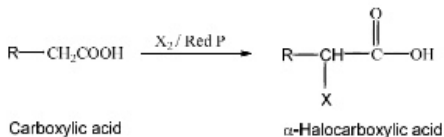

6.8 REACTIONS OF CARBOXYLIC ACIDS

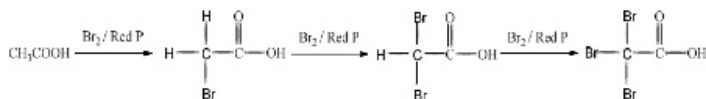
The carboxylic acids are reactive organic compounds because of $-OH$ and $-CO$ group and undergo many reactions some of them are as follows.

(1) α -Halogenation of aliphatic acids: Carboxylic acids undergo halogenation with chlorine or bromine in the presence of small amount of red phosphorus form α -halo or β -haloacids. The reaction is known as ***Hell Volhard Zelinsky reaction***. In this reaction a carboxylic acid containing an α -hydrogen atom is replaced by a chlorine or bromine atom to form an α -halo carboxylic acid. The general reaction is as:



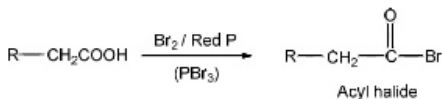
(Where, X = Cl, Br)

Bromination of acetic acid is a good example of this reaction.

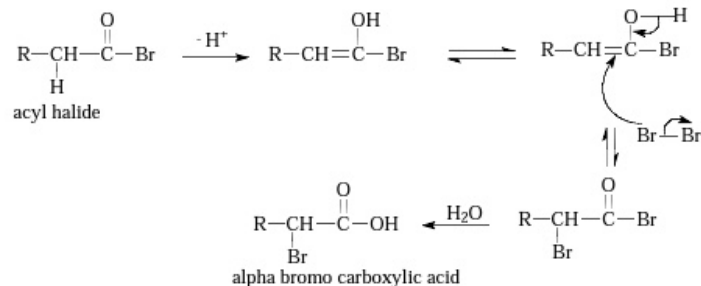


Mechanism: The stepwise mechanism is as follow of HVZ reaction

Step 1: Phosphorus reacts with bromine to form phosphorus tribromide, and in the first step this converts the carboxylic acid into an acyl bromide.



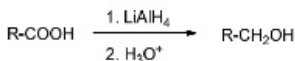
Step 2: The acyl bromide then tautomerizes to the enol form which subsequently attacks the halogen molecule to form a α -halo acyl halide. Water hydrolysis yields the final α -halo carboxylic acid product.



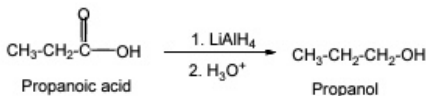
Although the α -bromination of some carbonyl compounds, such as aldehydes and ketones, can be accomplished with Br_2 under acidic conditions, this reaction will generally not occur with acids, esters, and amides because only aldehydes and ketones enolize to a sufficient extent to allow the reaction to occur.

(2) Reactions of -COOH group

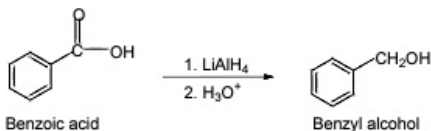
(i) a. Reduction of carboxylic acid to alcohols by LiAlH_4 : The carboxylic acids are reduced to primary alcohols with a strong reducing agent like lithium aluminium hydride (LiAlH_4). In this reaction the carbonyl group of a carboxyl group is reduced to - CH_2 group.



Propanoic acid is reduced to propanol in presence of lithium aluminium hydride (LiAlH_4).



Similarly, benzoic acid is reduced to benzyl alcohol in presence of lithium aluminium hydride (LiAlH_4).



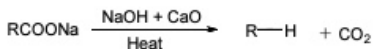
Higher carboxylic acids are also reduced to alcohols by hydrogen in presence of copper chromium oxide. This reaction is used to prepare detergents such as sodium lauryl sulphate from lauryl alcohol.



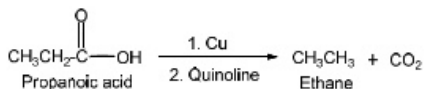
Carboxylic acids cannot be reduced by H_2/Ni , or $\text{Na}/\text{C}_2\text{H}_5\text{OH}$, or NaBH_4 , or catalytic hydrogenation.

b. Reduction by HI: Carboxylic acids can be reduced to either primary alcohols or alkanes depend upon the reducing agent involve in reaction

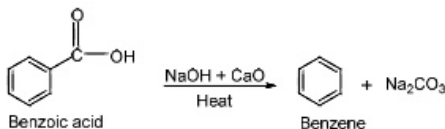
(ii) Decarboxylation reaction: When an anhydrous sodium salt of a fatty acid is heated with sodalime ($\text{NaOH} + \text{CaO}$) or $\text{Cu}/\text{quinoline}$, it loses carbon dioxide to form an alkane. This reaction is known as decarboxylation reaction. The general reaction is as:



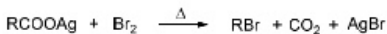
Simple copper salts such as copper chromate, copper hydroxide or copper carbonate can also be used in decarboxylation of aliphatic and aromatic acids.



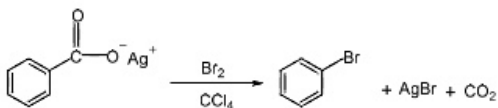
Aromatic carboxylic acids also react with sodalime to give benzene.



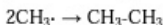
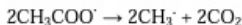
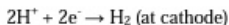
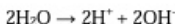
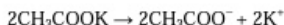
(iii) Hunsdiecker reaction: Silver salt of fatty acids on heating with a halogen (Cl or Br) undergo decarboxylate halogenations give alkyl or aryl halides. The general reaction is as:



For example,

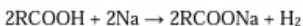


(iv) Kolbe electrolysis: The electrochemical oxidation of sodium or potassium salts of fatty acids give alkanes having twice the number of carbon atoms present in the alkyl group of the acid. This process is known as *Kolbe's electrolysis*. For example; the electrolysis of potassium ethanoate forms ethane with carbon dioxide gas and hydrogen gas as side products.

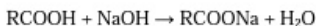


(3) Reactions with metals and alkalis: Some reactions which show the acidic character of carboxylic compounds are as follow:

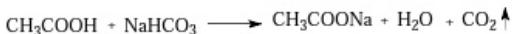
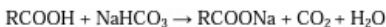
(i) Reaction with metal: Carboxylic acids react with active metals like K, Ca, Mg to form salts by releasing hydrogen gas.



(ii) Reaction with alkalis: Carboxylic acids react with alkalis like sodium hydroxide to form salts and water.



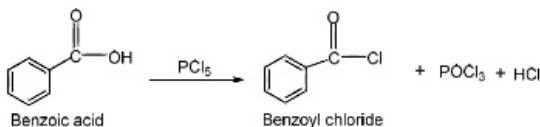
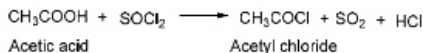
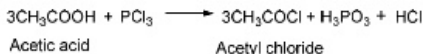
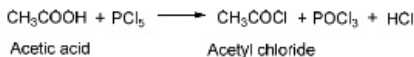
(iii) **Reaction with sodium bicarbonate:** Carboxylic acids are weaker than mineral acids like sulphuric acid or nitric acid and able to react with weaker bases like carbonates and bicarbonates to evolve carbon dioxide with water.

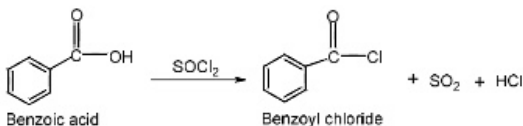
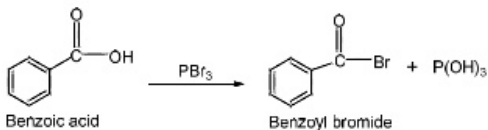


The reaction with sodium bicarbonate is also used as functional group determination of carboxylic acid

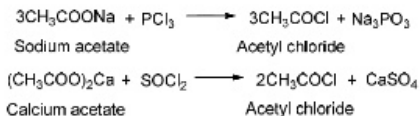
(4) **Formation of acid derivatives:** The carboxylic acid derivatives *viz.* acyl halides(RCOCl), acid anhydrides(RCOOCOR), esters(RCOOR) and acid amides(RCONH₂) can be derived from carboxylic acids(RCOOH) by the replacement of -OH part of a -COOH group by some other groups like -Cl, -OR, -NH₂.

(i) **Formation of acid halides:** Carboxylic acids react with halide derivatives like phosphorous trichloride (PCl₃), phosphorous tribromide (PBr₃), phosphorous pentachloride (PCl₅), and thionyl chloride (SOCl₂) to form acyl halides. Acyl halides are formed by the replacement of -OH part of -COOH group by a -Cl or -Br group.

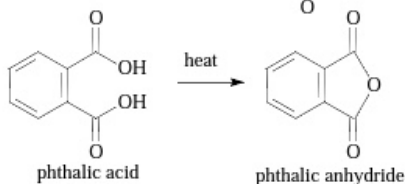
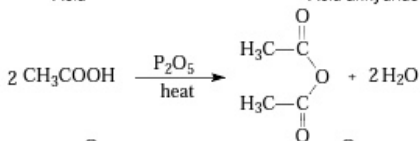
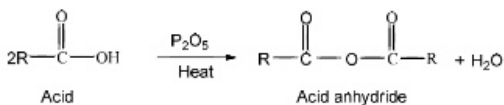




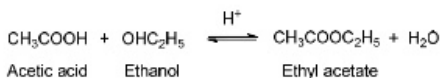
Acyl halides like acyl chlorides are also prepared by the reaction of sodium salts of carboxylic acids with phosphorous trichloride (PCl_3) or thionyl chloride (SOCl_2).



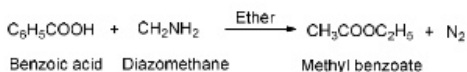
(ii) Formation of acid anhydride: The acid anhydrides can be obtained by the dehydration of carboxylic group in the presence of strong dehydrating agents like P_2O_5 or concentrated H_2SO_4 .



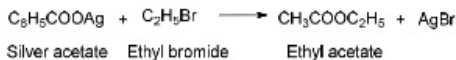
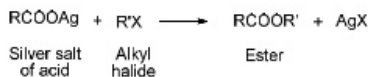
(iii) Formation of esters: Carboxylic acids react with alcohols to form esters in presence of concentrated H_2SO_4 . This reaction involves the replacement of $-\text{OH}$ group by $-\text{OR}$ group of alcohol or phenol and also known as Fischer-speier esterification. For example, ethanoic acid reacts with ethanol to form ethylethanoate.



Esters can also be prepared by the action of the ethereal solution of diazomethane on carboxylic acid.

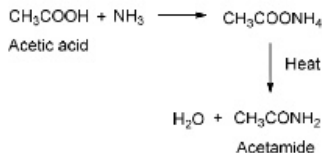


Esters can also be prepared by the reaction of silver salt of acids on alkyl halides.



(iv) Formation of amides

Carboxylic acids react with ammonia to form ammonium salts which on heating lose water molecule to form amides.

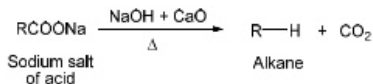


6.9 MECHANISM OF DECARBOXYLATION

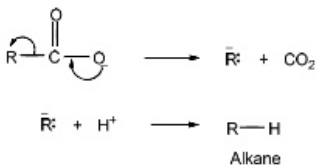
When anhydrous sodium salt of a fatty acid is heated with sodalime (NaOH + CaO) or Cu/quinine, it loses carbon dioxide to form an alkane. This reaction is known as decarboxylation reaction.

Decarboxylation is of two types:

1. Simple carboxylic acids

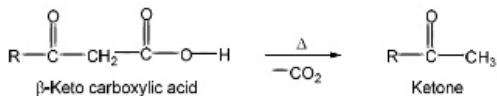


Mechanism



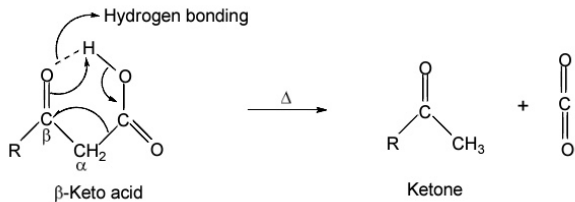
2. β -carbonyl carboxylic acids

The β -keto carboxylic acids lose CO_2 readily on heating at about 100°C .



Mechanism

Decarboxylation of β -keto acid takes place via a six membered cyclic transition state.



Note: Simple copper salts such as copper hydroxide and copper carbonate can also be used in decarboxylation of aliphatic and aromatic acids. For example:

