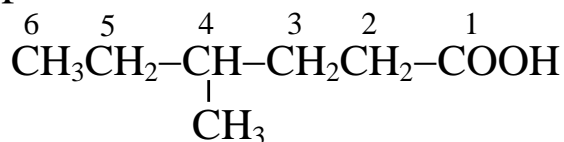


## CARBOXYLIC ACID & THEIR DERIVATIVES

The  $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{OH} \end{array}$  group, which apparently contains a carbonyl group, fails to show the reactivities of carbonyl compounds and acts as a separate functional group called carboxylic acid group.

### 1. Nomenclature

These are normally suffixed as “oic acid”, when  $\text{CO}_2\text{H}$  is the principal functional group and its carbon is counted while numbering longest chain. The carboxyl carbon is assigned number 1 in the IUPAC nomenclature. For example,

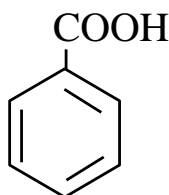


4-Methylhexanoic acid

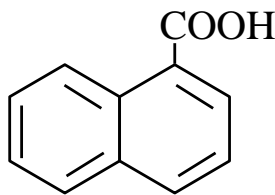
Name of the alkane without (-e)

Formic acid is called as methanoic acid and  $\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}_2\text{COOH}$  is called as 4-hexenoic acid.

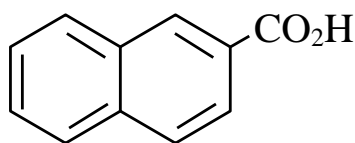
When  $\text{CO}_2\text{H}$  group is the main functional group but its carbon is not counted while selecting longest chain, then the suffix used is “carboxylic acid”. For example,



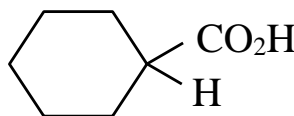
Benzene carboxylic acid



Naphthalene-1-carboxylic acid



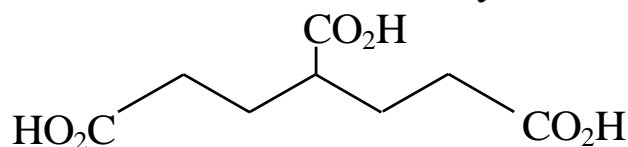
Naphthalene-2-carboxylic acid



Cyclohexane carboxylic acid

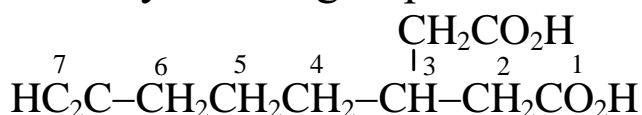
## CARBOXYLIC ACID & THEIR DERIVATIVES

If an unbranched chain is directly linked to more than 2 CO<sub>2</sub>H groups, these groups are named from the parent hydride by substitutive use of a suffix such as “tricarboxylic acid”.




Pentane-1,3,5-tricarboxylic acid

When all carboxylic acid groups cannot be described in the suffix, a carboxylic acid group is indicated by the prefix “carboxy”.

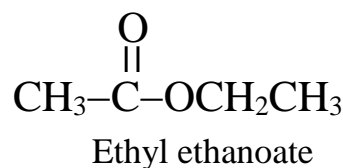


3-(Carboxymethyl)heptanedioic acid

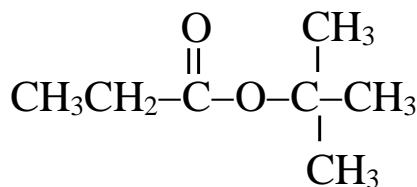
Dicarboxylic acids are named as “alkanedioic acids”. For example,  is named as ethanedioic acid, HO<sub>2</sub>C–CH<sub>2</sub>–CO<sub>2</sub>H is named as propanedioic acid and HO<sub>2</sub>C–CH<sub>2</sub>CH<sub>2</sub>–CO<sub>2</sub>H is named as butane-1,4-dioic acid.

### Esters:

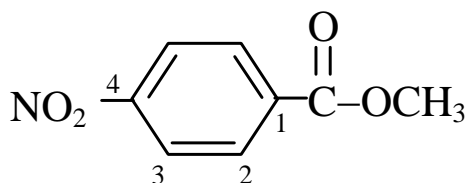
According to IUPAC nomenclature, esters are named as “alkyl alkanoate”. For example,



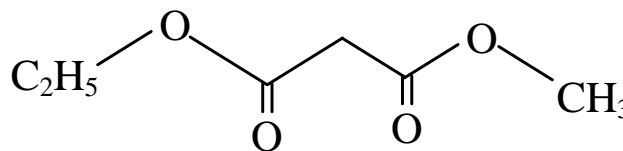
Ethyl ethanoate



tert-butyl propionate



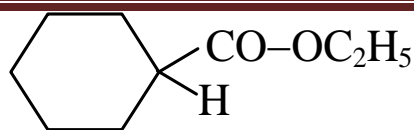
Methyl 4-nitrobenzoate



Ethyl methyl malonate

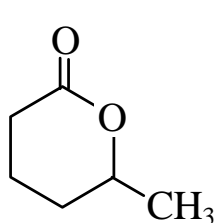
When ester is the main functional group but its carbon is not counted while selecting the longest chain, then the name of the ester is written as “Alkyl alkane carboxylate”.

## CARBOXYLIC ACID & THEIR DERIVATIVES

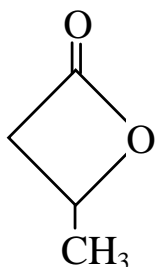


Ethyl cyclohexane carboxylate

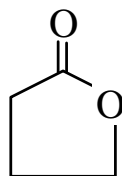
Lactones are named by replacing “lactone” for the “ic acid” ending of a systematic “-oic acid” name for the non-hydroxylated parent acid and inserting a locant designating the position of OH group between the “o” and “lactone”.



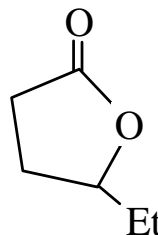
δ-Caprolactone  
or Hexane-5-lactone



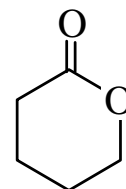
β-Butyrolactone  
or Butano-3-lactone



γ-Butyrolactone  
or Tetrahydrofuran-2-one  
or Butano-4-lactone



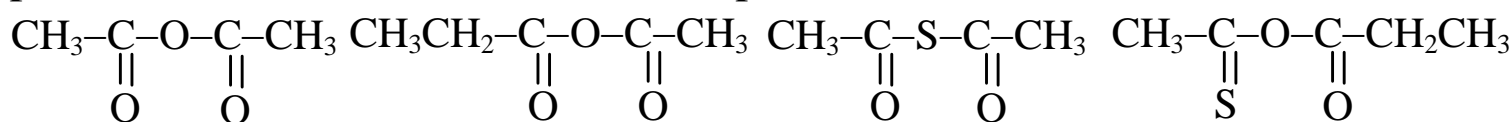
γ-Caprolactone  
or Hexano-4-lactone



δ-Valerolactone  
or Pentano-5-lactone

### Carboxylic acid anhydride:

Carboxylic acid anhydrides are named as “alkanoic anhydride” (if only one type of alkyl group is present) but when two different alkyl groups are present, then alkanoic are named in alphabetical order.

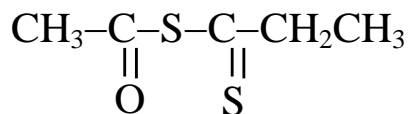


Ethanoic anhydride  
or Acetic anhydride

Ethanoic propionic anhydride  
or Acetic propionic anhydride

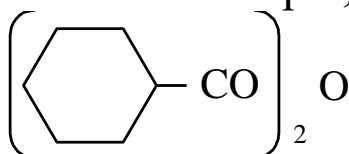
Acetic thioanhydride  
or Ethanoic thioanhydride

Propionic thioacetic  
anhydride



Acetic thiopropionic thioanhydride

When anhydride group is the main functional group but its carbon is not counted while selecting longest chain, then the suffix used is “carboxylic anhydride”. For example,

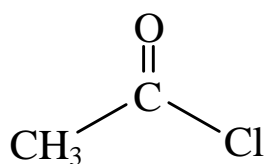


Cyclohexanecarboxylic anhydride

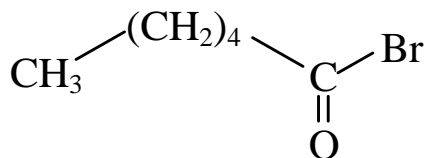
## CARBOXYLIC ACID & THEIR DERIVATIVES

### Acid halide:

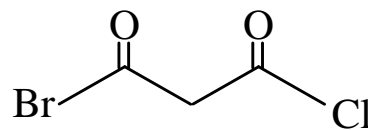
According to IUPAC nomenclature, acid halides are named as “alkanoyl halide”. For example,  $\text{CH}_3\text{COCl}$  is named ethanoyl chloride or acetyl chloride and  $\text{CH}_3\text{CH}_2\text{COCl}$  is called propanoyl chloride.



Acetyl chloride or Ethanoyl chloride

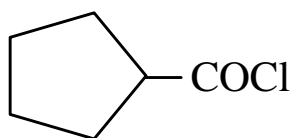


Hexanoyl bromide

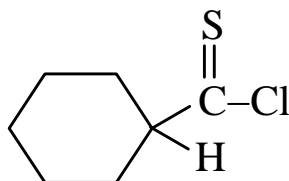


Malonyl bromide chloride

When COX group is the main functional group but its carbon is not counted while selecting the longest chain, then the suffix used is “carbonyl halide”. For example,



Cyclopentane carbonyl chloride

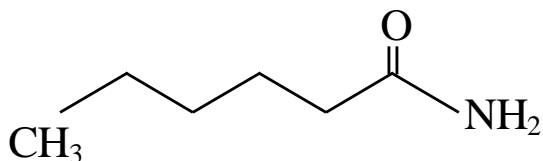


Cyclohexane carbothioyl chloride

### Acid amide:

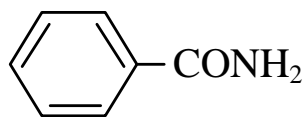
According to IUPAC nomenclature, primary acid amides are named as “alkanamide”.

For example,  $\text{CH}_3\text{CONH}_2$  is named acetamide or ethanamide and  $\text{CH}_3\text{CH}_2\text{CONH}_2$  is called propanamide.

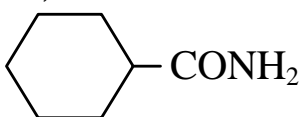


Hexanamide

When  $\text{CONH}_2$  group is the main functional group but its carbon is not counted while selecting the longest chain, then the suffix used is “carboxamide”. For example,



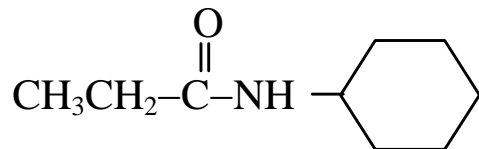
Benzene carboxamide



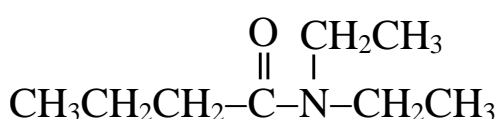
Cyclohexanecarboxamide

## CARBOXYLIC ACID & THEIR DERIVATIVES

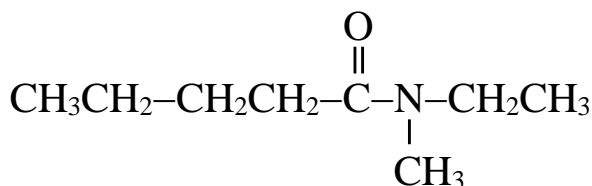
According to IUPAC nomenclature, secondary acid amides are named as N-alkyl alkanamide and tertiary acid amides are named as N,N-dialkyl alkanamide, if identical substituents are present but when the substituents present are different they are to be named in alphabetical order.



N-Cyclohexylpropanamide

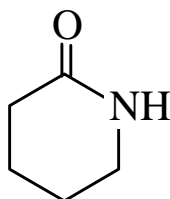


N,N-Diethylbutanamide

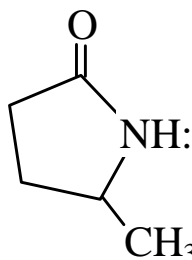


N-Ethyl-N-methylpentanamide

Cyclic amides (lactam) are named just as lactones by replacing “lactone” in the name by “lactam”.



$\delta$ -Valerolactam  
or Pentano-5-lactam



$\gamma$ -Valerolactam  
or Pentano-4-lactam

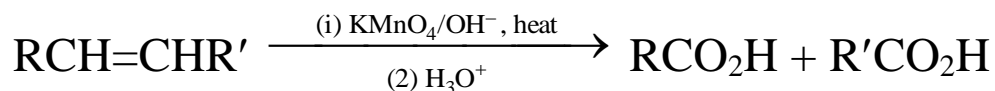
Tautomeric forms of lactam are called “lactim”.

## 2. Carboxylic Acids

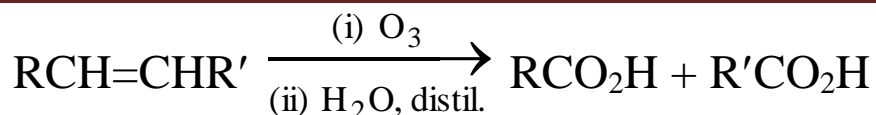
### 2.1 Preparation of Carboxylic Acids

#### 1. By oxidation of alkenes

When alkenes are treated with an oxidising agent such as  $\text{KMnO}_4$  or on oxidative ozonolysis, it forms carboxylic acids.

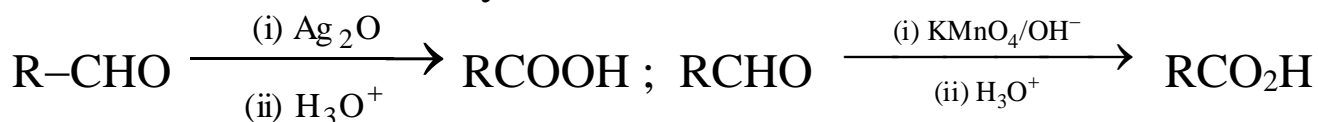


## CARBOXYLIC ACID & THEIR DERIVATIVES

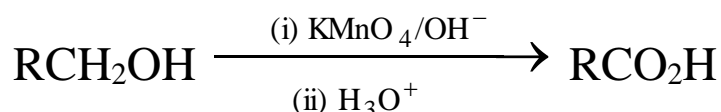


### 2. By oxidation of aldehydes or primary alcohols

When aldehydes are reacted with  $\text{Ag}_2\text{O}$ ,  $\text{H}_3\text{O}^+$  or with acidified or alkaline  $\text{KMnO}_4$ , it forms carboxylic acids.

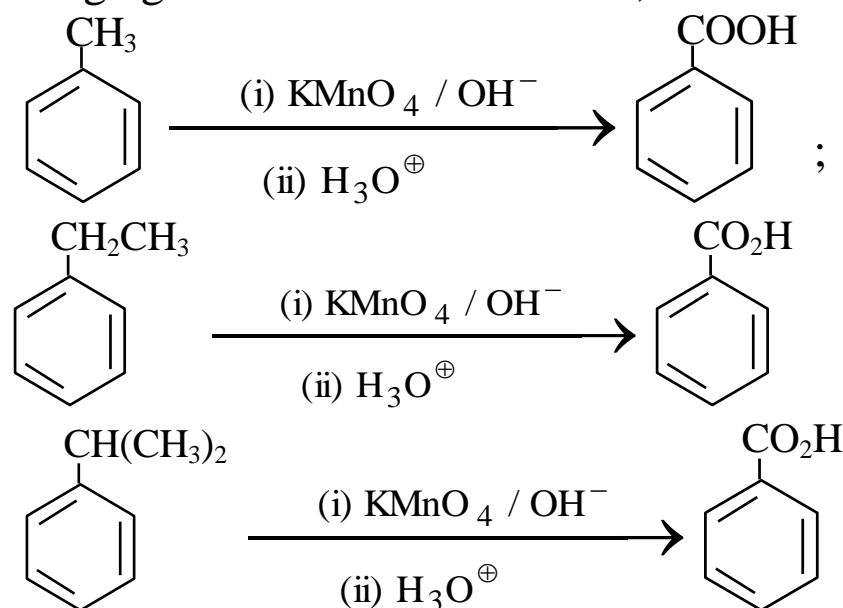


Primary alcohols can be oxidised to carboxylic acids by acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  or acidified/alkaline  $\text{KMnO}_4$ .



### 3. By oxidation of alkyl benzene (for aromatic acids)

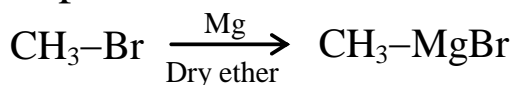
When the arenes containing an  $\alpha$ -hydrogen atom are reacted with a strong oxidising agent like alkaline  $\text{KMnO}_4$ , it forms benzoic acid.



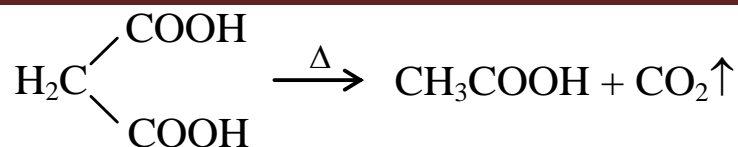
### 4. Using Grignard reagent

When Grignard reagent is reacted with  $\text{CO}_2$ , the alkyl part of  $\text{RMgX}$  reacts at the carbon of  $\text{CO}_2$  to form magnesium salt of carboxylate, which on acid hydrolysis gives carboxylic acid.

For example,

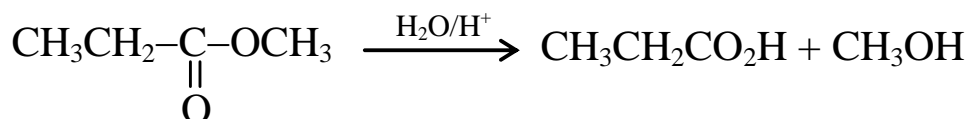
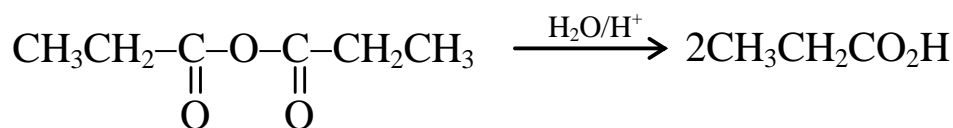
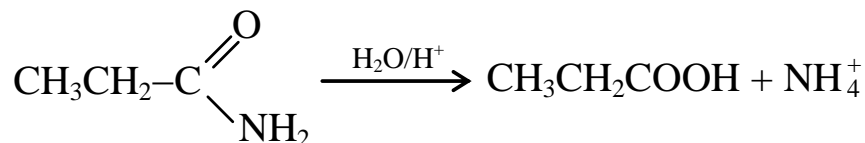
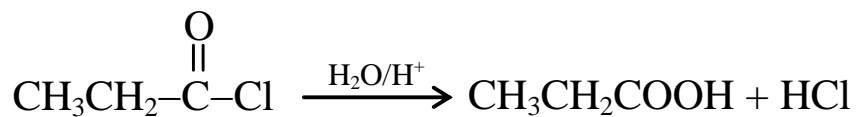


## CARBOXYLIC ACID & THEIR DERIVATIVES



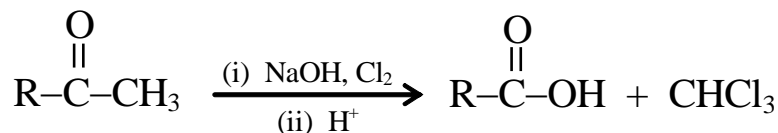
### 7. Hydrolysis of acid derivatives

Another useful method constitutes the hydrolysis of carboxylic acid derivatives such as acyl halides, acid amides, acid anhydrides or esters.



### 8. By the Oxidation of Methyl Ketones

Oxidation of  $-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$  group with sodium hypochlorite ( $\text{NaOH} + \text{Cl}_2$ ) results in a carboxyl group formation.



It is a specific reagent for this group. The reaction is commonly called “haloform reaction”.

## 2.3 Chemical Reactions

The most important properties of carboxylic acids are their conversion to important functional derivatives. The reactions of carboxylic acids may be discussed under the following categories.

(a) Reactions involving the  $-\text{OH}$  group.



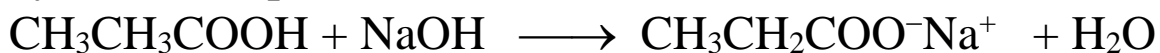
## CARBOXYLIC ACID & THEIR DERIVATIVES

(b) Reactions involving the  $\begin{array}{c} \diagup \\ \text{C=O} \\ \diagdown \end{array}$  group.

(c) Reactions involving the  $-\text{COOH}$  group.

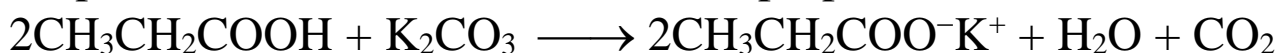
(d) Reactions involving the aliphatic moiety.

1. Carboxylic acids react rapidly with aqueous solutions of sodium hydroxide or potassium carbonate to form soluble salts.



Propionic acid

Sodium propionate

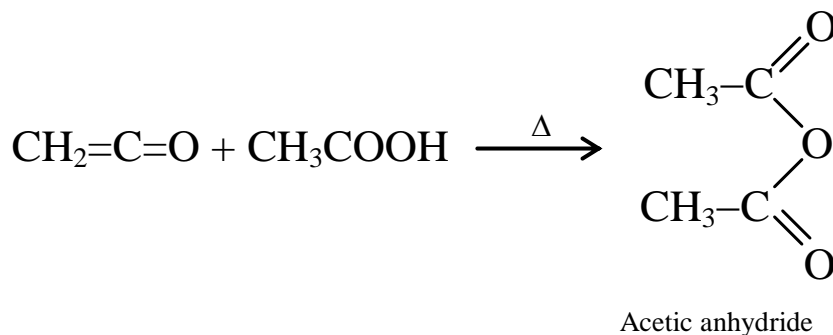
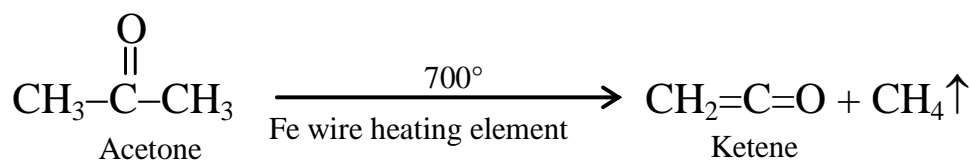
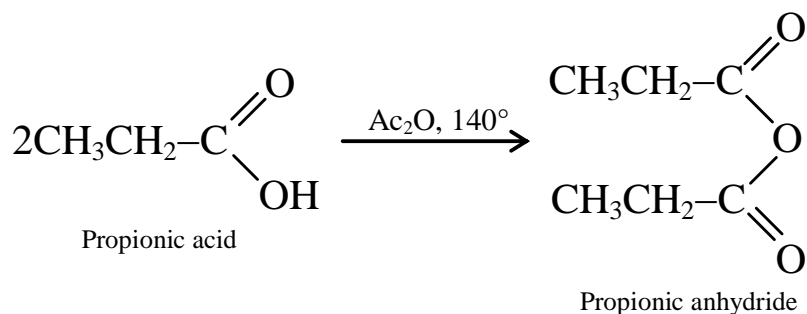


Propionic acid

Potassium propionate

Aqueous solutions of these salts are alkaline, they being salts of a strong base and a weak acid. The sodium or potassium salts of long chain fatty acids are known as “*soaps*”.

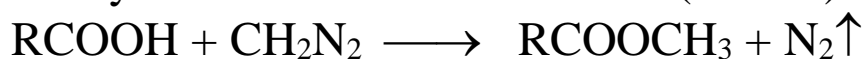
2. Symmetrical anhydrides are obtained by heating together a carboxylic acid and acetic anhydride. Acetic anhydride, however, is prepared by a special method from ketene and acetic acid.



## CARBOXYLIC ACID & THEIR DERIVATIVES

### 3. Reaction with Diazomethane:

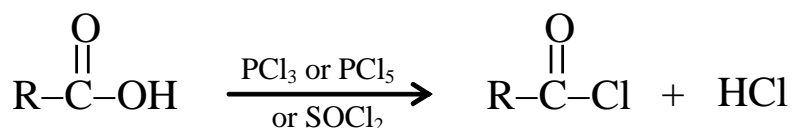
A synthetically useful reaction of carboxylic acid is the formation of methyl esters by reaction with diazomethane( $\text{CH}_2\text{N}_2$ ).



### 4. With $\text{LiAlH}_4$ or $\text{NaBH}_4$

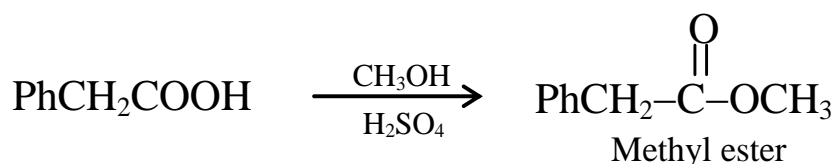


### 5. With $\text{PCl}_3$ or $\text{PCl}_5$ or $\text{SOCl}_2$



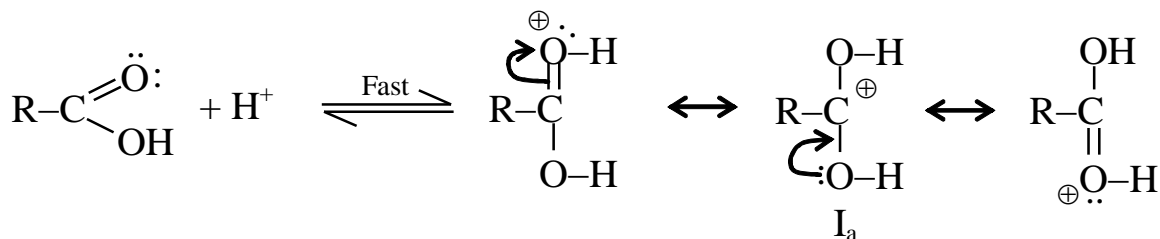
With  $\text{PCl}_3$ ,  $\text{H}_3\text{PO}_3$ ; with  $\text{PCl}_5$ ,  $\text{POCl}_3$  and with  $\text{SOCl}_2$ ,  $\text{SO}_2$  are the other products.

### 6. With $\text{ROH}$ and $\text{NH}_3$

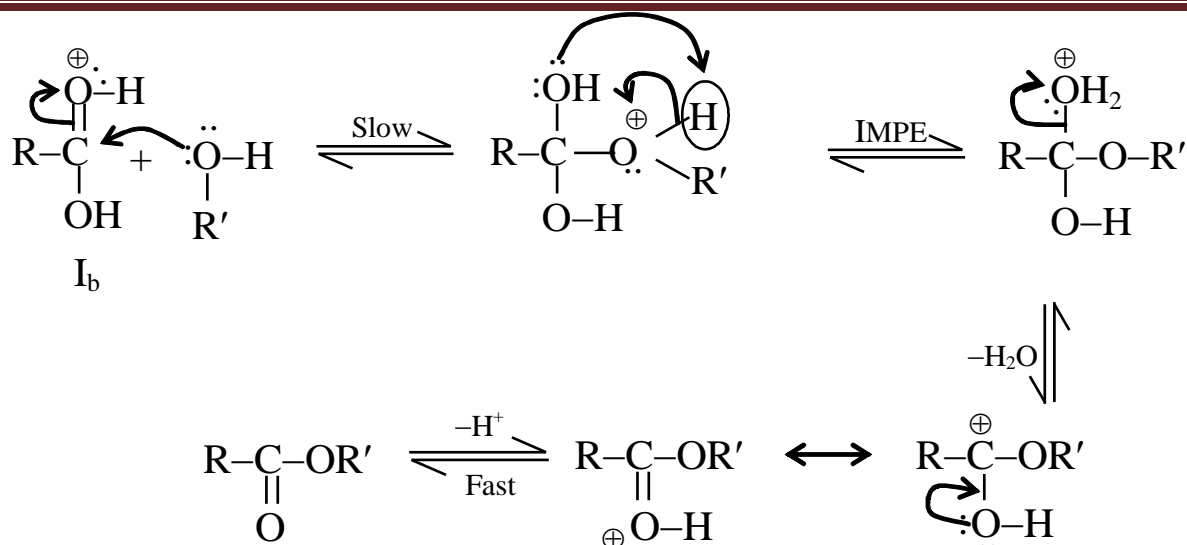


### Mechanism of esterification by acid catalysis:

A direct reaction between a carboxylic acid and alcohol under the catalytic effect of sulphuric acid yields an ester. This is a reversible reaction and is known as the “*Fischer esterification*”.

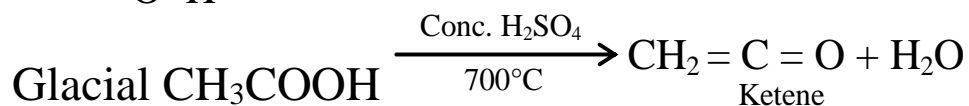
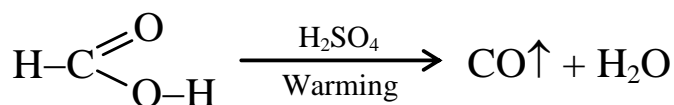
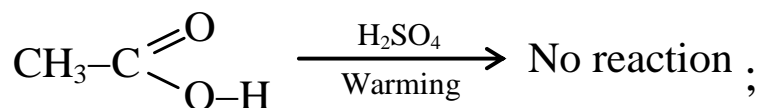


## CARBOXYLIC ACID & THEIR DERIVATIVES



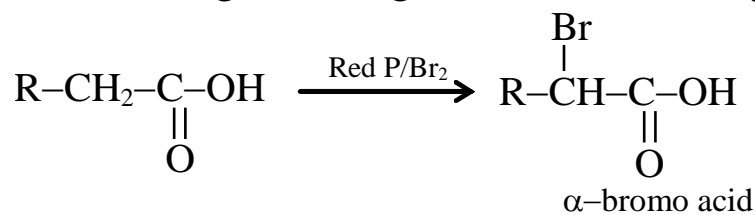
Base catalysed esterification is very rare. Molecularity of the above esterification reaction is two.

### 7. Conc. $\text{H}_2\text{SO}_4$ treatment



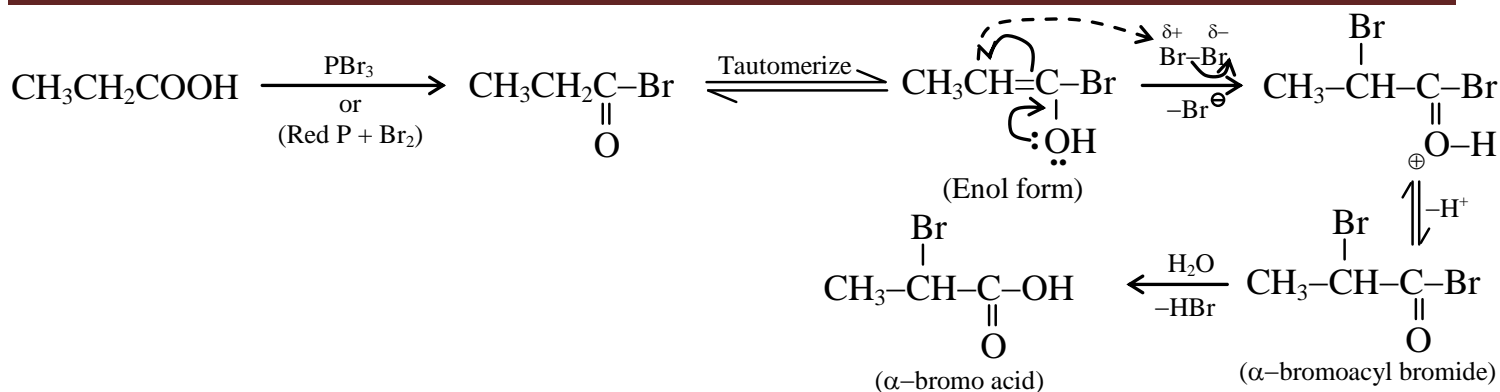
### 8. Hell–Volhard–Zelinsky (HVZ) reaction

This is a reaction affecting  $\alpha$ -halogenation of carboxylic acid.

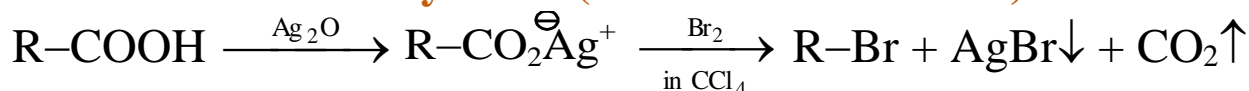


The possible mechanism for the reaction is

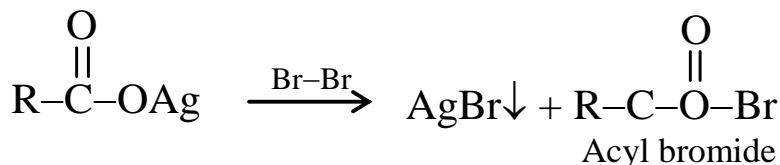
## CARBOXYLIC ACID & THEIR DERIVATIVES



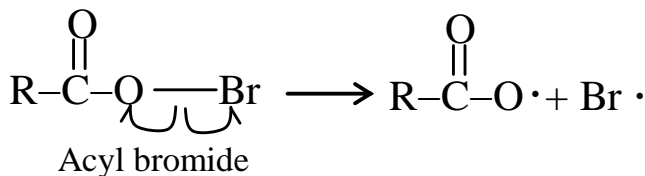
### 9. Brominative decarboxylation (Hunsdieker reaction)



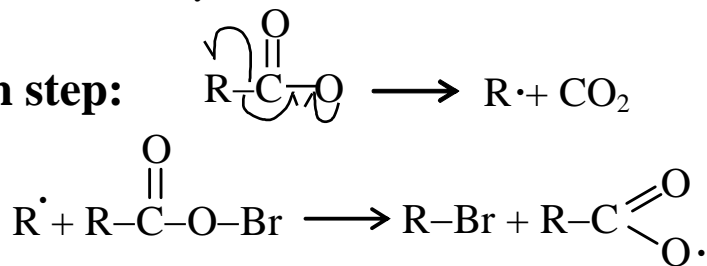
The mechanism of the reaction is via free radical and various steps in the mechanism are shown as below.



**Chain initiation step:**



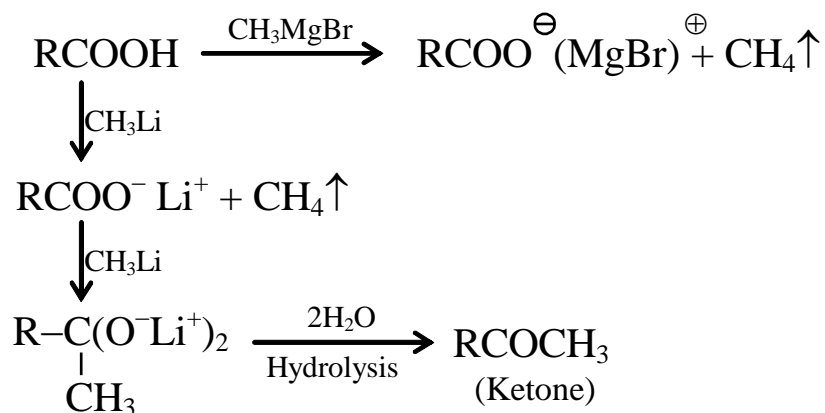
**Chain propagation step:**



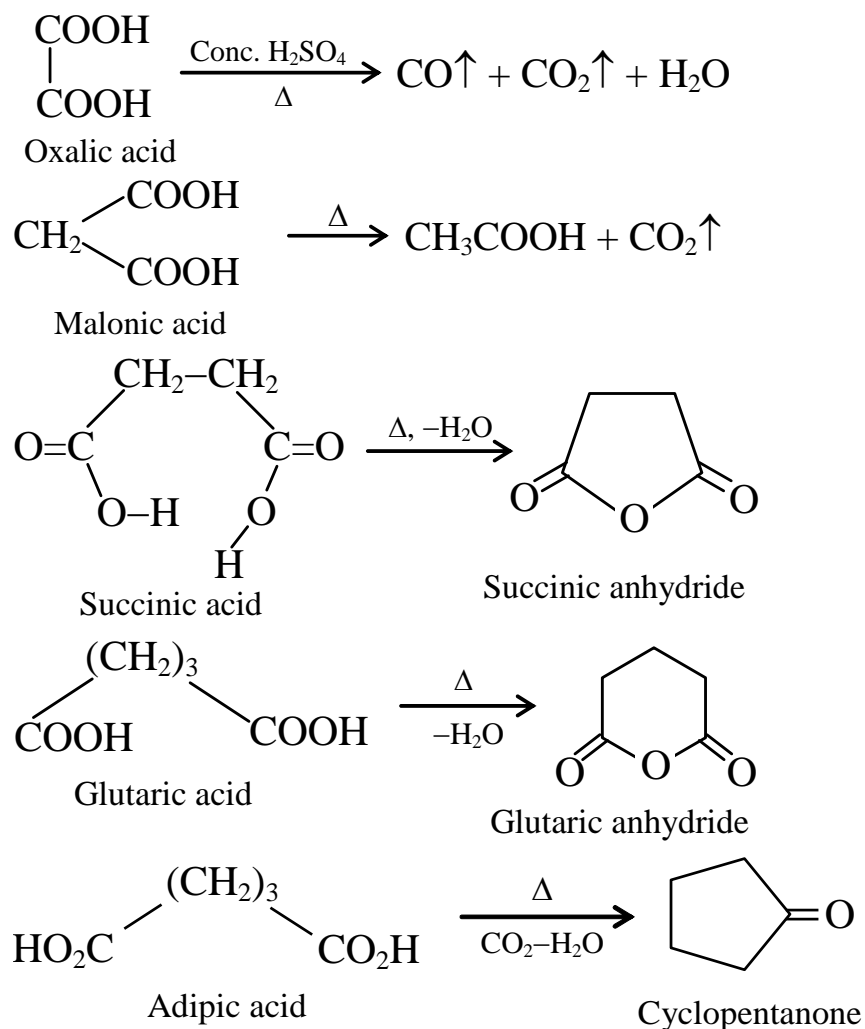
Then both the propagation steps are repeated till either the reactants are consumed or any two radicals collide.

## CARBOXYLIC ACID & THEIR DERIVATIVES

### 10. With excess of organometallic compounds:



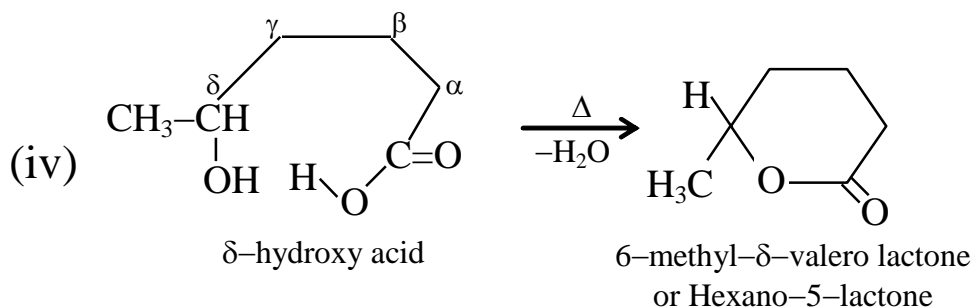
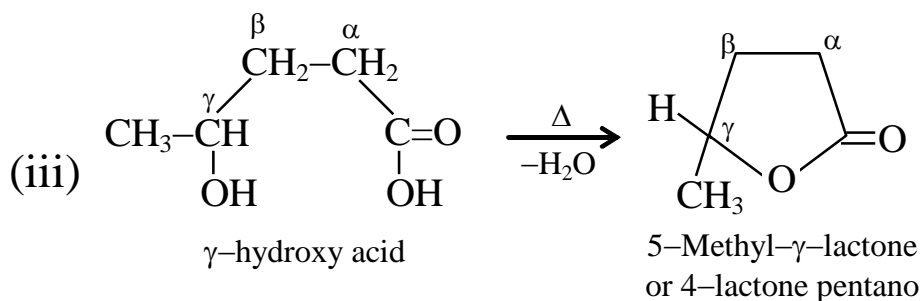
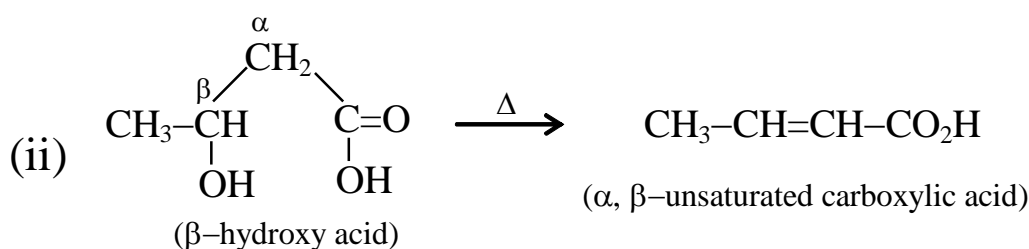
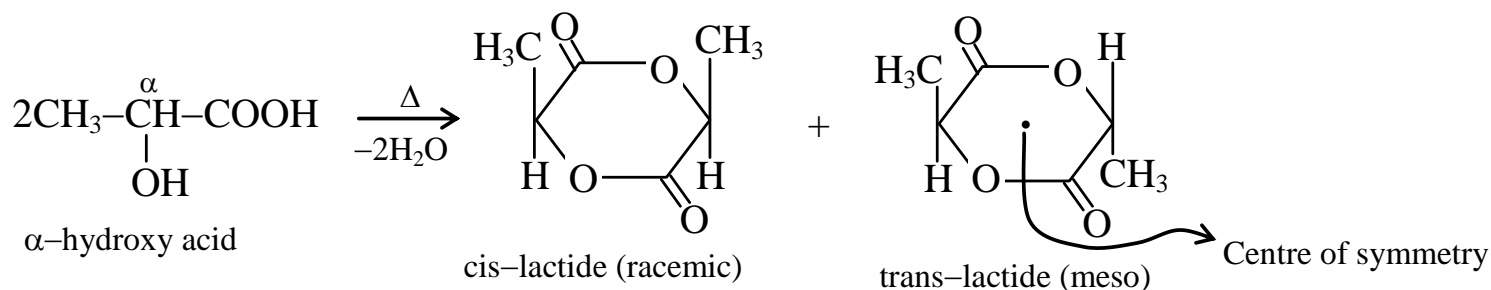
### 11. Action of heat on dicarboxylic acids:



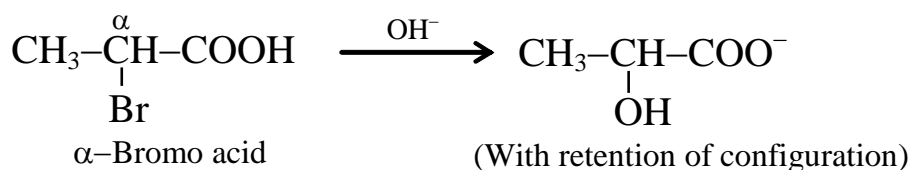
## CARBOXYLIC ACID & THEIR DERIVATIVES

### 12. Heating of $\alpha$ , $\beta$ and $\gamma$ - hydroxy carboxylic acids

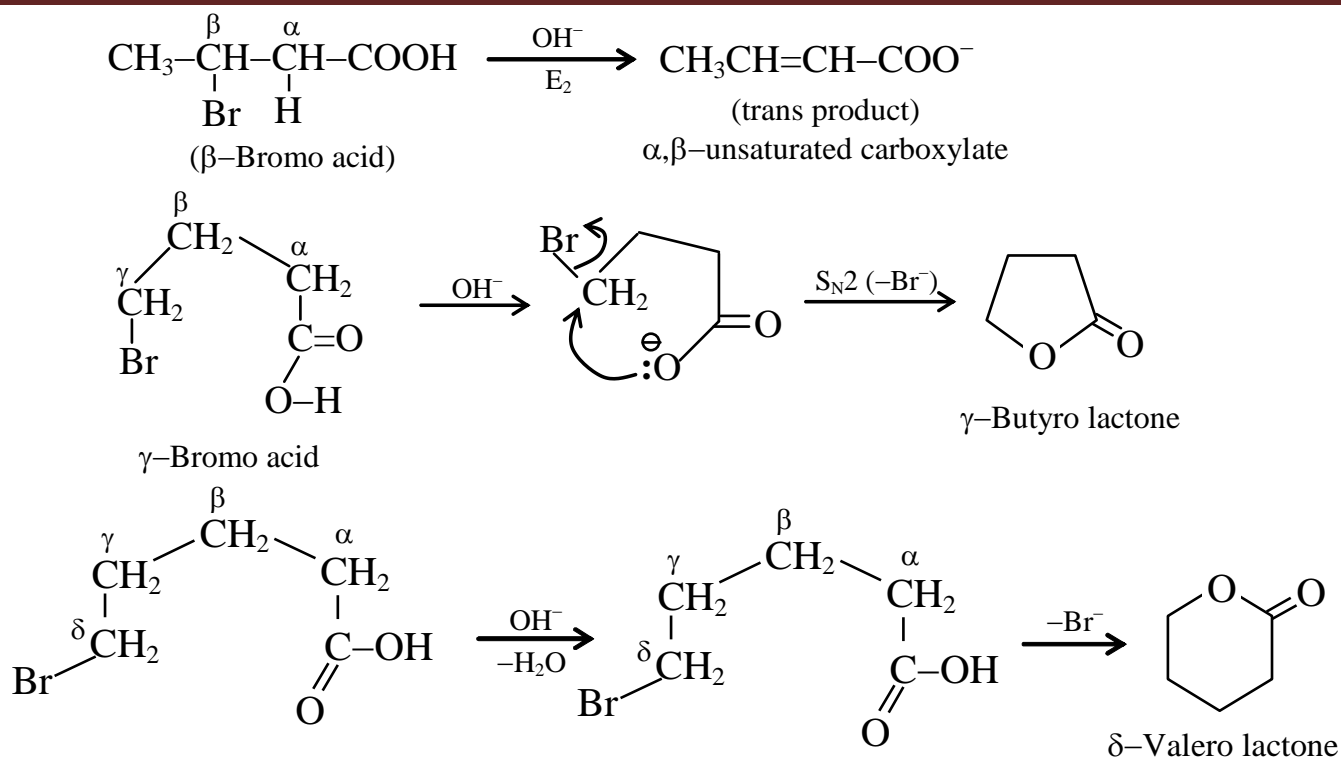
(i)



### 13. Treatment of $\alpha$ , $\beta$ and $\gamma$ -halo carboxylic acid with aqueous NaOH

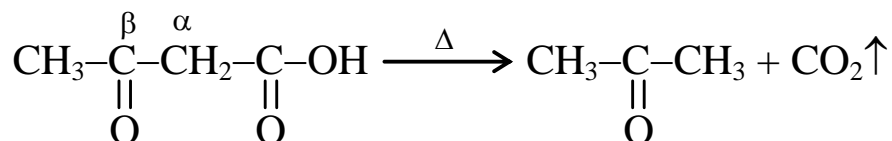


## CARBOXYLIC ACID & THEIR DERIVATIVES

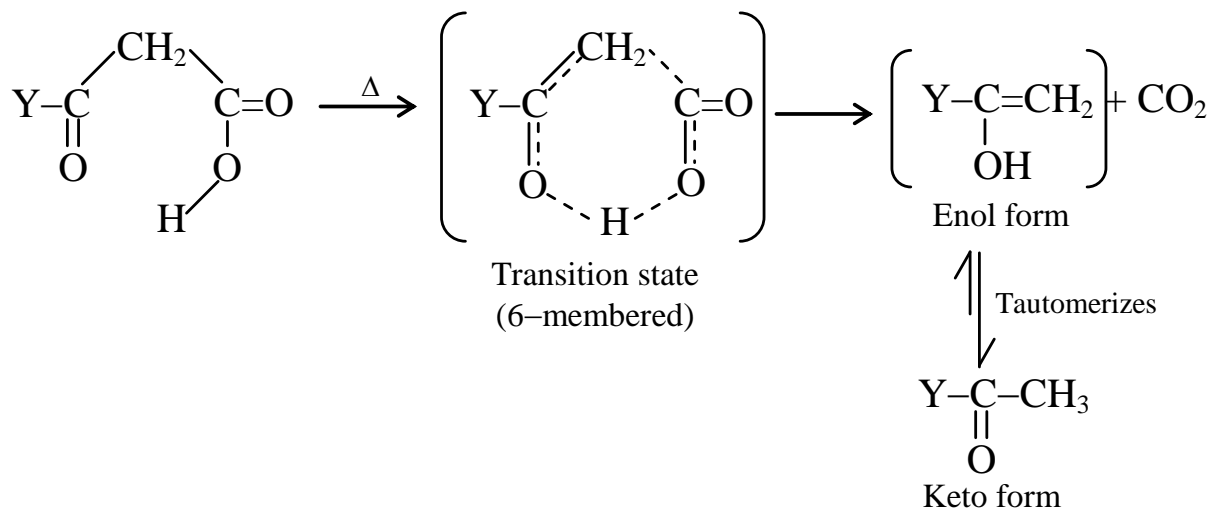


### 14. Decarboxylation

$\beta$ -keto acids on slightest warming alone or in presence of a base undergoes ready loss of  $\text{CO}_2$ . The process of loss of  $\text{CO}_2$  is called “decarboxylation”. For example,

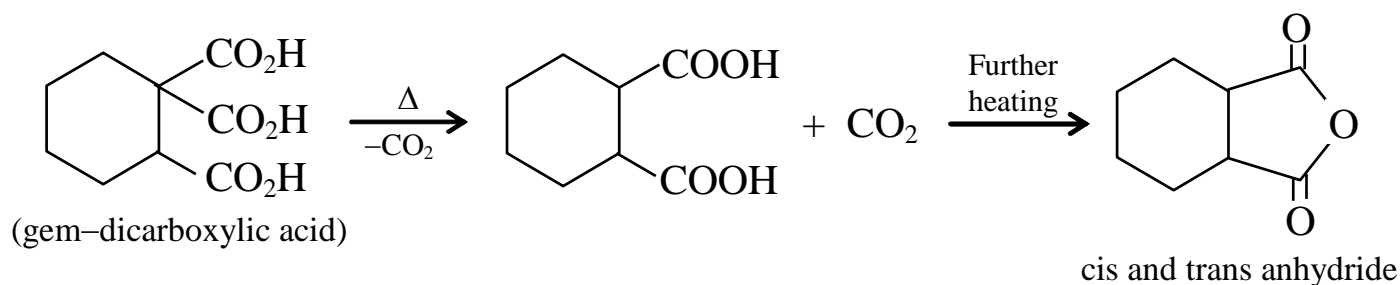


#### Mechanism:



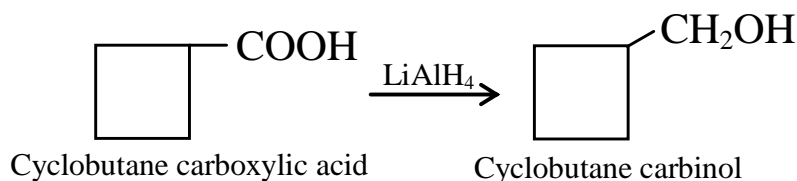
## CARBOXYLIC ACID & THEIR DERIVATIVES

Here Y can be substituents like CH<sub>3</sub>, OH etc.

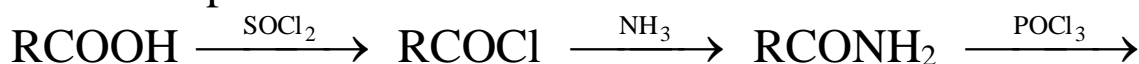


**15.** In the carboxyl group, the carbonyl and the hydroxyl groups are in close association. This tends to modify the chemistry associated with either group alone. In particular, the type of nucleophilic addition reactions identified with the carbonyl group in aldehydes or ketones are commonly not observed with acids. This may be accounted for by the fact that an attacking base preferentially abstracts an  $\text{H}^+$  ion. Because of its negative charge and large resonance energy, resists the addition of a second molecule of the attacking base. It thus does not form an oxime or phenyl hydrazone.

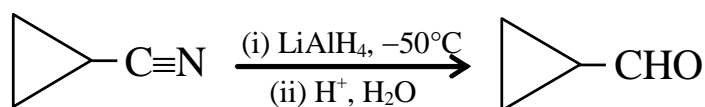
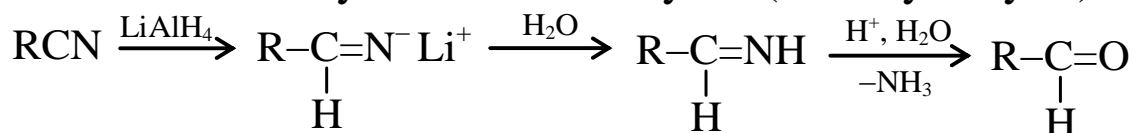
Lithium aluminium hydride reduces a carboxyl group to a primary alcohol. The reduction, however, does not take place with  $\text{NaBH}_4$ .



Reduction of the carboxyl group with  $\text{LiAlH}_4$  also takes place to an aldehyde at low temperature.



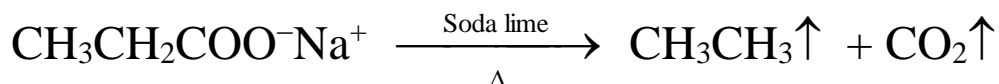
$\text{LiAlH}_4$  can also reduce cyamides to aldehydes (after hydrolysis).





## CARBOXYLIC ACID & THEIR DERIVATIVES

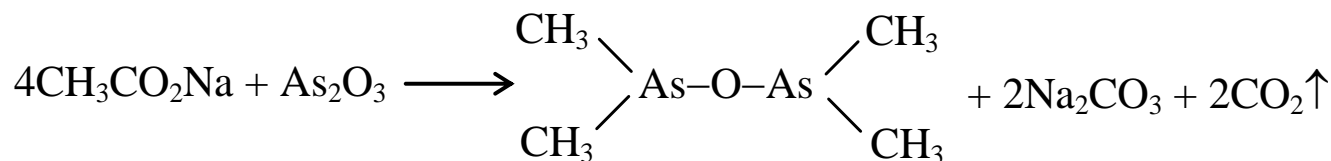
Sodium salts of the acid, on fusion with soda lime (NaOH + CaO) also suffer loss of carbon dioxide and the corresponding hydrocarbon is obtained.



A carboxylic acid can be decarboxylated without soda lime if it contains a  $\beta$ -carbonyl group or a ' $\beta, \gamma$ '  $-\text{C}=\text{C}-$  bond.

### 16. Cacodyl oxide test

Acetate salt on heating with solid  $\text{As}_2\text{O}_3$  gives cacodyl oxide, which have an extremely nauseating odour. The cacodyl oxide is poisonous also.

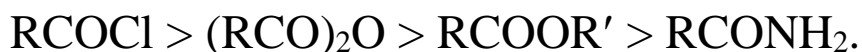


Cacodyl oxide (nauseating odour)

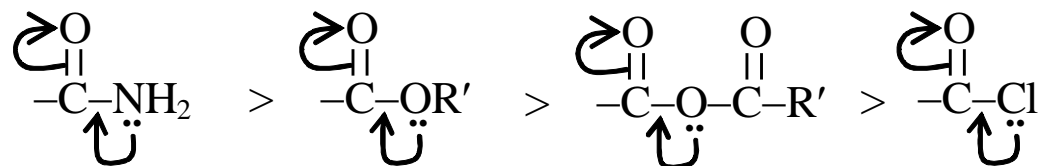
### Comparison of The Reactivity of Various Acid Derivatives

Partial positive charge of  $\overset{\text{O}}{\parallel}{-\text{C}-}$  bonds in esters, anhydride, amide and acyl halides determine how fast a nucleophile will attack on these compounds.

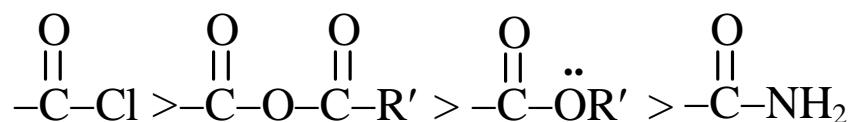
The order of nucleophilic attack is,



The above consideration is drawn on the fact that +R effect reduces in the order



But  $-I$  effect is in the order



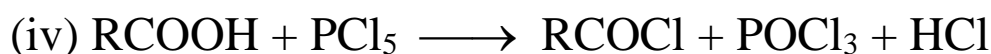
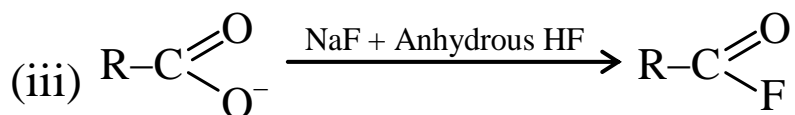
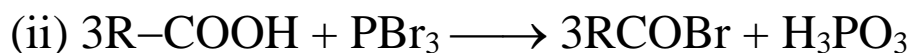
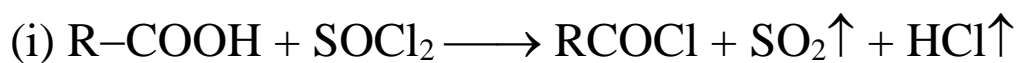
## CARBOXYLIC ACID & THEIR DERIVATIVES

Therefore, stronger the  $-I$  effect and lesser is the  $+R$  effect, stronger will be the electrophilicity of carbon in  $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-$  and more easily the nucleophile will attack that carbon.

### 3. Acid Derivatives

#### ACID HALIDES

##### (a) Preparation of acid halides

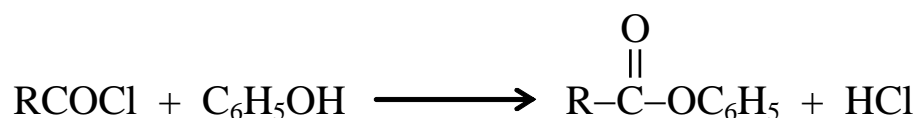
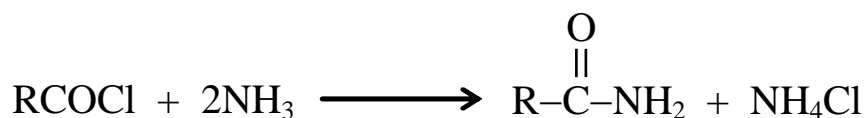
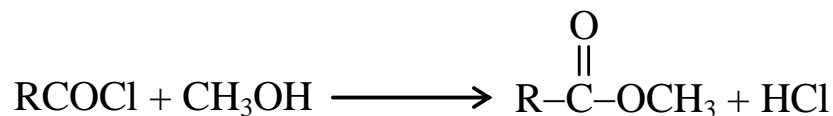


The lower acyl chlorides are colourless liquids with irritating odour. Higher members are colourless solids.

##### (b) Reactions of acid halides

###### (i) Formation of other acid derivatives

Acyl chlorides are the most reactive acid derivatives. Acyl chlorides may be converted into other acid derivatives as shown below:

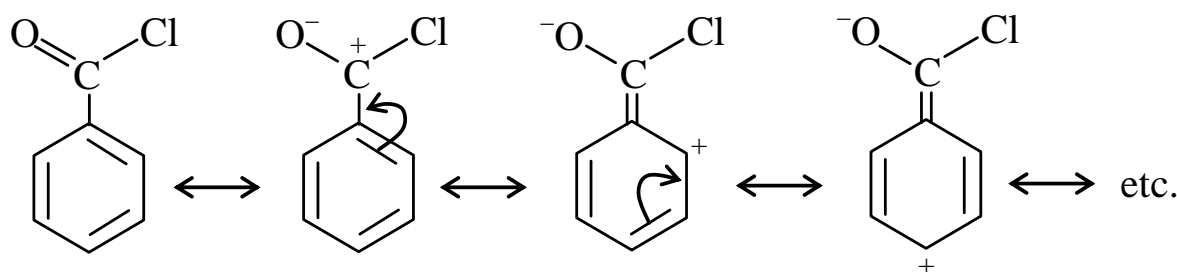


where R may be an alkyl or aryl group.

Acyl chlorides react rapidly with the above reagents. The reaction, however, with aliphatic acid chlorides is much more vigorous than with

## CARBOXYLIC ACID & THEIR DERIVATIVES

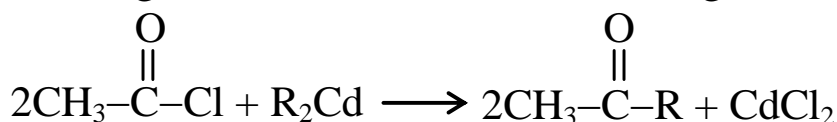
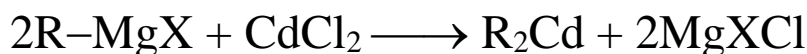
the aromatic acid chlorides. In the former, the carbonyl carbon atom is a centre of low electron density while in the latter this is not so because of resonance with the ring



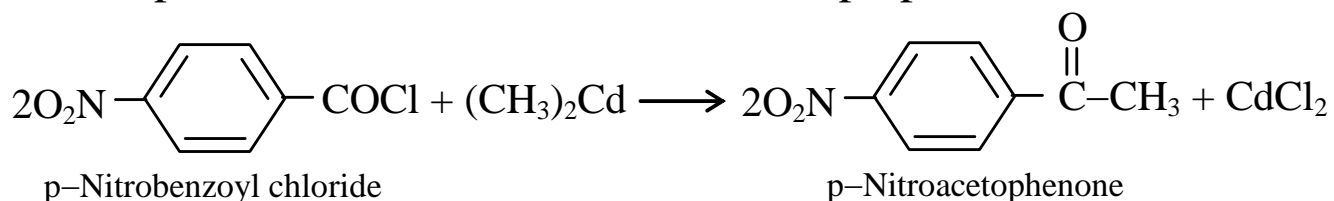
Benzoyl chloride, for instance, is so much less reactive that it can be used as water suspension.

### (ii) Formation of ketones

Alkyl Grignard reagent react with anhydrous cadmium chloride,  $\text{CdCl}_2$  to form a dialkylcadmium compound,  $\text{R}_2\text{Cd}$ . This intermediate, on reaction with an acyl chloride, yields a ketone. Organo cadmium compounds are less reactive than Grignard reagents and are thus more selective in their attack as nucleophiles.



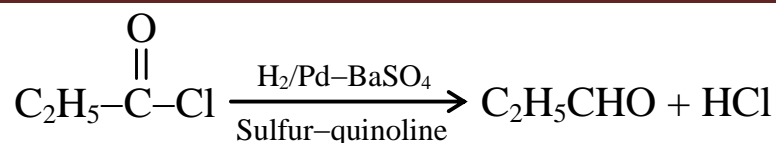
Both aliphatic and aromatic ketones can be prepared in this manner.



### (iii) Rosenmund Reduction

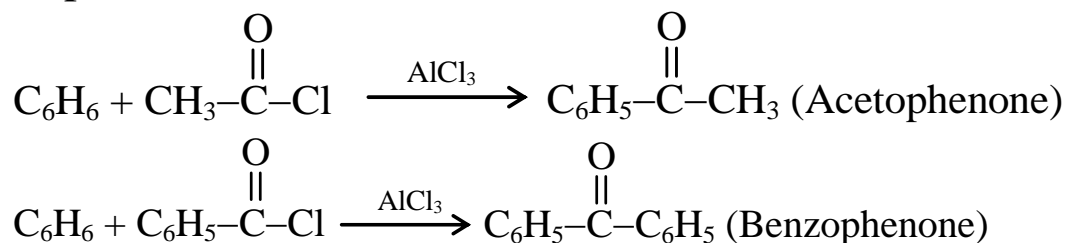
This reaction requires hydrogen and Pd, which is a catalyst, adsorbed on  $\text{BaSO}_4$  and a catalytic poison like quinoline to slow down the reaction. The result is the formation of an aldehyde. If the given catalytic poison is not employed the product would have been a primary alcohol.

## CARBOXYLIC ACID & THEIR DERIVATIVES



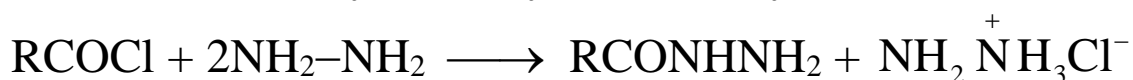
### (iv) Friedel–Crafts reaction

Preparation of aromatic ketones by the Friedel–Crafts reaction of acyl chlorides is an important method.



### (v) Acid Hydrazides

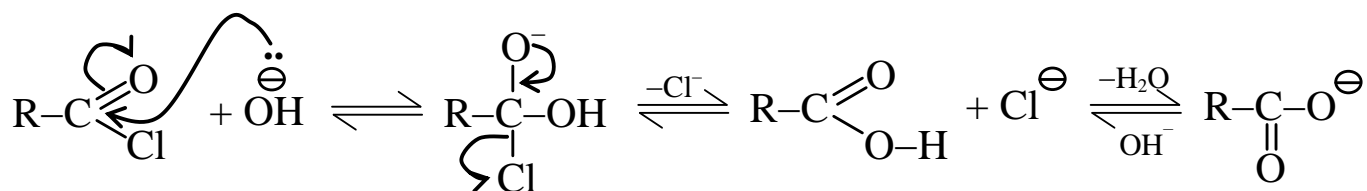
RCOCl on treatment with hydrazine yields acid hydrazides.



The acid halide, on heating with the salt of the corresponding acid, yields an anhydride.



### (vii) Hydrolysis of $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{Cl}$ by base catalysis



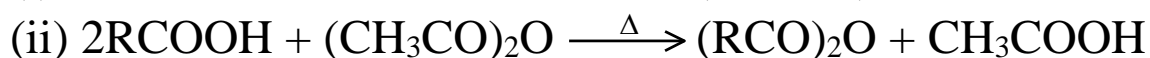
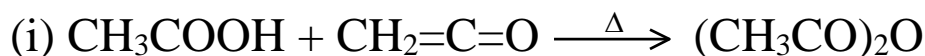
## Acid Anhydrides

Acid anhydrides are formed by the removal of a molecule of water from two molecules of a carboxylic acid. Most acid anhydrides are symmetrical. Unsymmetrical or mixed anhydrides are also known but are not much used. Acid anhydrides are also very reactive like the acid chlorides and

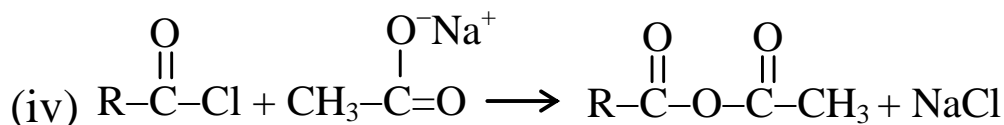
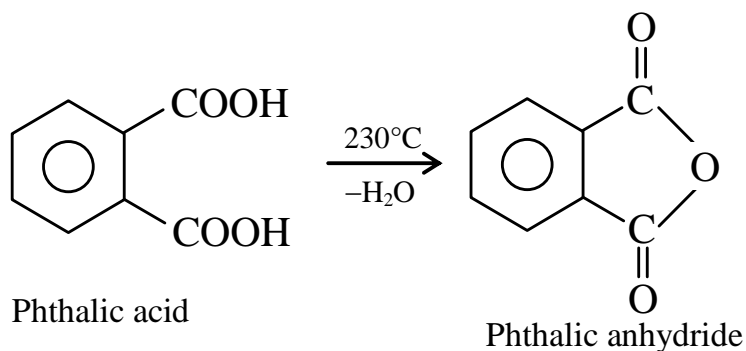
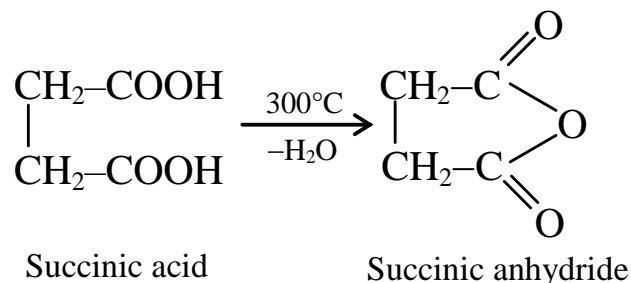
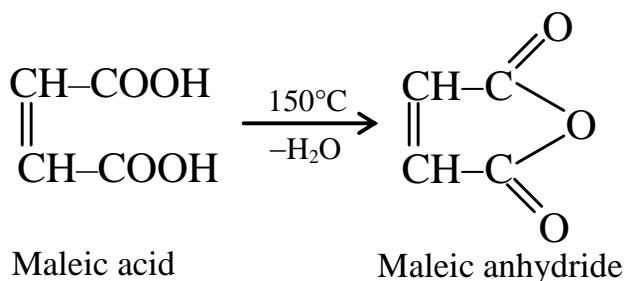
## CARBOXYLIC ACID & THEIR DERIVATIVES

have penetrating odour. They are useful for synthetic purposes because of their less corrosive action and greater stability.

### (a) Preparation of acid anhydrides



(iii) Heating of 2 moles of  $\text{R}-\text{C}(=\text{O})\text{OH}$  with dehydrating agents also produces  $(\text{RCO})_2\text{O}$ .



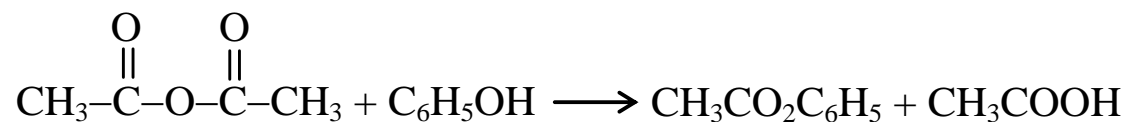
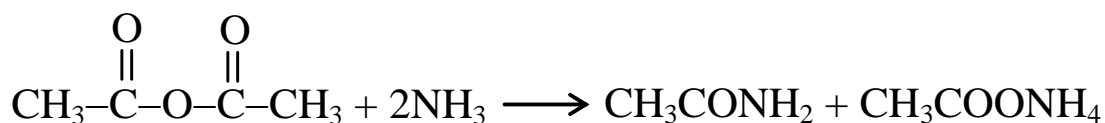
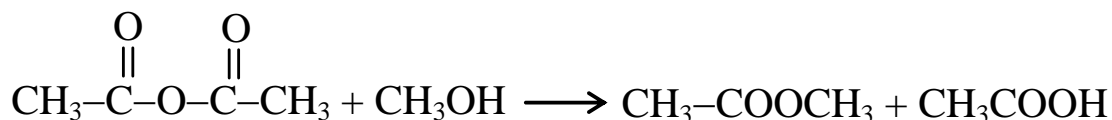
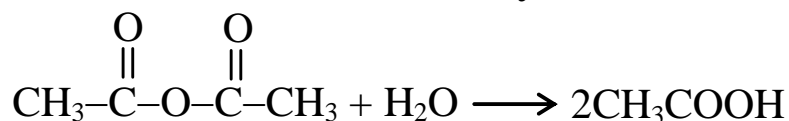
Acetic anhydride is a colourless liquid with irritating smell, slightly soluble in water but readily soluble in ether and benzene.

## CARBOXYLIC ACID & THEIR DERIVATIVES

### (b) Reactions of acid anhydrides

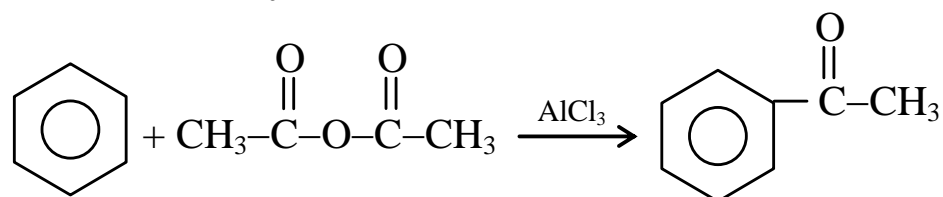
#### (i) Formation of acid and other acid derivatives

Acid anhydrides contain carbonyl groups and thus undergo nucleophilic attack by various electron donors to yield the corresponding products.



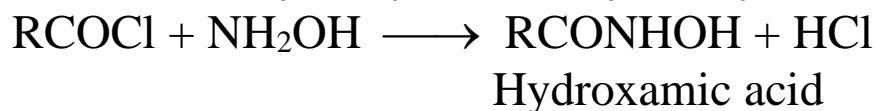
#### (ii) Friedel Crafts acylation

Ketones are obtained by the Friedel–Crafts acylation of aromatic hydrocarbons. Acetophenone is formed from acetic anhydride and benzene in presence of anhydrous  $\text{AlCl}_3$ .



#### (iii) Reaction with hydroxylamine

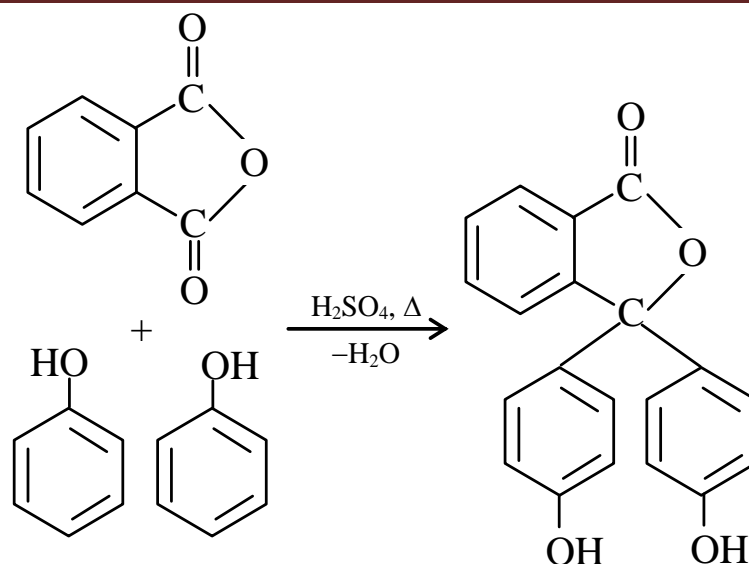
Acid anhydrides react with hydroxylamine to yield hydroxamic acid.



#### (iv) Formation of phenolphthalein

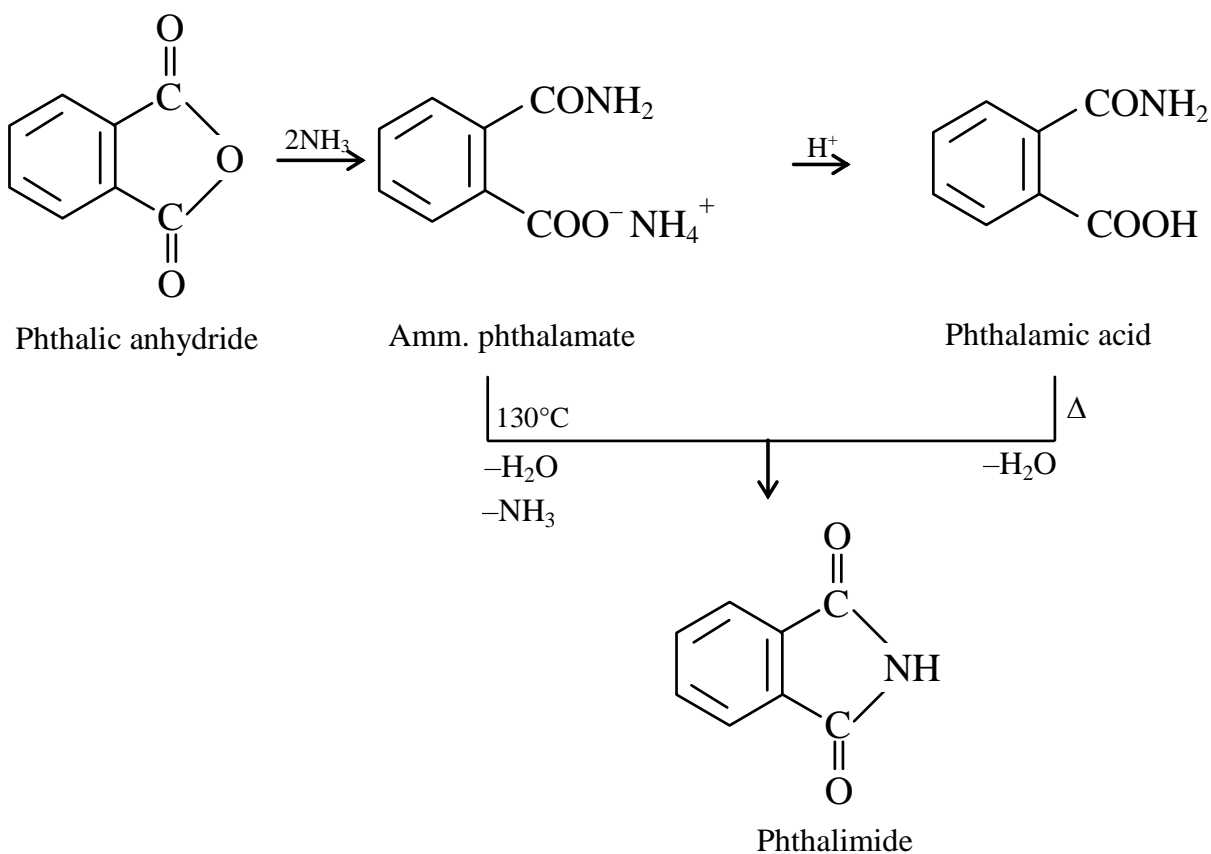
Phthalic anhydride condenses with two moles of phenol in the presence of concentrated  $\text{H}_2\text{SO}_4$  to form phenolphthalein.

## CARBOXYLIC ACID & THEIR DERIVATIVES



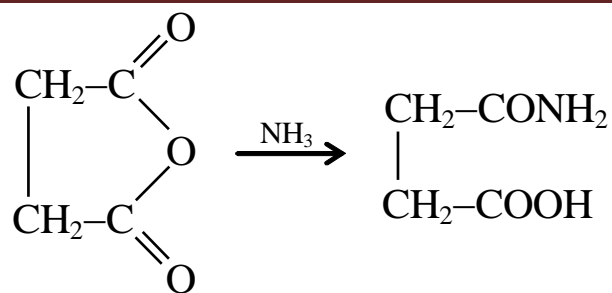
### (v) Formation of cyclic imides

Cyclic acid anhydrides react with ammonia to form amides, which on heating lose a molecule of water with the resultant formation of cyclic imides.

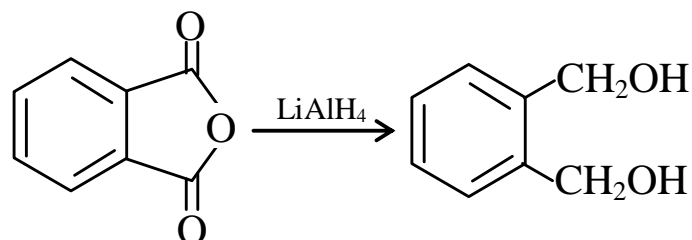


Succinic anhydride with ammonia forms succinamic acid.

## CARBOXYLIC ACID & THEIR DERIVATIVES

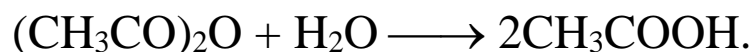


### (vi) Reduction



### (vii) Hydrolysis

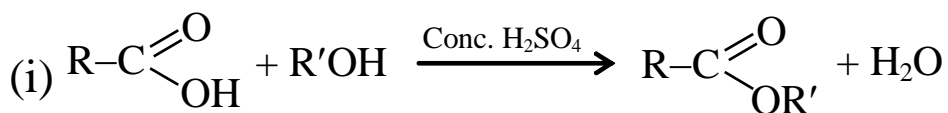
Acetic anhydride is hydrolysed in water slowly but rapidly by alkali.



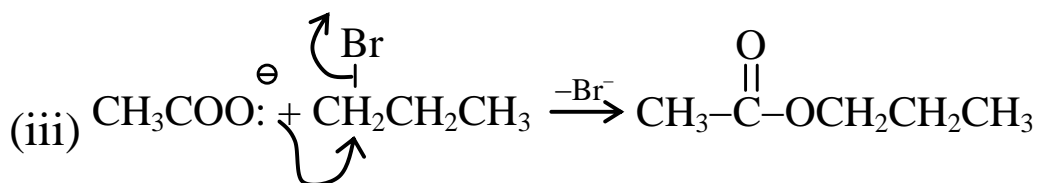
## Esters

Esters probably constitute the most important class of carboxylic acid derivatives. They occur widely in nature and are responsible for the fragrance of many fruits and flowers.

### (a) Preparation of esters

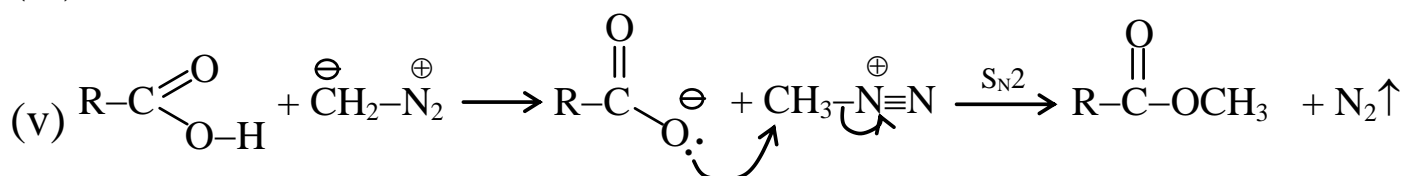
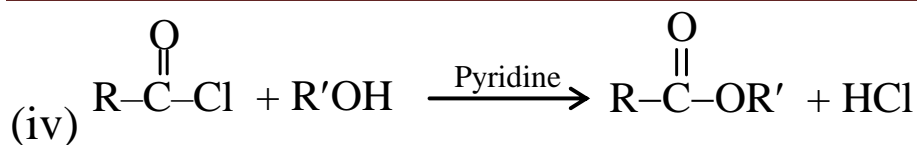


The mechanism of acid catalysed esterification has already been discussed.

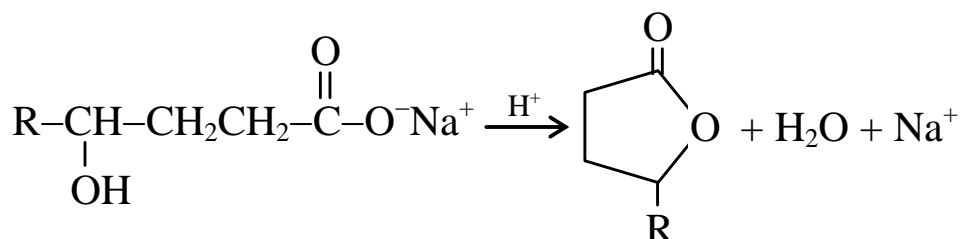




## CARBOXYLIC ACID & THEIR DERIVATIVES



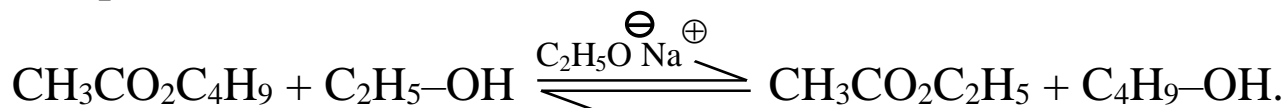
(vi) Cyclic esters (lactones) may be obtained by intramolecular esterification of hydroxy acids.



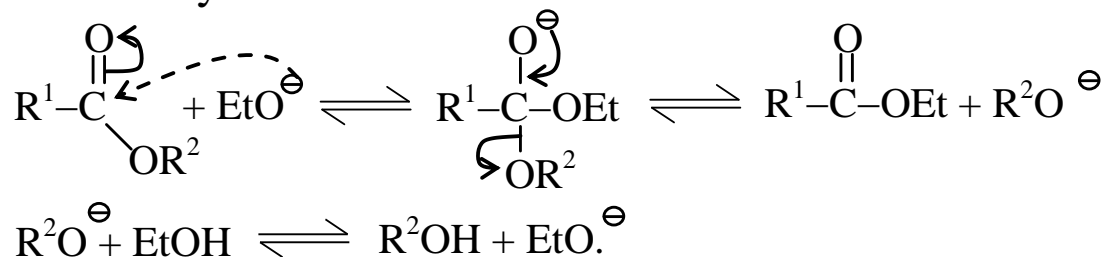
### (vii) Transesterification

This is basically a process called as “alcoholysis”. This is carried out by refluxing the ester with large excess of alcohol, preferably in the presence of small amount of acid or sodium alkoxide as catalyst. Alcoholysis is usually effective in replacing a higher alcohol by a lower one.

For example:



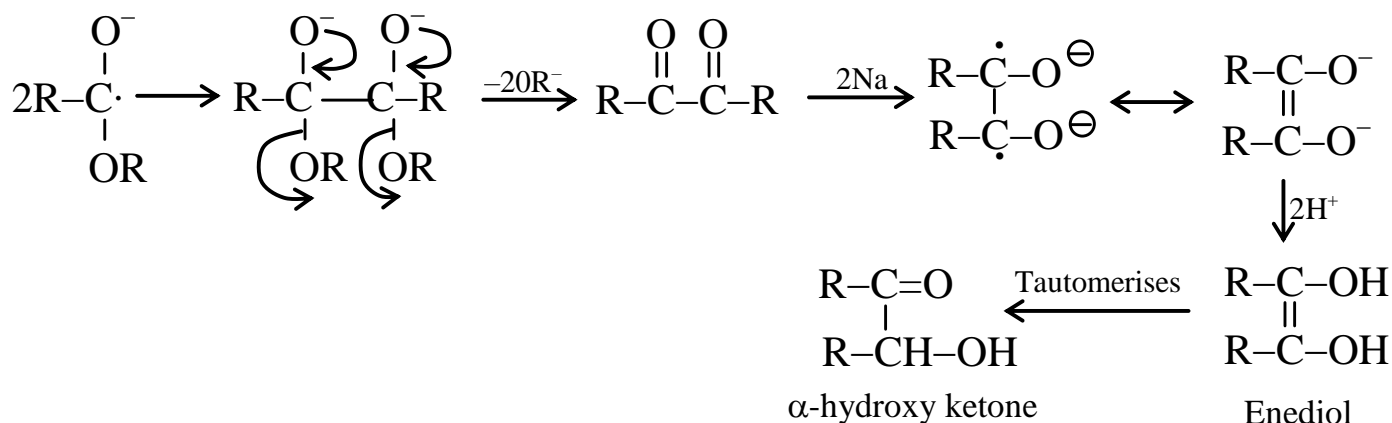
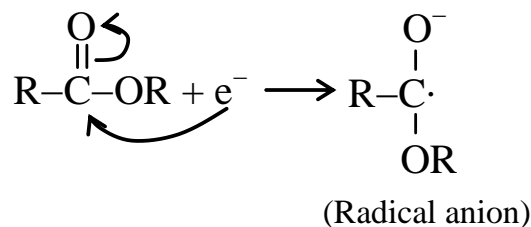
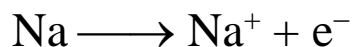
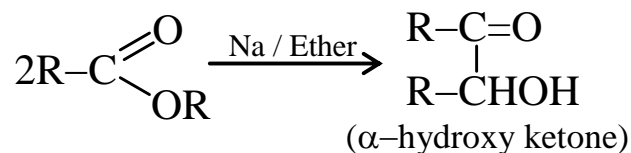
Plausible base catalysed mechanism of the reaction is



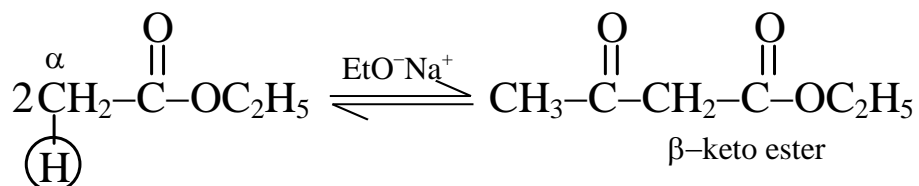
## CARBOXYLIC ACID & THEIR DERIVATIVES

### (b) Reaction of esters

#### (i) Acyloin condensation



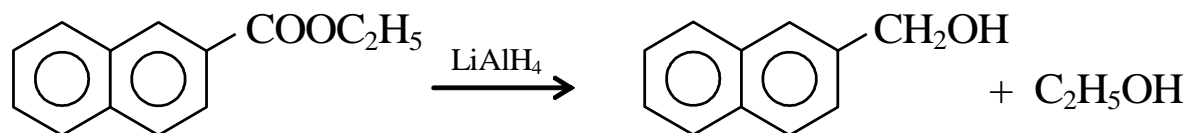
#### (ii) Claisen ester condensation



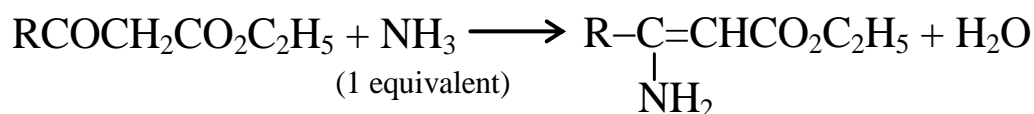
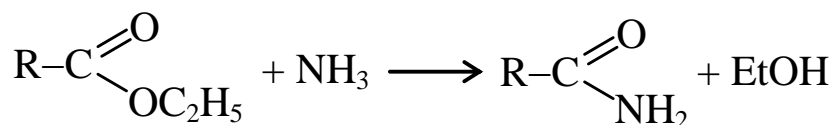
#### (iii) Reduction of ester

Esters can be reduced by  $\text{LiAlH}_4$  in a manner similar to carboxylic acid. The process results in the formation of two alcohols and is known as “hydrogenlysis”. One of the alcohols is essentially a primary alcohol while other alcohol unit could be  $1^\circ$ ,  $2^\circ$  or  $3^\circ$ . Esters are the only compound, which on reduction with  $\text{LiAlH}_4$  gives 2 units of alcohol.

## CARBOXYLIC ACID & THEIR DERIVATIVES

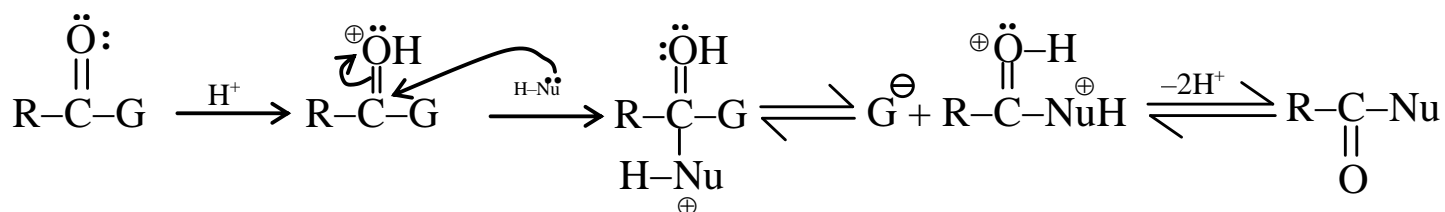


### (iv) Reaction of $\text{NH}_3$ with ester and keto ester

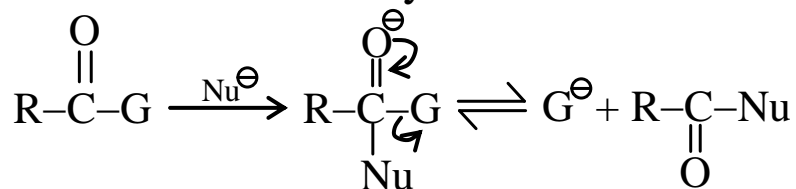


### (v) Hydrolysis

The basic feature of acid catalysed mechanism is



The basic feature of base catalysed mechanism is



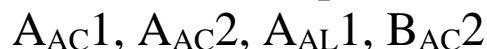
Esters undergo nucleophilic substitution reactions very slowly because their leaving groups are quite basic. The rate of hydrolysis of an ester can be increased by carrying out the reaction in the presence of a catalyst. Either  $\text{H}^+$  or  $\text{OH}^-$  can be used to increase the rate of reaction.

In an acid-catalysed reaction all organic reactants, intermediates and products are positively charged or neutral; there are no negatively charged organic reactants, intermediates or products in acidic solution. Also, in a reaction in which  $\text{OH}^-$  is used to increase the rate of the reaction, all organic reactants, intermediates and products are negatively charged or

## CARBOXYLIC ACID & THEIR DERIVATIVES

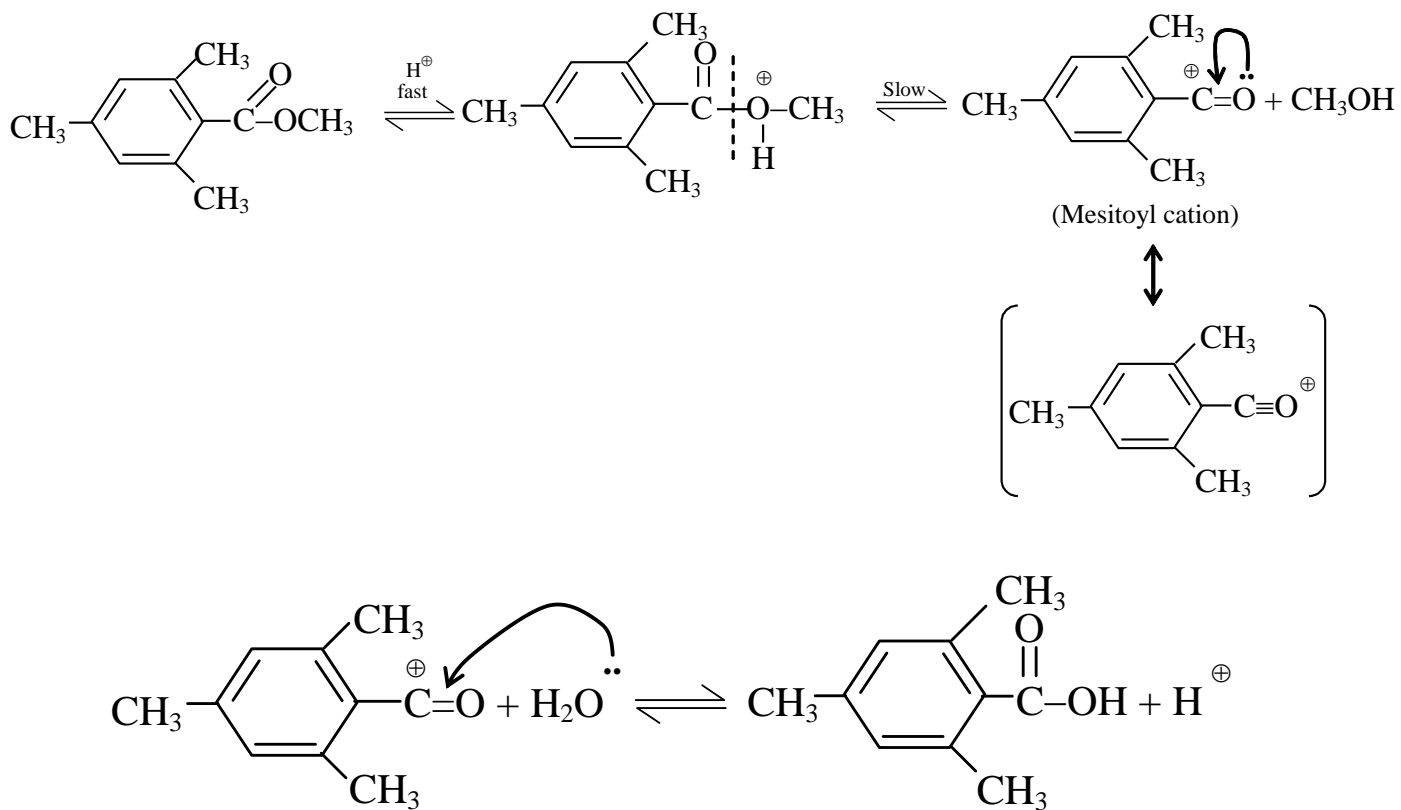
neutral ; there are no positively charged organic reactants, intermediates or products in basic solution.

Ester hydrolysis can be carried out in 8 possible ways.  $A_{AC1}$ ,  $A_{AC2}$ ,  $B_{AC1}$ ,  $B_{AC2}$ ,  $A_{AL1}$ ,  $A_{AL2}$ ,  $B_{AL1}$ ,  $B_{AL2}$ . Out of these possible mechanistic pathways, most common examples are

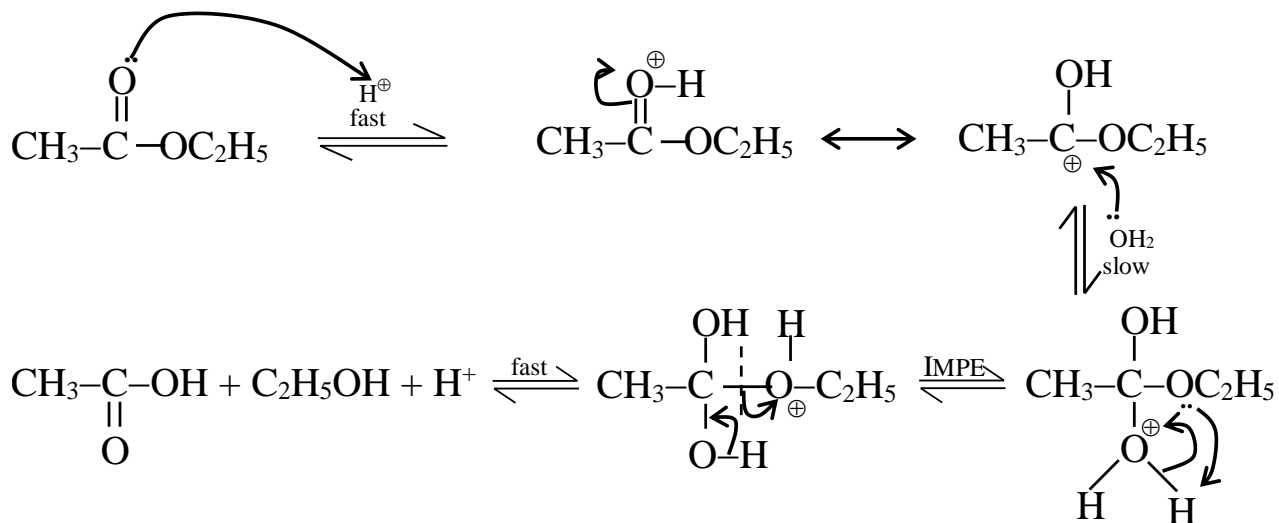
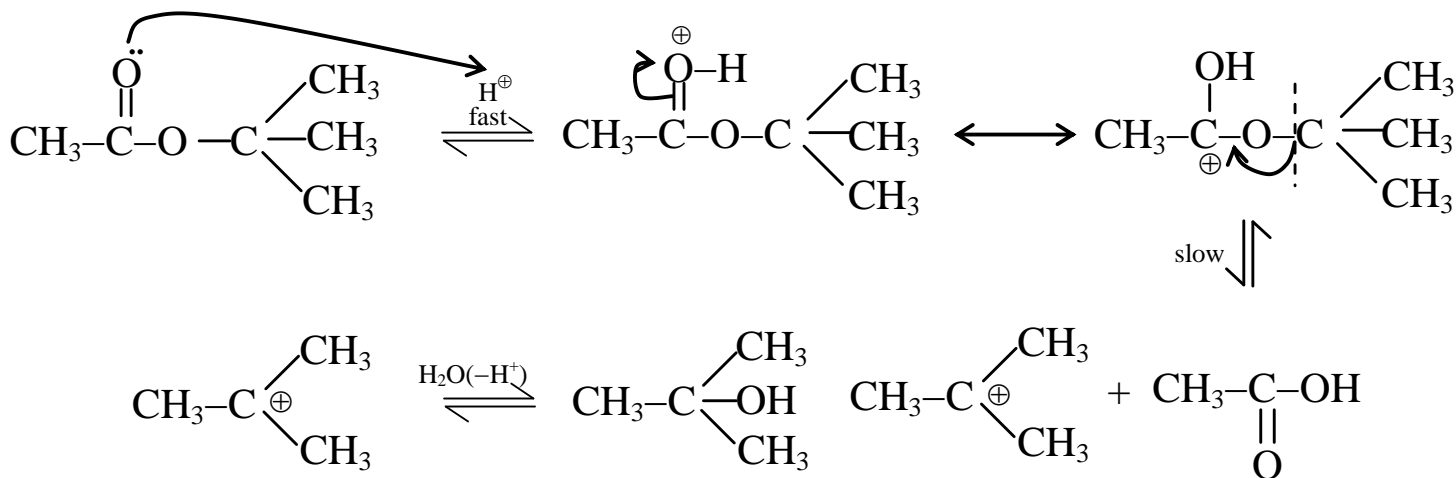


Here A or B stands for acid or base catalysed and AC or AL stands for acyl-oxygen or alkyl-oxygen cleavage and 1 or 2 stands for unimolecular or bimolecular.

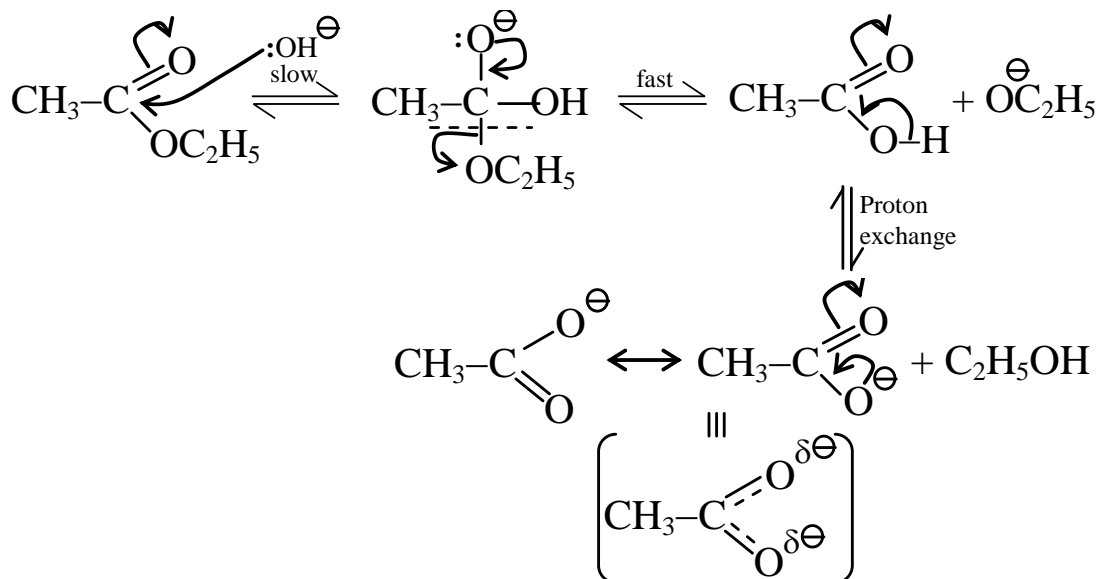
$A_{AC1}$ :



**A<sub>AC</sub>2:**

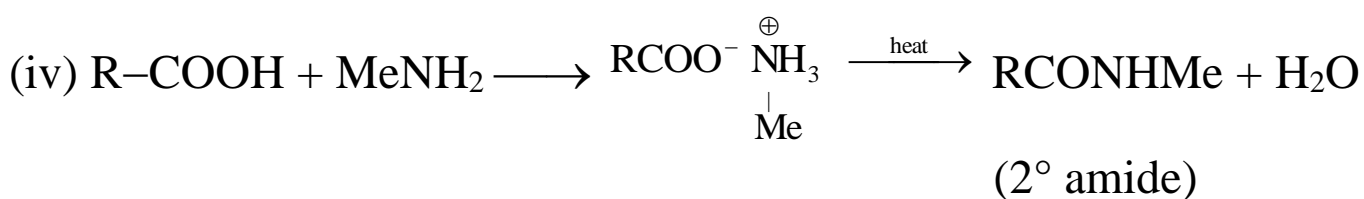
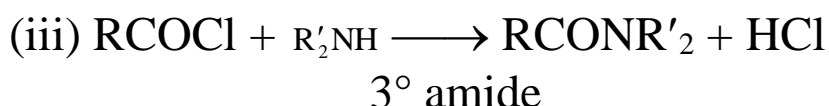
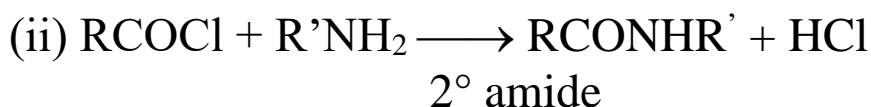
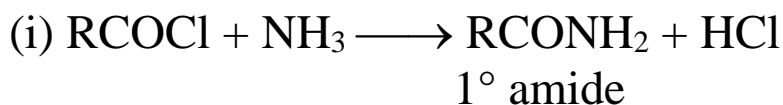
A<sub>AL</sub>1:

B<sub>AC</sub>2:

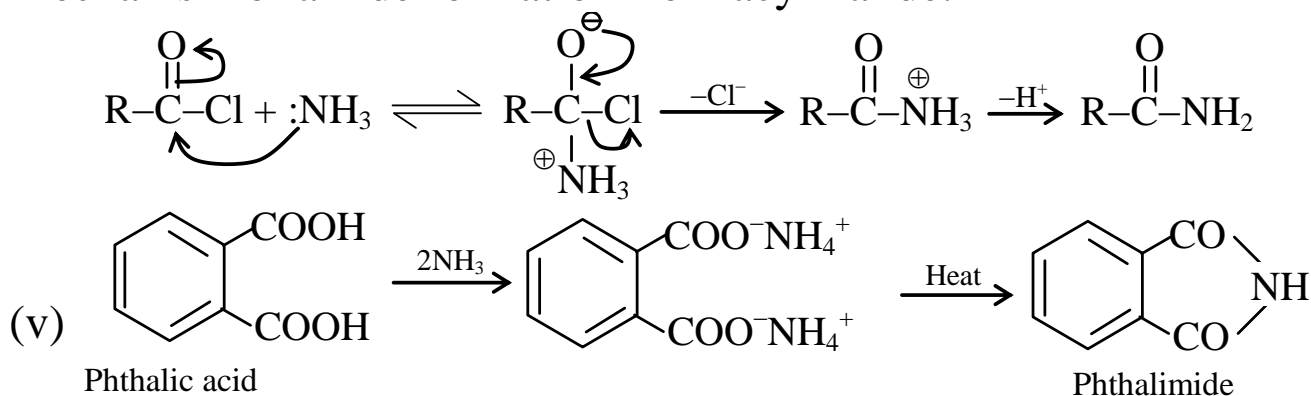


## Acid Amides

### (a) Preparation of acid amides



Mechanism of amide formation from acyl halide.



H-bonding makes the boiling points and melting points of amides higher than other acid derivatives.

### (b) Properties of Amides

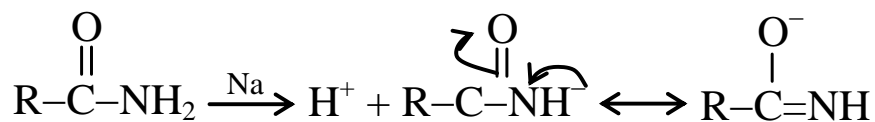
Amides are the least reactive of all the acid derivatives. Amides do not react with halide ions, carboxylate ions, alcohols or water because in each case the incoming nucleophile is a weaker base than the leaving group of the amide.

#### (i) Acidity of amides:

Although amides are considered to be weakly acidic (for instance,  $K_a$  for acetamide is  $\sim 10^{-15}$ ), they react with alkali metals to form salts. The

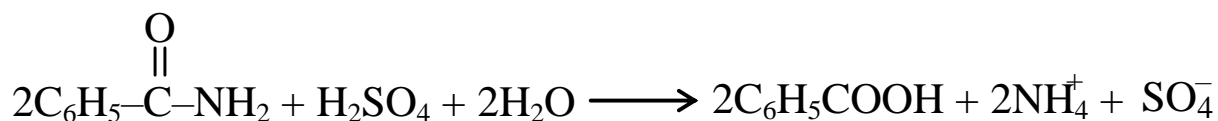
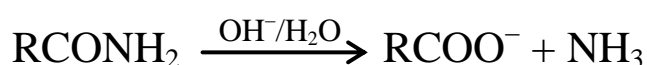
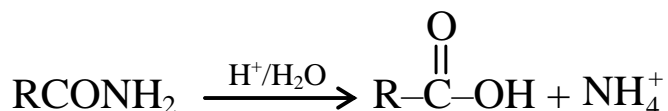
## CARBOXYLIC ACID & THEIR DERIVATIVES

reason for the acidity is that the resulting anion can be stabilized by resonance as shown below:



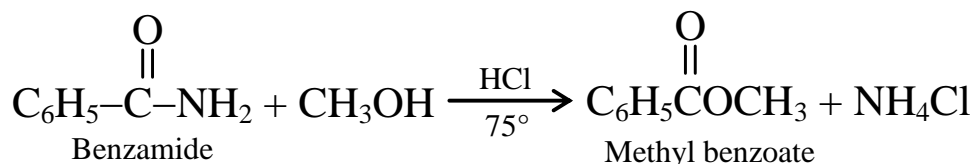
### (ii) Hydrolysis

Amides, however, may be hydrolyzed in the presence of either an acid or a base leading to the formation of the parent acid.



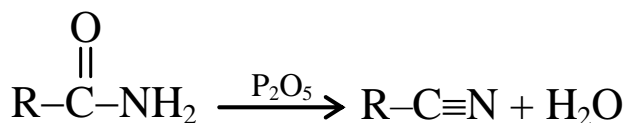
### (iii) Reaction with alcohol

Esters are obtained on heating amides with alcohols in the presence of a mineral acid.



### (iv) Dehydration

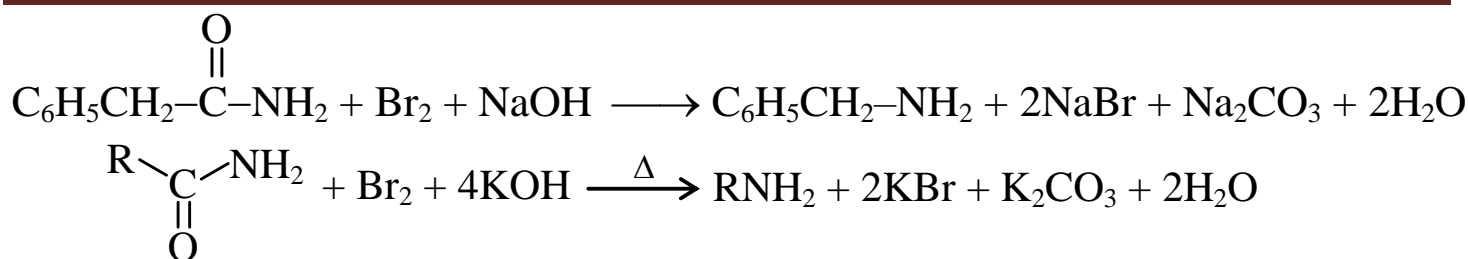
Amides lose a molecule of water in the presence of an efficient dehydrating agent such as phosphorus pentoxide to form a nitrile.



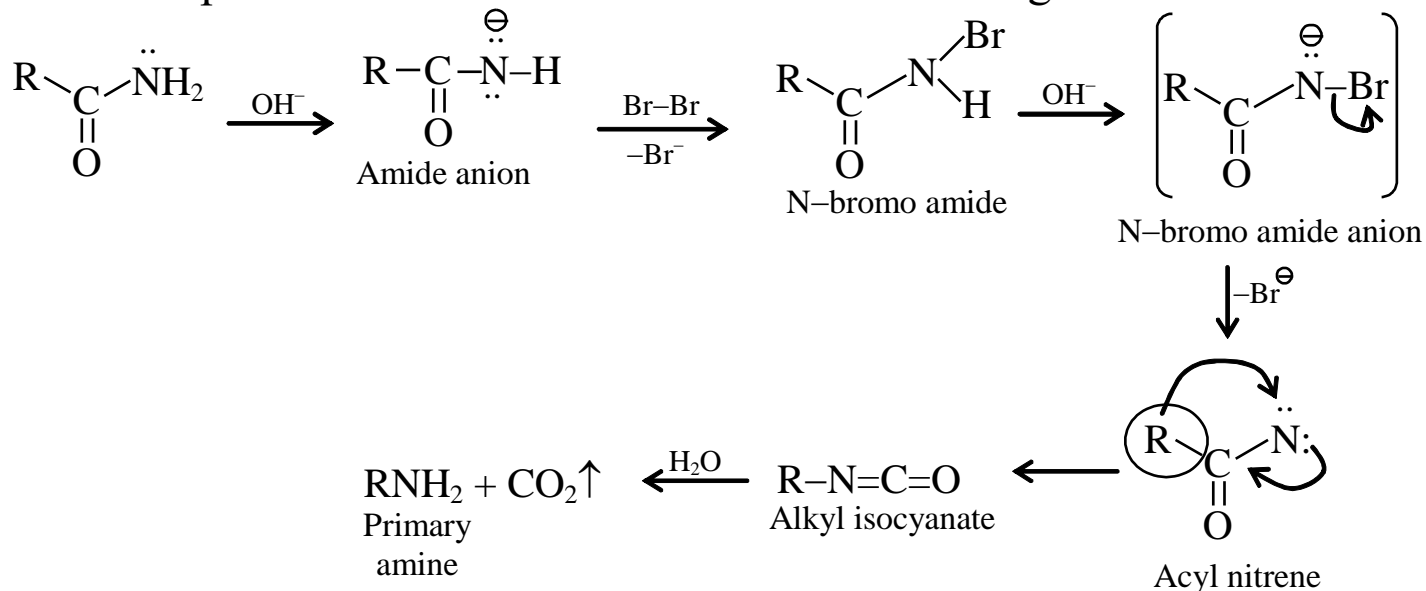
### (iv) Hoffmann degradation reaction

A primary amide (aliphatic or aromatic) on treatment with bromine in the presence of an aqueous base forms an amine. The reaction is referred to as “Hoffmann reaction”.

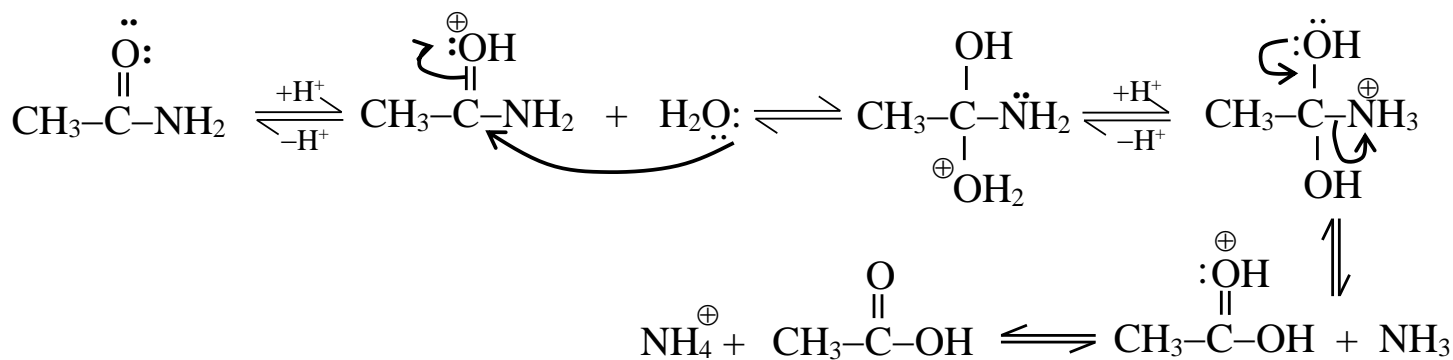
## CARBOXYLIC ACID & THEIR DERIVATIVES



The most plausible mechanism of the Hoffmann's degradation is



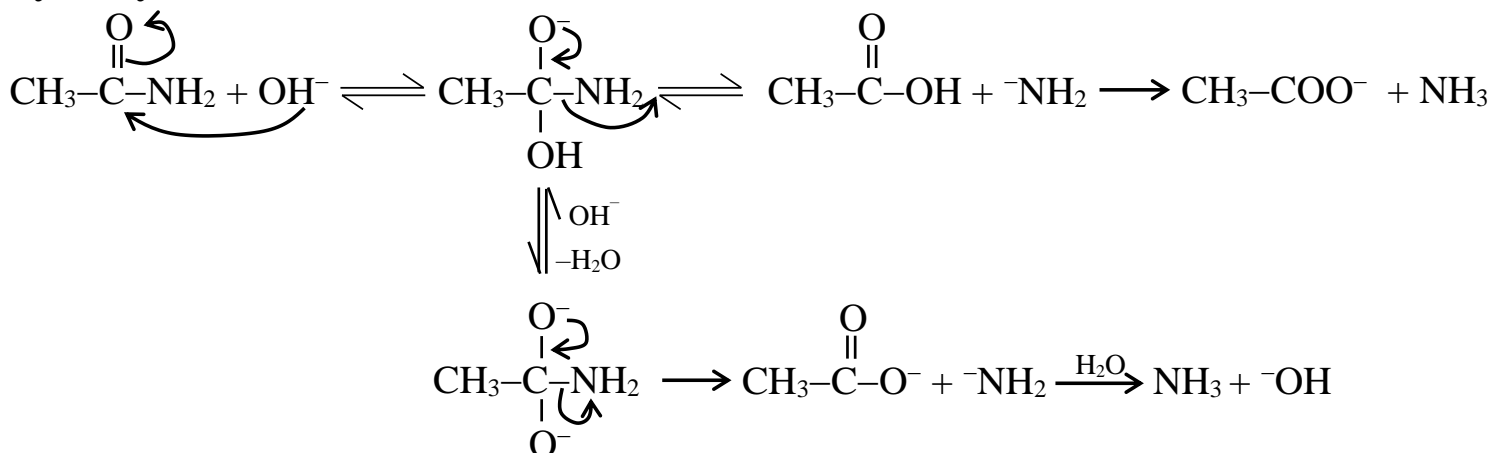
### (v) Acid catalysed hydrolysis



The hydrolysis of an amide does not occur without a catalyst. In the non-acid catalysed reaction, the amide is not protonated. Therefore, water, a very poor nucleophile, must attack a neutral amide that is much less susceptible to nucleophilic attack than a protonated amide would be. Consequently, the tetrahedral intermediate is formed very slowly. In addition, the  $\text{NH}_2$  group of the tetrahedral intermediate is not protonated in the non-acid catalysed reaction. As a result, the two leaving groups of the



tetrahedral intermediate are  $\text{HO}^-$  and  $\text{NH}_2^-$ . Because  $\text{OH}^-$  is the weaker base, it is more easily expelled, which reforms the amide. Base catalysed hydrolysis:

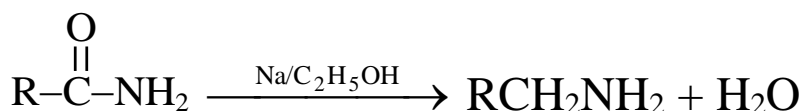


In the hydroxide ion promoted hydrolysis of an amide,  $\text{OH}^-$  rather than water is the nucleophile. Because  $\text{OH}^-$  is a better nucleophile than water, it is better at forming the tetrahedral intermediate. The two leaving groups of the tetrahedral intermediates are  $\text{OH}^-$  and  $\text{NH}_2^-$ . Because  $\text{OH}^-$  is the weaker base, it is more easily expelled, but occasionally an  $\text{NH}_2^-$  is ejected. When this happens, the carboxylic acid that is formed immediately loses a proton. Since this step is irreversible, it disturbs the equilibrium and drives the reaction towards products.

In strongly basic solutions, the hydrolysis reaction is second order in hydroxide ion. In other words, two equivalents of hydroxide ion participate in the reaction. When the new tetrahedral intermediate collapses, the possible leaving groups are  $\text{O}^{2-}$  or  $\text{NH}_2^-$ . Because  $\text{NH}_2^-$  is the weaker base, it is expelled and the hydrolysis reaction occurs.

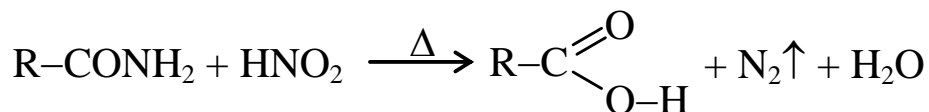
An amide reacts with an alcohol in the presence of  $\text{H}^+$  for the same reason it reacts with water in the presence of  $\text{H}^+$ .

Amides are reduced to amines.



## CARBOXYLIC ACID & THEIR DERIVATIVES

### (vi) Reaction with nitrous acid



The reaction proceeds via the attack of electrophilic species  $\text{NO}^+$  generated from  $\text{HNO}_2$ .

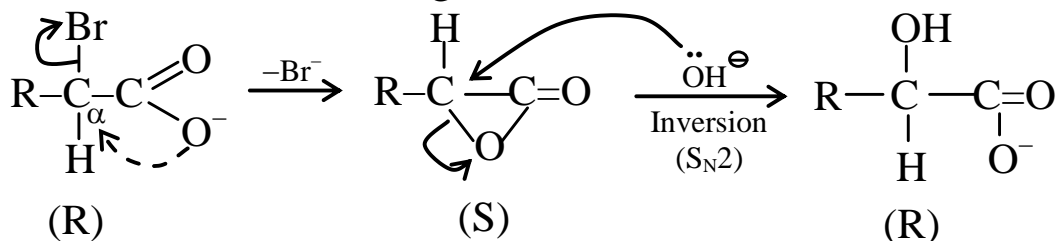
## Fundamental Solved Examples

### Example 1.

Predict the stereochemistry at  $\alpha$ -C for  $\beta$ -bromo acid (optically active) when treated with  $\text{NaOH}$ .

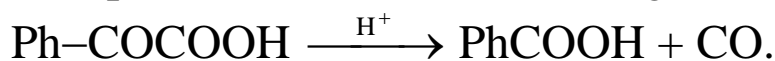
### Solution:

The configuration (if chiral carbon) at  $\alpha$ -carbon remains same i.e. reaction proceeds with retention of configuration.

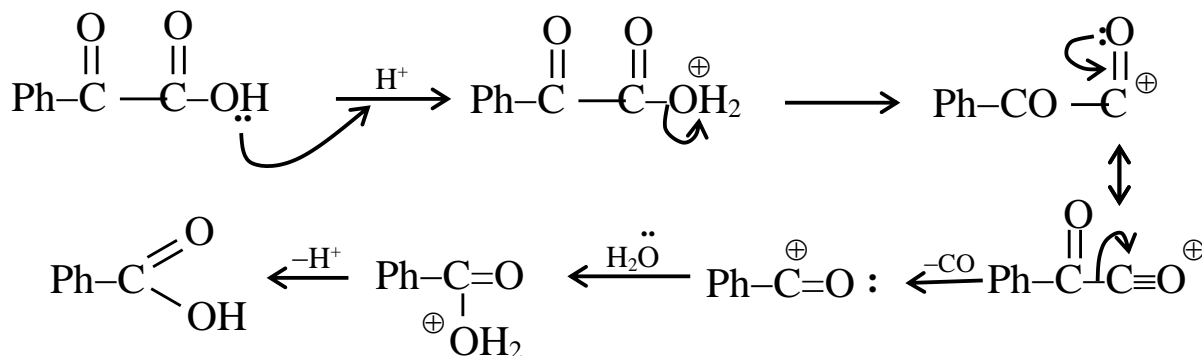


### Example 2.

Write the possible mechanism for the given reaction.



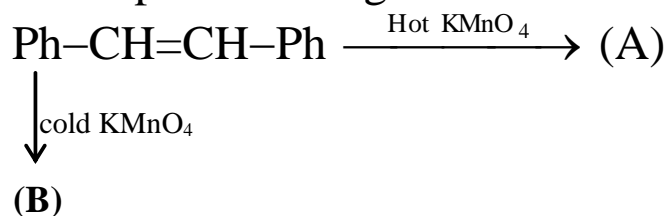
### Solution:



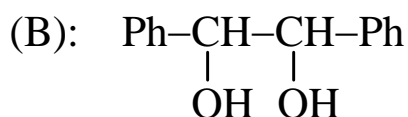
## CARBOXYLIC ACID & THEIR DERIVATIVES

### Example 3.

Predict the products of given reaction.



### Solution:



### Example 4.

- (a) Why are both p-Me and m-Me substituted acids weaker than  $\text{PhCO}_2\text{H}$  with the p-acid being the weakest one?
- (b) Why is the p-OH acid weaker than  $\text{PhCO}_2\text{H}$  while the m-OH acid is stronger?

### Solution:

- (a) Both p-Me and m-Me are electron-donating and acid weakening. m-Me is electron donating by induction while p-Me is electron-donating by induction as well as hyperconjugation. p-Me being more electron releasing is more acid weakening and p-Me and m-Me substituted acids both are weaker than  $\text{PhCO}_2\text{H}$ .
- (b) OH group shows -I effect from m-position while from p-position it shows -I and +R effects. Electron-donation by resonance (+R) is more prominent than electron withdrawal by induction (-I) for OH group. So m-OH is electron-withdrawing and acid strengthening, thus m-OH acid is stronger than  $\text{PhCO}_2\text{H}$ . p-OH is electron-donating and acid weakening, thus p-OH acid is weaker than  $\text{PhCO}_2\text{H}$ .

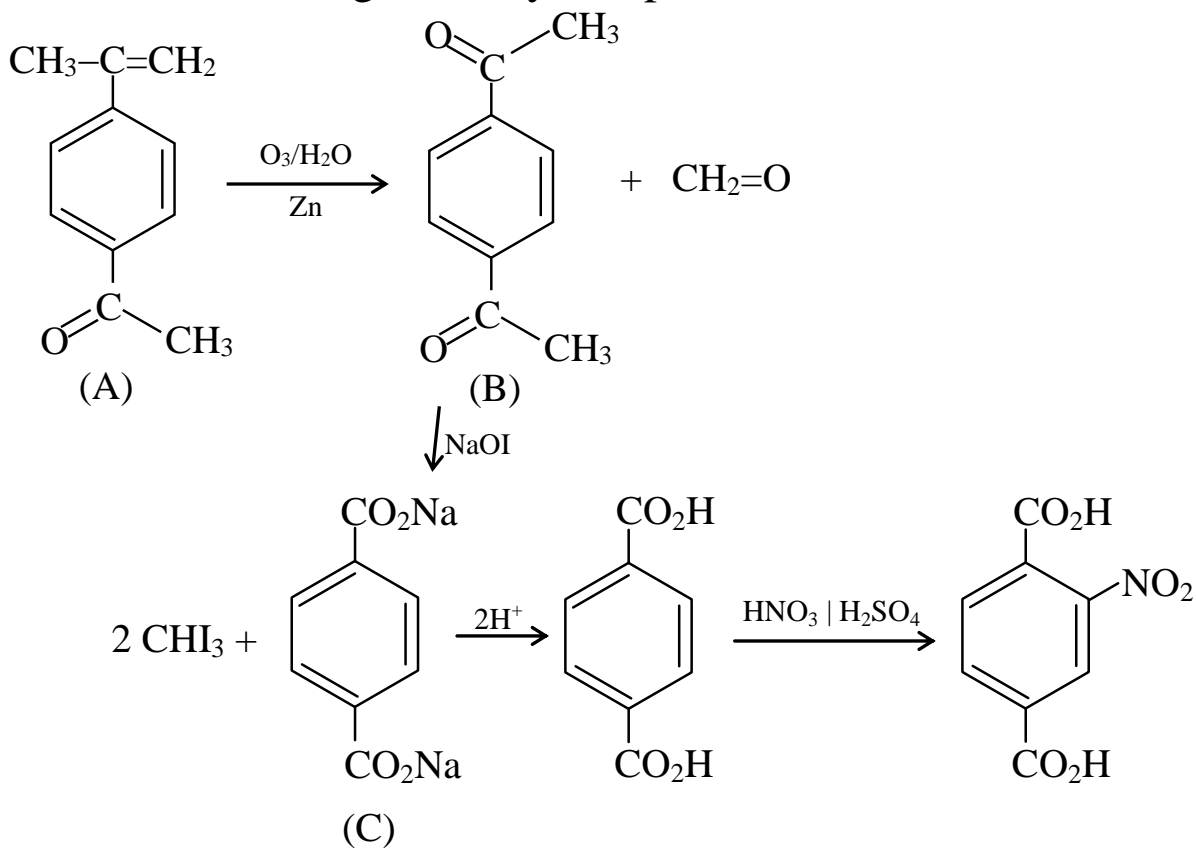
## CARBOXYLIC ACID & THEIR DERIVATIVES

### Example 5.

Reductive ozonolysis of (A) having molecular formula  $C_{11}H_{12}O$  gives  $CH_2O$  and (B) with molecular formula  $C_{10}H_{10}O_2$ . Both (A) and (B) gives a precipitate from reaction with NaOI. (B) on reaction with NaOI gives a precipitate of  $CHI_3$  along with the formation of compound (C) as sodium salt. Compound (C) on acidification gives a compound which on mononitration gives only one product. Identify compound (A), (B) & (C).

### Solution:

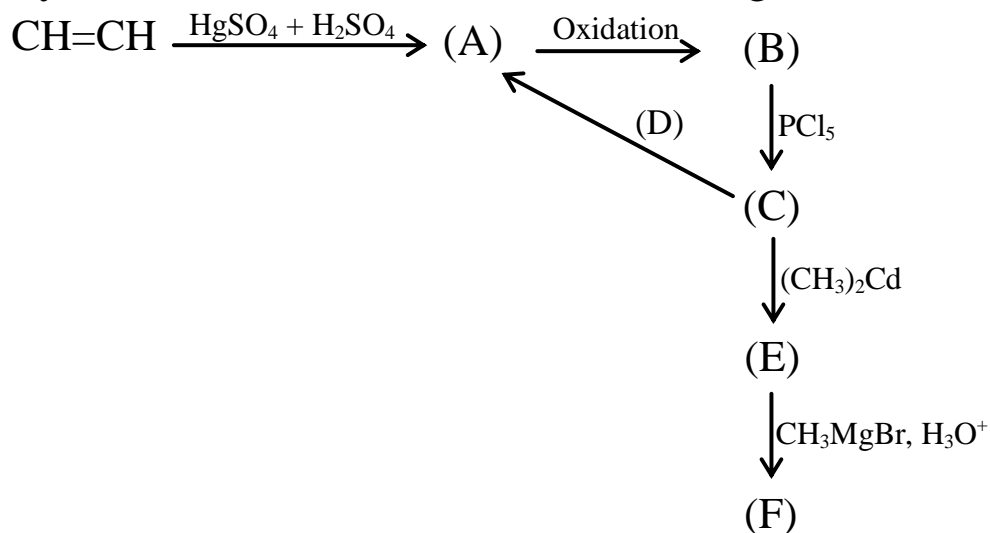
Compounds (A) and (B) responding positively to iodoform reaction reveals that they have either  $CH_3CO-$  or  $CH_3CH(OH)-$  structural unit. Compound (A) has  $6^\circ$  of unsaturation while (B) has  $5^\circ$  of unsaturation. Compound (A) has a benzene ring (accounting for 4 degree of unsaturation), a  $CH_3CO-$  unit and a double bond in the side chain (accounting for rest two degree of unsaturation).  $CH_3CO-$  unit and side chain with a double bond ( $=CH_2$  unit) must be at para position since (C) on mononitration gives only one product.



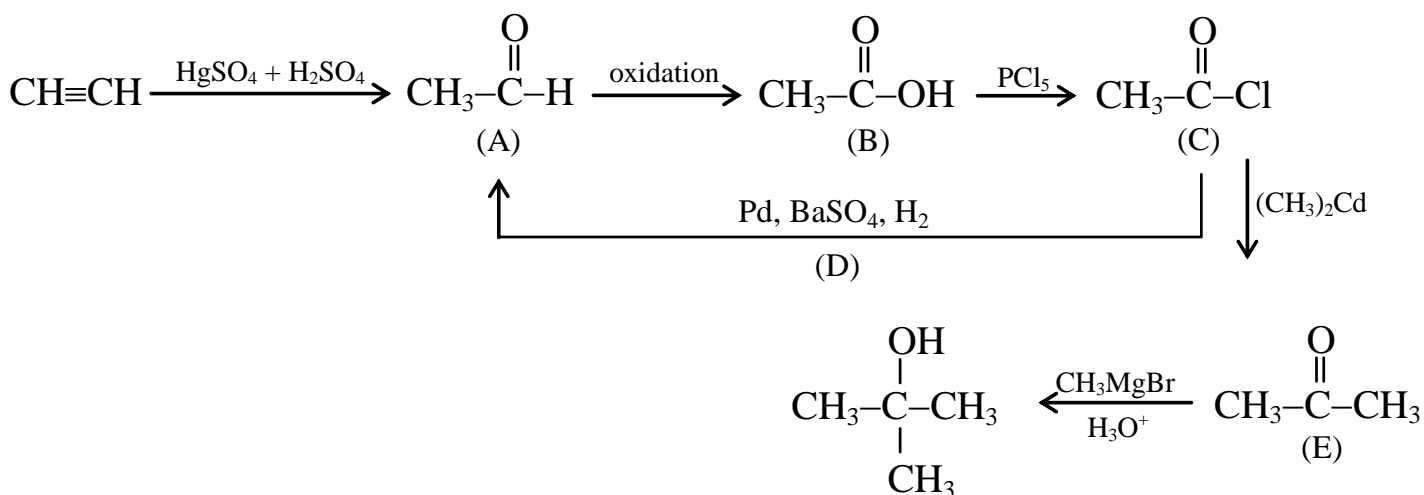
## CARBOXYLIC ACID & THEIR DERIVATIVES

### Example 6.

Identify A, B, C, D, E and F in the following reactions



### Solution:

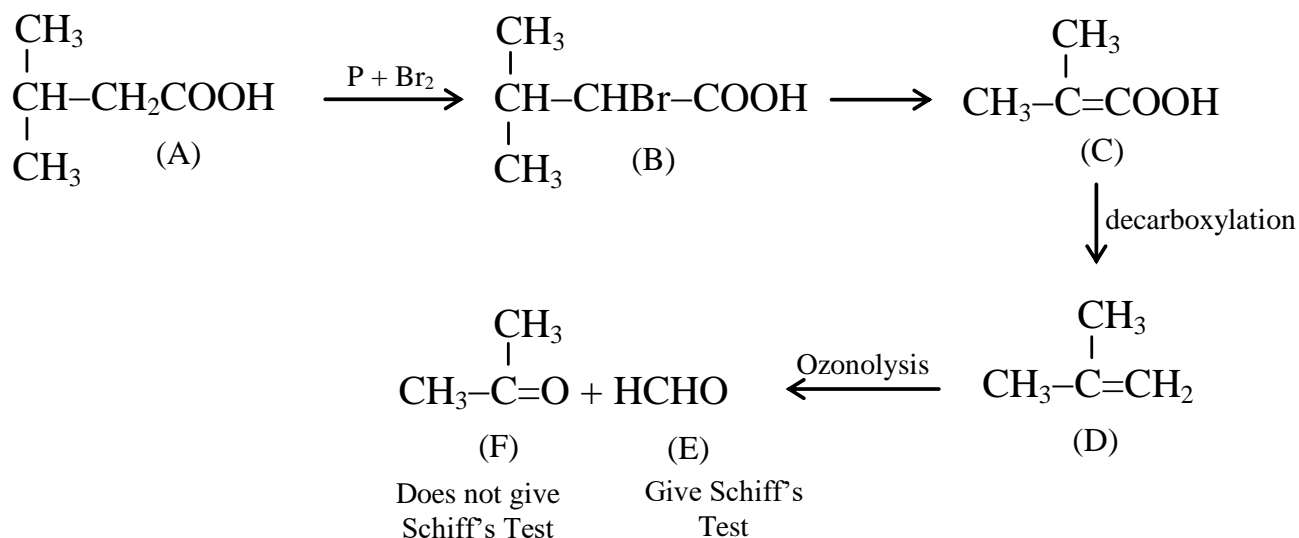


### Example 7.

An organic acid (A),  $\text{C}_5\text{H}_{10}\text{O}_2$  reacts with  $\text{Br}_2$  in the presence of phosphorus to give (B). Compound (B) contains an asymmetric carbon atom and yields (C) on dehydrobromination. Compound (C) does not show geometric isomerism and on decarboxylation gives an alkene (D) which on ozonolysis gives (E) and (F). Compound (E) gives a positive Schiff's test but (F) does not. Give structures of (A) to (F) with reasons.

## CARBOXYLIC ACID & THEIR DERIVATIVES

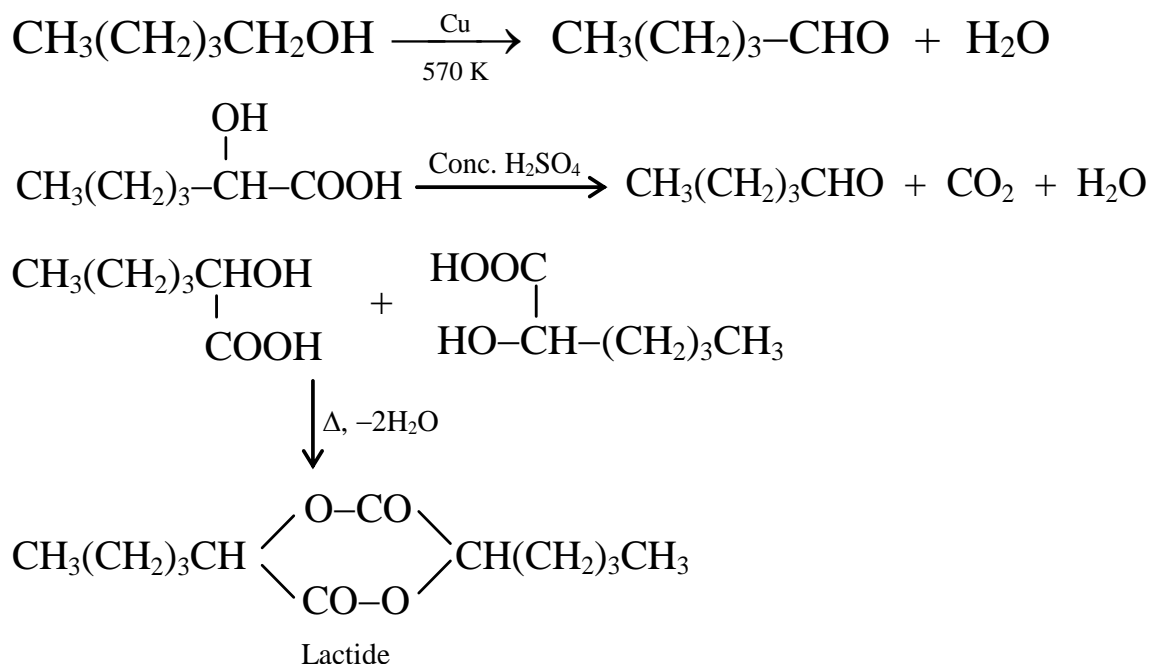
### Solution:



### Example 8.

An organic compound (A)  $\text{C}_6\text{H}_{12}\text{O}_3$  on treatment with concentrated  $\text{H}_2\text{SO}_4$  gives  $\text{CO}$ ,  $\text{H}_2\text{O}$  and (B). Compound (B) can be prepared by passing vapours of 1-pentanol over heated copper at 570 K. Compound (A) on heating gives (C)  $\text{C}_{12}\text{H}_{20}\text{O}_4$ . Give structures of (A) to (C) with proper reasoning.

### Solution:

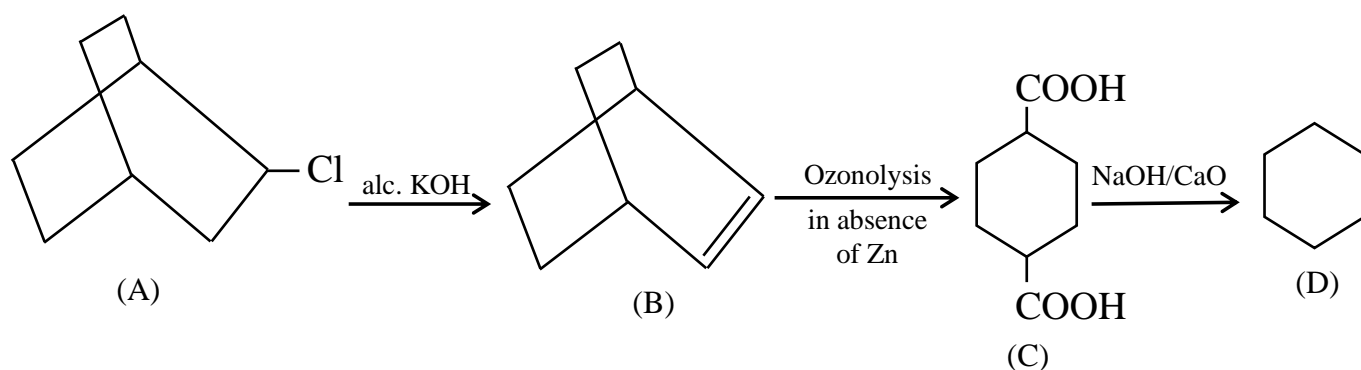


## CARBOXYLIC ACID & THEIR DERIVATIVES

### Example 9.

An optically active organic compound (A) ( $C_8H_{13}Cl$ ) does not decolourise bromine water solution. (A) on treatment with alcoholic KOH can produce 2 products in principle but infact only one product (B) ( $C_8H_{12}$ ) is obtained. (B) on treatment with ozone followed by work up with  $H_2O_2$  yields (C) ( $C_8H_{12}O_4$ ) which cannot be resolved into enantiomers. (C) on heating with NaOH/CaO yields (D) ( $C_6H_{12}$ ) which on monochlorination yields  $C_6H_{11}Cl$  single isomer. Deduce structures of (A) to (D).

### Solution:



### Example 10.

A cyclobutandicarboxylic acid exists in two stereo-isomeric forms in which one is polar but non-resolvable while other is non-polar but resolvable into enantiomers. Deduce structures of all these compounds.

### Solution:

The compound must be 1,2-cyclobutandicarboxylic acid since all other constitutional isomers are non-resolvable.

