

## Carboxylic Acids and their derivatives Part 2

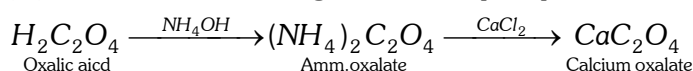
(ix) **Reaction with Glycerol** : At 100° – 110°C, formic acid is formed. At 260°, allyl alcohol is formed.

(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  $\text{NaHCO}_3$ .
- (iii) The neutral solution gives a white precipitate with calcium chloride solution. It is insoluble in acetic acid.

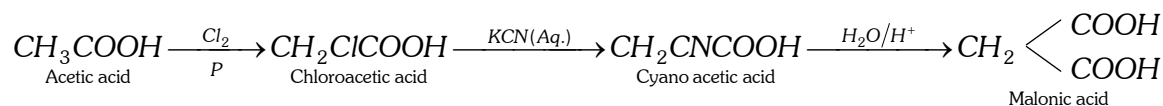


- (iv) Oxalic acid decolourises hot potassium permanganate solution having dilute sulphuric acid.
- (v) With hot conc.  $\text{H}_2\text{SO}_4$ , it evolves carbon monoxide which burns with blue flame.

**Malonic Acid or Propane-1,3-Dioic Acid** :  $\text{CH}_2 \begin{matrix} \swarrow \text{COOH} \\ \searrow \text{COOH} \end{matrix}$  or  $\text{CH}_2(\text{COOH})_2$  or  $(\text{C}_3\text{H}_4\text{O}_4)$

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

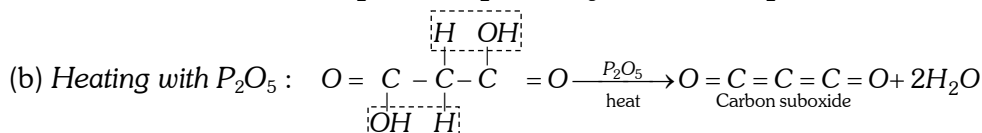
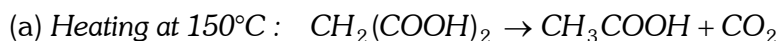


(2) **Physical Properties**

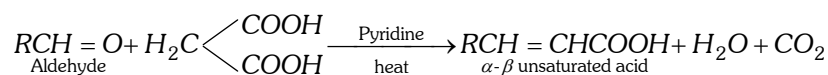
- (i) It is a white crystalline solid.
- (ii) It's melting point is 135°C.
- (iii) It is soluble in water and alcohol but sparingly soluble in ether.

(3) **Chemical Properties**

(i) **Action of heat**



(ii) **Reaction with aldehyde** : With aldehydes,  $\alpha$ - $\beta$  unsaturated acids are formed.



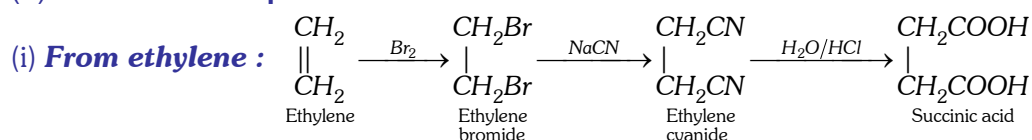
(4) **Uses** : Its diethyl ester (malonic ester) is a valuable synthetic reagent for preparation of a variety of carboxylic acids.

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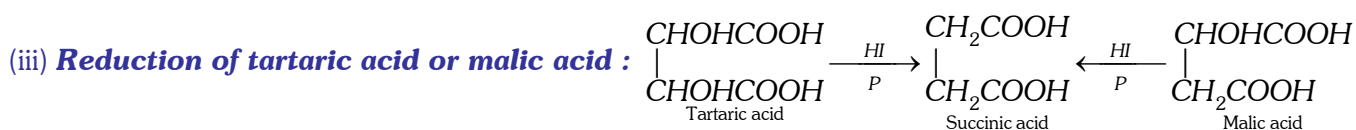
**Succinic Acid or Butane-1,4-Dioic Acid :**  $\begin{array}{c} \text{CH}_2\text{-COOH} \\ | \\ \text{CH}_2\text{-COOH} \end{array}$  or  $(\text{CH}_2)_2(\text{COOH})_2$  or  $(\text{C}_4\text{H}_6\text{O}_4)$

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



**Note :** \* This is an industrial method.



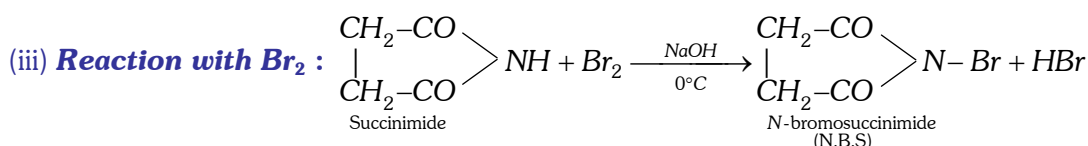
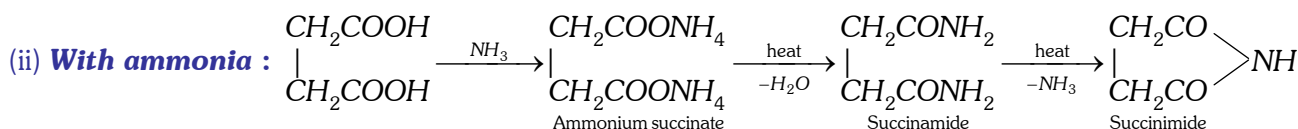
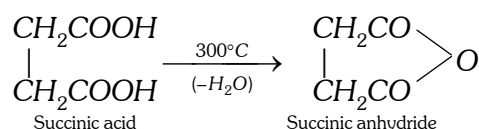
### (2) Physical properties

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

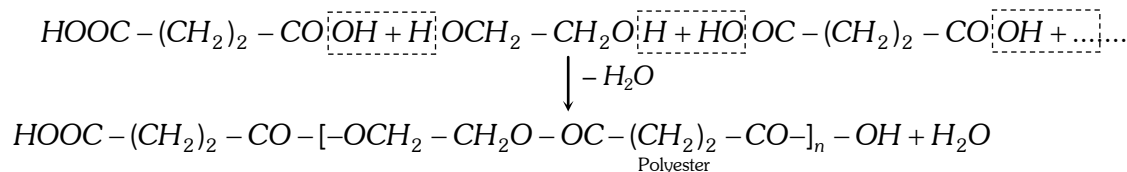
(ii) It is less soluble in water. It is comparatively more soluble in alcohol.

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

#### (i) Action of heat : At 300°C



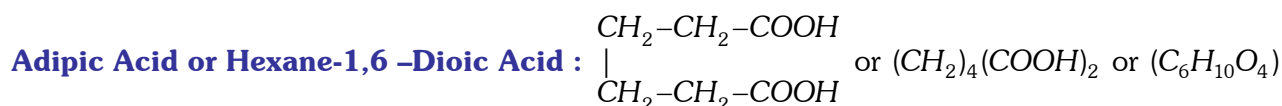
#### (iv) Reaction with ethylene glycol



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.

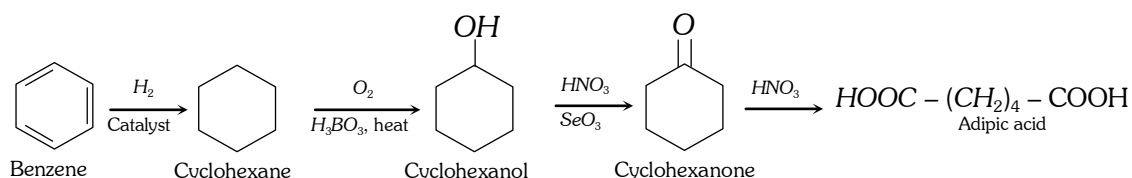
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It was first obtained by the oxidation of fats (Latin, adeps = fat.)

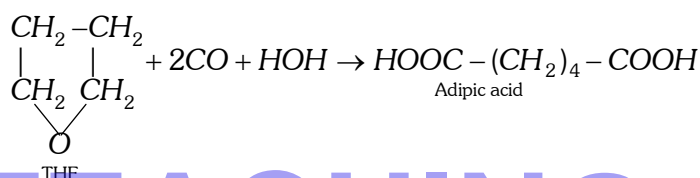
### (1) Methods of Preparation

#### (i) From benzene



**Note :** ✪ It is an industrial method.

#### (ii) From tetrahydrofuran (THF)



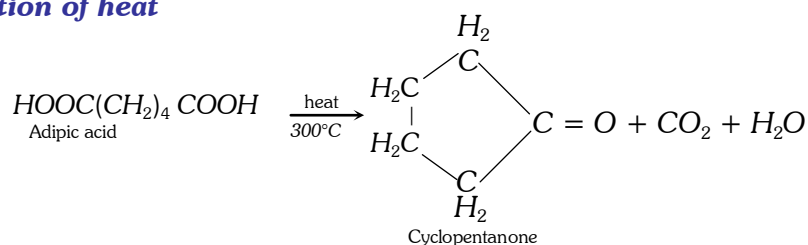
### (2) Physical Properties

- (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.

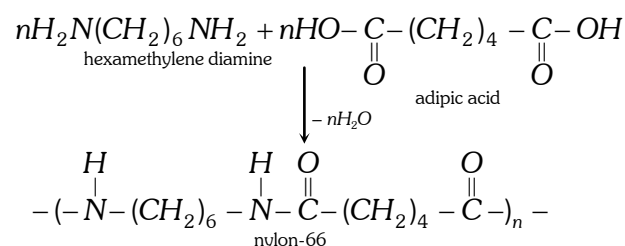
### (3) Chemical Properties

It shows all the general reaction of dicarboxylic acids.

#### (i) Action of heat



#### (ii) Formation of Nylon-66 [Reaction with hexa methylene diamine]



**(4) Uses :** It is used in the manufacture of several polymers.

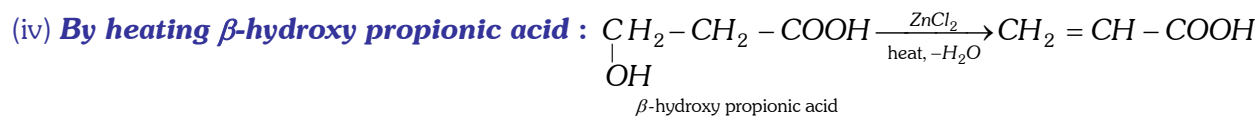
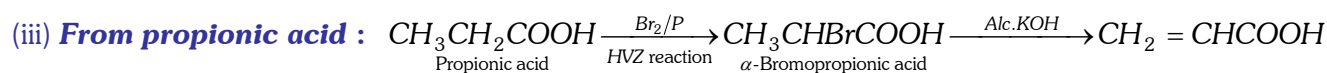
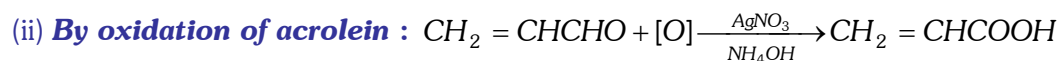
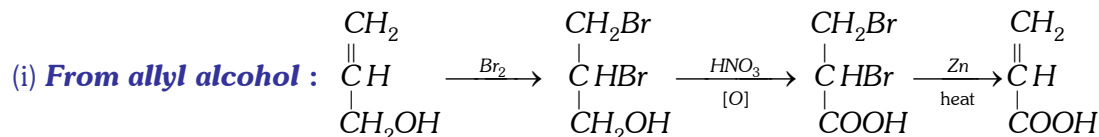
**Unsaturated Acids :** When the double bond presents in the carbon chain of an acid is called unsaturated acid.

## Carboxylic Acids and their derivatives Part 2

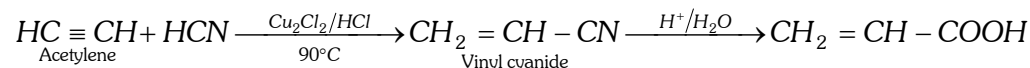


**Acrylic Acid or Prop-2-Enoic Acid** :  $CH_2 = CH - COOH$  or  $(C_3H_4O_2)$

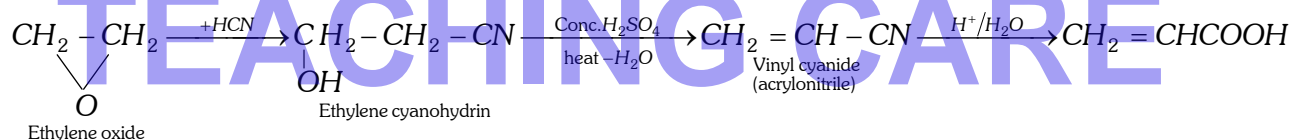
### (1) Methods of Preparation



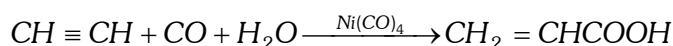
### (v) From vinyl cyanide



### (vi) From ethylene cyanohydrin



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



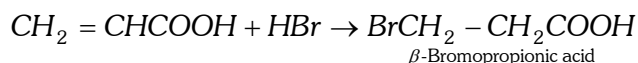
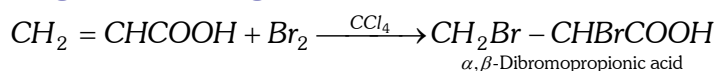
### (2) Physical Properties

- 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.

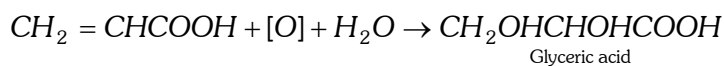
### (3) Chemical Properties



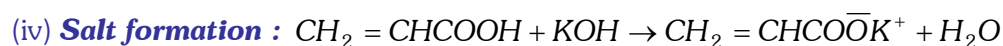
(ii) **With halogens and halogen acids** : Markownikoff's rule is not followed.



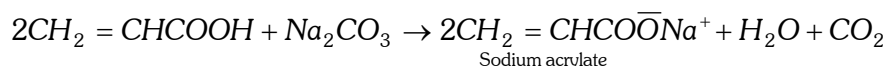
(iii) **Oxidation** : In presence of dilute alkaline  $KMnO_4$ .



**Note** : • On vigorous oxidation, oxalic acid is formed.



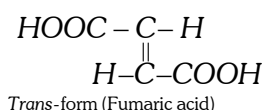
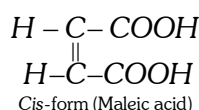
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(4) **Uses** : Its ester are used for making plastics such as Lucite and plexiglass.

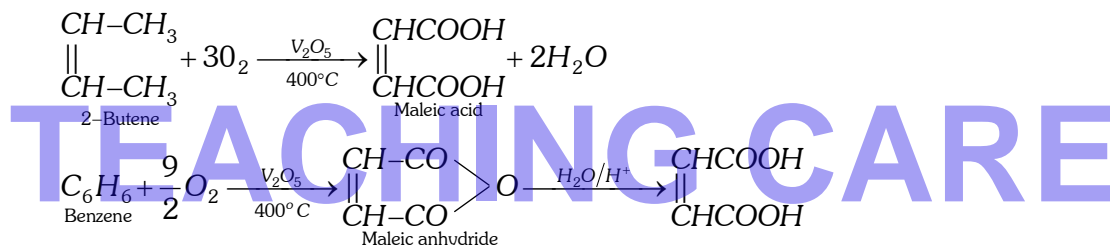
### Unsaturated Dicarboxylic Acids.

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

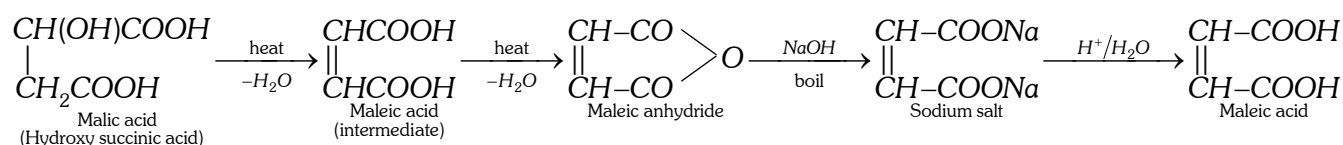


#### (1) Methods of Preparation of Maleic Acid

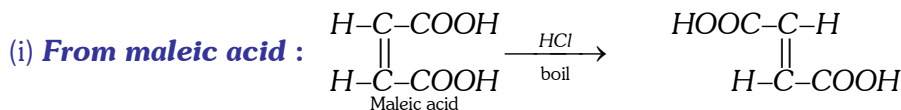
(i) **By catalytic oxidation of 2-butene or benzene**



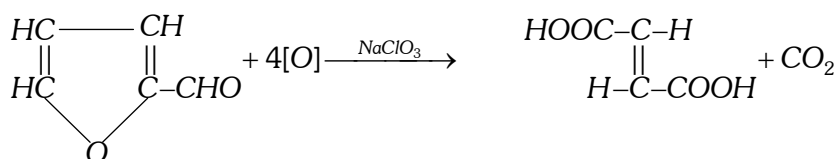
(ii) **From malic acid :**



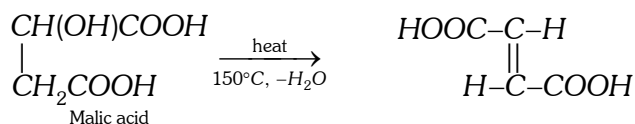
#### (2) Methods of Preparation of Fumaric Acid



(ii) **By oxidation of furfural with sodium chlorate**

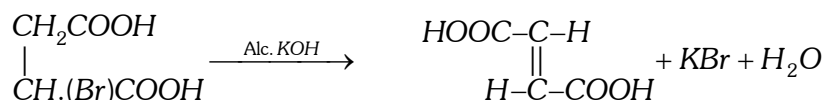


(iii) **By heating malic acid at about  $150^\circ\text{C}$  for long time**



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(iv) **By heating bromosuccinic acid with alcoholic potash** : By heating bromosuccinic acid with alcoholic potash.



### (4) Physical Properties

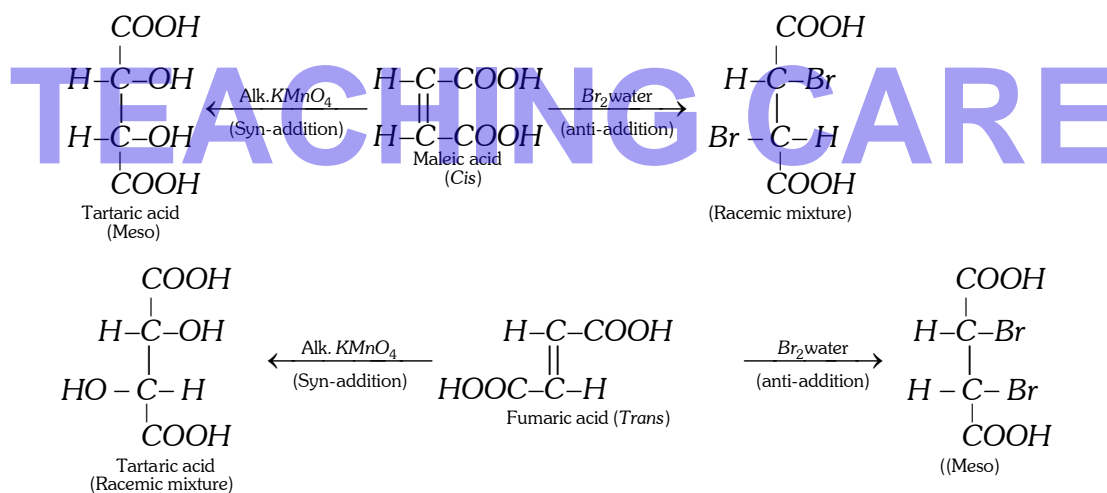
- (i) Both are colourless crystalline solids. Both are soluble in water.
- (ii) The melting point of maleic acid (130.5°C) is lower than the melting point of fumaric acid (287°C).

### (5) 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  $\text{KMnO}_4$  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.

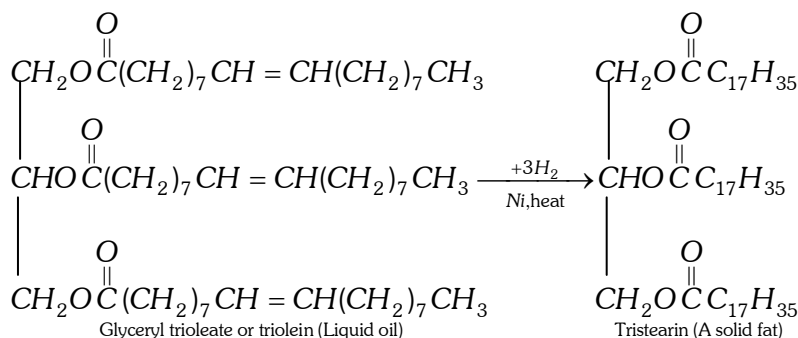
Name of acids	Source	Molecular formula
<b>Palmitic acid</b>	<b>Palm oil,</b>	$\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$
<b>Stearic acid</b>	<b>Stear (meaning tallow)</b>	$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$
<b>Oleic acid</b>	<b>Olive oil.</b>	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$

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.

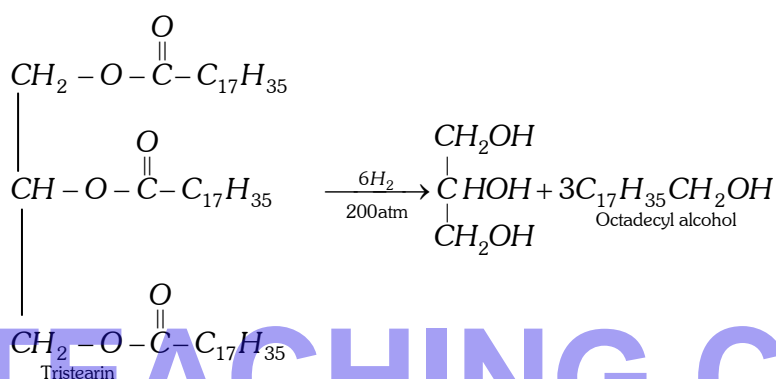


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(ii) **Hydrogenation** : In the presence of finely divided nickel, the hydrogenation process is called hardening of oils.



(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

$$\text{refluxing a Saponification number of fat or oil} = \frac{168,000}{M}$$

$M = \text{molecular mass}$

(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.



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(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

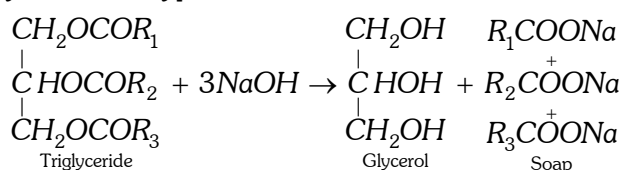
- (i) Many oils and fats are used as food material.
- (ii) Oils and fats are used for the manufacture of glycerol, fatty acids, soaps, candles, vegetable ghee, margarine, hair oils, etc.
- (iii) Oils like linseed oil, tung oil, etc., are used for the manufacture of paints, varnish, etc.
- (iv) Castor 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.

### (6) 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 <sub>12</sub> to C <sub>16</sub> .
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.

(7) **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 :

- (i) The cold process
- (ii) The hot process
- (iii) Modern process

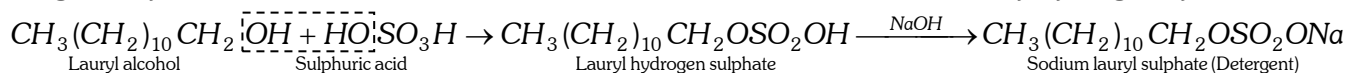
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**(8) Synthetic Detergents :** The synthetic detergents or **Syndets** are substitutes of soaps. They have cleansing power as good or better than ordinary soaps. Like soap, they contain both hydrophilic (water soluble) and hydrophobic (oil-soluble)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



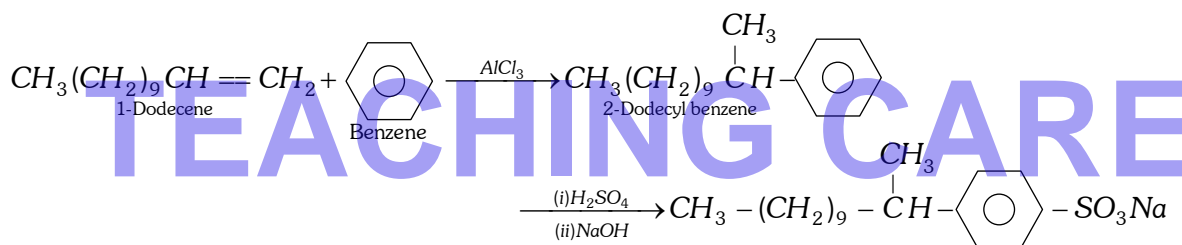
Some of the detergents used these days are given below:

**(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,  $C_{16}H_{33}OSO_2ONa$  and sodium stearyl sulphate,  $CH_3(CH_2)_{16}CH_2OSO_3Na$ . Unlike ordinary soaps, they do not produce  $OH^-$  ions on hydrolysis and thus can be safely used for woollen garments.

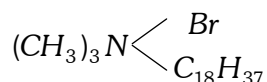
**(ii) Sodium alkyl benzene sulphonates :** Sodium *p*-dodecyl benzene sulphonate acts as a good detergent. It is most widely used since 1975.



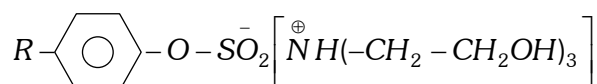
Sodium dodecyl benzene sulphonate (S.D.S.)

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

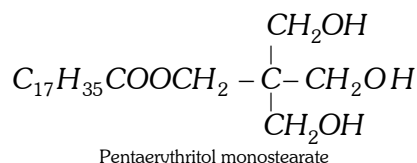
**(iii) Quaternary ammonium salts :** Quaternary ammonium salts with long chain alkyl group have been used as detergents, e.g., trimethyl stearyl ammonium bromide.



(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.

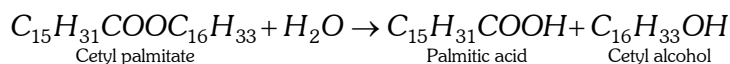
(i) These can be used both in soft and hard waters as the calcium and magnesium ions present in hard water form soluble salts with detergents. Ordinary soap cannot be used in hard water.

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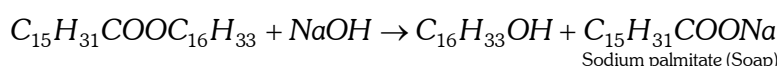
(ii) The aqueous solution of detergents are neutral. Hence these can be used for washing all types of fabrics without any damage. The solution or ordinary soap is alkaline and thus cannot be used to wash delicate fabrics.

(9) **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 ( $C_{25}H_{51}COOH$ ), melissic acid ( $C_{30}H_{61}COOH$ ) and cetyl alcohol ( $C_{16}H_{33}OH$ ), ceryl alcohol ( $C_{26}H_{53}OH$ ), myricyl alcohol ( $C_{30}H_{61}OH$ ), 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,  $C_{25}H_{51}COOC_{30}H_{61}$

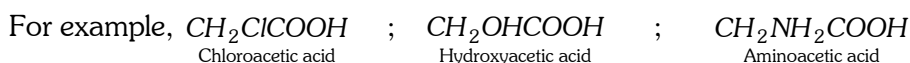
Waxes are used in the manufacture of candles, polishes, inks, water proof coating and cosmetic preparations.

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.

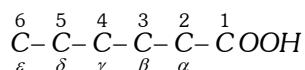
Candles are prepared by mixing paraffin wax (90%) with higher fatty acids like stearic and palmitic. The fatty acids are added to paraffin wax as to give strength to candles. The mixture is melted and poured into metal tubes containing stretched threads. On cooling candles are obtained.

### 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.



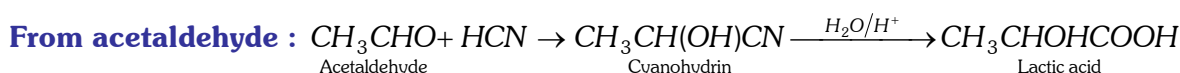
The position of the substituents on the carbon chain are indicated by Greek letters or numbers.



#### Lactic Acid or $\alpha$ -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 acidi lactici*-sour milk) in presence of  $CaCO_3$ .

#### (1) Method of Preparation



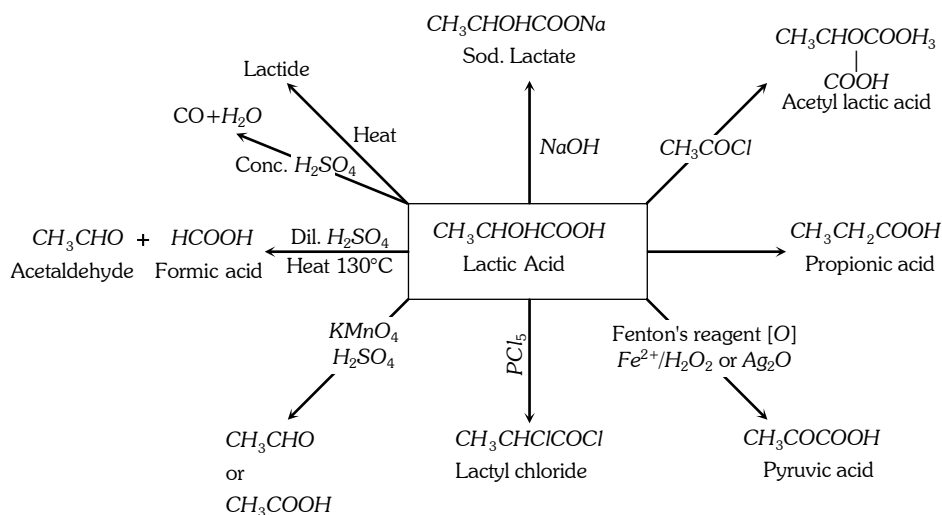
## Carboxylic Acids and their derivatives Part 2

### (2) Physical Properties

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

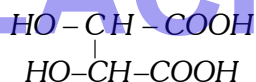
It is hygroscopic and very soluble in water. It is optically active and exists in three distinct forms.

(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.

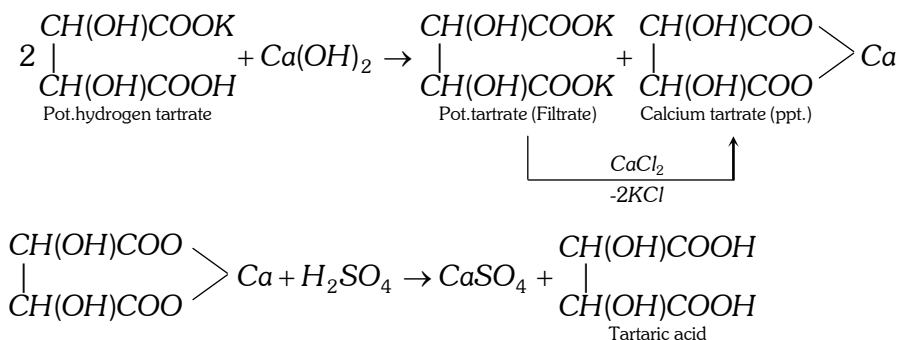
**Tartaric Acid. Or  $\alpha, \alpha'$ -Dihydroxy succinic acid or 2,3-Dihydroxy-Butane-1,4-Dioic acid**



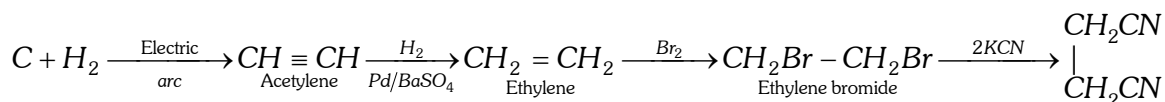
It is found as free or potassium salt in grapes, tamarind, and berries.

### (1) Methods of Preparation

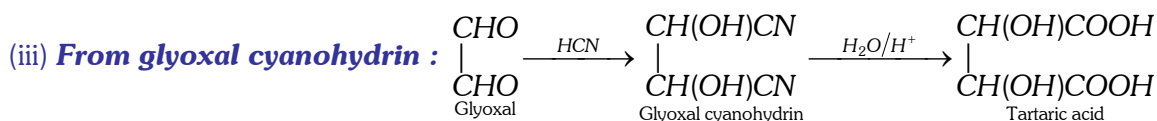
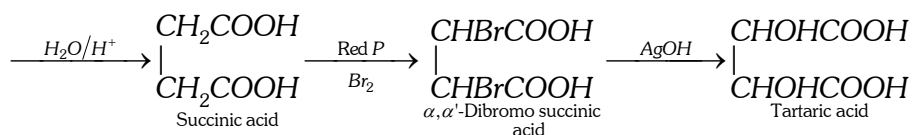
(i) **Argol** which separates as a crust during fermentation of grape juice is impure potassium hydrogen tartrate. Argol is boiled with limewater. Calcium tartrate is precipitated which is filtered. The solution contains potassium tartrate which is also precipitated by addition of  $\text{CaCl}_2$ . The calcium salt is then decomposed with calculated quantity of dilute  $\text{H}_2\text{SO}_4$ . The precipitate ( $\text{CaSO}_4$ ) is filtered and the filtrate on concentration gives the crystals of tartaric acid.



### (ii) Synthetic method

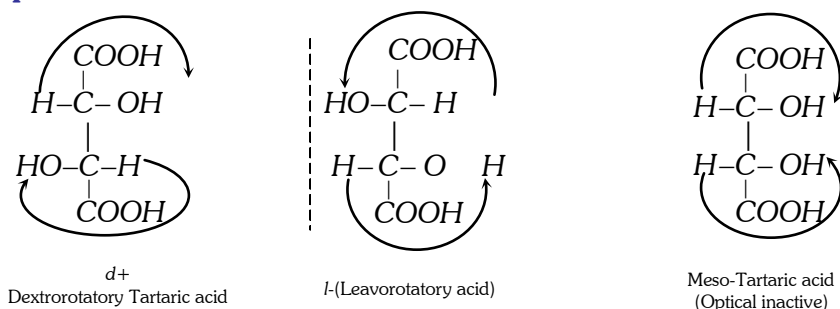


## Carboxylic Acids and their derivatives Part 2



**(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



Optical active

(i)  $d +$  Tartaric acid-Dextro-rotatory

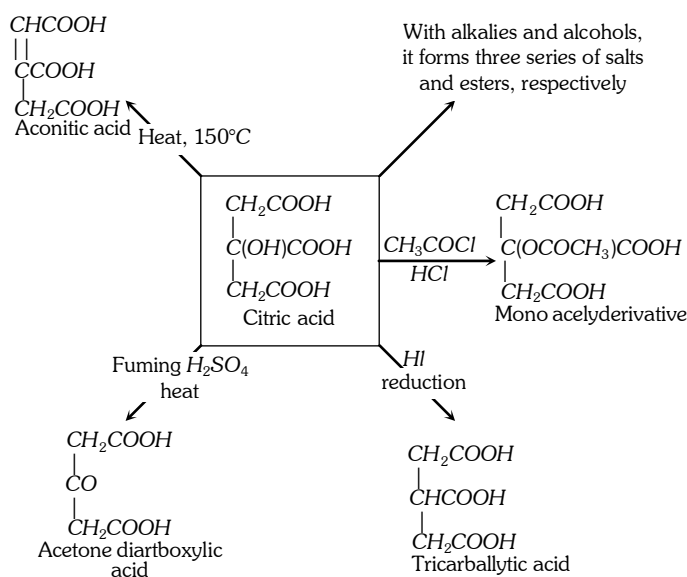
(ii)  $l -$ Tartaric acid-Levorotatory

Optical active

(iii) Meso tartaric acid-optically inactive due to internal compensation.

(iv) Racemic tartaric acid (Equimolar mixture of  $d +$ ,  $l$ -forms). Optically inactive due to external compensation

### (3) Chemical Properties



## Carboxylic Acids and their derivatives Part 2

(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  $\text{AgNO}_3$**  : 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** : ( $\text{H}_2\text{O}_2$  containing a little of ferrous salt) and caustic soda, It gives a violet colour.

(iv) **With Resorcinol and conc.  $\text{H}_2\text{SO}_4$**  : It gives blue colour.

### Citric Acid Or 2-Hydroxypropane Or 1,2,3-Tri Carboxylic Acid Or $\beta$ -Hydroxy Tricarballic Acid

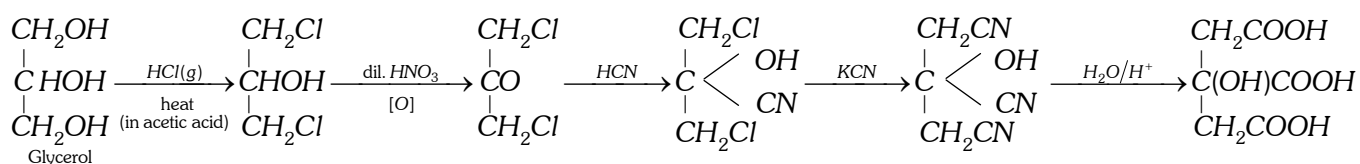
It occurs in the juice of citrus fruits such as lemon, galgal, orange, lime, etc. Lemon juice contains 6-10% of citric acid.

#### (1) Methods of Preparation

(i) **By Fermentation** : Citric acid is obtained by carrying fermentation of dilute solution of molasses with micro-organism, *Aspergillus nigar*, at 26-28°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  $\text{H}_2\text{SO}_4$ . The  $\text{CaSO}_4$  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  $\text{Ca}(\text{OH})_2$  as described in the above method.

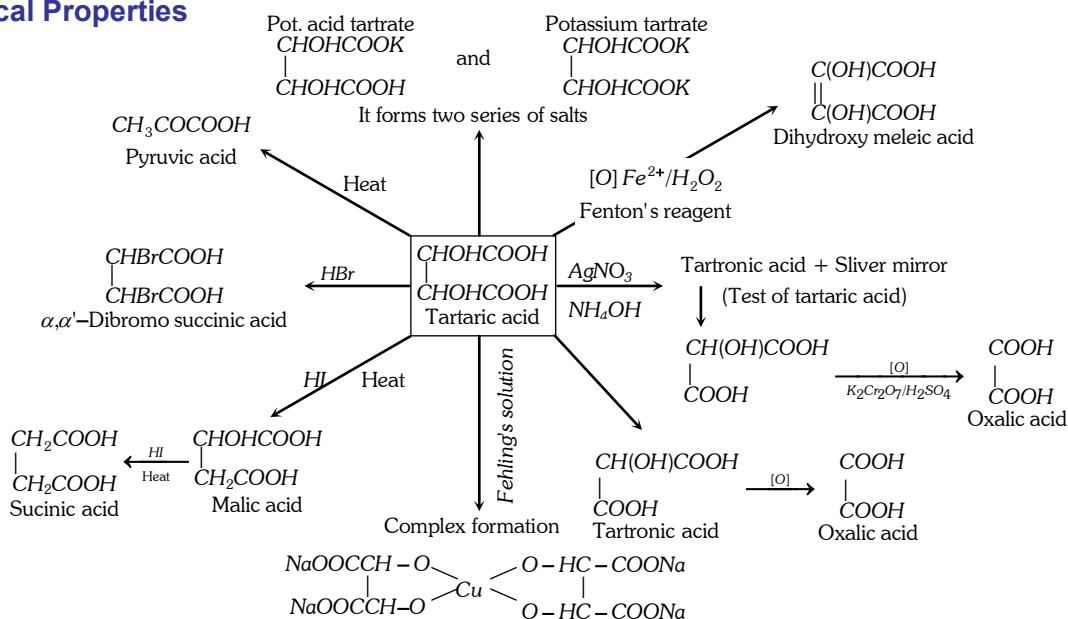
#### (iii) By synthetic method :



(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.

## Carboxylic Acids and their derivatives Part 2

### (3) Chemical Properties

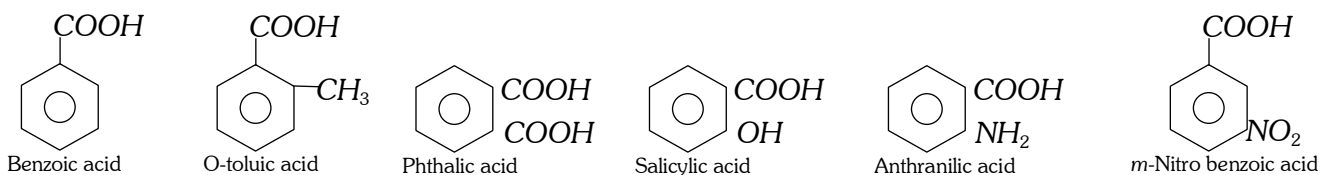


**(4) Uses :** It finds use in making lemonades, as acidulant in food and soft drinks and makes the lemon sour, as mordant in dyeing and calico printing. Ferric ammonium citrate, magnesium citrate (as an antacid and laxative), sodium or potassium citrate are used in medicine. Ferric ammonium citrate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

### Aromatic Carboxylic Acids.

Aromatic acid contain one or more carboxyl group ( $\text{COOH}$ ) attached directly to aromatic nucleus.

#### Examples

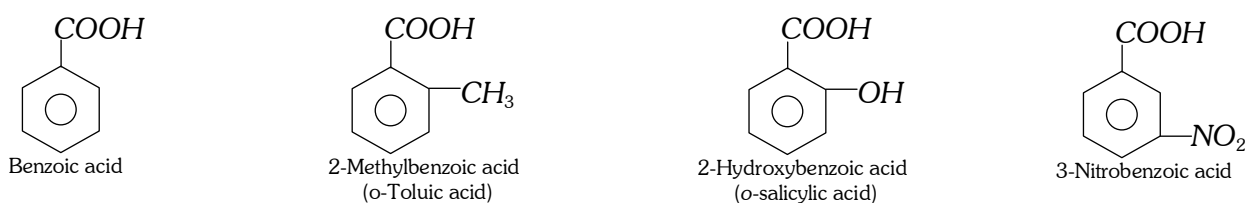


Aromatic acid containing  $\text{COOH}$  group in the side chain, they are considered as aryl substituted aliphatic acid.

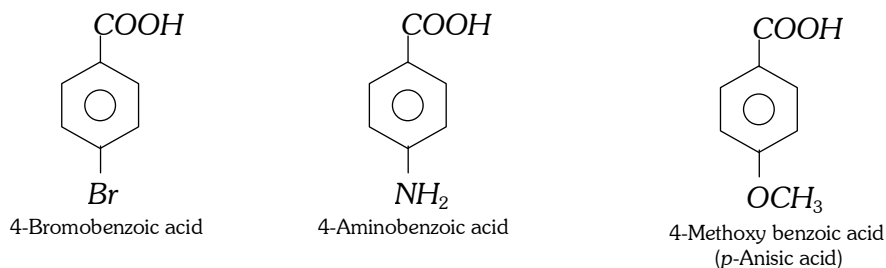
#### Examples



The IUPAC names of the substituted acids are derived by prefixing the name of the substituent to the name of parent acid *i.e.*, benzoic acid and the position is indicated by an arabic numeral with the carbon atom carrying the  $\text{COOH}$  group being numbered as 1. For example,



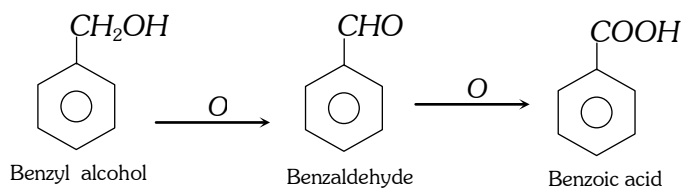
## Carboxylic Acids and their derivatives Part 2



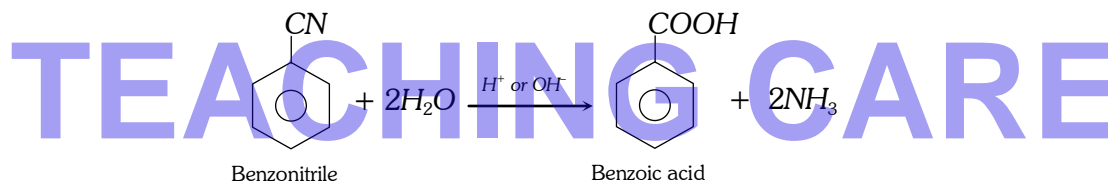
### Benzoic Acid

#### (1) Methods of Preparation

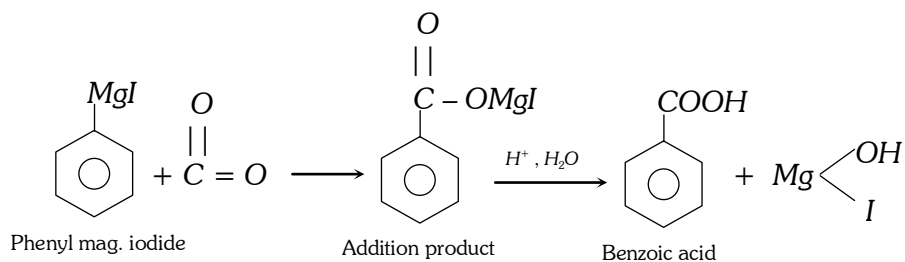
##### (i) From oxidation of Benzyl alcohol [Laboratory method]



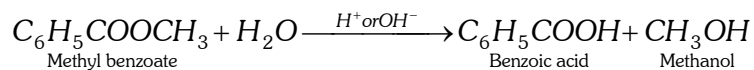
##### (ii) From hydrolysis of nitriles or cyanides



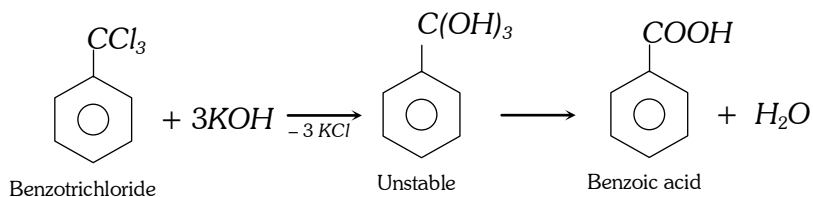
##### (iii) From Grignard reagent



##### (iv) By hydrolysis of esters



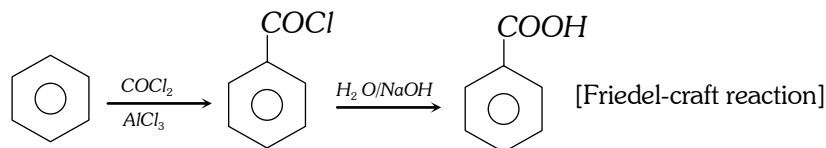
##### (v) From trihalogen derivatives of hydrocarbons



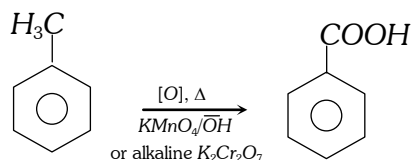


## Carboxylic Acids and their derivatives Part 2

### (vi) From benzene

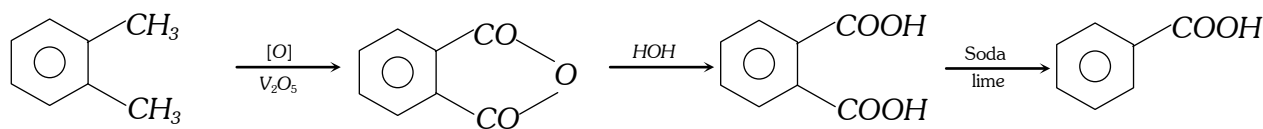


### (vii) From Toluene



**Note :** \* Chromic trioxide in glacial acetic acid or Co-Mn acetate can also be taken in place of alkaline  $\text{KMnO}_4$ .

### (viii) From o-xylene [Industrial method]



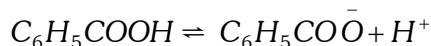
### (ix) From naphthalene [Industrial method]



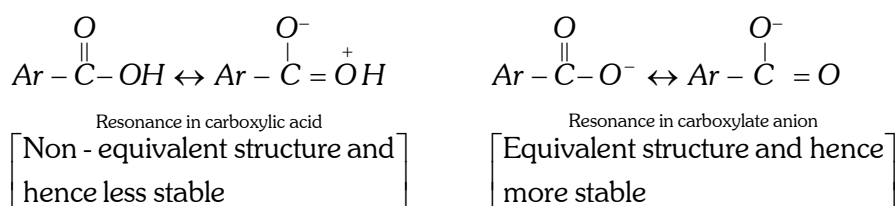
## (2) Physical Properties

- It is a white crystalline solid.
- It has m.p. 394 K.
- It is sparingly soluble in cold water but fairly soluble in hot water, alcohol and ether.
- 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 ( $\text{ArCOO}^-$ ) is resonance stabilised to a greater extent than the carboxylic acid ( $\text{ArCOOH}$ ).



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

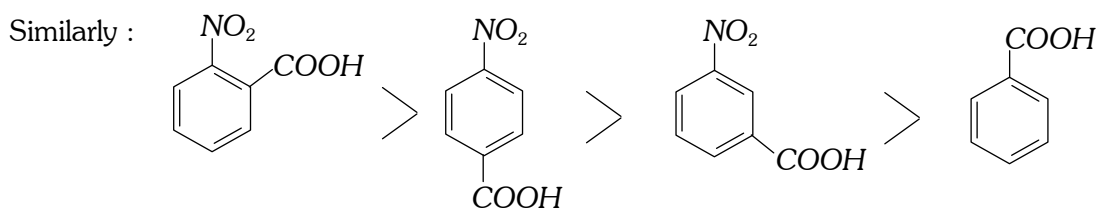
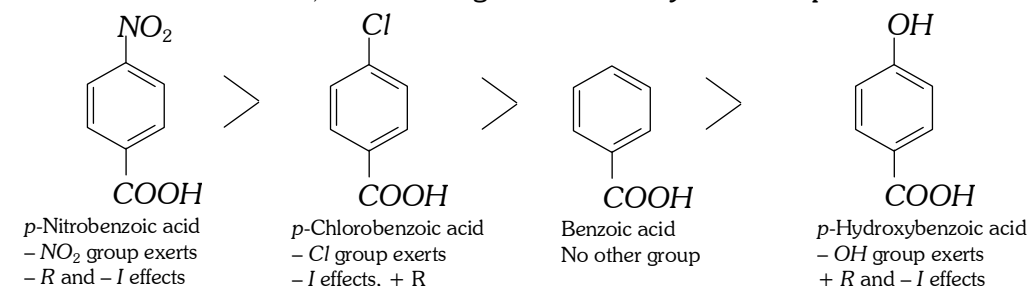
(i) **Inductive effect :** If the substituent exerts -I effect, it increases the acidity of carboxylic acids, while if it exerts + I effect it decreases the acidity. Inductive effect affects all positions, i.e., o-, m- and p-.

## Carboxylic Acids and their derivatives Part 2

(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.

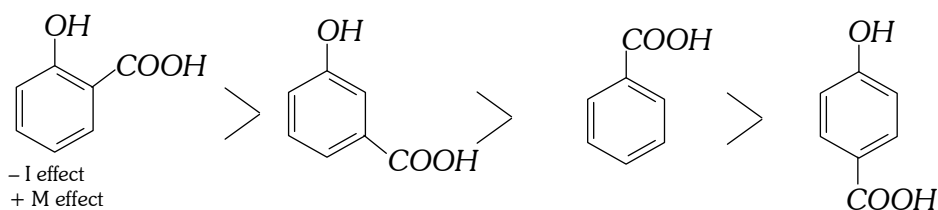
In case resonance and inductive effects both operate in the molecule, resonance effect being stronger overpowers the inductive effect.

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



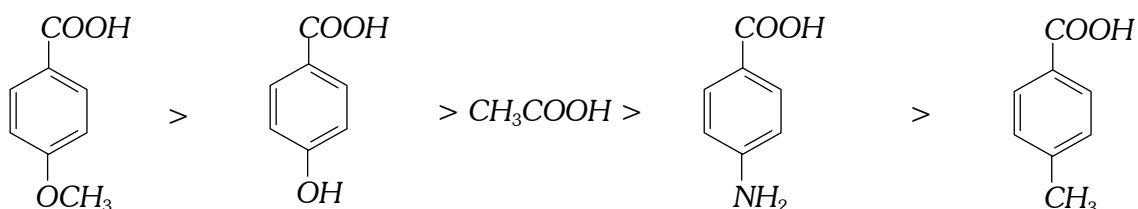
Acidity is only due to electron withdrawing inductive effect of the –  $\text{NO}_2$  group (resonance does not affect the *m*-position) while in the *p*-isomer acidity is due to electron withdrawing inductive as well as resonance effect.

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 :

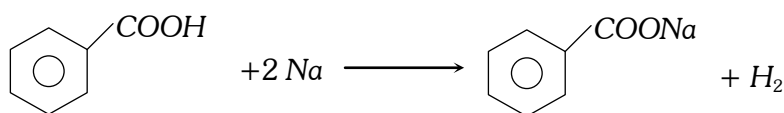
(i) Reactions of carboxylic group

(ii) Reactions of aromatic ring

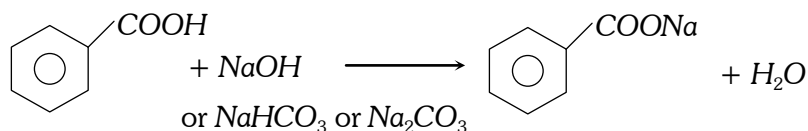
#### (i) Reactions of Carboxylic Group

(a) Reaction with metals

## Carboxylic Acids and their derivatives Part 2

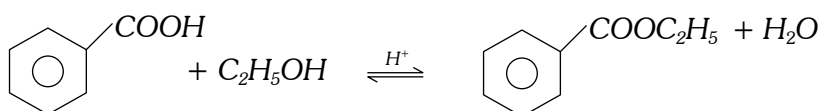


(b) Reaction with Alkalies Or  $\text{NaHCO}_3$  Or  $\text{Na}_2\text{CO}_3$  :



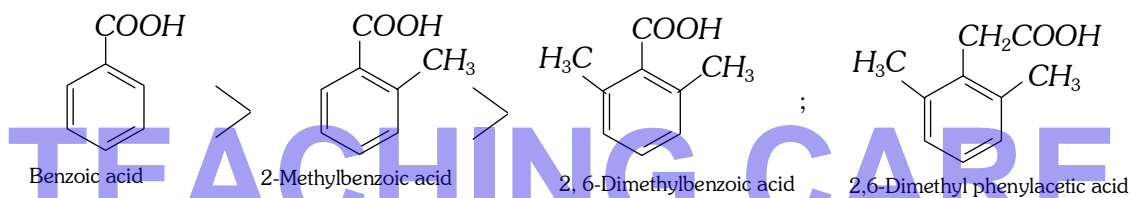
(c) Formation of Esters :

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



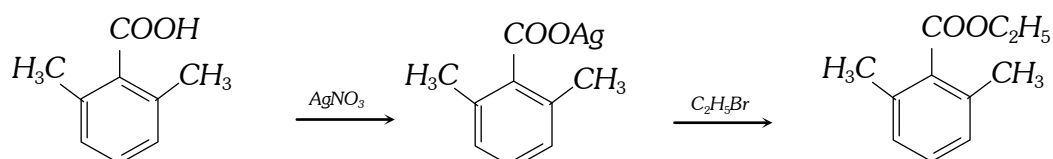
In presence of ortho substituent the rate of esterification is greatly decreased due to steric effect.

The esterification of the various benzoic acids :



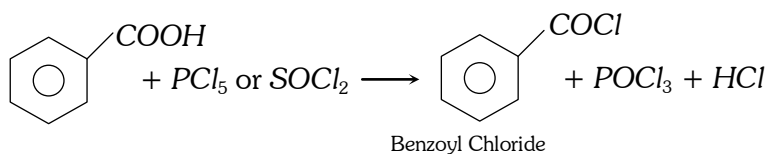
The substituted phenylacetic acid is easily esterified because  $-\text{COOH}$  group is separated from benzene ring by  $-\text{CH}_2-$  part.

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

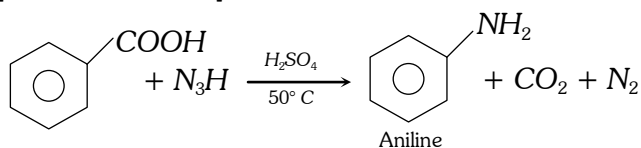


This is due to the fact that in such cases the attack of the alkyl moiety of the alkyl halides is on the oxygen atom of the  $-\text{COOH}$  group but not on the sterically hindered carbon atom.

(d) Formation of acid chloride

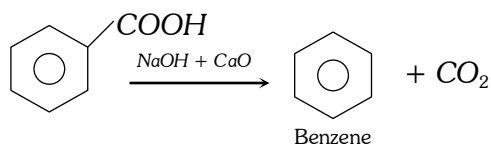


(e) Reaction with  $\text{N}_3\text{H}$  [Schmidt reaction]

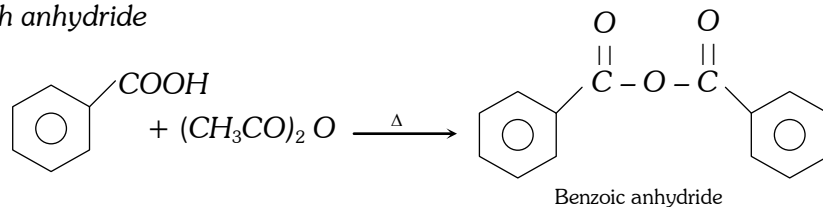


## Carboxylic Acids and their derivatives Part 2

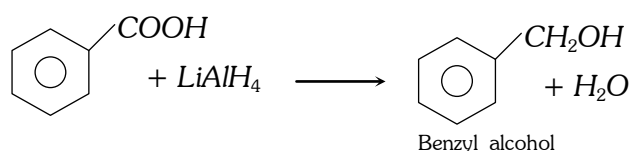
(f) Reaction with sodalime



(g) Reaction with anhydride



(h) Reduction



(i) Decarboxylation

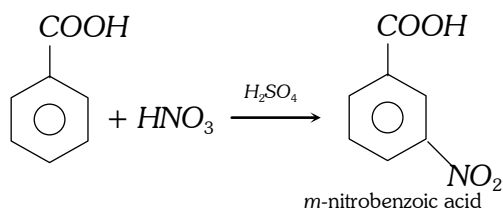


(j) Hunsdiecker reaction :  $\text{C}_6\text{H}_5\text{COOAg} + \text{X}_2 \xrightarrow[\text{heat}]{\text{in CCl}_4} \text{C}_6\text{H}_5\text{-X} + \text{CO}_2 \uparrow + \text{AgX}$

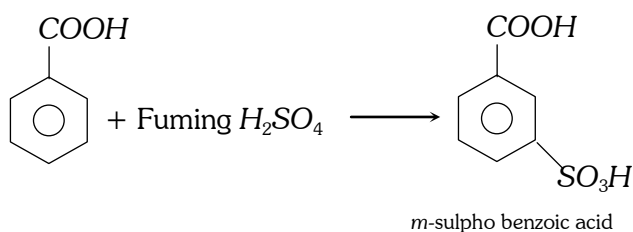
Silver benzoate (Br<sub>2</sub> or Cl<sub>2</sub>)      Phenyl halide

(ii) **Reactions of Aromatic Ring**

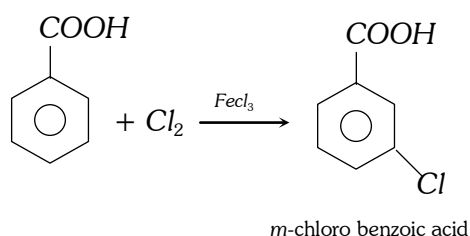
(a) Nitration



(b) Sulphonation

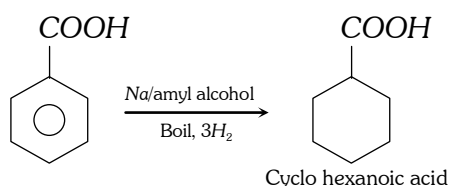


(c) Chlorination



## Carboxylic Acids and their derivatives Part 2

(d) Reduction



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

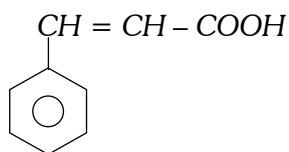
- (i) in medicine in the form of its salts especially as urinary antiseptic.
- (ii) As sodium benzoate for preservation of food such as fruit juices, tomato ketchup, pickles etc.
- (iii) In the preparation of aniline blue.
- (iv) In treatment of skin diseases like eczema.

(6) **General Tests**

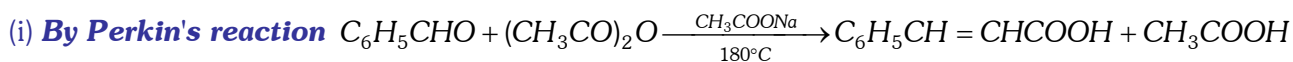
- (i) Benzoic acid dissolves in hot water but separates out in the form of white shining flakes on cooling.
- (ii) It evolves  $CO_2$  with sodium bicarbonate, i.e., it gives effervescence with sodium carbonate.
- (iii) Neutral ferric chloride gives a buff coloured precipitate.
- (iv) When warmed with 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.

# TEACHING CARE

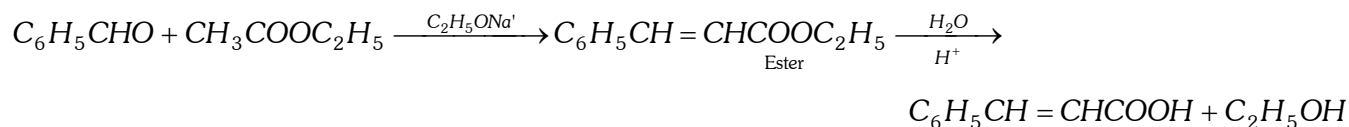
## Cinnamic Acid [ $\beta$ -Phenyl acrylic acid]



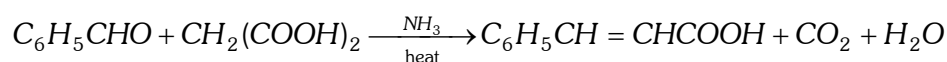
(1) **Methods of Preparation**



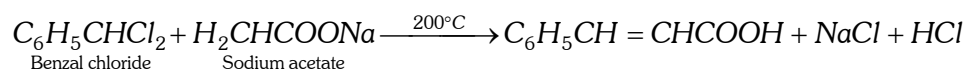
(ii) **By Claisen condensation**



(iii) **By Knoevenagel reaction**



(iv) **Industrial method**



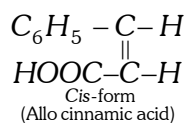
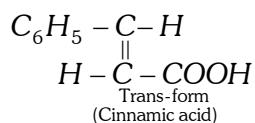
(2) **Physical Properties**

- (i) It is a white crystalline solid and its melting point  $133^\circ C$ .

## Carboxylic Acids and their derivatives Part 2

(ii) It is very 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** : It also gives reactions of benzene nucleus.

