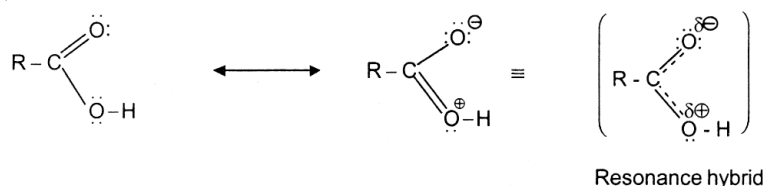


# Carboxylic, Acid & Its Derivatives

## 1. GENERAL INTRODUCTION

The organic compounds containing carboxyl ( $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$ ) group are known as carboxylic acids and the term 'Carboxylic' was firstly proposed by scientist 'Bayer'.

Resonance hybrid structure of carboxylic acid group is



due to resonance, the bond length value of both the bonds [C-O & C=O] are equal, which is 1.28 Å.

### 1.1 Classification :

On the basis of the group to which  $-\text{COOH}$  group is attached.

[a] Aliphatic carboxylic acid =  $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$  (R = H atom or alkyl group).

[b] Aromatic carboxylic acid =  $\text{Ar}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$  (Ar = Aryl group)

### 1.2 On the basis of number of $-\text{COOH}$ groups in their molecule.

No. of  $-\text{COOH}$  group

- [a] Mono carboxylic acids 1  
 [b] Dicarboxylic acids 2  
 [c] Tricarboxylic acids 3

General formula is  $\text{C}_n\text{H}_{2n}\text{O}_2$  or  $\text{C}_n\text{H}_{2n+1}\text{COOH}$

Saturated and unsaturated mono carboxylic acids are also called fatty acids, because higher acids like palmitic acid, steric acid, oleic acid, etc. were obtained by hydrolysis of fats and oils.

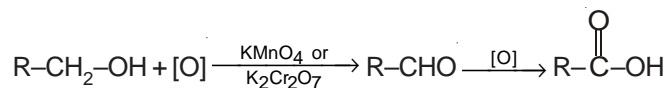
Isomerism – Chain, positional, functional group and optical.

Hybridisation state of C in the carboxyl group in  $\text{sp}^2$

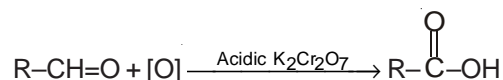
## 2. METHOD OF PREPARATION

### 2.1 By the oxidation of alcohols, aldehydes and ketones :

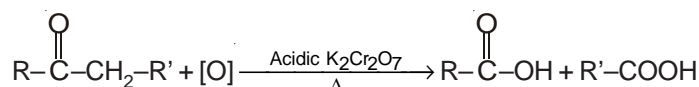
[a]  $1^\circ$  Alcohol  $\xrightarrow{[\text{O}]}$  corresponding carboxylic acids.

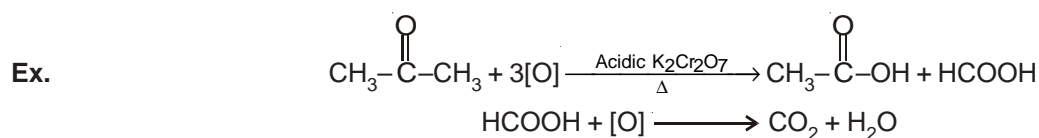


[b] Aldehyde  $\xrightarrow{[\text{O}]}$  corresponding acids



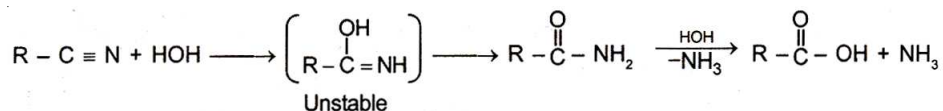
[c] Ketones  $\xrightarrow{[\text{O}]}$  mixture of acids of lesser no. of C atoms than the ketone.





## 2.2 By the hydrolysis of cyanides (nitriles) :

Cyanides on complete hydrolysis in the presence of dilute HCl form carboxylic acids.



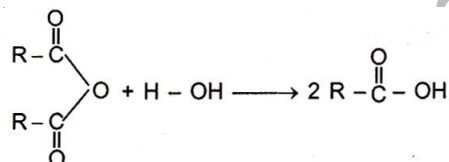
## 2.3 From hydrolysis of acid derivatives :



### [a] From acyl halides :



### [b] From acid anhydride :

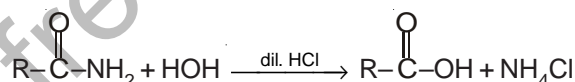


**Note :** Formic acid cannot be prepared by these two reactions (a & b) because its corresponding formyl chloride and formic anhydride are unstable compounds.

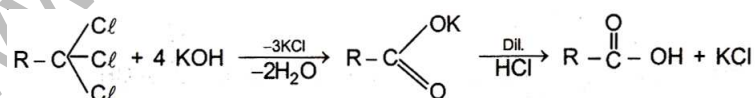
### [c] From carboxylic ester :



### [d] From acid amides :

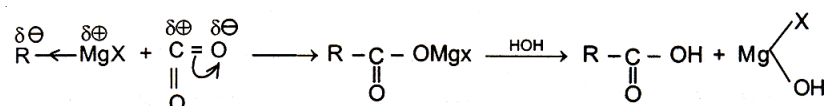


## 2.4 By alkaline hydrolysis of alkylidene trihalides :



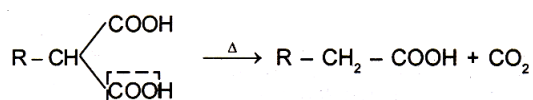
## 2.5 From carboxylation of grignard's reagent :

By passing  $\text{CO}_2$  in ether solution of Grignard's reagent

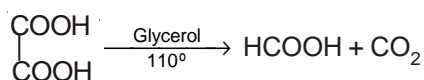


**Note :** Formic acid cannot be prepared by this method.

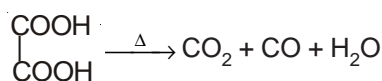
## 2.6 Partial decarboxylation of gem dicarboxylic acids :



**Note :** Formic acid is prepared from oxalic acid (laboratory method) by heating at about 110° in the presence of glycerol.

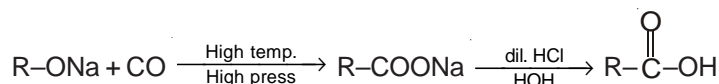
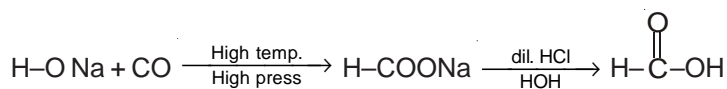


In absence of glycerol

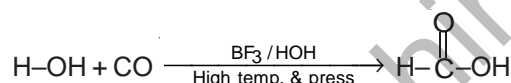
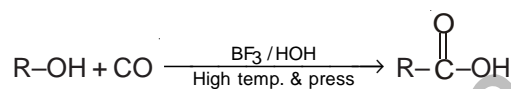


## 2.7 Carbonylation of :

[a] Sodium alkoxides or sodium hydroxide :



[b] Alcohols :

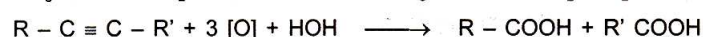
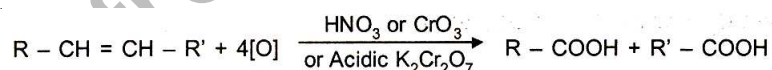


[c] Alkenes [Koch Reaction] :

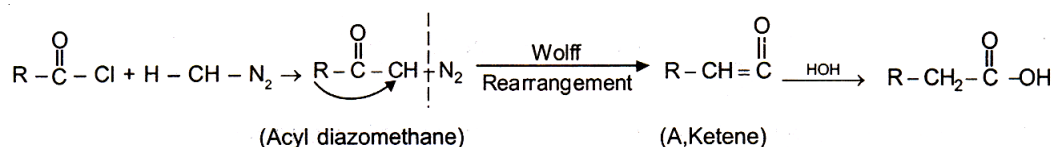


**Note :** Formic acid and acetic acid can not be prepared by this method.

## 2.8 Oxidation of alkenes and alkynes :

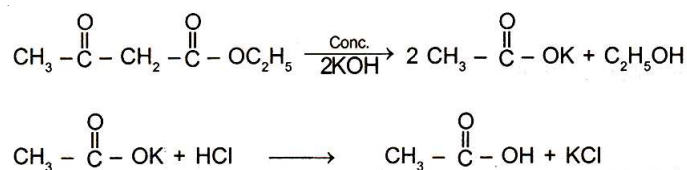


## 2.9 Arndt-Eistert reaction :



**Note :** [i] The method can be used in ascending up a homologous series.

[ii] The method can be used only for the synthesis of carboxylic acids having three or more carbon atoms and HCOOH or CH<sub>3</sub>COOH are not prepared by this reaction.

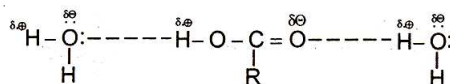
**2.10 From acetoacetic ester :**

**3. PHYSICAL POPERTIES**

- 3.1 Physical State :**  $\text{C}_1$  to  $\text{C}_3$  = Colour less pungent smelling liquids.  
 $\text{C}_4$  to  $\text{C}_9$  = Liquids having goat's butter like smell.  
 $\text{C}_{10}$  to  $\text{C}_{10+}$  = Colourless & odourless waxy solids.

- 3.2 Solubility :** Up to  $\text{C}_4$  = Highly soluble in water

With the increase in molecular weight of carboxylic acid, the solubility in water decreases.

Solubility of lower members of carboxylic acids family is due to the formation of hydrogen bond between  $-\text{COOH}$  group and water molecules.

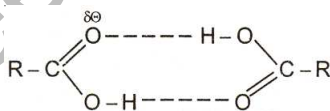


As the alkyl group increases in size in acids, the water repelling (hydrophobic) tendency of the hydrocarbon chain increases and it out weighs the effect of hydrogen bonding. This is why solubility decreases in higher members.

- 3.3 Boiling point (B.P.) :**

B.P. of acids > B.P. of alcohols

Because, A carboxylic acid molecular can enter into hydrogen bonding at two different points. This leads to the formation of cyclic dimers in acids. This is the fact that lower acids occur as dimers in solution.



- 3.4 Melting point (M.P.) :**

M.P. of carboxylic acids do not vary smoothly from one molecule to another

For first ten memebers

M.P. of  $\text{C}_{2n}$

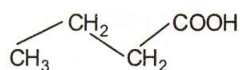
>

M.P. of  $\text{C}_{2n+1}$

( $n = 1, 2, 3, 4, 5$ )

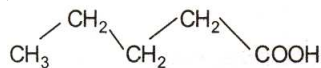
( $n = 0, 1, 2, 3, 4$ )

**Reasons :** In acids of even number of carbon atoms terminal  $-\text{CH}_3$  and  $-\text{COOH}$  group lie on the opposite side of the carbon chain.



Provide more effective packing of the molecule in the lattice.

While in acids of odd no. of carbon atoms



Less effective packing

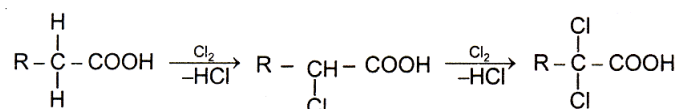
#### 4. CHEMICAL PROPERTIES

Carboxylic acids give following reactions :

- 4.1 Due to alkyl group
- 4.2 Due to acidic hydrogen
- 4.3 Due to  $>C = O$  group
- 4.4 Due to  $-OH$  group
- 4.5 Due to  $-COOH$  group
- 4.6 Special reaction of alkanolic acid

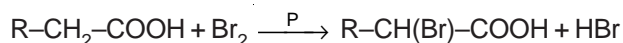
##### 4.1 Reactions due to alkyl group :

- [a] **Halogenation** : Acids having  $\alpha$ -H atom give this reaction. The  $\alpha$ -H atoms are easily replaced by chlorine or bromine atoms, forming halogen derivatives of acids.



**Note :** [i] The reaction is known as hell-volhard-Zelinisky (HVZ) reaction.

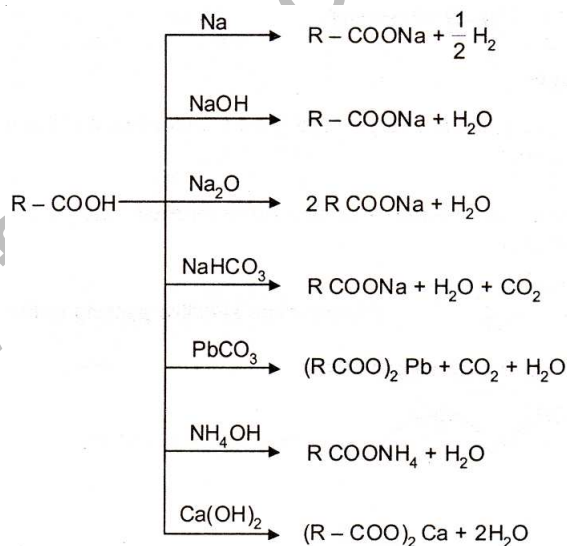
[ii] In the presence of phosphorus, monohalo product is formed as the main product.



[iii] Formic acid does not show HVZ reaction due to absence of alkyl group or  $\alpha$ -H atom.

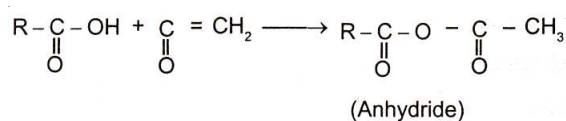
##### 4.2 Due to acidic hydrogen :

- [a] **Salt Formation** : Carboxylic acids form salts with metals, metal oxide, hydroxides, carbonates, bicarbonates and compounds showing basic nature.

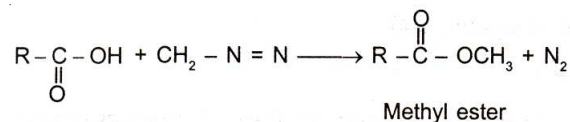


**Note :** Acids liberate  $\text{CO}_2$  with  $\text{NaHCO}_3$ . This reaction is used to distinguish carboxylic acid from phenol which does not react with  $\text{NaHCO}_3$ .

- [b] **Reaction with Ketene** :

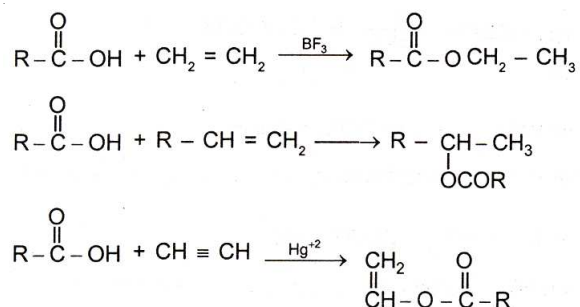


[c] **Reaction with diazomethane :**

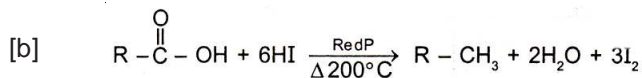
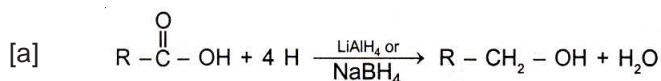


**Note :** Diazomethane is a powerful methylating agent. So by this method methyl ester can be prepared.

[d] **Reaction with alkene and alkyne :**

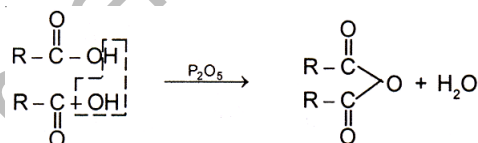


4.3 **Reaction due to (>C = O) group :**

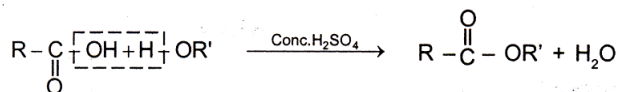


4.4 **Reactions due to (-OH) group :**

[a] **With P<sub>2</sub>O<sub>5</sub> (Dehydrations)**

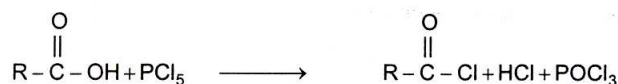


[b] **Esterification :**

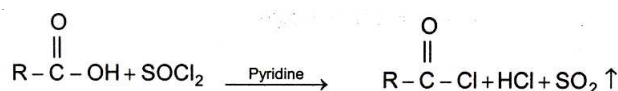


**Note :** The reaction is proton-catalysed esterification. In the reaction OH comes from the acid and H from the alcohol for release of H<sub>2</sub>O.

[c] **Reaction with Phosphorous Chlorides :**

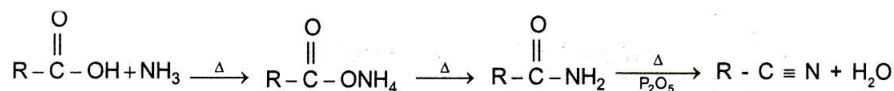


[d] **With Thionyl Chloride :**

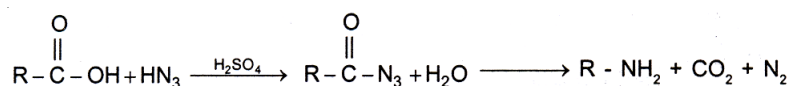


**Note :** In the reaction  $\text{SO}_2$  is gas so escapes out and  $\text{HCl}$  is an acid, gets absorbed by basic pyridine and pure acyl chloride is left. So its is best method for preparing acyl chloride from acids.

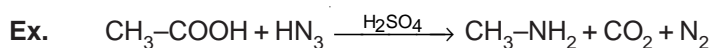
[e] **Formation of acid Amides and Alkane Nitriles :**



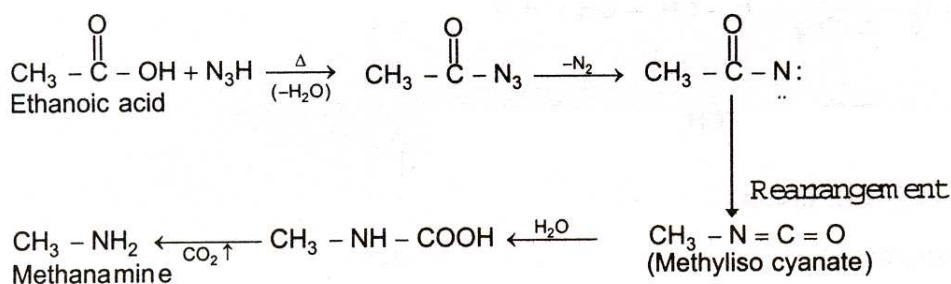
[f] **With Hydrazoic acid (Schmidt reaction) :**  $\text{N}_3\text{H}$  = Hydrazoic acid



The reaction is a modification of "curtius reaction".

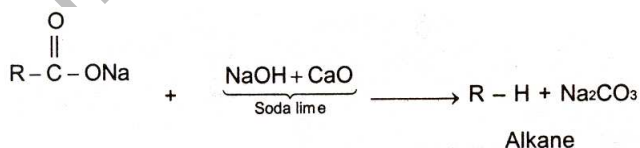


**Mechanism :**

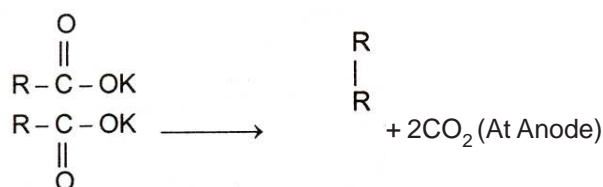


4.5 **Reaction due to (-COOH) group :**

[a] **Decarboxylation :**

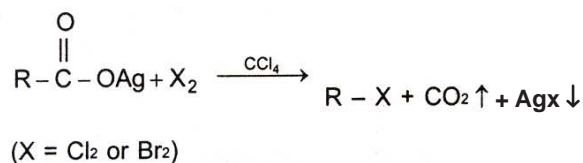


[b] **Kolbe's electrolytic synthesis :**



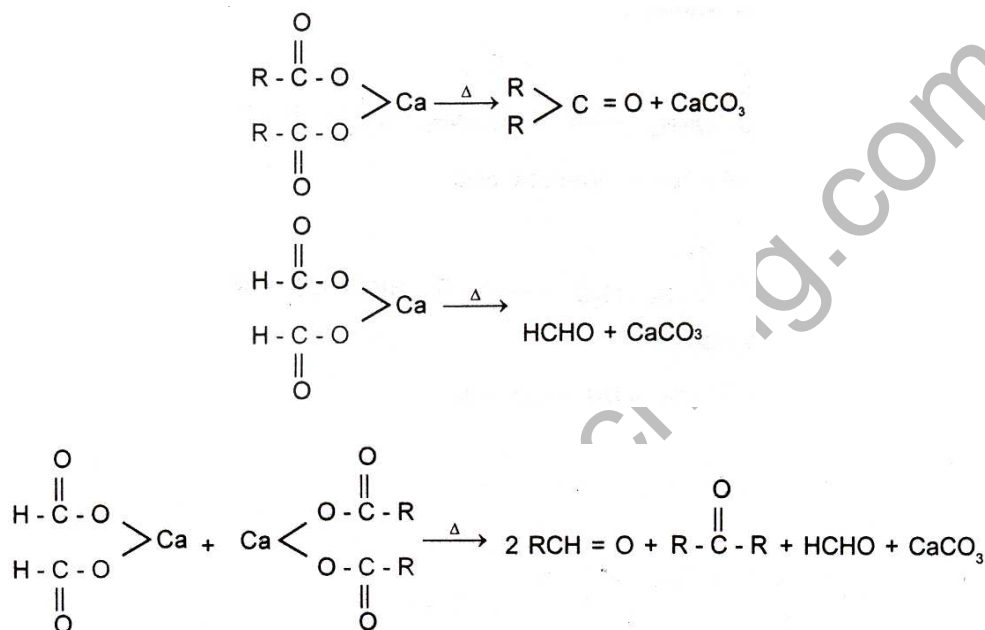
**Note :** Kolbe synthesis undergoes free radical mechanism.

[c] **Hundsdiecker reaction :**

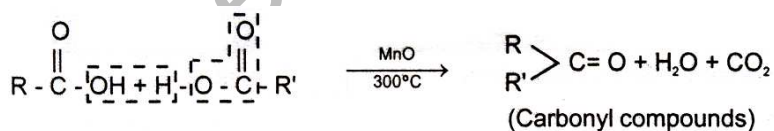


**Note :** In the reaction decarboxylative halogenation of the acid takes place. The reaction is useful in stepping down a homologous series.

[d] **Formation of carbonyl compounds [Dry distillation of calcium salt] :**



[e] **With Manganous oxide :**

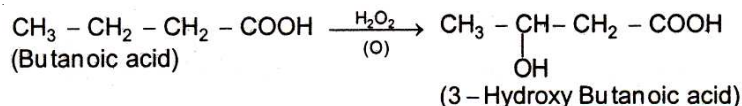


**4.6 Special reaction of alkanolic acid :**

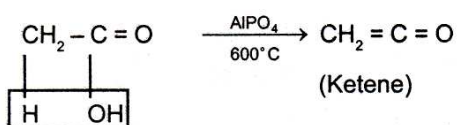
[a] **Oxidation :**

→ By SeO<sub>2</sub> α keto acid is formed

→ By H<sub>2</sub>O<sub>2</sub> -OH group comes at β -C atom.



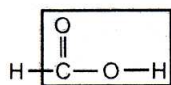
[b] **Pyrolysis :**



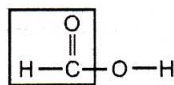


## 5. SPECIAL FEATURES OF FORMIC ACID

- [a] Formic acid shows acidic character due to the presence of  $-\text{COOH}$  group as well as shown reducing character due to the presence of  $-\text{CHO}$  group.

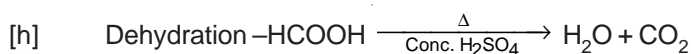


$-\text{COOH}$  group

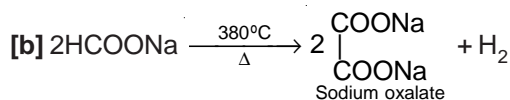
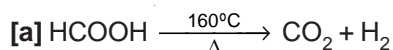


$-\text{CHO}$  group

- [b] It reduces Tollen's reagent and forms silver mirror.  
 [c] It reduces mercuric chloride and forms black ppt. of mercury.  
 [d] It decolourises the pink colour of acidic  $\text{KMnO}_4$   
 [e] It forms brown ppt. of  $\text{MnO}_2$  with basic  $\text{KMnO}_4$   
 [f] It converts the orange colour of acidic  $\text{K}_2\text{Cr}_2\text{O}_7$  into green colour.  
 [g] It reduces Fehling solution.



- [i] **Effect of heat :**

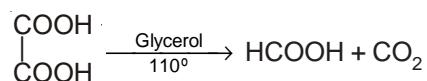


## 6. DISTINCTION BETWEEN FORMIC ACID AND ACETIC ACID

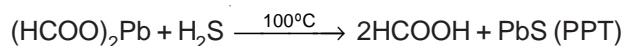
S. NO.	$\text{HCOOH}$	$\text{CH}_3\text{COOH}$
1.	Decomposed on heating to give carbon dioxide and hydrogen.	Stable
2.	With concentrated sulphuric acid gives carbon monoxide and water.	Stable
3.	With halogens, there is not action.	Substituted acids are formed.
4.	Reduces ammonical silver nitrate and Fehling's solution.	No action.
5.	Calcium salt on heating gives formaldehyde.	Calcium salt on heating gives acetone.
6.	Sodium salt on heating gives sodium oxalate hydrogen.	No action.
7.	Sodium salt + soda lime gives hydrogen on heating.	Methane is produced.
8.	Electrolysis of alkali solution gives hydrogen.	Ethane is obtained.
9.	Decolourises acidified $\text{KMnO}_4$ solution.	No action.
10.	Dichromate solution turns into green coloured solution.	No action.

## 7. FORMIC ACID (HCOOH)

### 1. Lab Reaction :



**Note :** BP of HCOOH is 100.5°, for removal of water from formic acid we can use PbCO<sub>3</sub> or PbO (Litharge) and H<sub>2</sub>S.



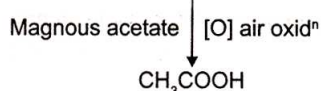
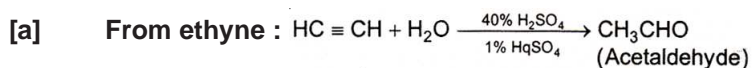
### 2. Industrial method :

It is prepared on large scale by reaction CO with aqueous sodium hydroxide under pressure 1 atm and 473 K

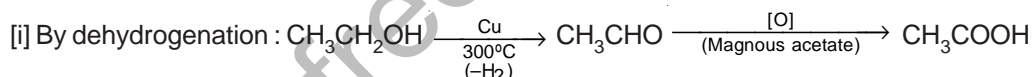


## 8. ACETIC ACID CH<sub>3</sub>COOH

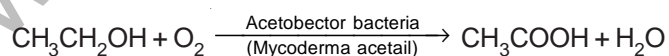
### Industrial methods :



### [b] From ethyl alcohol

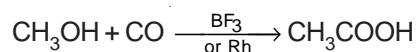


[ii] By fermentation (Quick vinegar process)



[dilute form 8 – 10% Called **VINEGAR**]

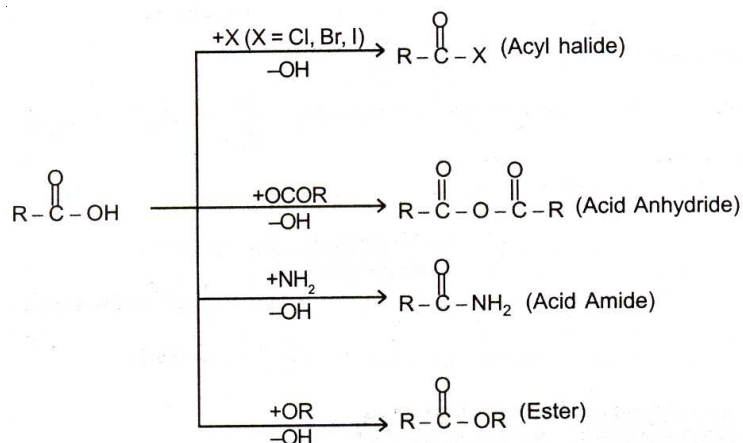
[iii] From CH<sub>3</sub>OH



# Acid Derivatives

## 1. GENERAL INTRODUCTION

Replacement of  $-OH$  group of the  $-COOH$  group in a carboxylic acid by an atom or by any other functional group give rise to certain new families of compounds. These compounds are called acid derivatives.

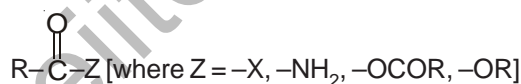


Acyl chlorides are the most important acid halides. The first member of this family is acetyl chloride because formylchloride is unstable.

Similarly acetic anhydride is the representative member of the acid anhydrides family, because formic anhydride is unstable.

The first two members of Acid Amide family are formamide and Acetamide. Acetamide is an important acid amide.

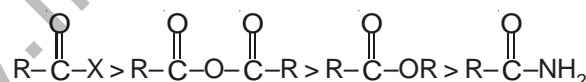
Esters have functional group isomerism with acids.



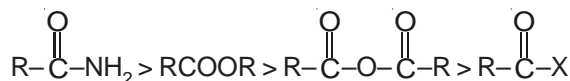
\* Order of basic character of group Z



\* Reactivity order/Rate of hydrolysis

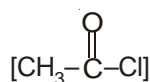


\* Order of stability



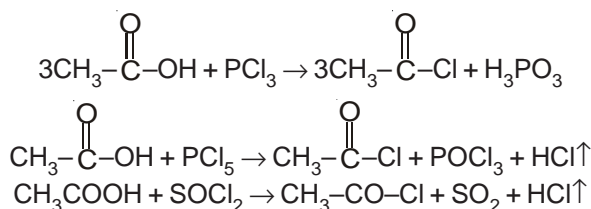
Derivatives regenerate the parent acid on hydrolysis.

## 2. ACETYL CHLORIDE

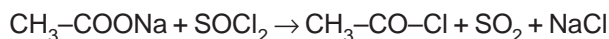
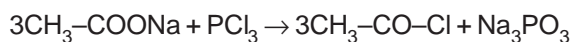
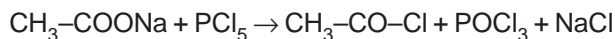


### 2.1 Method of preparation :

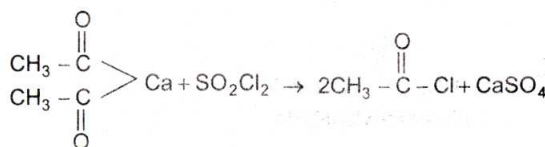
Laboratory method :



From Sodiumacetate :



By the reaction of sulphuryl chloride on calcium ethanoate :

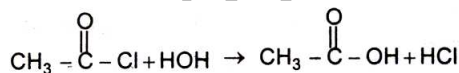


## 2.2 Physical Properties :

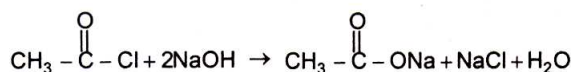
- [i] Colourless liquid, having pungent odour.
- [ii] Slowly soluble in water, soluble in organic solvents like  $\text{CHCl}_3$ ,  $\text{CCl}_4$ ,  $\text{CH}_3\text{-CO-CH}_3$ , etc.
- [iii] Produces blister on skin and its vapour causes irritation in eyes.
- [iv] Boiling point is  $51^\circ\text{C}$ .
- [v] Fumes strongly in moist air.

## 2.3 Chemical properties :

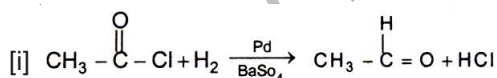
### [1] Hydrolysis :



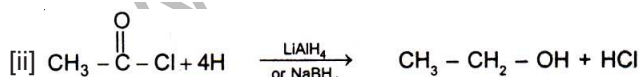
on alkaline hydrolysis



### [2] Reduction :

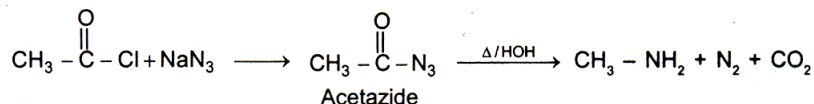


(Rosenmund's reduction, partial reduction)

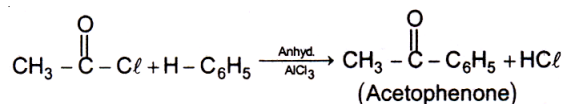


(Complete reduction)

### [3] Curtius Reaction :



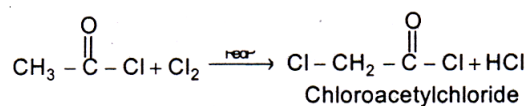
### [4] Friedel Craft's reaction :



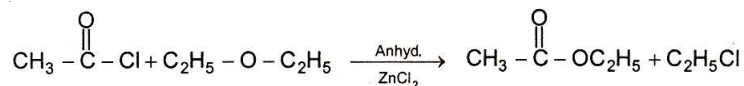
[5] With Grignard's reagent :



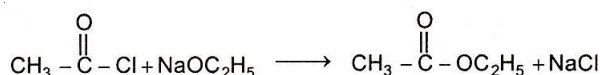
[6] Halogenation :



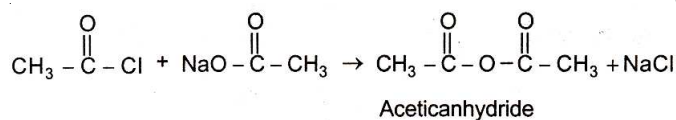
[7] With Ether :



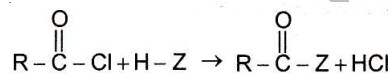
[8] With Sodium Ethoxide :



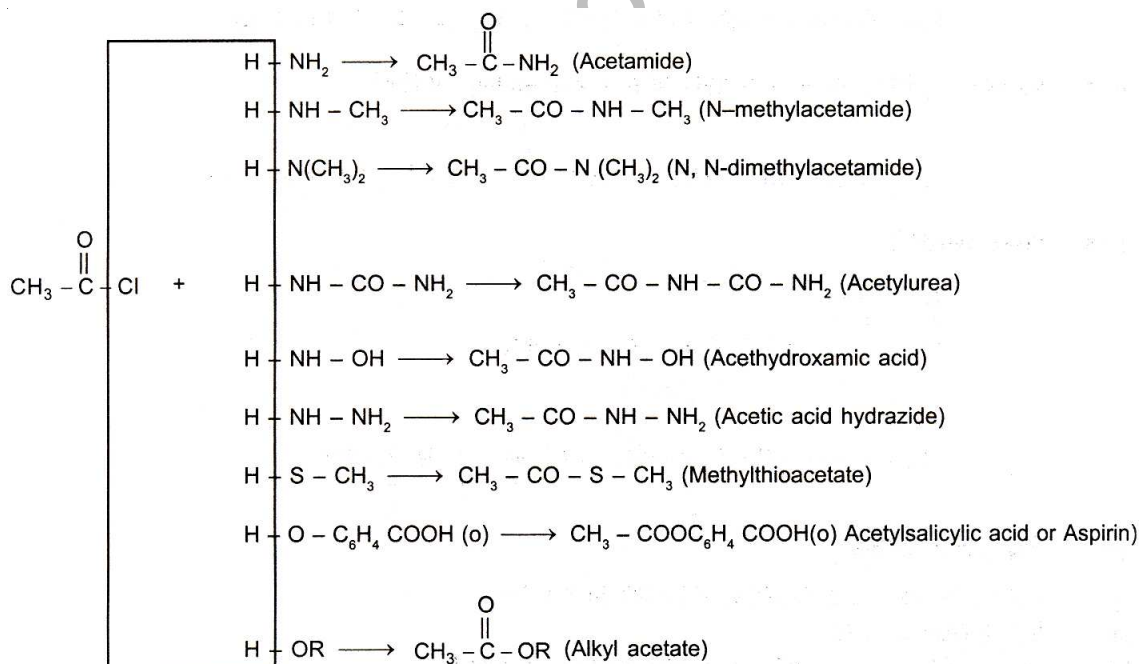
[9] With Sodium Acetate :



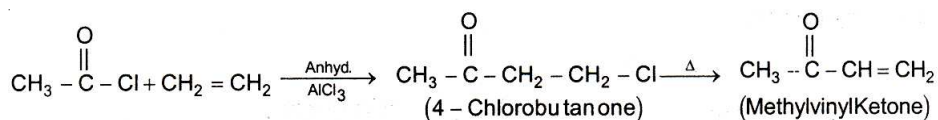
[10] Acetylation of Compounds having reactive hydrogen atom :



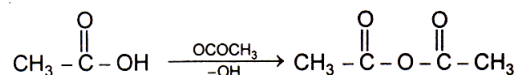
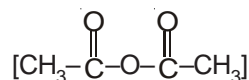
Ex.



[11] With Alkene :

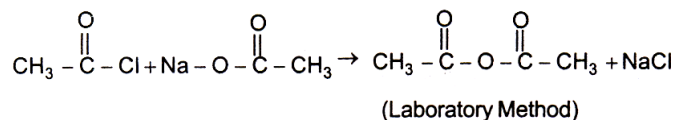
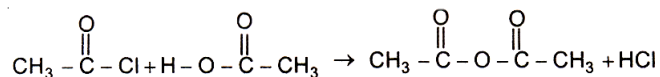


### 3. ACETIC ANHYDRIDE

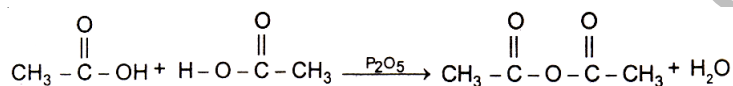


#### 3.1 Method of preparation :

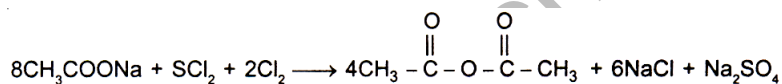
From Acetyl chloride :



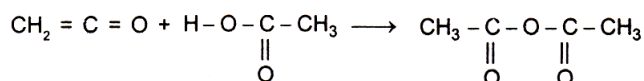
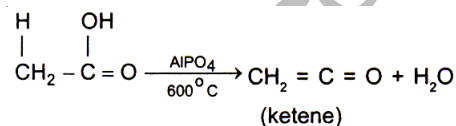
From Acetic acid :



By passing chlorine in a mixture of  $\text{SCl}_2$  and sodium acetate :



From Ketene :

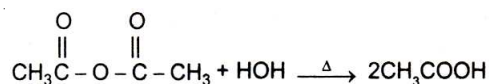


#### 3.2 Physical Properties :

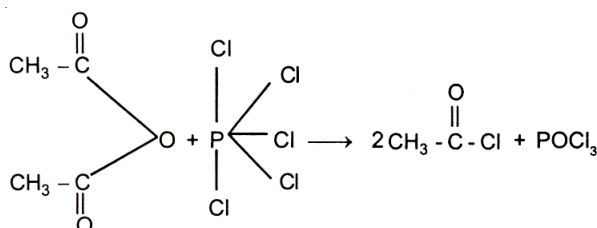
- [i] It is colourless liquid having pungent vinegar like odour.
- [ii] Boiling point is  $138^\circ\text{C}$ .
- [iii] Slowly soluble in cold water, but readily soluble in hot water

#### 3.3 Chemical Properties :

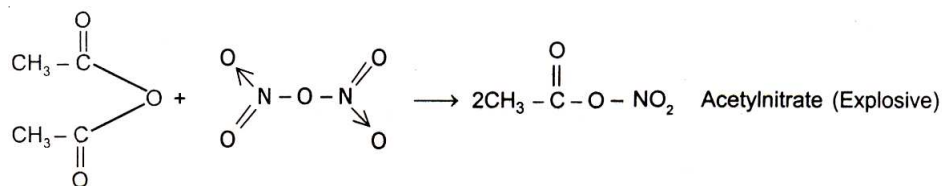
Hydrolysis :



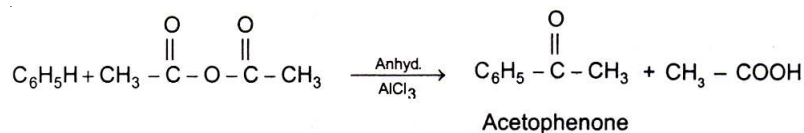
With  $\text{PCl}_5$  :



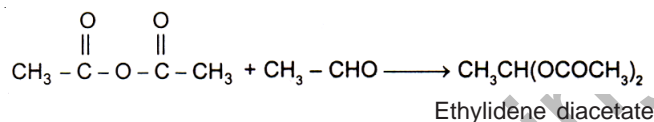
With  $N_2O_5$  :



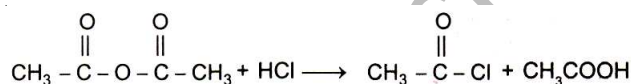
With Benzene [Friedel-Craft's Reaction] :



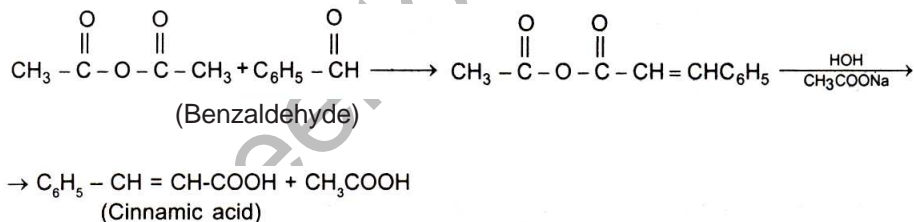
With Acetaldehyde :



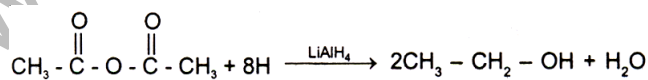
With Dry HCl gas :



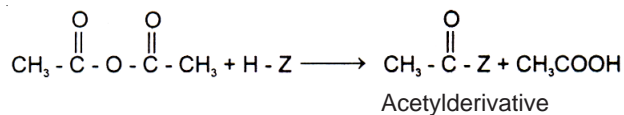
Perkin's Reaction :



Reduction :

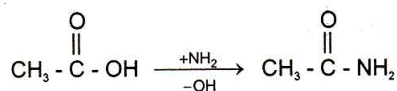
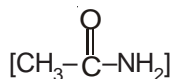


With Compounds having reactive H-atom :



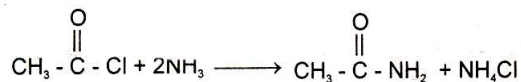
**Note :** Products are similar as in case of Acetyl chloride.

## 4. ACETAMIDE

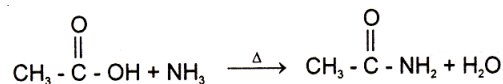


### 4.1 Method of Preparation :

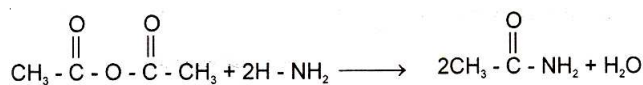
#### From Acetylchloride :



#### From Acetic Acid :



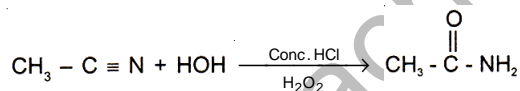
#### From acetic Anhydride :



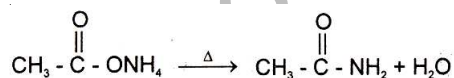
#### From Ethyl Acetate :



#### Partial hydrolysis of Acetonitrile :



#### By thermal decomposition of Ammonium acetate :

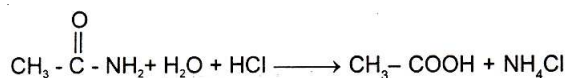


### 4.2 Physical properties :

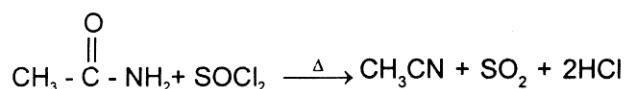
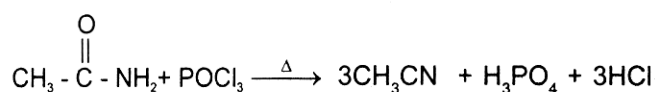
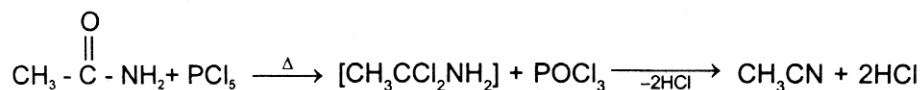
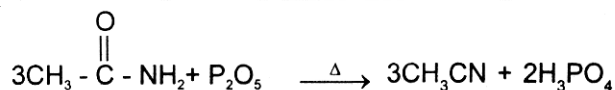
- [i] It is a hygroscopic white crystalline solid.
- [ii] It has faint smell in pure state, but a rat like smell in impure state.
- [iii] It is soluble in water and alcohol, but sparingly soluble in ether.
- [iv] Melting point 82°C and boiling point is 222°C.

### 4.3 Chemical properties :

#### Hydrolysis :

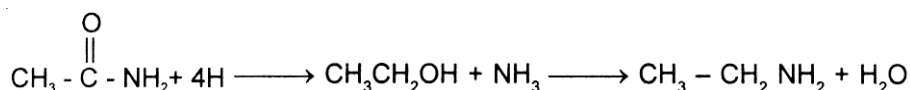
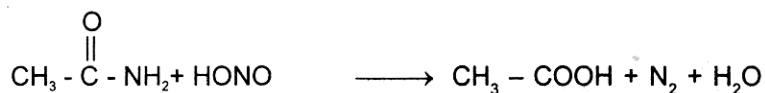


#### Dehydration :

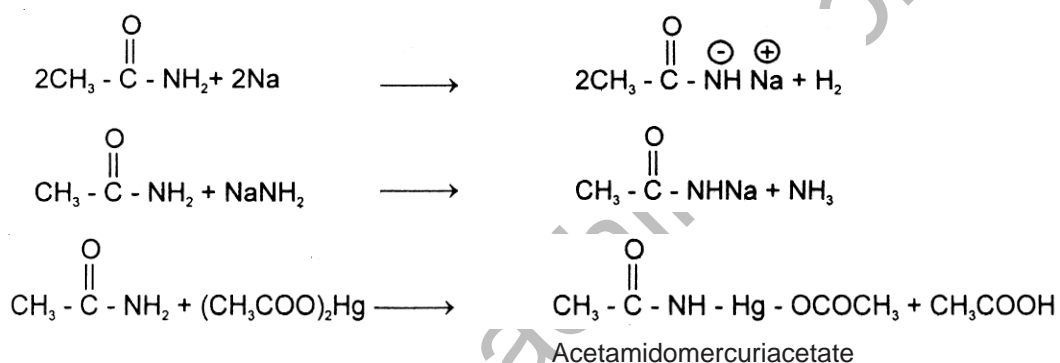
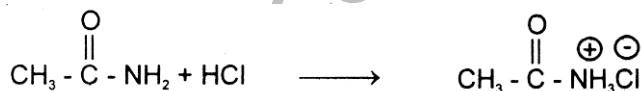
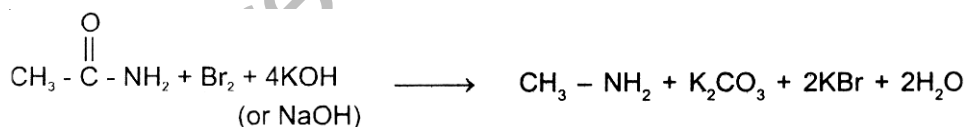
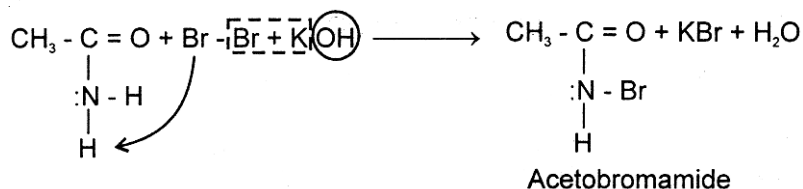
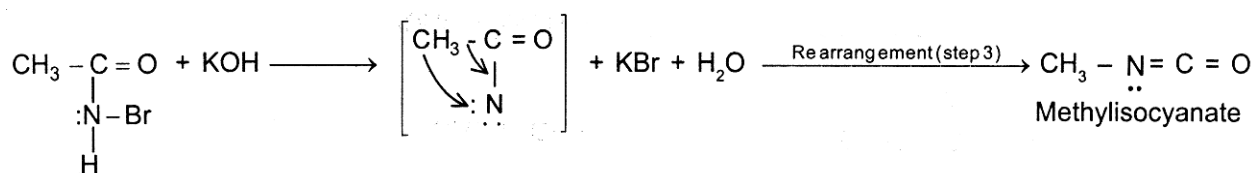




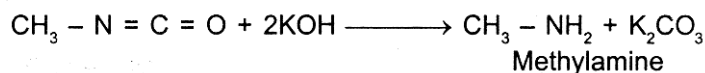
**Reduction :**

 Reducing Agent : Metal Catalyst + H<sub>2</sub>, Na + Ethanol, LiAlH<sub>4</sub> etc.

**With Nitrous Acid :**

**Amphoter character :**

Acetamids forms salts on reacting with strong bases as well as strong acids. Therefore it behaves like a weak base as well as weak acid. i.e. it shows amphoteric character.

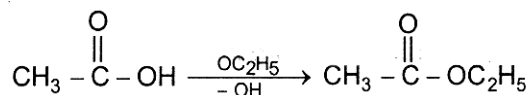
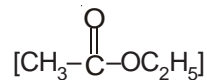
 [i] **Weak acidic behaviour :**

 [ii] **Weak basic behaviour :**

**Hofmann Bromamide Reaction or Hypobromite Reaction :**

**Slightly Mechanism :**
**Bromination :**

**Dehydrobromination :**


**Hydrolysis :**



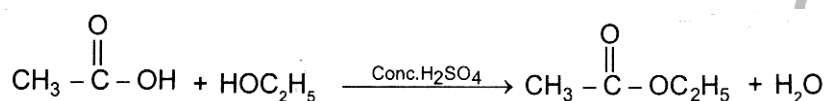
**Note :** In the reaction decrease of one carbon atom takes place. Therefore it can be used in descending down a homologous series and it is also called Hofmann degradation.

## 5. ETHYL ACETATE AND ACETIC ESTER

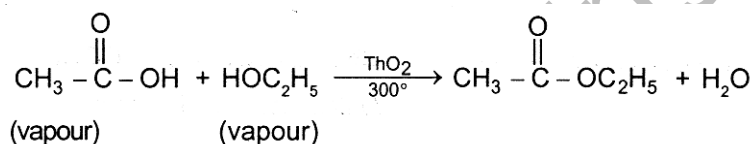


5.1 **Methods of preparation :**

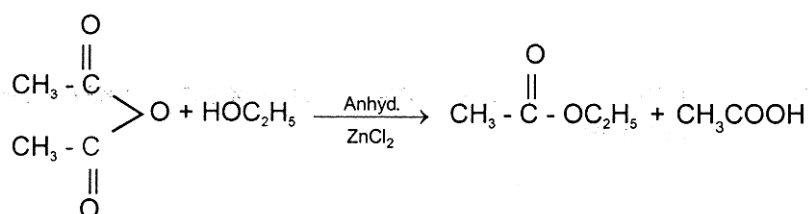
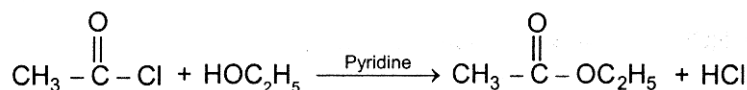
**By liquid phase Esterification :**



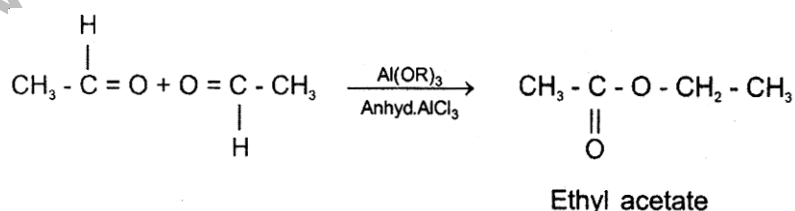
**By vapour phase Esterification :**



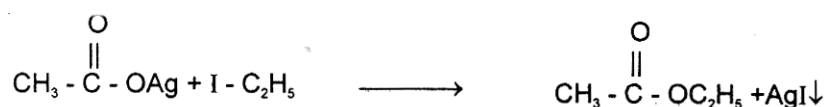
**By Aacylation of Ethanol :**

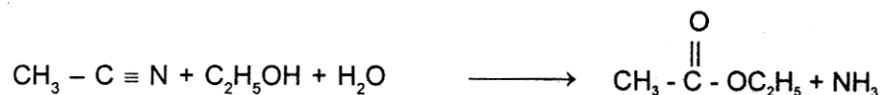
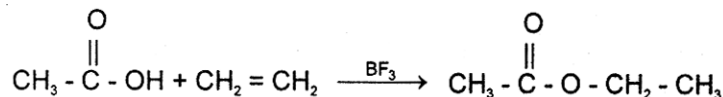


**Tischenko Reaction :**



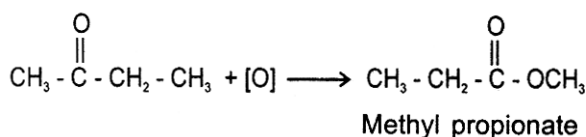
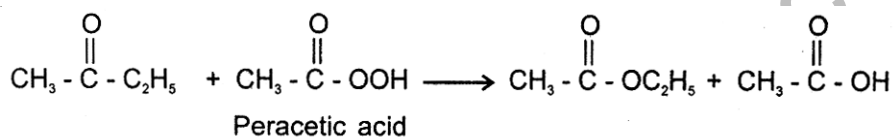
**Ethylation of Silver halides :**



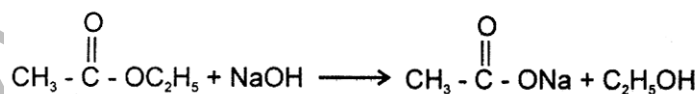
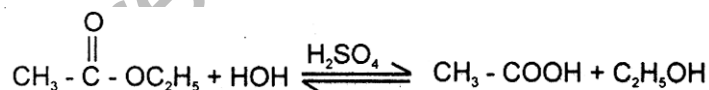
**Ethanolysis of Ethanenitrile :**

**By addition of Acetic acid on Ethylene :**

**By reaction of sodium Ethoxide on Acetyl chloride :**

**Baeyer–Villiger Oxidation :**

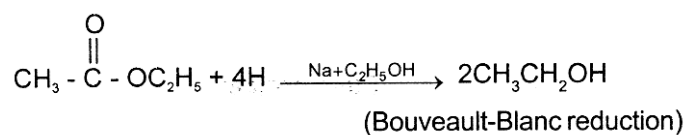
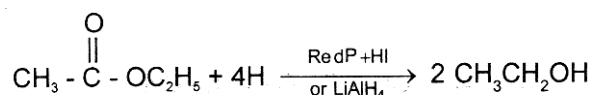
Ethyl acetate is formed on reacting butanone with a peracid, Methyl propionate is also formed in small amounts.

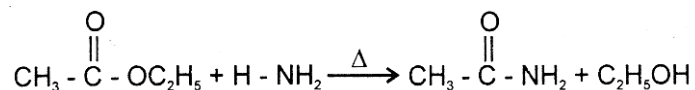
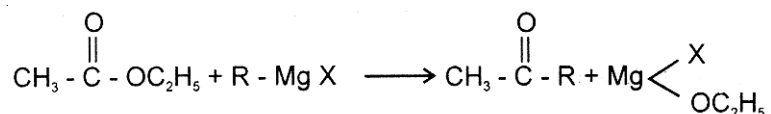

**5.2 Physical Properties :**

- [i] Colourless, sweet smelling steamvolatile, inflammable liquid.
- [ii] Very sparingly soluble in water, but soluble in organic solvents.
- [iii] Boiling point 78°.

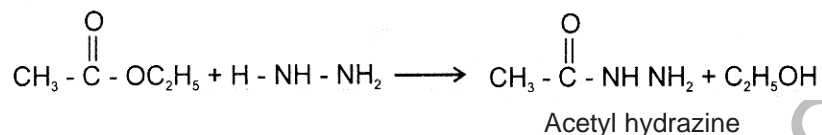
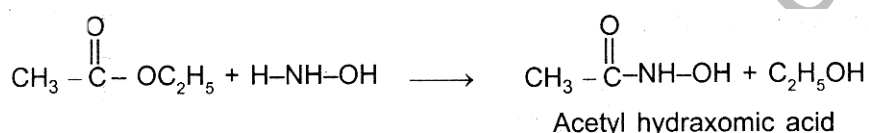
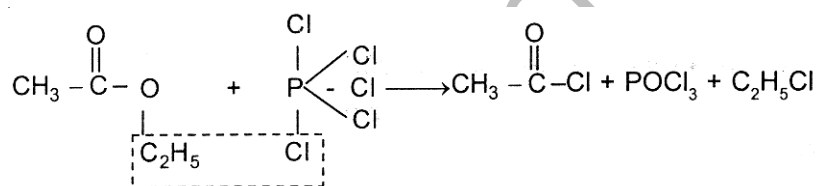
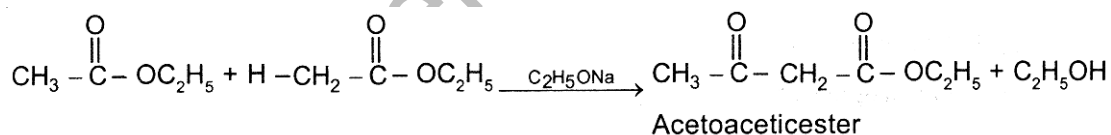
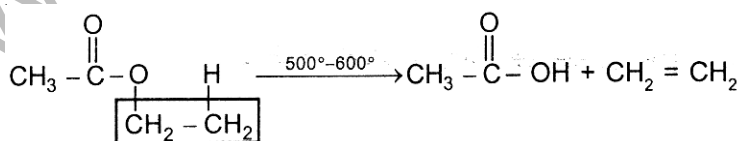
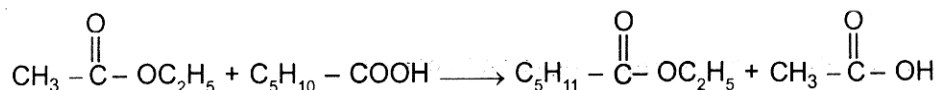
**5.3 Chemical Properties :**
**Hydrolysis :**


**Note :** In esters caustic alkalies hydrolysis is rapid and complete. Alkaline hydrolysis of esters is called "Saponification".

**Reduction :**


**Ammonolysis :**

**With Grignard's Reagent :**


**Note :** The product will be tertiary alcohol when 2 mole of Grignard's reagent are taken.

**With Hydrazine :**

**With Hydroxyl Amine :**

**With  $\text{PCl}_5$  :**

**Claisen Ester Condensation :**

**Pyrolysis or Thermal decomposition :**

**Acidolysis :**


# Benzoic Acid

## BENZOIC ACID (C<sub>6</sub>H<sub>5</sub>COOH)

Benzoic acid was first obtained by Schiele from gum benzoin. It is also present in Peru balsam and Tolu balsam in the form of its benzyl ester (benzyl benzoate).



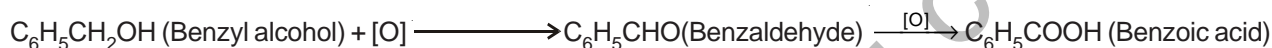
In combined form it is found as benzoylglycine in horse urine.



### 1.1 PREPARATION

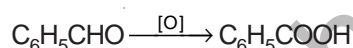
#### [1] Oxidation of Benzyl Alcohol :

Benzoic acid is formed on permanganate oxidation of benzyl alcohol.



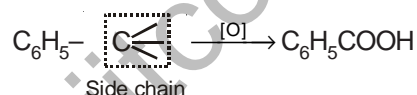
#### [2] Oxidation of Benzaldehyde :

Oxidation of benzaldehyde takes place very readily and benzoic acid is formed.



#### [3] Oxidation of Alkanes and Their Derivatives :

A side chain (alkyl group or substituent alkyl group) bonded directly to the benzene ring is converted to a carboxyl group on oxidation. Dilute nitric acid or chromic acid or alkaline permanganate can be used as oxidant.



Benzoic acid is obtained on oxidation of many compounds like alkanes (toluene, ethylbenzene, n-propylbenzene, cumene, etc.) and their oxygenated derivatives (benzyl alcohol, benzaldehyde, acetophenone, benzophenone, etc.) halogenated derivatives (benzyl chloride, benzal chloride, benzotrichloride etc) nitrogenated derivatives (cyanobenzene benzamide, etc.)

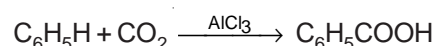
#### [4] Carboxylation of Grignard's Reagents :

Benzoic acid is formed on hydrolysis of the product obtained by passing carbon dioxide in ethereal solution of phenylmagnesium bromide.



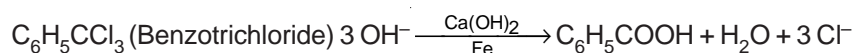
#### [5] Carboxylation of Benzene :

Benzoic acid is obtained on heating benzene and carbon dioxide in nitrobenzene medium in the presence of anhydrous aluminium chloride.



#### [6] Alkaline Hydrolysis of Benzotrichloride :

Benzoic acid is formed on hydrolysis of benzotrichloride by lime water in the presence of iron catalyst.

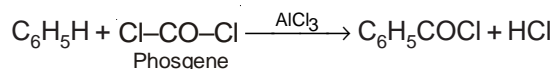


**[7] Hydrolysis of Benzoyl Chloride :**

Benzoic acid is obtained by hydrolysis of benzoyl chloride



Benzoyl chloride is prepared by Friedel–Crafts chloroformylation of benzene, Benzoic acid is obtained in 60% yield by the method.


**[8] Hydrolysis of Cyanobenzene :**

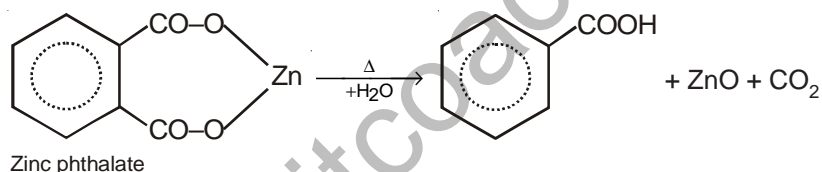
Benzoic acid is formed on hydrolysis of cyanobenzene i.e., benzonitrile by dilute hydrochloric acid.


**[9] Dehydroxylation of Hydroxybenzoic Acid :**

Benzoic acid is formed on dry distillation of o-, m- or p-hydroxybenzoic acid with zinc dust. The ortho isomer is called salicylic acid.


**[10] Decarboxylation of Phthalic Acid :**

o-Benzendicarboxylic acid is called phthalic acid. On heating its zinc or nickel or chromium salt at 200–300° with water vapours, benzoic acid is formed by partial decarboxylation.


**[11] Hydrolysis of Benzoic Acid Derivatives :**

Benzoic acid is formed on hydrolysis of esters, anhydride, acid chloride and amide of benzoic acid.



Benzoyl chloride and benzoic anhydride very readily get hydrolysed by water, but with little bit more difficulty as compared to aliphatic acid chlorides. Hydrolysis by alkali takes place faster.



Hydrolysis of benzoic esters takes place on heating with an alkali.



Hydrolysis of benzamide takes place on boiling with dilute acid or alkali solution.



Liberation of ammonia gas on heating the solution after adding sodium hydroxide solution is the test for amides.

**1.2 PHYSICAL PROPERTIES**

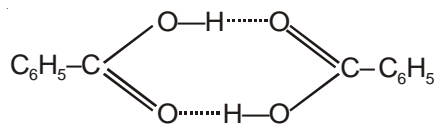
Benzoic acid is a crystalline solid (melting point 122°) which is sparingly soluble in cold water, but readily soluble in hot water. It is also soluble in organic solvents like alcohol ether, etc. Its acid strength is more than that of the alkanolic acids due to weak negative inductive effect of phenyl group.

### 1.3 RESONANCE IN BENZOIC ACID

The COOH group present in benzoic acid is a strong electron-attracting group due to which the benzene ring is deactivated and rate of  $S_E$  reaction decreases as compared to unsubstituted benzene. Therefore, the COOH group exerts a deactivating effect on the benzene ring.

#### Dimerisation in Benzoic Acid due to Hydrogen Bonding :

Benzoic acid in liquid phase (in benzene solution or in molten form) exists in the form of a dimer by association due to intermolecular hydrogen bonding in the same fashion as in alkanolic acids. This is the reason why the experimental value of the molecular weight of benzoic acid is twice the calculated value.



Hydrogen bonded dimer of benzoic acid

### 1.4 REACTIONS

Benzoic acid gives the following two types of reactions.

[A] Reactions due to COOH group

[B] Reactions due to  $C_6H_5$  group

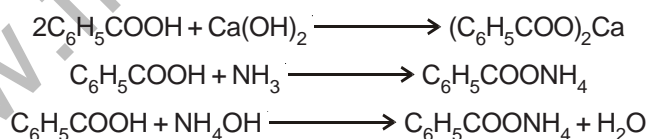
#### [A] Reaction Due to Carboxyl Group :

##### 1. With Bases :

Many alkaline compounds form benzoate salts on reacting with benzoic acid.

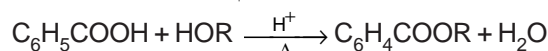


Phenol (a weak acid) does not react with sodium bicarbonate, whereas benzoic acid gives effervescence of  $CO_2$ , although both are acidic organic compounds toward litmus. Therefore, distinction between phenol and carboxylic acids can be done by using  $NaHCO_3$ .



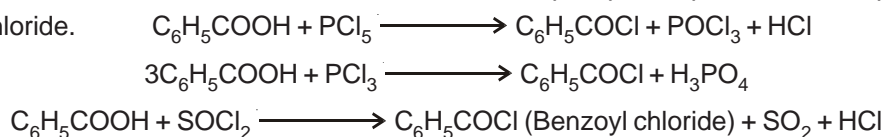
##### 2. With Alcohols :

An alkyl benzoate is formed by esterification on heating a mixture benzoic acid and an alkanol in the presence of a few drops of concentrated  $H_2SO_4$ .



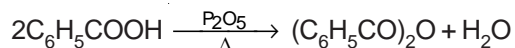
##### 3. With Inorganic Chloride :

Benzoyl chloride is formed on the reaction of benzoic acid with phosphorous pentachloride or phosphorous trichloride or thionyl chloride.



**4. With P<sub>2</sub>O<sub>5</sub> :**

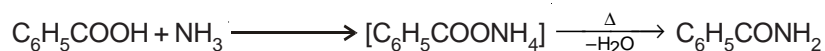
Benzoic anhydride is formed on heating benzoic acid with P<sub>2</sub>O<sub>5</sub>.



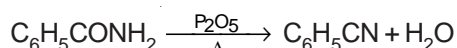
Acetic anhydride also dehydrates two molecules of benzoic acid to give benzoic anhydride.

**5. With Ammonia :**

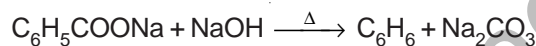
Benzamide is formed on heating benzoic acid with ammonia.



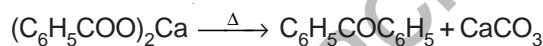
Benzonitrile or cyanobenzene can be obtained by heating benzamide with P<sub>2</sub>O<sub>5</sub>.


**6. With Soda Lime :**

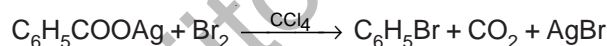
Benzene is obtained on dry distillation of sodium salt of benzoic acid with sodalime.


**7. Dry Distillation of Calcium Salt :**

Benzophenone is obtained on dry distillation of calcium salt of benzoic acid.


**8. Hunsdiecker Reaction :**

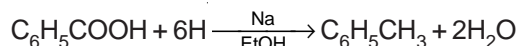
Bromobenzene is formed on heating the silver salt of benzoic acid with bromine in carbon tetrachloride solution


**9. Reduction by Lithium Aluminium Hydride :**

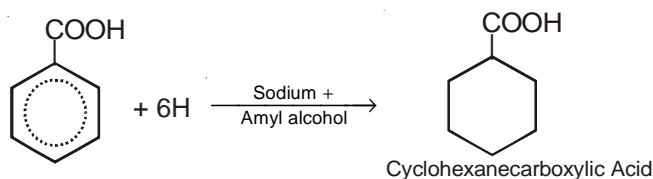
Benzyl alcohol is formed on reduction of benzoic acid by lithium aluminium hydride (LiAlH<sub>4</sub>).


**10. Reduction by Sodium and Ethanol :**

Toluene is formed on reduction of benzoic acid by sodium and ethanol.


**[B] Reduaction Due to Aromatic Ring :**
**Hydrogenation by Sodium and Amyl Alcohol :**

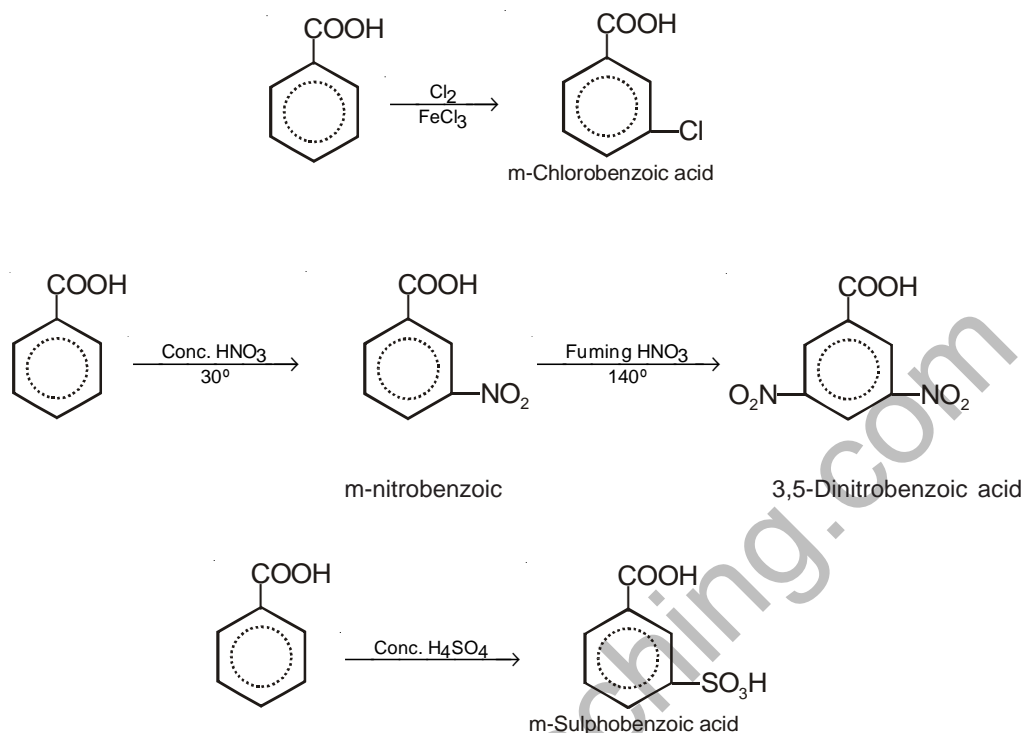
The COOH group is not affected on reduction of benzoic acid by sodium and amyl alcohol but benzene ring of benzoic acid is completely hydrogenated to form Cyclohexanecarboxylic acid.





**Aromatic Electrophilic Substitution Reaction :**

Meta substitution products are formed on halogenation nitration and sulphonation of benzoic acid.



**Note :** Due to the presence of a deactivating m-directing COOH group in benzoic acid, the latter does not give Friedel-Crafts reaction.

**1.5 TESTS****1. Formation of Ferric salt :**

A red-brown precipitate is obtained on adding a small amount of neutral ferric chloride solution in benzoic acid solution.

**2. Esterification :**

A sweet odour of ethyl benzoate is perceived on heating benzoic acid after adding a few drops of ethyl alcohol and concentrated sulphuric acid.

**3. Decarboxylation :**

Inflammable vapours of benzene are liberated out on heating benzoic acid after mixing it thoroughly with soda lime.

**1.6 USES**

**Benzoic acid is used as follows :**

1. As a germicide.
2. Benzoic acid and its salts are used in the form of medicines.
3. Sodium benzoate is used as a preservative of canned food products.
4. Benzoic acid is used in the manufacture of many synthetic dyes, like aniline blue dye.
5. Ethyl ester of benzoic acid (ethyl benzoate) is used as a flavouring agent.