c) CH_3
 $\quad \quad \quad |$
 $\quad \quad \quad CH(OOC-CH_3)_2$ (d) None of these
126. Acetic acid reacts with PCl_5 to form
 (a) CH_3COCl (b) $CHCl_2COOH$ (c) $CH_2ClCOOH$ (d) CH_3COOCl
127. $CH_3COOC_2H_5$ with excess of C_2H_5MgBr and hydrolysis gives
 (a) $CH_3 - \overset{\overset{C_2H_5}{|}}{C} = O$ (b) $CH_3 - \overset{\overset{C_2H_5}{|}}{C} - OH$ (c) $CH_3 - \overset{\overset{C_2H_5}{|}}{C} = O$ (d) $CH_3 - \overset{\overset{C_2H_5}{|}}{C} = O$
 $\quad \quad \quad |$ $\quad \quad \quad |$ $\quad \quad \quad |$ $\quad \quad \quad |$
 $\quad \quad \quad C_2H_5$ $\quad \quad \quad C_2H_5$ $\quad \quad \quad CH_3$ $\quad \quad \quad CH_3$
128. Urea upon hydrolysis yields
 (a) Acetamide (b) Carbonic acid (c) Ammonium hydroxide (d) NO_2
129. $CH_3CHO \xrightarrow{HCN} A \xrightarrow{HOH} B$. The product B is
 (a) Malonic acid (b) Glycolic acid (c) Lactic acid (d) Malic acid
130. What is the % of acetic acid present in vinegar?
 (a) 6 – 10% (b) 70 – 80% (c) 7 – 8% (d) 90 – 100%
131. Fruity smell is given by
 (a) Esters (b) Alcohols (c) Chloroform (d) Acid anhydrides

132. Lactic acid molecule has
 (a) One chiral carbon atom (b) Two chiral carbon atoms
 (c) No chiral carbon atom (d) Asymmetric molecule

133. 4-methyl benzene sulphonic acid reacts with sodium acetate to give



134. In a set of reactions acid yielded a product D

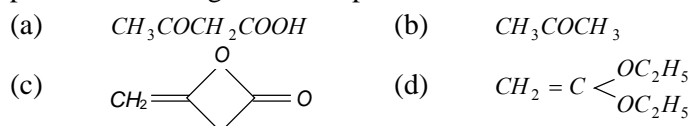


135. $C_6H_5CHO + HCN \rightarrow C_6H_5 - \overset{\overset{H}{|}}{\underset{\underset{OH}{|}}{C}} - CN$

The product would be

- (a) A racemate (b) Optically active
 (c) A meso compound (d) A mixture of diastereomers
136. What happens when 2-hydroxy benzoic acid is distilled with zinc dust, it gives
 (a) Phenol (b) Benzoic acid (c) Benzaldehyde (d) A polymeric compound

137. $CH_3CO_2C_2H_5$ on reaction with sodium ethoxide in ethanol gives A, which on heating in the presence of acid gives B compound B is



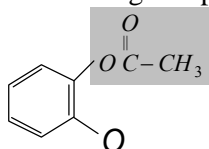
138. $C_6H_5CONHCH_3$ can be converted into $C_6H_5CH_2NHCH_3$ by
 (a) $NaBH_4$ (b) $H_2 - Pd / C$ (c) $LiAlH_4$ (d) $Zn - Hg / HCl$

139. Among the following acids which has the lowest pK_a value
(a) CH_3COOH (b) $HCOOH$ (c) $(CH_3)_2CH - COOH$ (d) CH_3CH_2COOH
140. X is heated with soda lime and gives ethane. X is
(a) Ethanoic acid (b) Methanoic acid (c) Propanoic acid (d) Either (a) or (c)
141. Which of the following is an amphoteric acid
(a) Glycine (b) Salicylic acid (c) Benzoic acid (d) Citric acid
142. Colouration of Br_2 / CCl_4 will be discharged by
(a) Cinnamic acid (b) Benzoic acid (c) *o*-phthalic acid (d) Acetophenone
143. Order of hydrolysis for the following
(I) $RCOCl$ (II) $RCOOR$
(III) $RCONH_2$ (IV) $(RCO)_2O$
(a) I>IV>II>III (b) I>II>III>IV (c) I>III>II>IV (d) IV>III>II>I
144. If the enolate ion combines with carbonyl group of ester, we get
(a) Aldol (b) α, β -unsaturated ester (c) α -keto aldehyde (d) Acid
145. Which of the following compounds will react with $NaHCO_3$ solution to give sodium salt and carbon dioxide
(a) Acetic acid (b) *n*-hexanol (c) Phenol (d) Both (a) and (c)
146. A carboxylic acid is converted into its anhydride using
(a) Thionyl chloride (b) Sulphur chloride
(c) Sulphuric acid (d) Phosphorus pentoxide

EXERCISE - IV

Uses of Carboxylic Acids and Their Derivatives

1. The following compound is used as

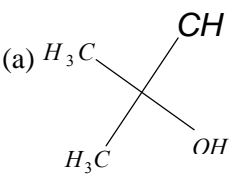


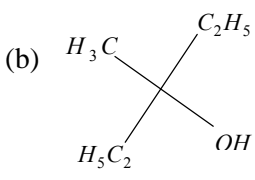
- (a) An anti-inflammatory agent (b) Analgesic
(c) Hypnotic (d) Antiseptic
2. To which of the following groups does soap belongs
(a) Esters (b) Amines
(c) Salts of organic higher fatty acids (d) Aldehydes
3. Aspirin is an acetylation product of
(a) *o*-hydroxybenzoic acid (b) *o*-dihydroxybenzene
(c) *m*-hydroxybenzoic acid (d) *p*-dihydroxybenzene
4. Which one is used as a food preservative
(a) Sodium acetate (b) Sodium propionate
(c) Sodium benzoate (d) Sodium oxalate
5. What makes a lemon sour
(a) Tartaric acid (b) Oxalic acid (c) Citric acid (d) Hydrochloric acid
6. The reagent used for protection of amino group during the nitration of aniline is
(a) $SOCl_2$ / Pyridine (b) PCl_5 (c) Acetic acid (d) Acetic anhydride

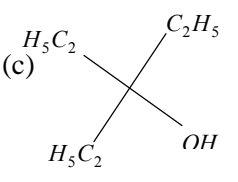
EXERCISE - V

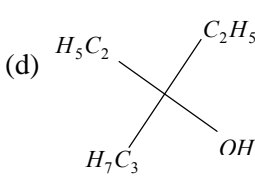
OBJECTIVE QUESTIONS

- Ethyl ester $\xrightarrow[\text{excess}]{CH_3MgBr}$ P . The product P will be

(a) 

(b) 

(c) 

(d) 
- Hydrogenation of $C_6H_5CHOH - COOH$ over $Rh - Al_2O_3$ catalyst in methanol gives

(a) $C_6H_5CH_2COOH$

(b) $C_6H_{11}CHOHCOOH$

(c) $C_6H_5CHOHCH_2OH$

(d) $C_6H_{11}CH_2COOH$
- Which of the following has the most acidic proton

(a) CH_3COCH_3

(b) $(CH_3)_2C = CH_2$

(c) $CH_3COCH_2COCH_3$

(d) $(CH_3CO)_3CH$
- In the anion $HCOO^-$ the two carbon-oxygen bonds are found to be of equal length. What is the reason for it

(a) Electronic orbitals of carbon atom are hybridised

(b) The $C = O$ bond is weaker than the $C - O$ bond

(c) The anion $HCOO^-$ has two resonating structures

(d) The anion is obtained by removal of a proton from the acid molecule
- An organic compound of molecular formula $C_4H_{10}O$ does not react with sodium. With excess of HI , it gives only one type of alkyl halide. The compound is

(a) Ethoxyethane

(b) 2-Methoxypropane

(c) 1-Methoxypropane

(d) 1-Butanol
- When $CH_2 = CH - COOH$ is reduced with $LiAlH_4$, the compound obtained will be

(a) $CH_3 - CH_2 - COOH$

(b) $CH_2 = CH - CH_2OH$

(c) $CH_3 - CH_2 - CH_2OH$

(d) $CH_3 - CH_2 - CHO$
- In a set of the given reactions, acetic acid yielded a product C

$$CH_3COOH + PCl_5 \rightarrow A \xrightarrow[\text{anh. } AlCl_3]{C_6H_6} B \xrightarrow[\text{ether}]{C_2H_5MgBr} C$$
 Product C would be

(a) $CH_3 - \overset{\overset{C_2H_5}{|}}{C}(OH)C_6H_5$

(b) $CH_3CH(OH)C_2H_5$

(c) $CH_3COC_6H_5$

(d) $CH_3CH(OH)C_6H_5$

8. Carboxylic acids are more acidic than phenol and alcohol because of
(a) Intermolecular hydrogen bonding
(b) Formation of dimers
(c) Highly acidic hydrogen
(d) Resonance stabilization of their conjugate base
9. $R-CH_2-CH_2OH$ can be converted into RCH_2CH_2COOH . The correct sequence of the reagents is
(a) PBr_3, KCN, H_3O^+ (b) PBr_3, KCN, H_2 (c) HCN, PBr_3, H^+ (d) KCN, H^+
10. When propionic acid is treated with aqueous sodium bicarbonate CO_2 is liberated. The 'C' of CO_2 comes from
(a) Methyl group (b) Carboxylic acid group
(c) Methylene group (d) Bicarbonate
11. Benzoyl chloride is prepared from benzoic acid by
(a) Cl_2, hv (b) SO_2Cl_2 (c) $SOCl_2$ (d) Cl_2, H_2O
12. Identify the correct order of boiling points of the following compounds
 $CH_3CH_2CH_2CH_2OH$ (1), $CH_3CH_2CH_2CHO$ (2), $CH_3CH_2CH_2COOH$ (3)
(a) $1 > 2 > 3$ (b) $3 > 1 > 2$ (c) $1 > 3 > 2$ (d) $3 > 2 > 1$
13. The compound not soluble in acetic acid is
(a) $CaCO_3$ (b) CaO (c) CaC_2O_4 (d) $Ca(OH)_2$
14. The *ortho/para* directing group among the following is
(a) $COOH$ (b) CN (c) $COCH_3$ (d) $NHCOCH_3$
15. Iodoform test is not given by
(a) Acetone (b) Ethyl alcohol
(c) Acetic acid (d) None of these
16. How will you convert butan-2-one to propanoic acid
(a) Tollen's reagent (b) Fehling's solution
(c) $NaOH / I_2 / H^+$ (d) $NaOH / NaI / H^+$
17. Which of the acids cannot be prepared by Grignard reagent
(a) Acetic acid (b) Succinic acid
(c) Formic acid (d) All of these

EXERCISE - VI

Assertion & Reason

Read the assertion and reason carefully to mark the correct option out of the options given below :

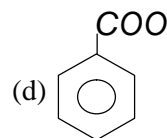
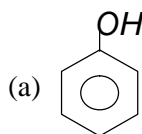
- (a) If both assertion and reason are true and the reason is the correct explanation of the assertion.
- (b) If both assertion and reason are true but reason is not the correct explanation of the assertion.
- (c) If assertion is true but reason is false.
- (d) If the assertion and reason both are false.
- (e) If assertion is false but reason is true.

1. Assertion : Carboxylic acid exist as dimer.
Reason : Carboxylic acid shows hydrogen bonding.
2. Assertion : Trichloroacetic acid is stronger than acetic acid.
Reason : Electron withdrawing substituents decrease the activity.
3. Assertion: First four aliphatic monocarboxylic acids are colourless.
Reason : Carboxylic acids with more than five carbon atoms are insoluble in water.
4. Assertion : Carboxylic acids do not give characteristic reactions of carbonyl group.
Reason : Carboxylic acids exist as cyclic dimers in solid, liquid and even in vapour state.
5. Assertion : Pure acetic acid is converted into ice like solid called glacial acetic acid.
Reason : Acetic acid is stronger than $HCOOH$.
6. Assertion : The second dissociation constant of maleic acid is greater than fumaric acid.
Reason : Higher the dissociation constant of acid more is acidic character.
7. Assertion : Lower acids on reacting with strong electropositive metals give effervescences of H_2 .
Reason : $MeCOOC_4H_9$ hydrolyses rapidly than $MeCOOCH_3$.
8. Assertion : Melting point of carboxylic acids shows a regular pattern.
Reason : Carboxylic acids are reduced to alkanes on reduction with HI in presence of red phosphorus.
9. Assertion : Electron withdrawing groups decrease the acidity of carboxylic acids.
Reason : Substituents affect the stability of the conjugate base and acidity of carboxylic acids.
10. Assertion : Fluoroacetic acid is stronger acid than bromoacetic acid.
Reason : Acidity depends upon the electron withdrawing effects of the fluorine and chlorine.

11. Assertion : Aminoacetic acid is less acidic than acetic acid.
Reason : Amino group is electron donating in nature.
12. Assertion : Carboxylic acids have higher boiling points than alkanes.
Reason : Carboxylic acids are resonance hybrids.
13. Assertion : Both formic acid and oxalic acid decolourize $KMnO_4$ solution.
Reason : Both are easily oxidised to CO_2 and H_2O .
14. Assertion : Esters which contain α – hydrogens undergo Claisen condensation.
Reason : $LiAlH_4$ reduction of esters gives acids.

Self Evaluation Test

1. Which of the following is the weakest acid



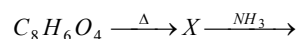
2. Pyruvic acid is obtained by

- (a) Oxidation of acetaldehyde cyanohydrin
 (b) Oxidation of acetone cyanohydrin
 (c) Oxidation of formaldehyde cyanohydrin
 (d) None of these

3. The product obtained by dry distillation of calcium formate on reacting with ammonia yields

- (a) Formamide (b) Acetamide
 (c) Acetaldehyde ammonia (d) Urotropine

4. In the reaction



The compound X is

- (a) Phthalic anhydride (b) Phthalic acid
 (c) *o*-xylene (d) Benzoic acid

5. Ethyl acetate reacts with CH_3MgBr to form

- (a) Secondary alcohol (b) Tertiary alcohol
 (c) Primary alcohol and acid (d) Acid

6. In quick vinegar process of acetic acid, the temperature of mixture is

- (a) 300 K (b) 427 K (c) 500 K (d) 350 K

7. Formic acid can reduce

- (a) Tollen's reagent (b) Mercuric chloride
 (c) KMnO_4 (d) All of these

8. 0.2 gm of fine animal charcoal is mixed with half litre of acetic acid (–SM) solution and shaken for 30 minutes

- (a) The concentration of the solution decreases
 (b) Concentration increases
 (c) Concentration remains same
 (d) None of these

9. Dimerisation in carboxylic acid is due to

- (a) Ionic bond (b) Covalent bond
 (c) Coordinate bond (d) Intermolecular hydrogen bond

10. A colourless organic compound gives brisk effervescences with a mixture of sodium nitrite and dil. HCl . It could be
(a) Glucose (b) Oxalic acid (c) Urea (d) Benzoic acid
11. What is formed when benzoyl chloride reacts with aniline in presence of sodium hydroxide
(a) Acetanilide (b) Benzanilide (c) Benzoic acid (d) Azobenzene
12. Strong acid among the following is
(a) CF_3COOH (b) CBr_3COOH (c) CH_3COOH (d) CCl_3COOH
13. Aspirin is obtained by the reaction of salicylic acid with
(a) Acetone (b) Acetaldehyde (c) Acetyl chloride (d) Acetic anhydride
14. Oxalic acid when reduced with zinc and H_2SO_4 gives
(a) Glyoxallic acid (b) Glyoxal (c) Glycollic acid (d) Glycol
15. A distinctive and characteristic functional group in fats is
(a) A ketonic group (b) An ester group
(c) A peptide group (d) An alcoholic group
16. Which substance will give amide when heated with NH_3
(a) Potassium (b) Hydrogen (c) Ethane (d) Nitrogen
17. Which acid has least pK_a value
(a) $Cl_3C.COOH$ (b) $Cl_2CH.COOH$ (c) $Cl.CH_2COOH$ (d) CH_3COOH

ANSWER KEY

EXERCISE -I

General Introduction of Carboxylic Acids and Their Derivatives

1	d	2	d	3	c	4	d	5	a
6	c	7	d	8	c	9	c	10	d
11	a	12	c	13	d	14	d	15	b
16	c	17	d	18	d	19	c	20	b,d
21	a	22	a	23	c	24	b	25	b
26	b	27	c	28	d	29	a	30	a
31	c	32	b	33	d	34	c	35	a
36	d	37	a	38	d				

EXERCISE -II

Preparation of Carboxylic Acids and Their Derivatives

1	d	2	a	3	a	4	c	5	c
6	a	7	a	8	c	9	a	10	b
11	d	12	a	13	b	14	d	15	a
16	c	17	c	18	a	19	c	20	b
21	a	22	b	23	b	24	a	25	c
26	d	27	c	28	b	29	a	30	b
31	c	32	a	33	b	34	c	35	a
36	b	37	b	38	c	39	b	40	a
41	d	42	b	43	b	44	a	45	b
46	d	47	c	48	a	49	a		

EXERCISE -III

Properties of Carboxylic Acids and Their Derivatives

1	c	2	b	3	d	4	b	5	d
6	b	7	ad	8	b	9	a	10	a
11	a	12	d	13	b	14	b	15	d
16	b	17	c	18	a	19	d	20	d
21	b	22	b	23	b	24	d	25	c
26	c	27	b	28	c	29	c	30	c
31	b	32	c	33	d	34	c	35	d
36	c	37	d	38	c	39	c	40	c
41	a	42	b	43	d	44	c	45	b
46	b	47	c	48	d	49	c	50	c
51	c	52	b	53	b	54	b	55	d
56	b	57	c	58	a	59	c	60	a
61	c	62	c	63	b	64	c	65	b
66	a	67	c	68	b	69	c	70	a

71	b	72	b	73	c	74	b	75	a
76	d	77	c	78	a	79	c	80	d
81	a	82	a	83	b	84	b	85	b
86	b	87	d	88	d	89	d	90	d
91	d	92	d	93	c	94	b	95	d
96	d	97	b	98	a	99	a	100	a
101	a	102	a	103	a	104	a	105	c
106	a	107	c	108	d	109	d	110	a
111	d	112	b	113	b	114	a	115	d
116	c	117	c	118	d	119	b	120	b
121	a	122	c	123	a	124	d	125	c
126	a	127	b	128	b	129	c	130	a
131	a	132	a	133	a	134	a	135	b
136	b	137	c	138	d	139	b	140	c
141	a	142	a	143	a	144	c	145	a
146	d								

EXERCISE -IV**Uses of Carboxylic Acids and Their Derivatives**

1	b	2	c	3	a	4	c	5	c
6	d								

EXERCISE -V**Critical Thinking Questions**

1	a	2	b	3	d	4	c	5	a
6	b	7	a	8	d	9	a	10	d
11	c	12	b	13	c	14	d	15	c
16	c	17	c						

EXERCISE -VI**Assertion & Reason**

1	a	2	c	3	c	4	b	5	c
6	e	7	c	8	e	9	e	10	a
11	c	12	b	13	a	14	c		

HINTS & SOLUTIONS

EXERCISE -I

General Introduction of Carboxylic Acids and Their Derivatives

- (d) Methyl salicylate occurs in natural essential oils like winter green.
- (d) Tartaric acid have the chiral carbon (*) atom. So it is optically active.

$$\begin{array}{c} OH \\ | \\ H - C^* - COOH \\ | \\ H - C^* - COOH \\ | \\ OH \\ \text{Tartaric acid} \end{array}$$
- (c) Formula of palmitic acid is $C_{15}H_{31}COOH$.
- (d) Amide group represent by the formula $-CONH_2$
- (a) $Cl - \underset{3}{CH_2} - \underset{2}{CH_2} - \underset{1}{COOH}$
3 chloro propanoic acid
- (d) Soaps are sodium salt of fatty acids *e.g.*- $C_{17}H_{35}COONa$ Sodium Stearate acid.
- (c) $R - CONH_2$ (Primary amide) $(RCO)_2NH$ (Secondary amide)
- (c) $\begin{array}{c} CHO HCOOH \\ | \\ CHO HCOOH \end{array}$ is known as tartaric acid and its potassium salt is known as Tartaremetic.
- (a) $R - \overset{\curvearrowright}{C} \leftarrow OH \leftrightarrow R - \overset{O^-}{C} - O \cdots \cdots H$
It represent the acidic nature.
- (c) $CH_3 - \overset{O}{\parallel} C - CH_2 - \overset{O}{\parallel} C - O - C_2H_5 \rightleftharpoons$
Acetoacetic ester (keto form)

$$CH_3 - \overset{OH}{\underset{|}{C}} = CH - \overset{O}{\parallel} C - O - C_2H_5$$

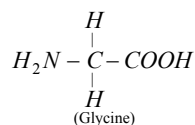
(enolic form)
- (d) $2RCOOH \xrightarrow{-H_2O} (RCO)_2O$
Acid anhydride
- (d) $HOOC - CH_2 - \overset{OH}{\underset{|}{C}} - CH_2 - COOH$

$$\quad \quad \quad |$$

$$\quad \quad \quad COOH$$

It is citric acid consist three carboxylic group.
- (c) Wax are long chain ester.

17. (d) Glycine do not have the chiral carbon so it is not optically active acid.



18. (d) Except phenyl acetic acid all rest acid are fatty acid.

19. (c) Vinegar contain 8-10% acetic acid.

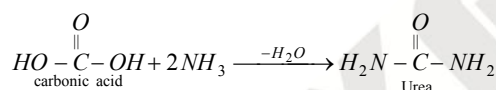
20. (b,d) General formula of monocarboxylic acid is $\text{C}_n\text{H}_{2n+1}\text{COOH}$ or $\text{C}_n\text{H}_{2n}\text{O}_2$.

21. (a) Formula of Acetamide is CH_3CONH_2 which consist single oxygen atom.

22. (a) Urea behaves as a monoacidic base and react with nitric acid and form sparingly soluble nitrate.

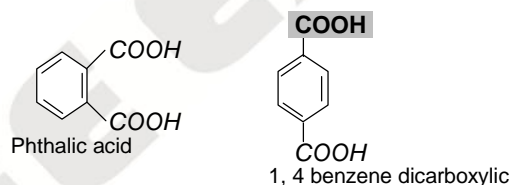
23. (c) Fats and oil jointly known as lipid which are the ester of glycerol with high fatty acid.

26. (b) Urea is the diamide of carbonic acid.



So two mole of NH_3 required that why it is the diamide of carbonic acid.

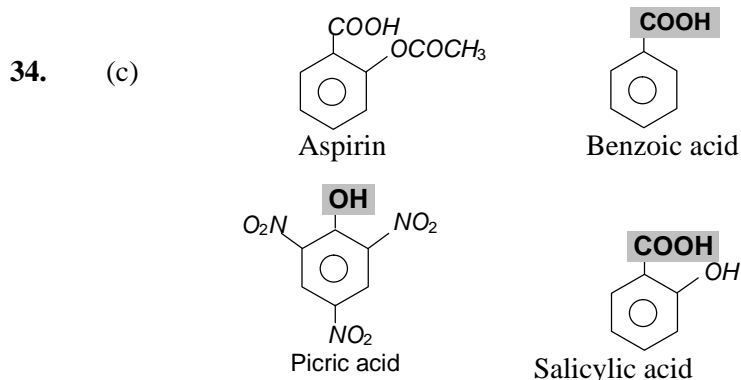
27. (c) Phthalic acid is the isomer of 1, 4 benzene dicarboxylic acid because both have the same molecular formula but differ in their structure.



28. (d) Esters are RCOOR' , where OR' = alkoxy group and $R = \text{H}$ or alkyl or aryl group.

29. (a) Soaps are the sodium or potassium salts of higher fatty acids.

33. (d) Vinegar is the diluted solution of acetic acid (CH_3COOH). It is formed by the fermentation of ethyl alcohol in the presence of enzyme acetobacter.

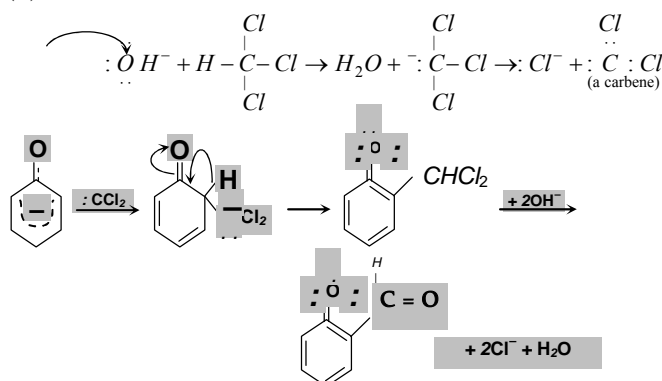


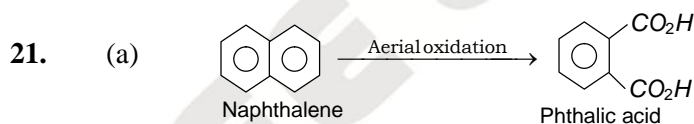
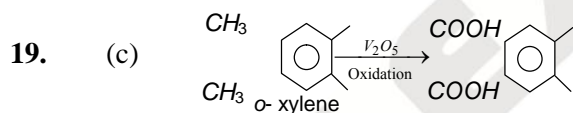
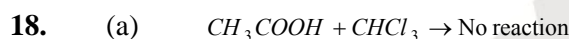
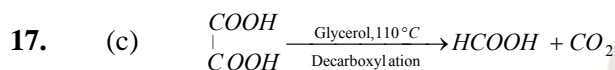
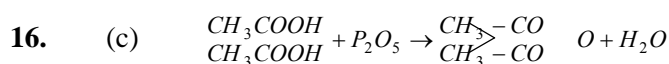
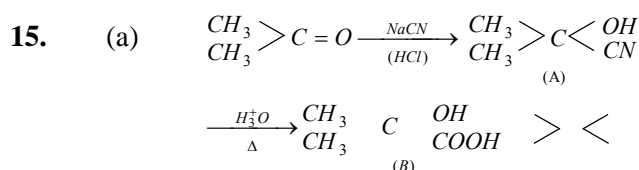
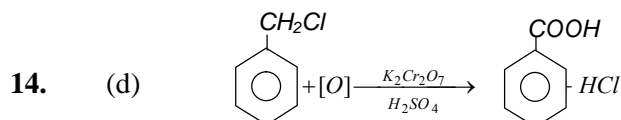
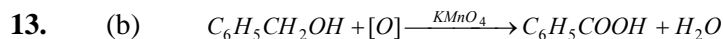
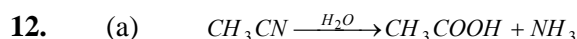
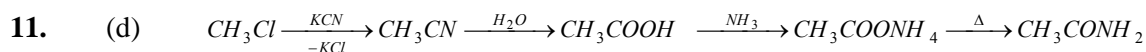
35. (a) Acetic acid is the chief constituent of vinegar and hence its name (Latin : acetum = vinegar).
36. (b) Phenol was discovered by Runge in the middle oil fraction of coal-tar distillation and named it 'carbolic acid' (carbo-coil, oleum = oil) or phenol containing 5% water in liquid at room temperature and it is termed as carbolic acid.
37. (a) Any electron withdrawing substituent (having-I-effect) stabilises the anion by dispersing the negative charge and therefore, increases the acidity. Chlorine is an electron withdrawing group.
38. (d) The order of reactivity of acid derivatives towards different reactions decreases in the order,
- $$RCOCl > (RCO)_2O > RCOOR' > RCONH_2$$
- In other words, the reactivity decreases as the basicity of the leaving group increases i.e.,
- $$Cl^- < RCOO^- < RO^- < NH_2^-$$

EXERCISE -II

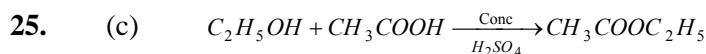
Preparation of Carboxylic Acids and Their Derivatives :

1. (d) $CH_3CH_2NO_2 + H_2O \xrightarrow{H_2SO_4} CH_3COOH + NH_2OH$
2. (a) $HCOOH + PCl_5 \rightarrow HCOCl + POCl_3 + HCl$
Formic acid Formyl chloride
4. (c) $2CH_3CHO \xrightarrow{Al(OC_2H_5)_3} CH_3CH_2OH + CH_3COOH \rightarrow CH_3COOC_2H_5 + H_2O$
Ethylacetate
5. (c) $CH_3CHO \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3COOH$
6. (a) $C_2H_5OH \xrightarrow{\text{Acetobacter}} CH_3COOH$
7. (a) $CO + NaOH \xrightarrow{\Delta} HCOONa$
9. (a) $CH \equiv CH \xrightarrow[H_2SO_4]{1\% Hg^{+2}} CH_3 - CH \begin{matrix} \text{OH} \\ \text{OH} \end{matrix} \rightarrow CH_3CHO \xrightarrow{[O]} CH_3COOH$
Unstable acetic acid
10. (b) Reimer-Tiemann reaction involves a carbene intermediate.

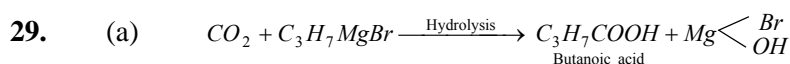
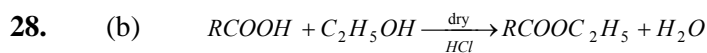


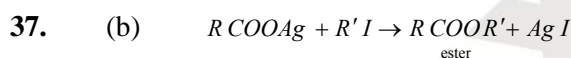
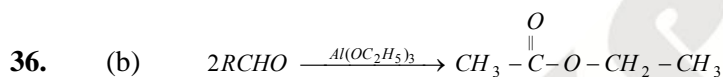
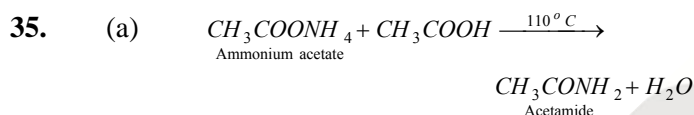
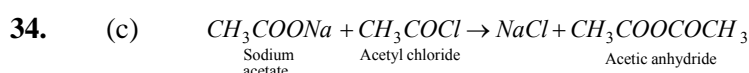
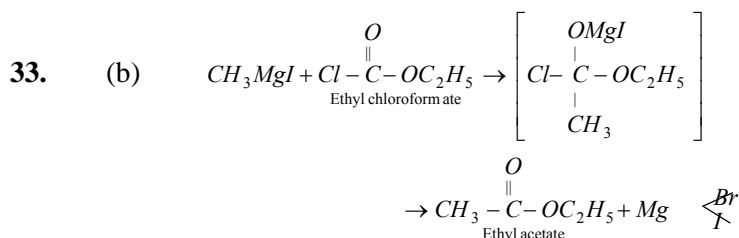
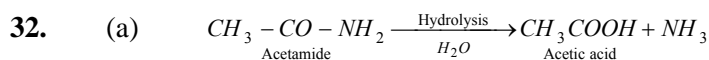
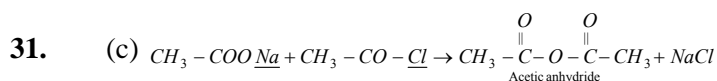


23. (b) Acetic acid freezes at $16.6^\circ C$ while water freezes at $0^\circ C$. So glacial acetic acid is obtained by crystallizing, separating and melting acetic acid.

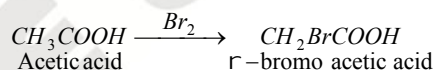


It is called esterification reaction.



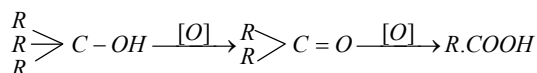


38. (c) When Cl_2 or Br_2 is react with carboxylic acid in the presence of red phosphorus then α -hydrogen of carboxylic acid is replaced by Cl_2 or Br_2

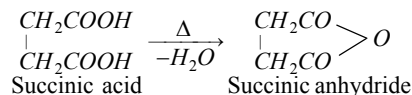


This reaction is known as Hell Volhard Zelinsky reaction.

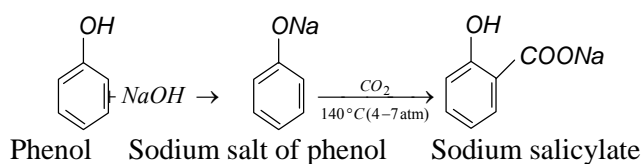
39. (b) Tertiary alcohol are not oxidised easily but on drastic conditions, these oxidise to give first ketone and then acid by losing one carbon at each step

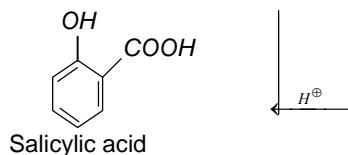


40. (a) When succinic acid is heated it forms. Succinic anhydride

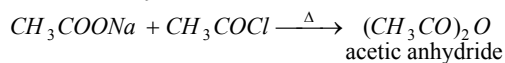


41. (d) Treatment of sodium salt of phenol with CO_2 under pressure bring about substitution of the carbonyl group $-COOH$, for the hydrogen of the ring. This is called as Kolbe's reaction



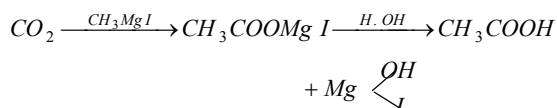


42. (b) When an acyl halide is heated with acid salt, anhydrides are formed

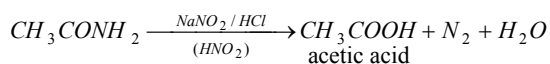


+ NaCl

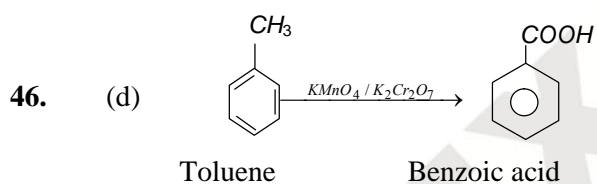
43. (b) CO_2 adds to Grignard's reagent to yield acids.



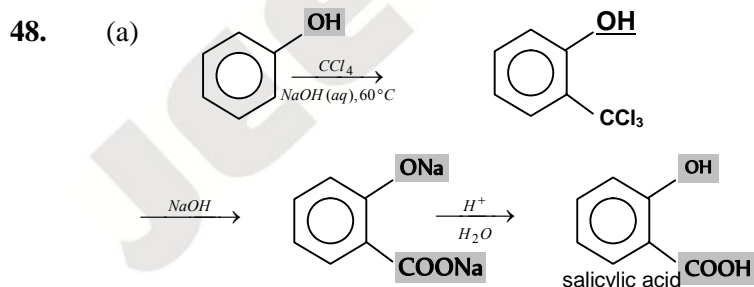
44. (a) Amide, on treating with HNO_2 , give acids.



45. (b) Aldehydes are easily oxidised to carboxylic acids on treatment with common oxidising agents like nitric acid, potassium permanganate and dichromate etc.



47. (c) This is an example of Perkin's reaction.
Therefore, (X) is Acetic anhydride.



The above given reaction is known as Reimer- Tiemann reaction.

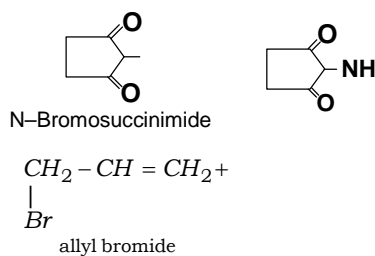
49. (a) $C_2H_5OH \xrightarrow{[O]} CH_3COOH$

EXERCISE -III

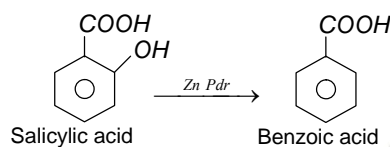
Properties of carboxylic acids and Their derivatives:

1. (c) $BrCH_2CH_2COOH$ is least acidic or has less K_a i.e., dissociation constant. It is (a) due to lesser $-I$ effect of Br than F and (b) Br atom further away from $-COOH$ group.

2. (b) $CH_3 - CH = CH_2 + N - Br \rightarrow$
Propene

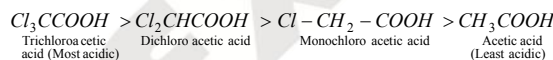


- 3. (d)**



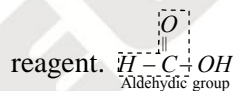
4. (b) $2CH_3COOH \xrightarrow[573\text{ K}]{MnO} CH_3COCH_3 + CO_2 + H_2O$

5. (d) Presence of $-I$ effect chlorine atom increases the acidic nature by withdrawing electrons




8. (b) The reaction of acetamide with water is an example of hydrolysis.

9. (a) Methanoic acid resemble with aldehyde due to its structure. So it reduce fehling




11. (a)
$$R-\overset{\overset{O}{\parallel}}{C}-R' \xrightarrow{LiAlH_4} R-CH_2OH + R'OH$$

Two units of alcohols

12. (d)
- 

Anisol

$+ HI \rightarrow$



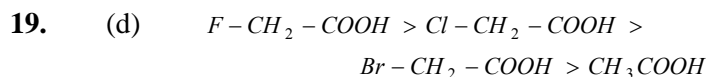
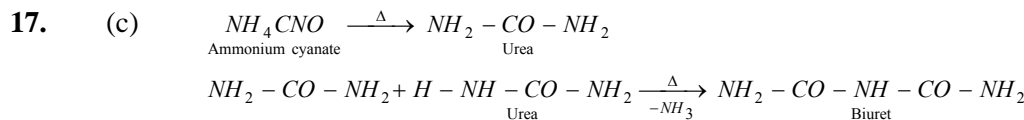
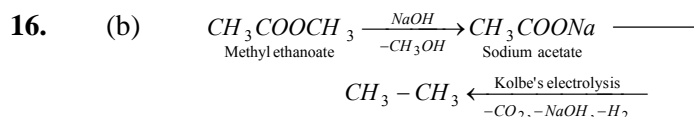
Phenol
- CH_3I
Methyl iodide

13. (b) $CH_3COOH + CH_3 - Mg - X \rightarrow CH_3 - CH_3$

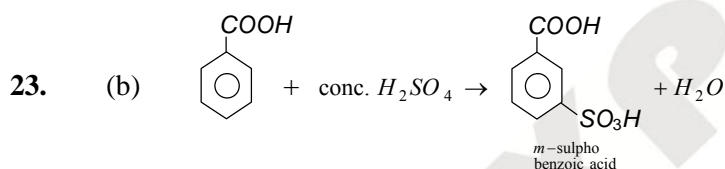
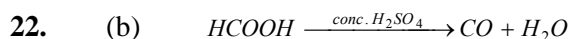
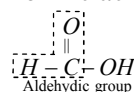
- 14.** (b) Forms *H*-bonding by means two highly electronegative atoms present in it.

15. (d)
$$\text{CH}_3\text{CH}_2\text{CONH}_2 \xrightarrow[\text{Hofmann bromamide reaction}]{\text{Br}_2 / \text{KOH}} \text{CH}_3\text{CH}_2\text{NH}_2$$

Propionamide Ethylamine

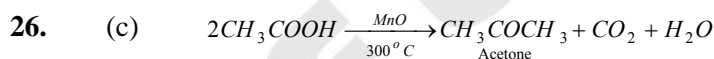


20. (d) Formic acid resemble with aldehyde due to its structure so it reduce Tollen's reagent.



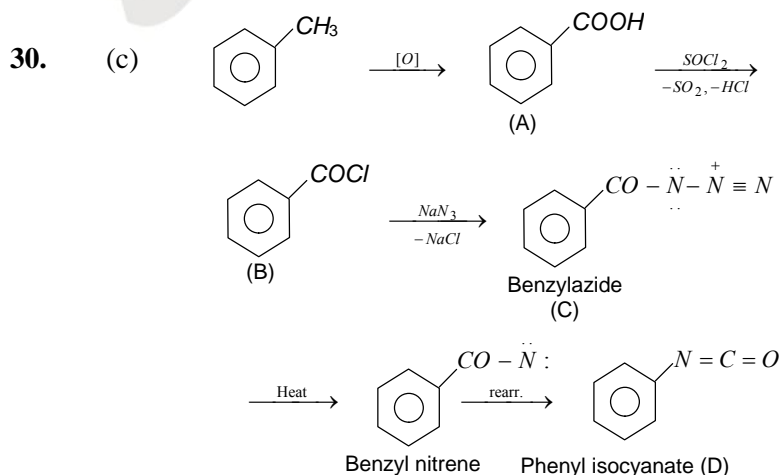
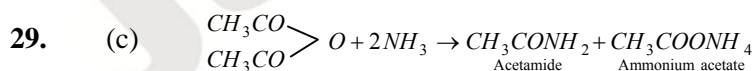
24. (d) $\text{CHF}_2 - \text{COOH}$. Difluoroacetic acid is strongest because presence of two *F* atoms increases its acidic nature.

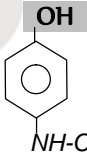
25. (c) CH_3COOH does not give silver mirror test.

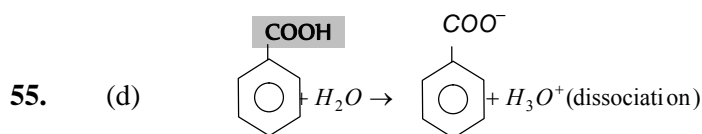


27. (b) CH_3COOH is slightly ionised than H_2SO_4 .

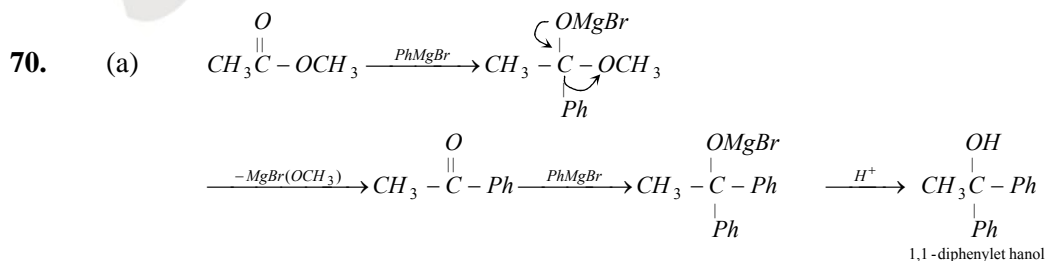
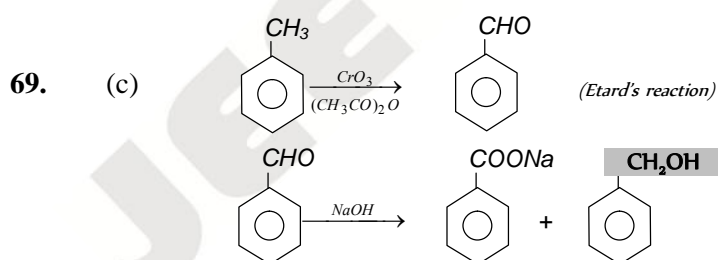
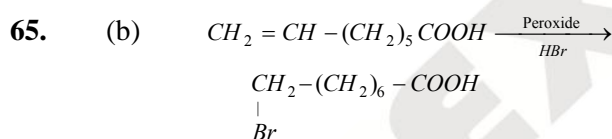
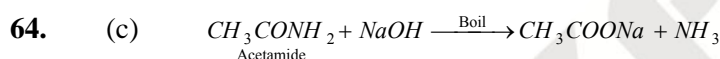
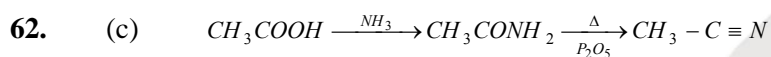
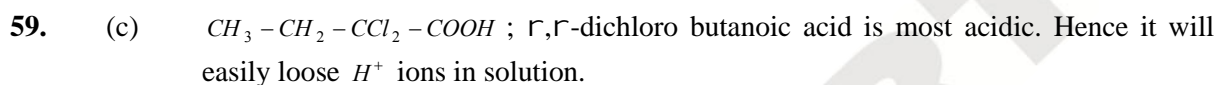
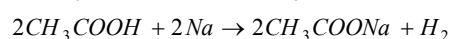
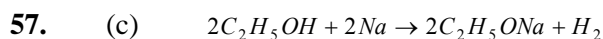
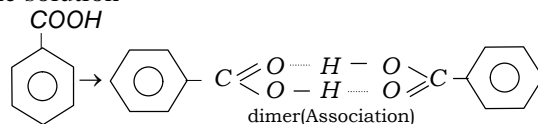
28. (c) Presence of methyl group decreases the acidic character of acetic acid due to positive inductive effect (+*I*).

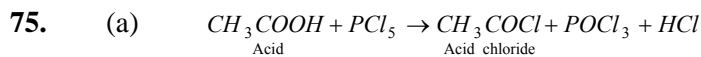
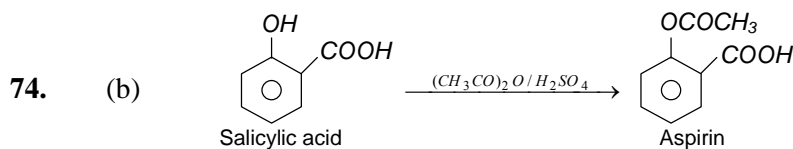


32. (c) $CH_3COOH \xrightarrow{LiAlH_4} CH_3CH_2OH$
 $CH_3CH_2OH \xrightarrow{I_2 / NaOH} CHI_3 \xrightarrow{Ag} C_2H_2$
34. (c) $HCOOH + 2Cu^{+2} \xrightarrow[\text{Solution}]{\text{Fehling}} \underset{\text{Red ppt}}{Cu_2O} + H_2O + CO_2$
 Whereas $CH_3COOH \xrightarrow[\text{Solution}]{\text{Fehling}} \text{No reaction}$
35. (d) $HCOOH + NaHCO_3 \rightarrow HCOONa + H_2O + CO_2$
 $HCHO + NaHCO_3 \rightarrow \text{No reaction}$
37. (d) $CH_3 - C \begin{matrix} \nearrow O \\ \searrow OH \end{matrix} \cdots \begin{matrix} HO \\ \nearrow O \\ \searrow \end{matrix} C - CH_3$
 Due to H-bonding
38. (c) $CH_3COOH + NaHCO_3 \rightarrow CH_3COONa + H_2O + CO_2$
39. (c) Acetic acid forms dimer in benzene due to which molecular mass becomes doubles.
42. (b) $CH_3COOH \xrightarrow{I_2 / Red p} CH_2Cl - COOH$
44. (c) $CH_3COOH \xrightarrow{\Delta / P_2O_5} (CH_3CO)_2O$
47. (c) $\begin{matrix} COOH \\ | \\ COOH \end{matrix} + KMnO_4 + H_2SO_4 \rightarrow 2CO_2 + H_2O$
 $+ K_2SO_4 + MnSO_4$
49. (c) $R - X \xrightarrow{KCN} R - CN \xrightarrow[H_2O]{NaOH} R - COONa + NH_3$
50. (c) $CH_3CH_2COOH \xrightarrow{Cl_2 / Fe} CH_3 - \underset{\substack{| \\ Cl}}{CH} - COOH$
 $CH_2 = CH - COOH \xleftarrow[\text{KOH}]{\text{Alcohol}}$
52. (b)  N-acetyl paraamino phenol
53. (b) Because it does not have α -hydrogen atom.
54. (b) Molecular Mass increases due to dimer formation $CH_3COOH \rightarrow CH_3 - \overset{\overset{O}{||}}{C} - OH \rightarrow$
 $CH_3 - C \begin{matrix} \nearrow O \\ \searrow O \end{matrix} \begin{matrix} -H-O \\ -H-O \end{matrix} C - CH_3$
 Dimer is formed



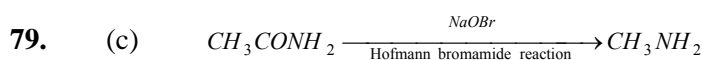
In benzene solution





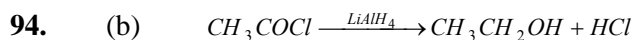
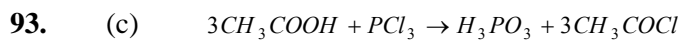
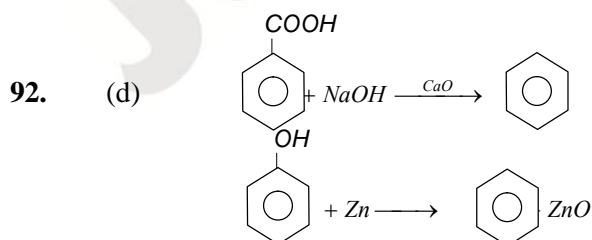
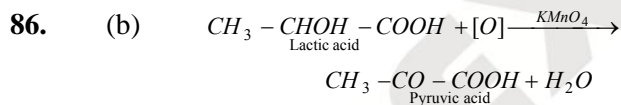
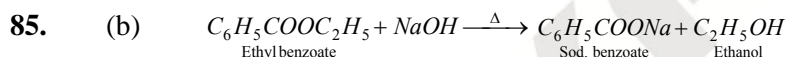
77. (c) Alcohols react with acids to form esters which have fruity smell.

78. (a) Acidity decreases with the decrease in electronegativity of halogen *i.e.*,
 $FCH_2COOH > ClCH_2COOH > BrCH_2COOH$



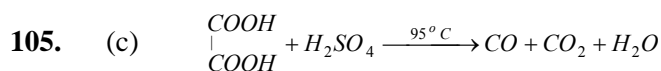
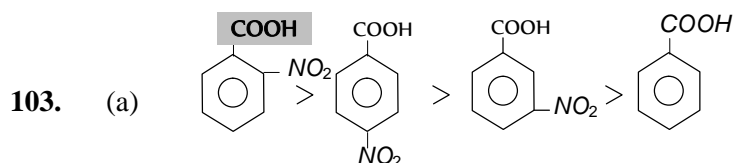
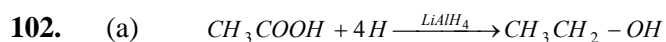
80. (d) Formic acid, $HCOOH$ shows reducing property.

81. (a) $HCOOH$ reduces ammoniacal silver nitrate solution, *i.e.*, Tollen's reagent but acetic acid does not.



99. (a) In this reaction γ -H is replaced by chlorine.

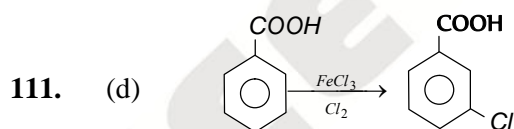
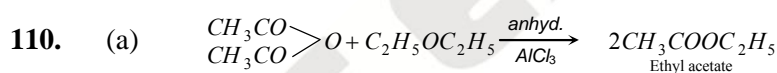
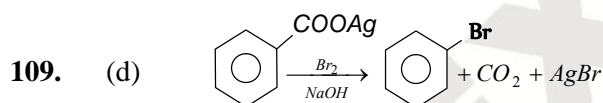
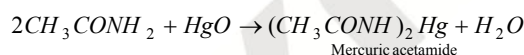
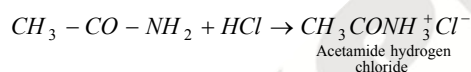
100. (a) Urea are neutral in nature in aqueous solution.



106. (a) Due to intramolecular hydrogen bonding.

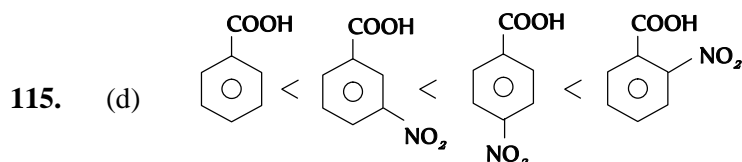


108. (d) Acetamide can behave as weak acid as well as base.



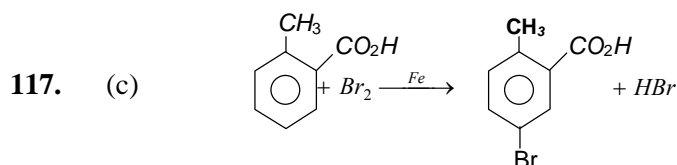
112. (b) Benzene sulphonyl chloride is called Hinsberg's reagent.

114. (a) $CH_3COOH < ClCH_2COOH < Cl_2CH_2COOH < Cl_3CCOOH$
Increasing order of acidic nature.



Electron withdrawing group, increases the acidity of benzoic acid, *O*-isomer will have higher acidity than corresponding *m* and *p*-isomer due to ortho effect.

116. (c) $CH_3COOC_2H_5 + NaCl_{(aq)} \rightarrow \text{no reaction}$
 $(CH_3COOC_2H_5 + NaCl_{(aq)})$



$-COOH$ is meta directing group

118. (d) $R-COOR' + R''OH \xrightleftharpoons{H^+} RCOOR'' + R'OH$

The exchange of alcohol residue known as alcoholysis or trans esterification

119. (b) $RCOOH + PCl_5 \rightarrow RCOCl + POCl_3 + HCl \xrightarrow{KCN} RCOCN + KCl$
 $RCOCN + KCl \xrightarrow{2H_2O} RCOCOOH + 2NH_3$
 $\xrightarrow[\text{Zn-Hg / Conc. HCl}]{\text{Clemenson reduction}} RCH_2COOH + H_2O$

120. (b) $CH_3COOH + Cl_2 \rightarrow CH_2ClCOOH + HCl$
 $CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$
 $CH_3COOH + SOCl_2 \rightarrow CH_3COCl + SO_2 + HCl$
 $3CH_3COOH + PCl_3 \rightarrow 3CH_3COCl + H_3PO_3$

121. (a) $C_6H_5COOC_2H_5 + KOH (alc) \rightarrow C_6H_5COOK + C_2H_5OH$
 $C_2H_5OH \xrightarrow{HCl} C_6H_5COOH + KCl$

122. (c) $ROH + PCl_5 \rightarrow R-Cl + POCl_3 + HCl$
 $RCOOH + PCl_5 \rightarrow RCOCl + POCl_3 + HCl$

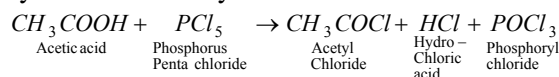
123. (a) It is picric acid because it has three $-NO_2$ group are arranged which are ortho and para position

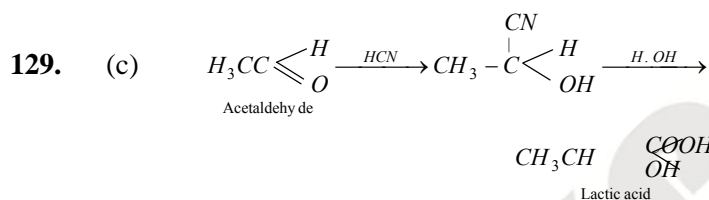
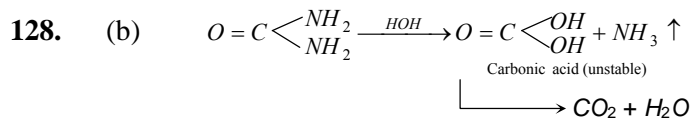
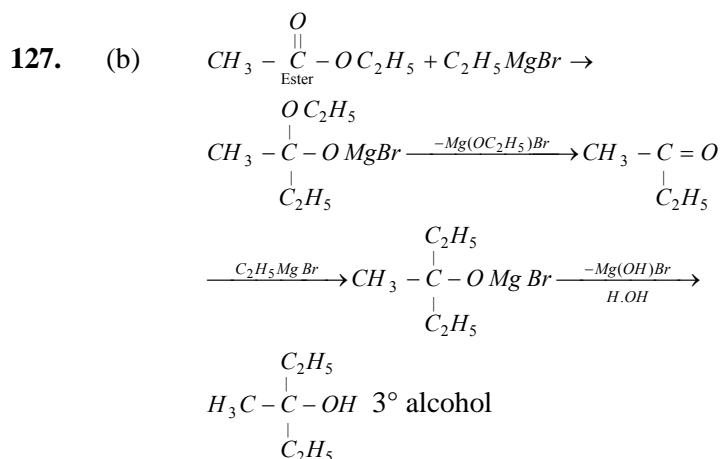
124. (d) Benedict solution is readily reduced by aldehyde. It does not oxidise anhydrides

125. (c) $CH \equiv CH + CH_3COOH \xrightarrow{[Hg^{2+}]} H_2C = CH - OCOCH_3 \xrightarrow{CH_3COOH} CH_3 - CH(O - COCH_3)_2$
 Vinylacetate Ethylidene acetate

This reaction is an example of addition reaction.

126. (a) When acetic acid is reacted with PCl_5 the product formed are acetyl chloride, phosphoryl chloride and hydrochloric acid

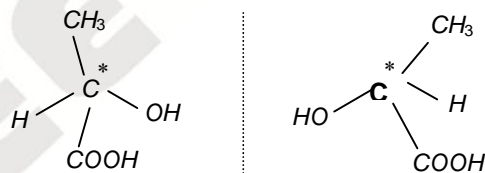




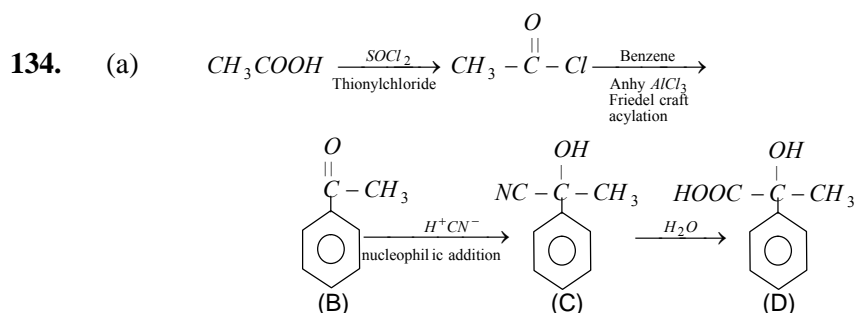
130. (a) Vinegar is 6 – 10% aqueous solution of acetic acid

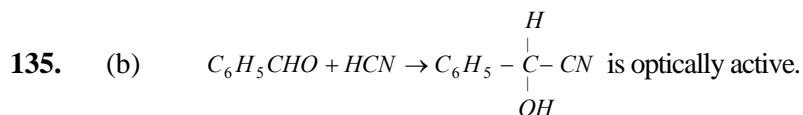
131. (a) All esters are pleasant liquid having pleasant fruity smell. Many of them are used in perfumery, e.g. Benzyl acetate etc.

132. (a) Lactic acid has one asymmetric (chiral) carbon atom, hence it has ($2^n = 2$) optical isomers.



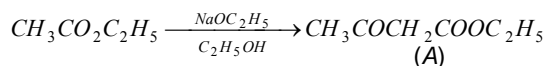
133. (a) 4-methyl benzene sulphonic acid is stronger than acetic acid thus it will release acetic acid from sodium acetate.



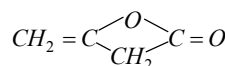


137. (c) Claisen condensation

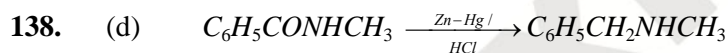
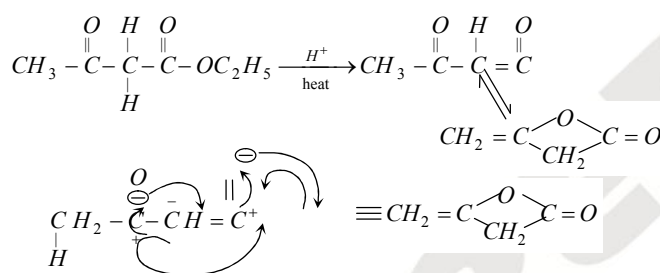
step I



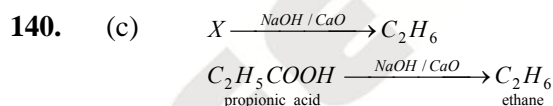
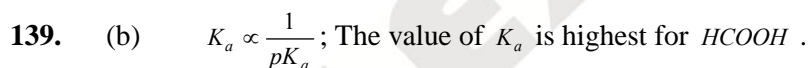
step II \downarrow heated in presence of acid



Step II :

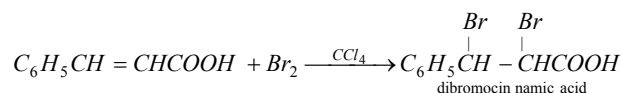


This reaction is known as Clemmenson reduction.



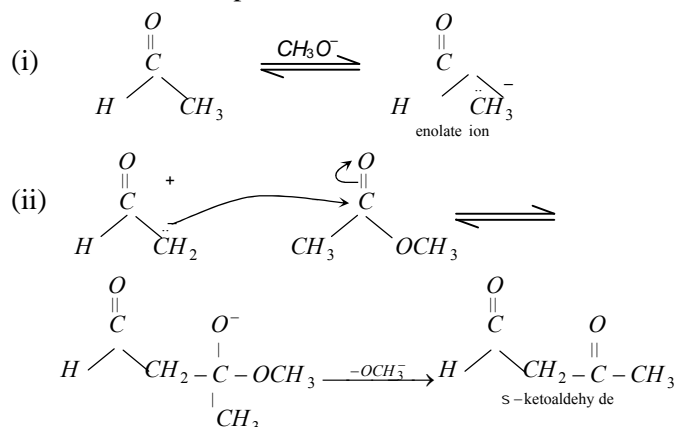
141. (a) Glycine is an amphoteric acid as it contains both acidic as well as basic groups.

142. (a) Cinnamic acid reacts with bromine in carbon tetrachloride to give dibromocinnamic acid.



143. (a) Of all the acid derivatives, acid chlorides, i.e. CH_3COCl is most reactive. The order of reactivity of acid derivatives decreases in the following order,
 $RCOCl > (RCO)_2O > RCOOR > RCONH_2$.

144. (c) Reaction can be explained as follows

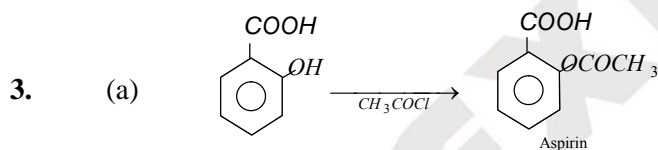


145. (a) $\text{CH}_3\text{COOH} + \text{NaHCO}_3 \rightarrow \text{CH}_3\text{COONa} + \text{CO}_2 + \text{H}_2\text{O}$

146. (d) $\text{RCOOH} \xrightarrow{\text{P}_2\text{O}_5} \text{RCO} > \text{O} + \text{H}_2\text{O}$
 P_2O_5 acts as a dehydrating agent.

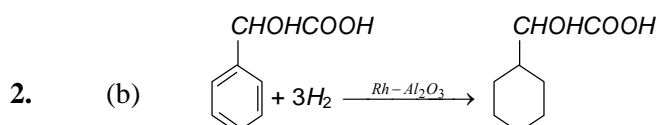
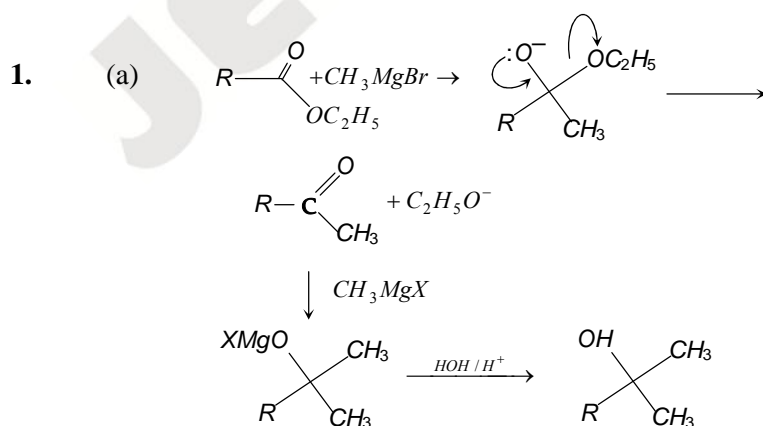
EXERCISE -IV

Uses of Carboxylic Acids and Their Derivatives:



EXERCISE -V

Critical Thinking Questions:



3. (d) $\begin{array}{c} \text{CH}_3\text{CO} \swarrow \\ \text{C} - \text{H} \\ \nwarrow \text{CH}_3\text{CO} \\ \downarrow \text{OCCCH}_3 \end{array}$ So most acidic in nature.
4. (c) Anion HCOO^- has two resonating structure (identical).
 $\begin{array}{c} \text{O} \\ \parallel \\ \text{H} - \text{C} - \text{O}^- \end{array} \leftrightarrow \begin{array}{c} \text{O}^- \\ | \\ \text{H} - \text{C} = \text{O} \end{array}$
5. (a) Since a single alkyl halide is formed on treatment with HI , it must be a symmetrical ether *i.e.*, ethoxyethane.
 $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5 + 2\text{HI} \rightarrow 2\text{C}_2\text{H}_5\text{I} + \text{H}_2\text{O}$
6. (b) $\text{CH}_2 = \text{CH} - \text{COOH} \xrightarrow{\text{LiAlH}_4} \text{CH}_2 = \text{CH} - \text{CH}_2\text{OH} + \text{H}_2\text{O}$
7. (a) $\text{CH}_3\text{COOH} + \text{PCl}_5 \rightarrow \text{CH}_3\text{COCl} \xrightarrow[\text{anh. AlCl}_3]{\text{C}_6\text{H}_6}$
 $\text{CH}_3\text{COC}_6\text{H}_5 \xrightarrow[\text{Ether}]{\text{C}_2\text{H}_5\text{MgBr}} \text{CH}_3 - \overset{\text{C}_2\text{H}_5}{\underset{|}{\text{C}}}(\text{OH})\text{C}_6\text{H}_5$
8. (d) Resonance stabilization of their conjugate base *i.e.*, carboxylate ion.
9. (a) $\text{R} - \text{CH}_2\text{CH}_2\text{OH} \xrightarrow{\text{PBr}_3} \text{R} - \text{CH}_2\text{CH}_2 - \text{Br}$
 $\xrightarrow{\text{KCN}} \text{R} - \text{CH}_2 - \text{CH}_2 - \text{CN} \xrightarrow{\text{H}_3\text{O}^+} \text{R} - \text{CH}_2 - \text{CH}_2\text{COOH} + \text{NH}_3$
10. (d) $\text{CH}_3\text{CH}_2\text{COOH}(\text{aq}) + \text{NaHCO}_3(\text{aq}) \rightarrow \text{CH}_3\text{CH}_2\text{COONa} + \text{CO}_2 + \text{H}_2\text{O}$
 Propionic acid sod. bicarbonate
11. (c) $\text{C}_6\text{H}_5\text{COOH} + \text{SOCl}_2 \rightarrow \text{C}_6\text{H}_5\text{COCl} + \text{SO}_2 + \text{HCl}$
 Benzoic acid Benzoyl chloride
12. (b) $-\text{COOH}$ and $-\text{OH}$ group form the hydrogen bond by which they have high boiling point. $-\text{COOH}$ group show strong hydrogen bonding so it form dimer and have more boiling point than $-\text{OH}$ group. While $-\text{CHO}$ group do not form hydrogen bond. Thus the reactivity order are as $3 > 1 > 2$.
13. (c) CaC_2O_4 is a salt of oxalic acid which is more acidic than acetic acid, so it is insoluble in acetic acid.
14. (d) $-\text{COOH}$ and COCH_3 are meta directing group due to the presence of $-\overset{\text{O}}{\parallel}{\text{C}}-$, similarly CN is also meta directing due to the presence of multiple bond while NHCOCH_3 is ortho/para directing group because of less electron density over $-\overset{\text{O}}{\parallel}{\text{C}}-$ group.
15. (c) Iodoform test is given by all the compounds having $\text{CH}_3 - \overset{\text{O}}{\parallel}{\text{C}} -$ or $\text{CH}_3 - \overset{\text{O}}{\underset{\text{OH}}{\text{C}}} -$ group.

16. (c)
$$C_2H_5-\underset{\begin{array}{c} || \\ O \end{array}}{C}-CH_3 + I_2 + NaOH \rightarrow C_2H_5CO_2^-Na^+ + CHI_3$$
$$C_2H_5CO_2^-Na^+ \xrightarrow{H^+} C_2H_5COOH + Na^+$$
17. (c) Formic acid can not be prepared by grignard's reagent. Higher acids are prepared by the reaction of CO_2 on grignard's reagent
- $$\overset{u-}{R} \overset{u+}{Mg} X + \overset{u+}{C} \begin{array}{l} \swarrow \\ \searrow \end{array} \begin{array}{l} Ou- \\ Ou- \end{array} \rightarrow R-\underset{\begin{array}{c} || \\ O \end{array}}{C}-O \overset{u+}{Mg} X \xrightarrow{H.OH} R-\underset{\begin{array}{c} O \\ || \\ \text{acid} \end{array}}{C}-OH + Mg(OH)X$$

EXERCISE - VI

Assertion & Reason

- (a) Carboxylic acid exist as dimer due to the formation of hydrogen bonding.

$$\begin{array}{c}
 R-C \begin{array}{l} \nearrow O \cdots H-O \\ \searrow O \cdots H-O \end{array} \nearrow C-R \\
 \text{H-bonding (dimer)}
 \end{array}$$
- (c) Trichloro acetic acid is stronger than acetic acid because the electron withdrawing group withdraw electrons from the carboxylate base and thus increasing the acid strength.

$$\begin{array}{ccc}
 \begin{array}{c} Cl \\ | \\ Cl-C \leftarrow C \begin{array}{l} O \\ || \end{array} \leftarrow OH \\ | \\ Cl \end{array} & & CH_3 \rightarrow \begin{array}{c} O \\ | \\ C \end{array} \rightarrow OH \\
 -I \text{ effect} & & +I \text{ effect} \\
 \text{(Stronger acid)} & & \text{(Weaker acid)}
 \end{array}$$
- (c) Carboxylic acids ($RCOOH$) dissolves in water due to hydrogen bonding between H -atom of $-COOH$ group and O -atom of water. As alkyl portion R -is non polar and lyophobic, this effect predominates as $-R$ gets larger (over five carbon atoms).
- (b) As carboxylic acids are resonance stabilized they do not contain true carbonyl group as is present in carbonyl compounds.

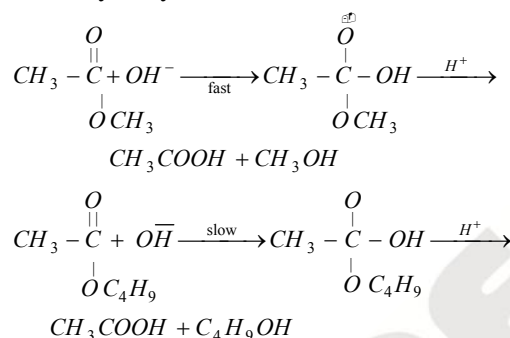
$$\begin{array}{ccc}
 \begin{array}{c} :\ddot{O}: \\ || \\ R-C-\ddot{O}-H \end{array} & \leftrightarrow & \begin{array}{c} :\ddot{O}: \\ | \\ R-C=\overset{+}{O}-H \end{array}
 \end{array}$$
- (c) Formic acid is stronger than acetic acid

$$\begin{array}{ccc}
 H-C \begin{array}{l} \nearrow O \\ \searrow O \end{array} -OH & \rightleftharpoons & H-C \begin{array}{l} \nearrow O \\ \searrow O \end{array} -O^- + H^+ \\
 CH_3-C \begin{array}{l} \nearrow O \\ \searrow O \end{array} -OH & \rightleftharpoons & CH_3-C \begin{array}{l} \nearrow O \\ \searrow O \end{array} -O^- + H^+
 \end{array}$$

Presence of CH_3 group in acetate ion shows $+I.E$, and there by intensifying charge on O^- of acetate ion than formate ion or acetate ion is destabilized. Thus

formate ion is more stable than acetate ion or $HCOOH$ loses proton more easily than CH_3COOH .

6. (e) Both fumaric and maleic acids have two ionisable H^+ i.e. protons. The maleate monoanion shows intramolecular H -bonding and thus requires more energy to give maleate dianion. It is therefore second dissociation of fumaric acid is more than maleic acid since former does not show intramolecular H -bonding.
7. (c) Larger is the size of alkyl group of ester, greater is the steric effect and thus lesser will be rate of hydrolysis.



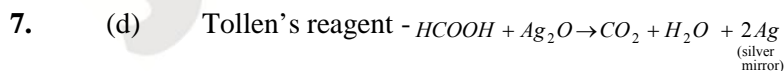
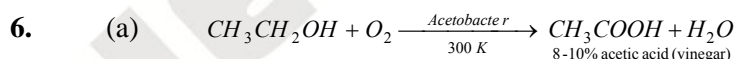
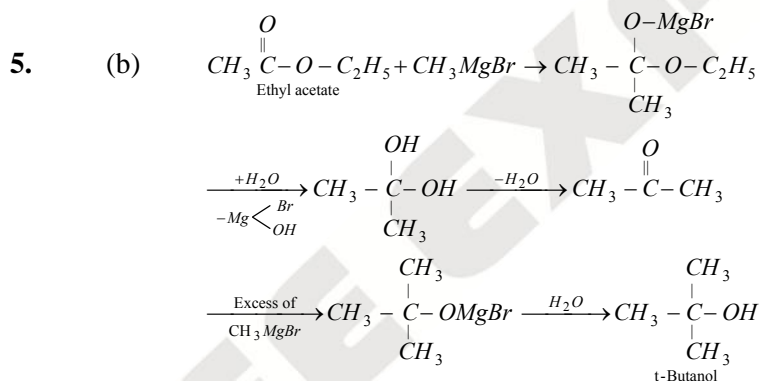
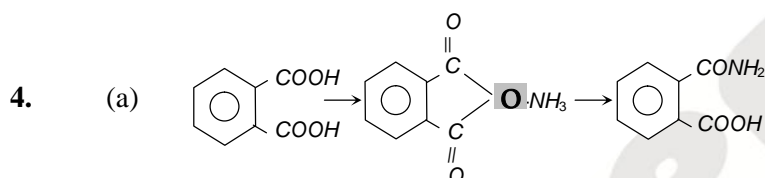
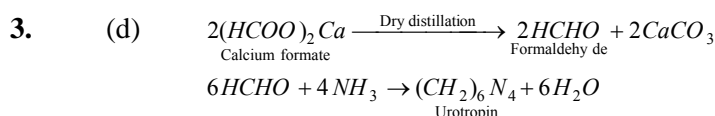
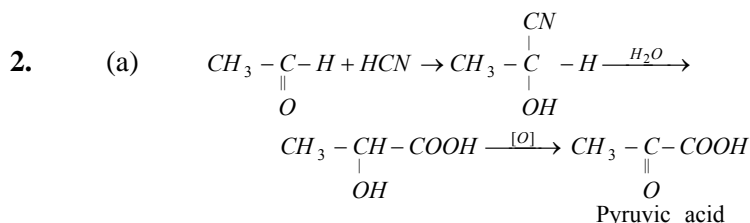
8. (e) The melting point of an aliphatic carboxylic acid containing an even number of carbon atoms is higher than the next lower and next higher homologue containing odd number of carbon atoms.
9. (e) Electron withdrawing groups increase the acidity of carboxylic acids by stabilising the conjugate base through delocalisation of the negative charge by inductive and resonance effects.
10. (a) The larger the electron withdrawing inductive effect the greater is the acidity.
11. (c) In aminoacetic acid, NH_2 group is electron repelling in nature.
12. (b) Boiling points of carboxylic acids are higher due to their tendency to associate and form dimers to a greater extent by hydrogen bonding.
13. (a) Both formic acid and oxalic acid behave as reducing agent and decolourise acidified $KMnO_4$ solution.

$$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$
14. (c) Esters containing α -hydrogens on treatment with a base form a carbanion which brings about nucleophilic acyl substitution at the carbonyl group of the other molecule of the ester to form β -keto esters.

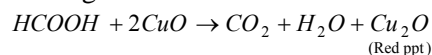
Self Evaluation Test

ANSWER & SOLUTIONS

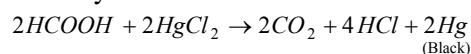
1. (a) Phenol is a weaker acid than carboxylic acids.



Fehling solution -



Mercury chloride -



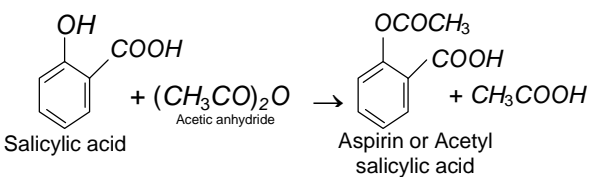
8. (a) Activated charcoal adsorbed the impurity of acetic acid by which the concentration of acetic acid solution decrease.

9. (d) Intermolecular hydrogen bonding leads to dimerisation of carboxylic acid in non-aqueous solvents.

10. (c) $\text{NaNO}_2 + \text{HCl} \rightarrow \text{HNO}_2 + \text{NaCl}$
 $\text{H}_2\text{NCONH}_2 + \text{HNO}_2 \rightarrow \text{CO}_2 + \text{NH}_3 + \text{H}_2\text{O} + \text{N}_2$
 Urea
 CO_2 evolve with brisk effervescence.

11. (b) It is known as Schotten Baumann reaction.
 $\text{C}_6\text{H}_5\text{NH}_2 + \text{ClCOC}_6\text{H}_5 \xrightarrow{\text{NaOH}} \text{C}_6\text{H}_5\text{NHCOC}_6\text{H}_5 + \text{HCl}$
 Aniline Benzoyl chloride Benzanilide

12. (a) Due to $-I$ effect of three F atom CF_3COOH is a strong acid.

13. (d) 

14. (c) $\begin{array}{c} \text{COOH} \\ | \\ \text{COOH} \\ \text{Oxalic acid} \end{array} + 4[\text{H}] \xrightarrow[\text{H}_2\text{SO}_4]{\text{Zn}} \begin{array}{c} \text{CH}_2\text{OH} \\ | \\ \text{COOH} \\ \text{Glycolic acid} \end{array} + \text{H}_2\text{O}$

15. (b) Fat is the ester of higher acids & glycerol.

16. (a) $2\text{K} + 2\text{NH}_3 \rightarrow 2\text{KNH}_2 + \text{H}_2$

17. (a) $(\text{Cl}_3\text{C}-\text{COOH})$ Trichloroacetic acid has least pK_a value and is most acidic.
