01 Carboxylic Acids and Its Derivatives

Organic compounds having –COOH group called Carboxylic group. This functional group is composed of Carbonyl ($-\overset{\overset{O}{\|}}{C}-$) and hydroxyl (–OH) group.

The properties of the carboxylic group are not simply the combined properties of these two groups, but it has its own distinctive properties. The acidic nature of carboxylic acids is due to the presence of replaceable H-atom in the Carboxylic group. The general formula is $C_nH_{2n}O_2$.

Classification :

Monocarboxylic acid (RCOOH) :

Having one carboxylic group, also called monobasic acid.

General formula - $C_nH_{2n}O_2$ (n = 1, 2, 3, ...).Higher mono carboxylic acids are called **fatty acids**.

Example : CH_3COOH acetic acid

Dicarboxylic acid : Having two carboxylic groups, also called dibasic acid.

Example : $\begin{matrix}COOH\\|\\COOH\end{matrix}$ Oxalic acid

Tricarboxylic acid : Having three carboxylic groups also called tribasic acid.

Example : $HO-\overset{\overset{CH_2COOH}{|}}{\underset{\underset{CH_2COOH}{|}}{C}}-COOH$ Citric acid

NOMENCLATURE :

Acid	Common name	IUPAC name
HCOOH	Formic acid (formica-red ants)	Methanoic acid
CH_3COOH	Acetic acid (acetum-vinegar)	Ethanoic acid
CH_3CH_2COOH	Propionic acid (Propan-first pion-fat)	Propanoic acid
$CH_3CH_2CH_2COOH$	Butyric acid (Butter-butyrums)	Butanoic acid
$CH_3CH_2CH_2CH_2COOH$	Valeric acid (valerian-plant root)	Pentanoic acid
$C_5H_{11}COOH$	Caproic acid	Hexanoic acid
$C_7H_{15}COOH$	Caprylic acid	Octanoic acid
$C_9H_{19}COOH$	Capric acid	Decanoic acid

Last three acids are found in goat fat word - (Caper-Goat).

General Method of Preparation :

1. By oxidation of primary alcohol with acidic $KMnO_4$ or acidic $K_2Cr_2O_7$:

$$R—CH_2OH + [O] \xrightarrow[K_2Cr_2O_7/H^{\oplus}]{KMnO_4} RCHO + H_2O \xrightarrow{[O]} RCOOH$$

2. By oxidation of aldehydes :

Aldehydes on oxidation with usual oxidizing agent gives carboxylic acid with same number of carbon atoms as in the aldehyde.

$$R—CHO + [O] \xrightarrow{\text{Tollen's Reagent}} R—COO^{\ominus} \xrightarrow{H^{\oplus}} R—COOH$$

$$C_6H_5CHO + [O] \xrightarrow{\text{Tollen's Reagent}} C_6H_5COO^{\ominus} \xrightarrow{H^{\oplus}} C_6H_5COOH$$

3. By oxidation of alkenes :

(a) $RCH = CHR' \xrightarrow[(ii)\ H_3O^{\oplus}]{(i)\ \text{conc. } KMnO_4/OH^{\ominus}} RCOOH + R'COOH$

(b) $RCH = CHR' \xrightarrow[(ii)\ H_2O,\ \text{Distill}]{(i)\ O_3} RCOOH + R'COOH$

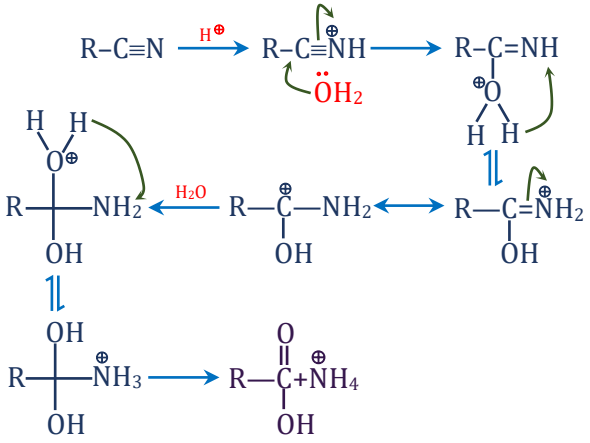
4. By Carboxylation of Grignard Reagent :

$$R–Br \xrightarrow[\text{Dry ether}]{Mg} RMgBr \xrightarrow{CO_2} R–\overset{O}{\overset{\|}{C}}–O^{\ominus}Mg^{\oplus}Br \xrightarrow[-MgBr\ (OH)]{H_2O/H^{\oplus}} R–\overset{O}{\overset{\|}{C}}–OH$$

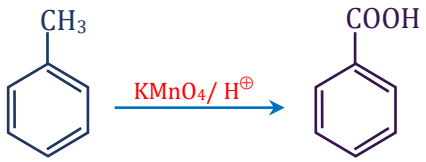
5. Cyanide hydrolysis with dilute acids :

$$R—CN \xrightarrow{H_3O^{\oplus}} RCOOH$$

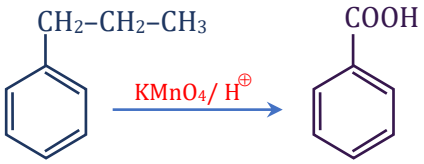
The mechanism of hydrolysis of R–CN is as follows.



6. By oxidation of alkyl benzene :



Alkyl group having no α-H atom will not be oxidized to –COOH. Any alkyl group containing at least one α-H atom will be oxidized to –COOH. The product of oxidation will be benzoic acid.



The order of benzoic acid formation by oxidation of alkyl benzene.

Methyl benzene >1° alkyl benzene >2° alkyl benzene

Solve the following questions.

1. Identify Z in the sequence

$CH_3COONH_4 \xrightarrow[(ii)P_2O_5]{(i)heat} Y \xrightarrow{H_2O(H)^{\oplus}} Z$

(A) $CH_3CH_2CONH_2$ (B) CH_3CN

(C) CH_3COOH (D) $(CH_3CO)_2O$

2. A halogen compound 'A' on hydrolysis with dilute alkali followed by acidification gives acetic acid. The compound X is -

(A) $ClCH_2CH_2Cl$ (B) CH_3CHCl_2

(C) $ClCH_2CHCl_2$ (D) CH_3CCl_3

3. Acetic acid is obtained when -

(A) Methyl alcohol is oxidised with potassium permangnate

(B) Formaldehyde is oxidised with potassium dichloromate and sulphuric acid

(C) Acetonitrile is hydrolysed with a dilute mineral acid

(D) Glycerol is heated with sulphuric acid

4. Identify Z in the following reaction sequence $CH_3I \xrightarrow[Ether]{Mg} X \xrightarrow[H^{\oplus}]{CO_2} Y \xrightarrow[Red\,P]{Cl_2} Z$

(A) CH_3COOH (B) CH_3MgI (C) CH_3COCl (D) $ClCH_2COOH$

5. Kolbe's electrolysis of aqueous potassium ethanoate leads to the formation of -

(A) Ethene (B) Methane (C) Ethane (D) Ethyne

6 $A \xleftarrow[HI]{red\,P} CH_3COOH \xrightarrow{LiAlH_4} B$. What is not true for A and B -

(A) A is hydrocarbon of general formula C_nH_{2n+2} while B belongs to alkanol

(B) A can be obtained by reducing CH_3CH_2Cl while B by its hydrolysis

(C) A is alkane while B is alkanal

(D) A and B both belongs to different homologous series

7. Arrange the following compounds in decreasing order of acidity -

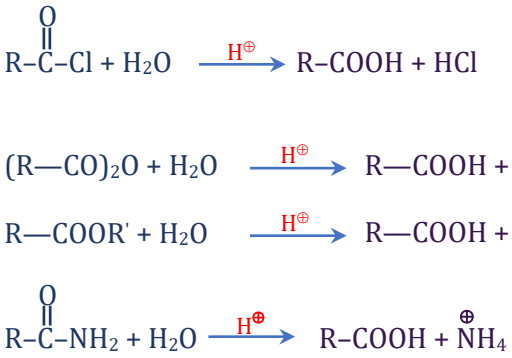
$ClCH_2CH_2CH_2COOH$ (I) $CH_3CHClCH_2COOH$ (II) $CH_3CH_2CHClCOOH$ (III)

(A) I > II > III (B) III > II > I (C) I > III > II (D) III > I > II

8. Arrange $OHCH_2COOH$ (I), $HOCH_2CH_2COOH$ (II) and CH_3COOH (III) in order of acidity -

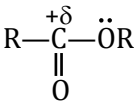
(A) I > II > III (B) III > II > I (C) I > III > II (D) II > III > I

7. By hydrolysis of acyl derivatives of carboxylic acid:

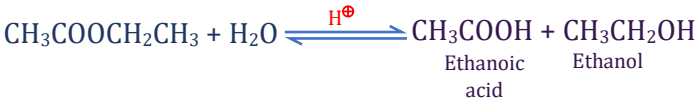


HYDROLYSIS OF ESTER :-

Esters are less reactive than acid chlorides because magnitude of +δ charge on carbonyl carbon is less. That's why hydrolysis of ester carries out under acidic or basic conditions.



Acidic medium :

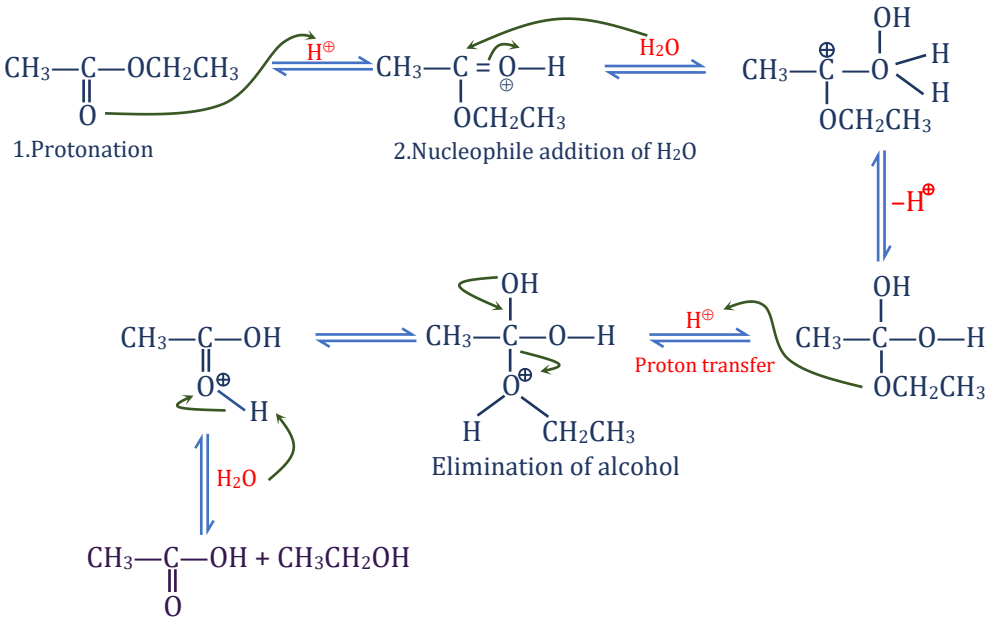


Ester is heated under reflux with dilute HCl. This reaction is reversible.

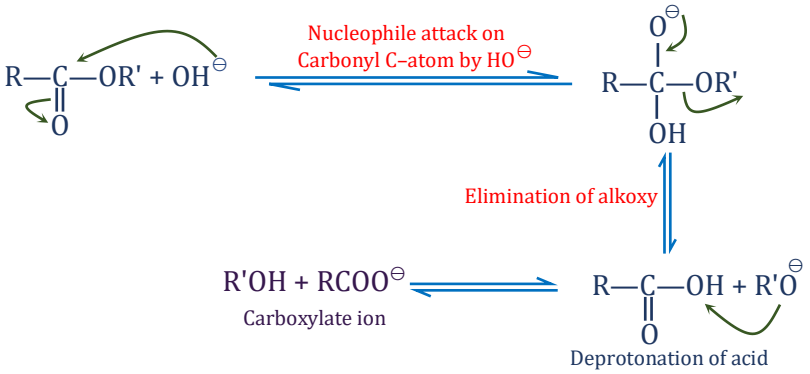
Hydrolysis of ester in acid medium

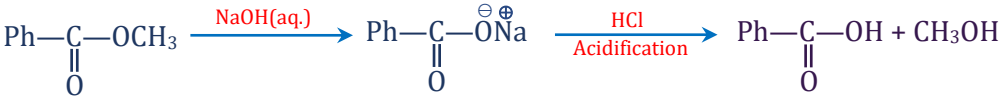
Mechanism

⇒ **It is a reversible reaction**



Hydrolysis of ester in Basic medium :



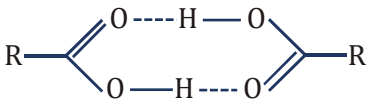


NOTE :

(1) The base-catalyzed ester hydrolysis is also known as saponification because it is used in the production of soaps from fats.

Physical Properties of Carboxylic Acid :

These are polar substances and can form H-bonds with each other to form dimer structures.



Boiling Point : Due to dimeric structure, the effective molecular mass of the acid becomes double of the actual molecular mass. Hence carboxylic acids have higher boiling points than alcohols of comparable molecular masses. Due to hydrogen bonding carboxylic acids show appreciable solubility in water. Its solubility in water is greater than alcohol because H-bonding strength is greater in carboxylic acid than alcohol.

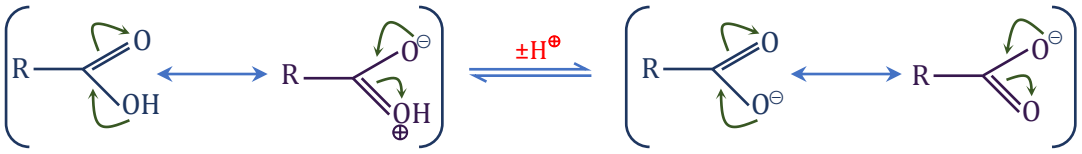
Melting Point : Melting point of the carboxylic acid with even number of carbon atoms is higher than acid with odd number of carbon atoms. Such effect is observed in first ten members of the homologous series. This feature is based on the fact that in the carboxylic acids with even number of carbon atoms, the terminal methyl group and carboxylic group are on the opposite sides of zig-zag carbon chain. Hence they fit better in the crystal lattice resulting in stronger inter molecular forces on the other hands acids with odd number of carbon atom have carboxyl and terminal methyl group on the same side of zig-zag carbon chain which result in poor fitting in the crystal lattice. This causes a weak forces among molecules and result for the relatively lower melting point.

The melting point and boiling points are usually higher than those of aliphatic acid of comparable molecular masses. This is due to planar structure of benzene ring in the acid which can pack closely in the crystal than aliphatic acids.

Chemical Properties of Carboxylic Acid :

1. Acidity of carboxylic acid :

Acidity is relative case with which it loses a proton leaving behind the anion. Its acid strength depends upon the difference in the stability of the acid and its anion.



non-equivalent structures of resonance hybrid

equivalent structures of resonance hybrid

both acid and its anion are stabilized by resonance, stabilization is far greater for the anion than for acid because anion gives two identical resonating structure.

2. Effect of substituents on Acidity :

Any factor that stabilizes the anion more than it stabilizes the acid should increase the acidity and any factor that makes the anion less stable should decrease the acidity of the carboxylic acid.

(a) An electron withdrawing substituents stabilizes the anion by dispersing the –ve charge and therefore increases the acidity of carboxylic acid.

(b) Electron releasing substituents intensify the –ve charge on the anion resulting in decrease of stability of the carboxylate anion and therefore decreases the acidity of the acid.

Carboxylic acids are weak acids and their carboxylate ions are strong conjugate bases. They are slightly alkaline due to the hydrolysis of carboxylate anion compared to other species. The order of acidity and basicity of corresponding conjugate bases are as follow.

$$\text{Acidity}--\text{RCOOH} > \text{HOH} > \text{ROH} > \text{CH} \equiv \text{CH} > \text{NH}_3 > \text{RH}$$

$$\text{Basicity}--\text{RCOO}^{\ominus} < \text{OH}^{\ominus} < \text{HC} \equiv \text{C}^{\ominus} < \text{NH}_2^{\ominus} < \text{R}^{\ominus}$$

Acidity increase Acidity decrease

The effect of various number of the substituent and their distance from the carboxylic group has been illustrated with the help of following examples.

(i) The effect of number of the substituent is shown by the chloro substituted acetic acids. The acid strength increases in the order given below :

$\text{ClCH}_2\text{—COOH} < \text{Cl}_2\text{CHCOOH} < \text{Cl}_3\text{CCOOH}$

The increase in the no. of chloro substituent on α-carbon atom of acetic acid make the electron withdrawing effect more pronounced and hence make carboxylate ion more stable.

When electron releasing substituent is attached to the carboxylic group then acid strength decreases as the electron releasing power increases.

$$\text{R} \rightarrow \text{CH}_2 \rightarrow \text{COOH} > \text{R} \rightarrow \underset{\displaystyle \underset{\displaystyle \text{R}}{\downarrow}}{\text{CH}} \rightarrow\rightarrow \text{–COOH} > \text{R} \rightarrow \underset{\displaystyle \underset{\displaystyle \text{R}}{\uparrow}}{\overset{\displaystyle \overset{\displaystyle \text{R}}{\downarrow}}{\text{C}}} \rightarrow\rightarrow\rightarrow \text{–COOH}$$

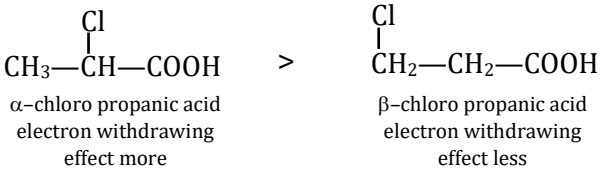
(ii) The effect of nature of the substituent is illustrated by the various halo acetic acids. Their acid strength follows the order :

$$ICH_2–COOH < BrCH_2COOH < ClCH_2COOH < F\,CH_2COOH$$

$$CH_3–CH_2–CH_2–COOH < CH_2 = CH–CH_2–COOH < N \equiv C–CH_2–COOH$$

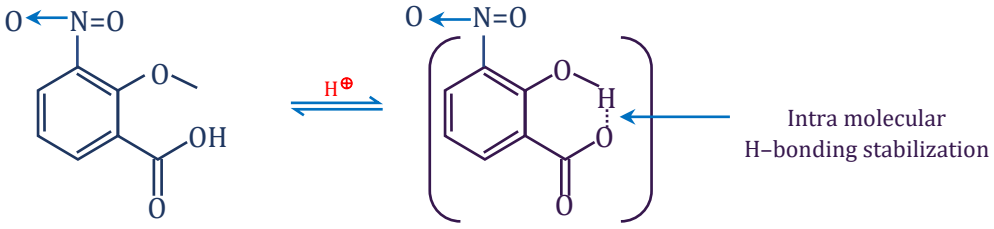
$$(sp^2) \qquad (sp)$$

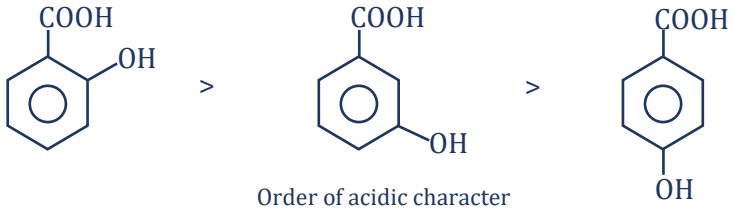
(ii) Effect of the position of the substituent : The effect of the substituent decreases as its distance from —COOH group increases.



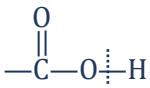
Ortho Effect:

The ortho substituted benzoic acid (whether the substituent is electron withdrawing or releasing) is comparatively stronger acid than the para and meta isomers. This effect is called ortho effect. It occurs due to the joint operation of steric and intra molecular H-bonding where ever it takes chance to stabilize the carboxylate anion due to nearness of the substituent. Groups like –OH, –Cl, $–NO_2$ will cause more stabilization to anion due to direct interaction through intra molecular H-bonding.





Reaction due to cleavage of (—O—H)bond as acid



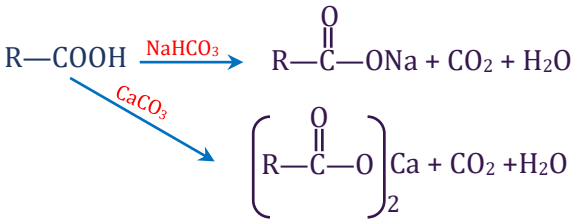
(i) Reaction with active metals [alkali and alkaline metal] :

(ii) Reaction with CaO :

$2R-COOH + CaO \longrightarrow (RCOO)_2Ca + H_2O$

(iii) Reaction with Bicarbonates and Carbonates :

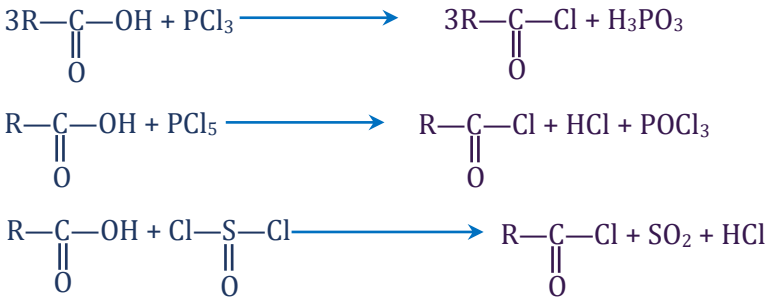
Carboxylic acid reacts with carbonates and bicarbonates to liberate CO_2 gas



Reaction with PCl_5, PCl_3, $SOCl_2$:

By carboxylic acid

Carboxylic acids react with PCl_5, PCl_3 and $SOCl_2$ (thionyl chloride) give acyl chloride by replacing –OH group



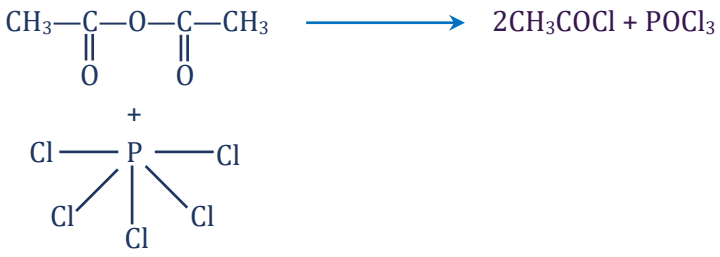
Example

$3CH_3COOH + PCl_3 \longrightarrow 3CH_3COOCl + H_3PO_3$

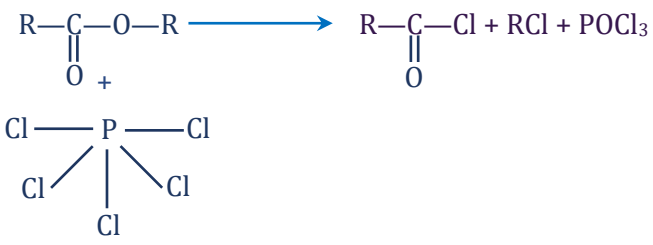
Note:

$SOCl_2$ is a better reagent because all by products are in gaseous form

By anhydride



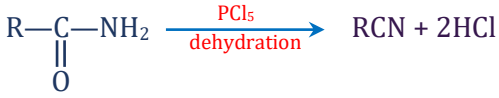
By Ester



Example

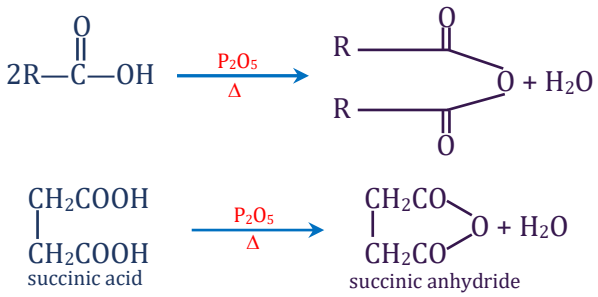
By Amide

Amide on reaction with PCl_5, PCl_3 and $SOCl_2$ give dehydration reaction and alkyl cyanide is formed



Formation of Acid Anhydride:

Carboxylic acid on treatment with any dehydrating agent as P_2O_5 to form anhydride by elimination of water molecule.

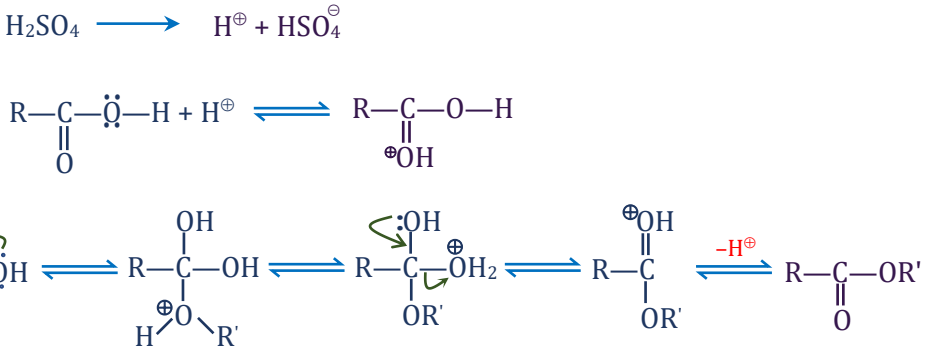


Reaction Involving Cleavage of –OH Group :

1. Esterification :

When carboxylic acid reacts with alcohol in the presence of conc. H_2SO_4 to form ester, it is known as esterification

Mechanism :



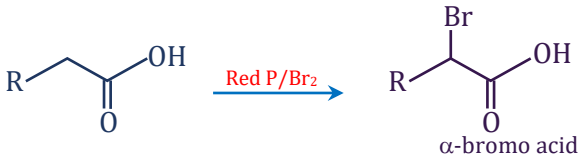
The relative reactivity of alcohol to ester formation markedly dependent on their structure. The greater the bulk of the substituents near the –OH group, the slower the reaction would be same facts is followed by acid as well

$CH_3OH > CH_3CH_2OH > (CH_3)_2CHOH > (CH_3)_3COH$

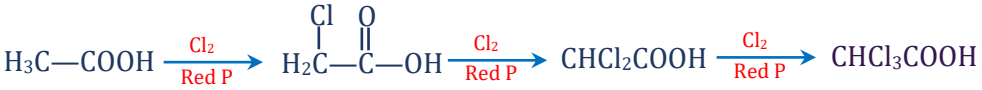
$H{-}{-}COOH > CH_3COOH > (CH_3)_2CHCOOH > (CH_3)_3CCOOH$

2. Hell-Volhard-Zelinsky Reaction (HVZ Reaction) :

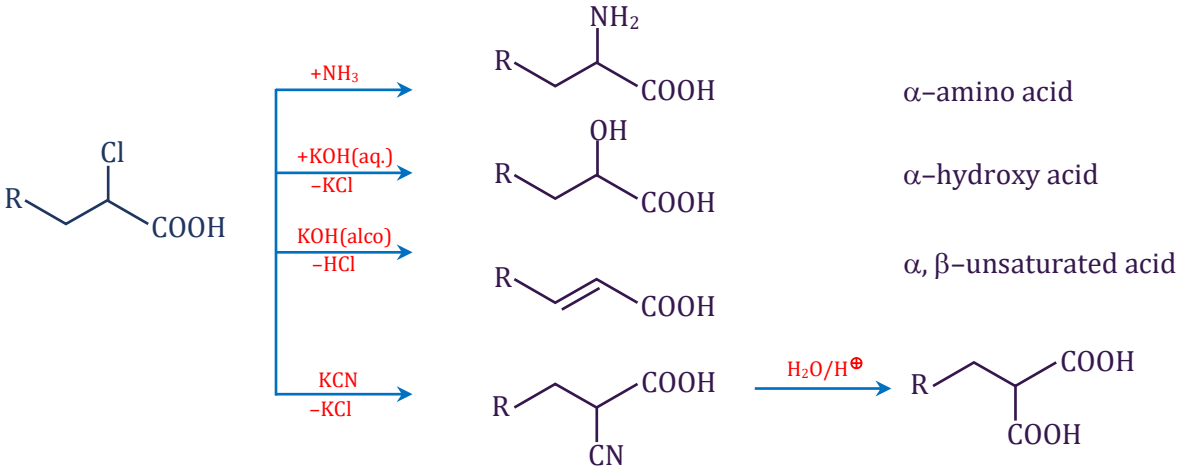
This is a-halogenation of a carboxylic acid.



The purpose of PBr_3 is to convert –OH into –Br to make a-hydrogen atom more acidic to be replaced by Br atom of Br_2. The reaction does not stop at monosubstitution but continues till the α-hydrogen are replaced.

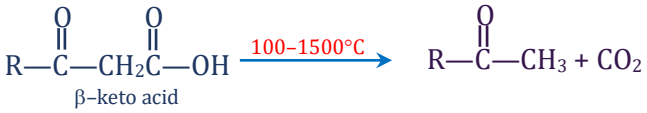


The reaction has a great synthetic importance as the halogen atom can be replaced by a number of other groups giving useful products.



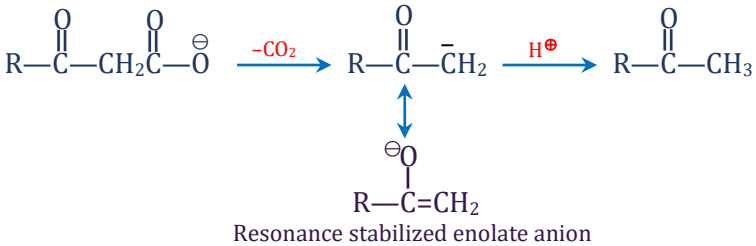
3. Hunsdicker Reaction :

4. Heating of b-keto acid :



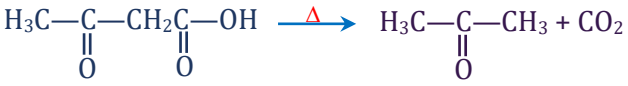
There are two facts on which ease of decarboxylation depends.

(i) When the carboxylate ion decarboxylate, it forms a resonance stabilized enolate anion.

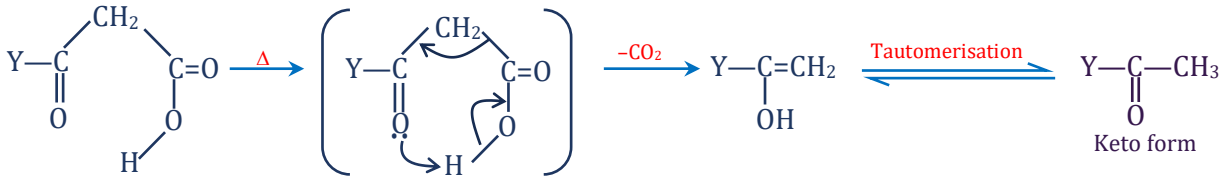


This anion is much more stable than the anion $RC^{\ominus}H_2$ formed by decarboxylation of an ordinary carboxylic acid anion.

(ii) When the acid itself decarboxylates it can do so through a six-membered cyclic transition state β-keto acid on warming alone or in presence of a base undergoes rapid removal of CO_2.



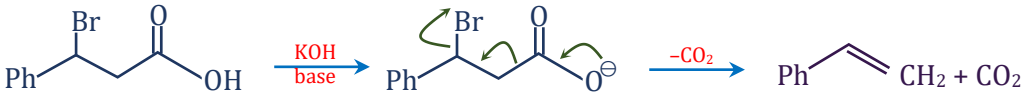
Mechanism :



Here y can be substituents like

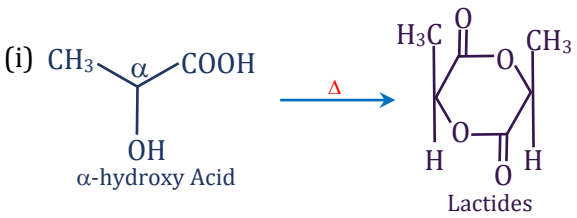
OH → diacid ; R → β-keto acid

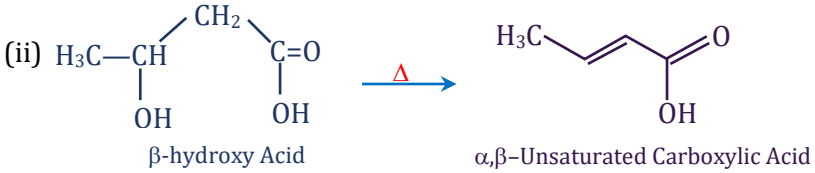
H → β aldehyde acid ; X → β halo acid

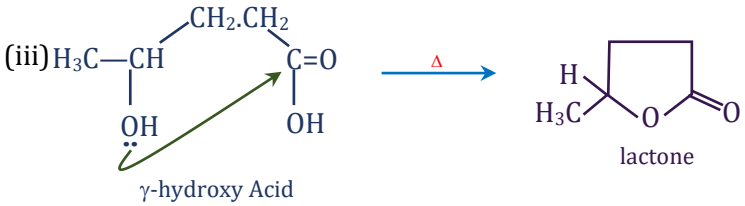


This decarboxylation proceeds through elimination.

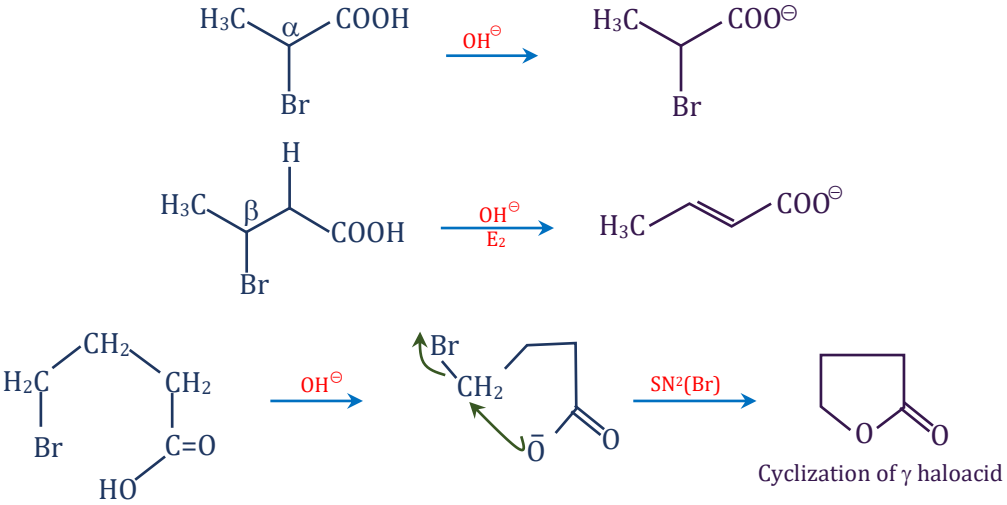
5. Heating of α, β and γ Hydroxy Acid :

(i) 

(ii) 

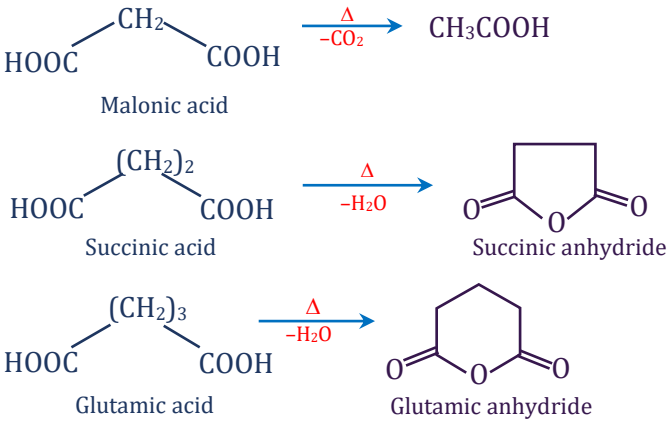
(iii) 

Reaction of α, β and γ halo carboxylic acid with aq. NaOH :



Cyclization of γ haloacid

Heating of Dicarboxylic Acids :

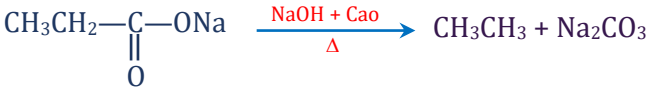


De-carboxylation, Kolbe's electrolysis:

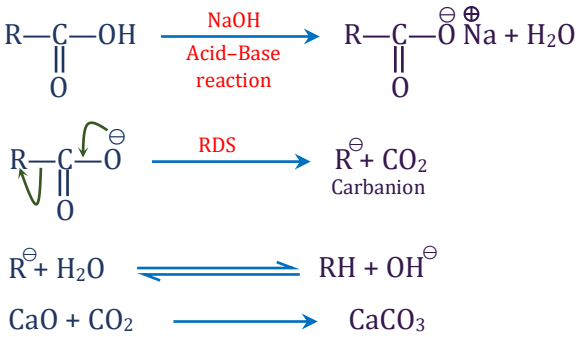
De-carboxylation

When alkali salt of carboxylic acid are heated With soda lime (NaOH and CaO in 3 : 1) formed hydrocarbon by losing CO_2.

This is known as decarboxylation :



Mechanism :

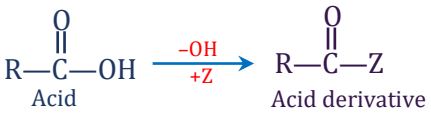


Kolbe's electrolysis:

Alkanes are formed on electrolysis of concentrated aqueous solution of sodium or potassium salt of saturated monocarboxylic acids.

Derivatives of Carboxylic Acid :

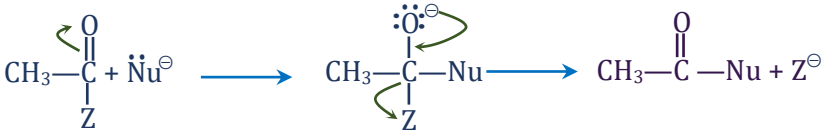
The –OH of an acid can be replaced by –Cl, –OR, or $-NH_2$ group to yield an acid chloride an ester or an amide. These compounds are called functional derivatives of acid and they all contain acyl group. The functional derivatives are all readily converted into the acid by simple hydrolysis.



$R-\overset{\overset{O}{\|}}{C}-$ is Acyl group and Z is nucleophile $Cl^{\ominus}$, $CH_3COO^{\ominus}$, $C_2H_5O^{\ominus}$, $NH_2^{\ominus}$ etc.

Characteristic reaction for acid derivatives is nucleophilic substitution reaction :

Mechanism :



sp^2 hybrid C - atom sp^3 hybrid C - atom

In this reaction Z is leaving group. Weak bases are good leaving groups.

Reactivity order - depends on the basic Character of Z

basicity : $Cl^{\ominus} < CH_3COO^{\ominus} < C_2H_5O^{\ominus} < NH_2^{\ominus}$

In the given groups, $Cl^{\ominus}$ is the weakest base so it is best leaving group.

Reactivity order : $CH_3COCl > CH_3COOCOCH_3 > CH_2COOC_2H_5 > CH_3CONH_2$

In acid derivatives the carbonyl group $\rangle CO$ is attached to highly electronegative $Cl^{\ominus}$, $CH_3COO^{\ominus}$, $NH_2^{\ominus}$ etc. group due to electron withdrawing effect of these groups, the electron density on the carbonyl carbon is reduced further. Thus acetyl group is readily attacked by $\ddot{N}u$ shows nucleophilic substitution reaction.

Basicity of leaving groups :

Weaker the basic character of the leaving group more will be the ease with which the leaving group eaves the compound and hence more is the leaving power

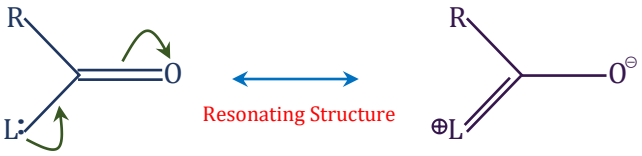
The order of basicity of the leaving group and their leaving tendency follows the order.

$H_2N^{\ominus} > RO^{\ominus} > RCOO^{\ominus} > Cl^{\ominus}$

Basicity ⟵

Leaving power ⟶

Resonance Effect :



Due to resonance, the carbon–leaving group (L) bond acquires a double bond character due to which stabilization occurs. Now more is stabilization, lesser is the reactivity and vice-versa. As the stabilization is the least in the case of acid chloride because of high magnitude of –I effect of Cl atom. Therefore its reactivity is the most.

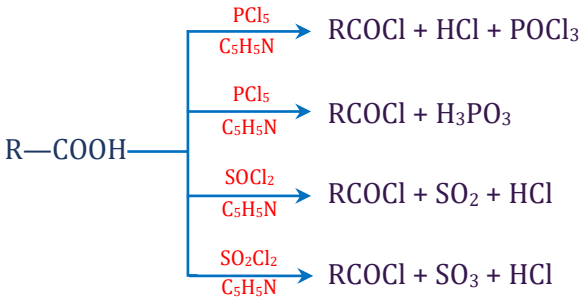
Nucleophilic acyl substitution should be catalysed by acids becasuse the protonation of the acyl compound would facillitate nuceleophilic attack.

Acyl Chloride (RCOCℓ):

These are the derivatives of carboxylic acid in which hydroxyl (–OH) part of carboxyl group is replaced by halo group. The most reactive compound of halo leaving group is chloro compounds.

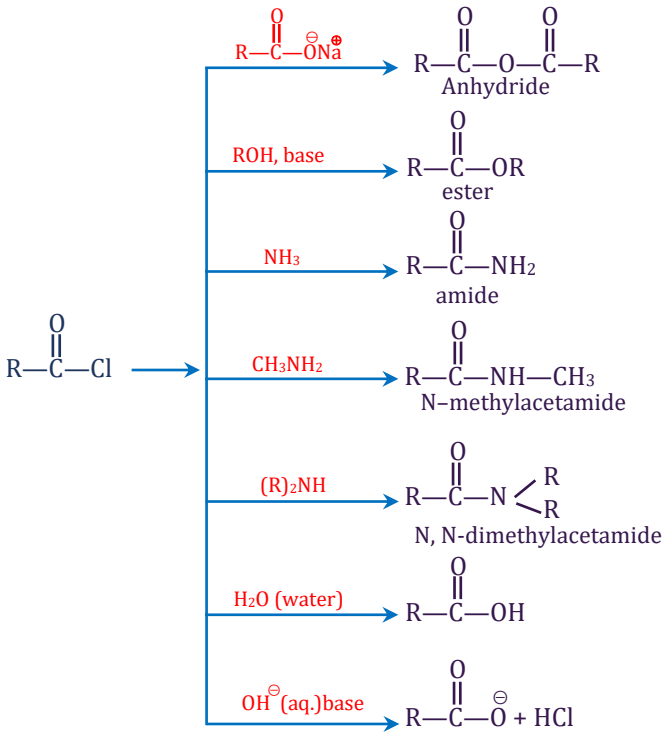
Method of Preparation :

Carboxylic acid chloride can be prepared by the reaction of carboxylic acid with PCl_5 or $SOCl_2$ of PCl_3 or SO_2Cl_2.

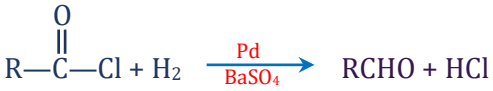


Chemical Properties :

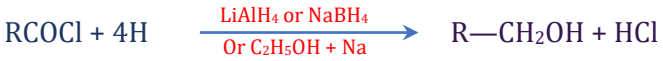
1. Acylation Reaction :



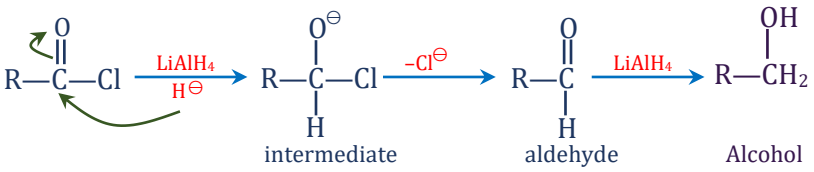
2. Reduction reactions :



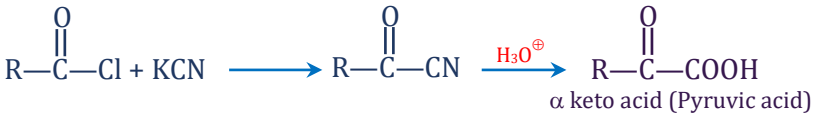
(Rosenmund's reduction)



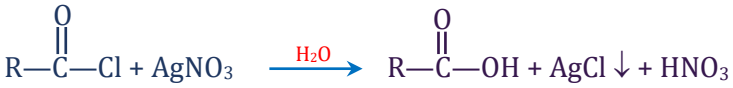
Mechanism :



3. Reaction with KCN :



4. Reaction with $AgNO_3$:



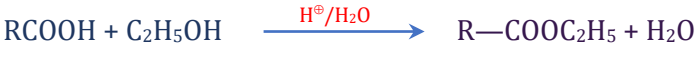
The aliphatic acid chlorides are readily decomposed by water therefore aqueous solution of acid chloride gives white ppt. with aqueous $AgNO_3$.

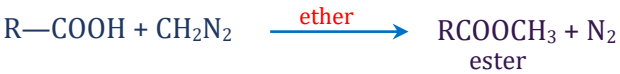
Esters (RCOOR) :

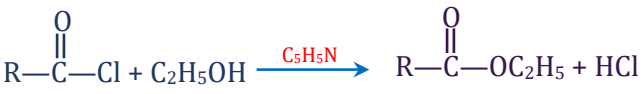
Ester are the derivative of the carboxylic acid in which the –OH part of the carboxylic group has been replaced by –OR group where R may be alkyl or aryl group.

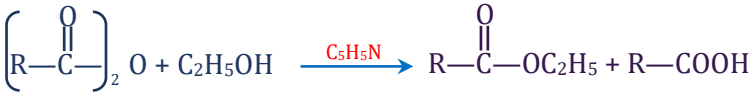
Method of Preparation :

By reaction of acids with alcohol or diazomethane in presence of ether.



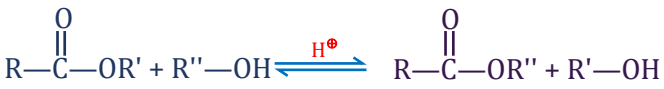




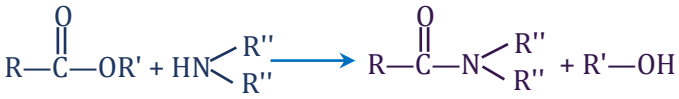


Chemical Properties :

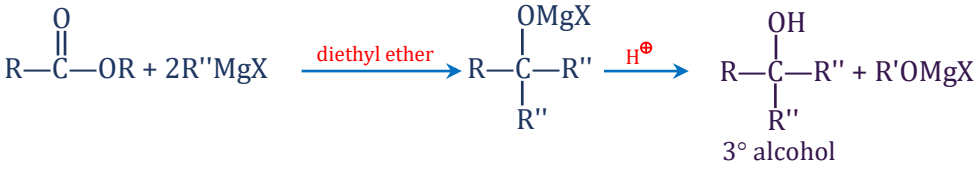
1. Conversion to other esters : Transesterifications



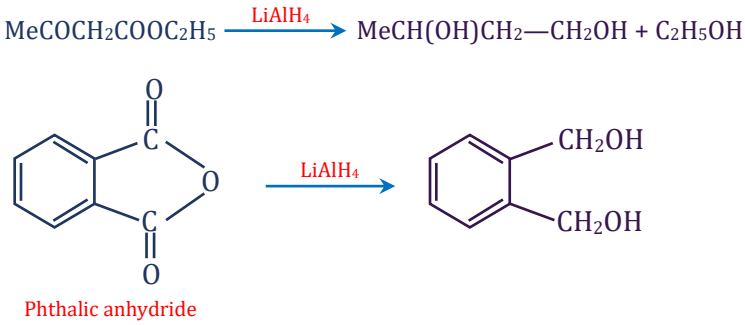
2. Conversion to amides :



3. Reaction with Grignard Reagent :

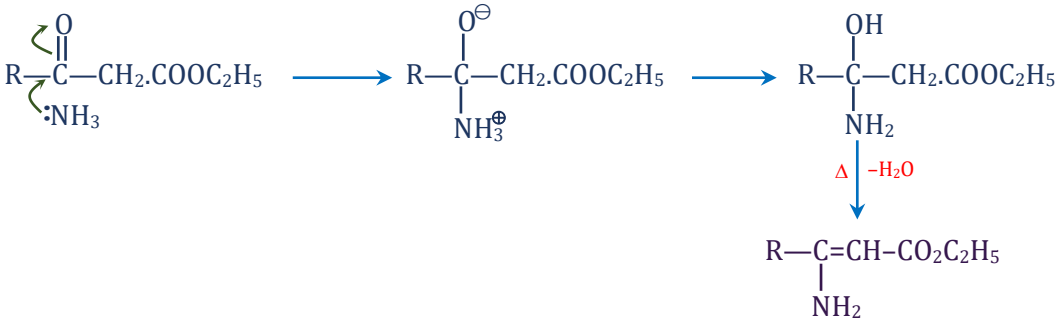


4. Reduction of ester :



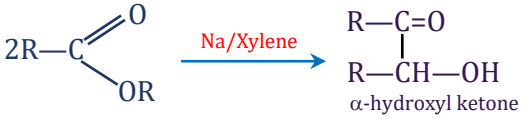
5. Reaction of NH_3 with keto ester :

Mechanism :



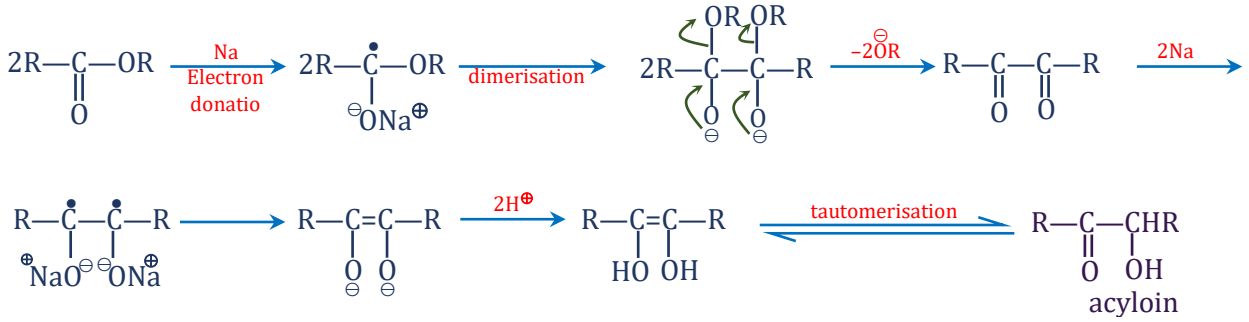
Attack will occur at carbonyl group first because of high degree of +ve charge on carbonyl carbon atom.

6. Acyloin condensation :



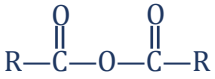
Mechanism :

It is the intermolecular, sodium promoted condensation of two moles of ester or the intra molecular condensation of a ester to a-hydroxy ketone (acyloin).

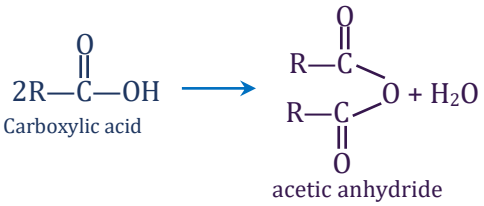


Hydrolysis of Acyl Derivatives :

Ester hydrolysis can be carried out in mechanistic pathways A_{AC^1} , A_{AC^2} , A_{AL^1} , B_{AC^2}



Acid anhydrides are considered to be derived from carboxylic acids by the removal of a molecule of water from two molecules of the acid.



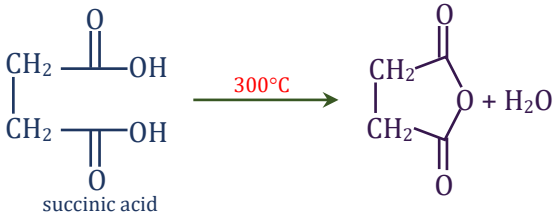
Method of preparation :

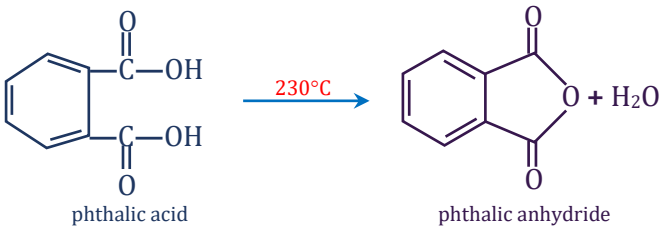
1. **Acylation :** Carboxylic acid reacts with acyl chloride in the presence of pyridine to give carboxylic acid anhydride.

2. **Sodium salt of carboxylic acids also react with acyl chlorides to give :**

In this reaction a carboxylate ion acts as a nucleophile and brings about a nucleophilic substitution reaction at the acyl carbon of acyl chloride.

3. **Cyclic anhydrides :** By simple heating the appropriate dicarboxylic acid. This method leads to a five or six membered ring.

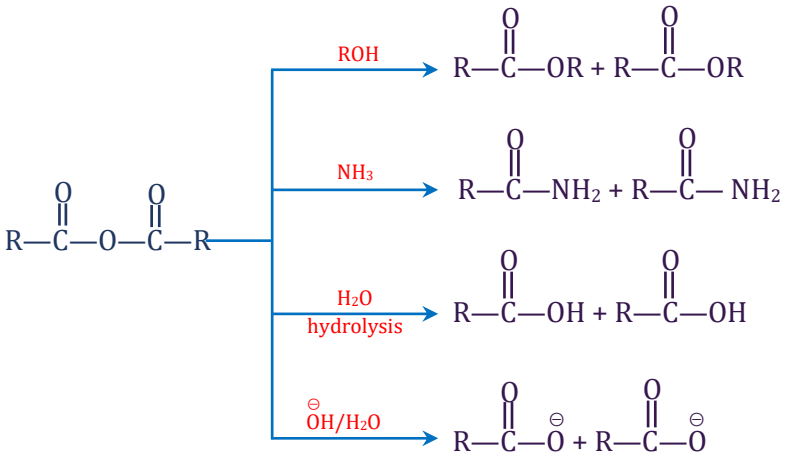




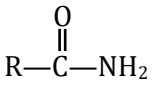
phthalic acid phthalic anhydride

4. Chemical Properties :

Acid anhydride are good acylating agents. Their reactions are less vigorous than the corresponding acyl halides.



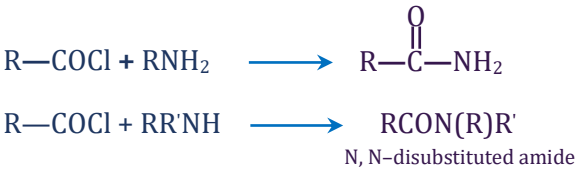
Amides ($RCONH_2$)

Structure of amide 

Method of Preparation :

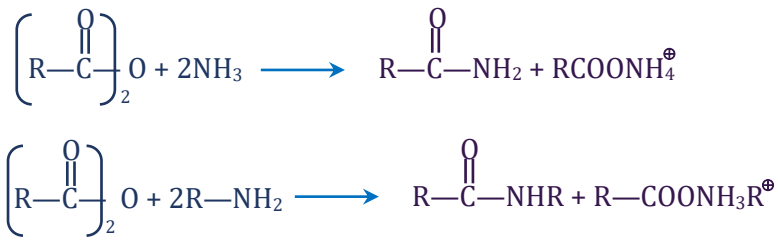
1. Amides from Acyl chloride :

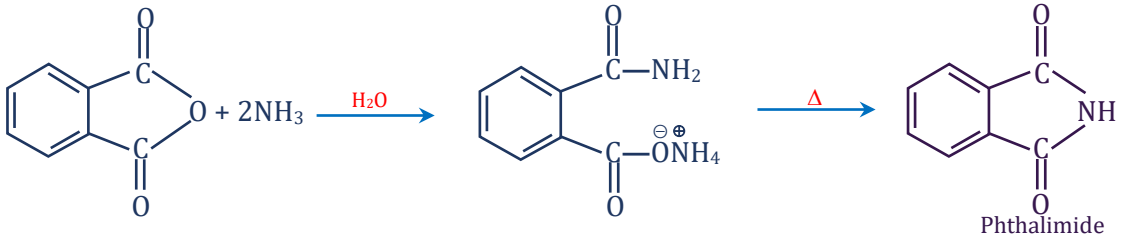
Primary amines, secondary amines and ammonia all react rapidly with acid chloride to form amides. An excess of ammonia or amine is used to neutralize the HCl that would be formed otherwise.



N, N–disubstituted amide

2. Amides from acid anhydride :





Carbene & Nitrene:

Carbene

Carbene are divalent carbon intermediate.

Carbon atom from only two bond in their molecules and two unshared electrons which may be paired or unpaired.

Eg:- :CCl2 :CCl2 :CH—C(=O)—CH3

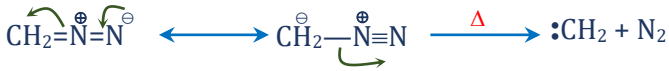
Formation of carbene

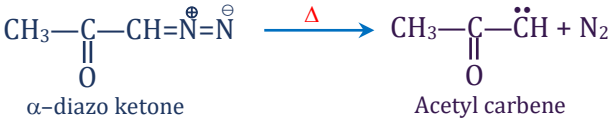
(1) By α- elimination

α- elimination mean ⟶ Removal of two atom from the same carbon

(2) From diazo compounds

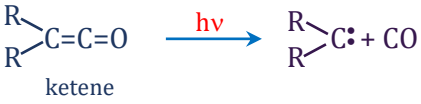
Diazo compound generate carbene on photolysis or thermolysis.





(3) From Ketene

Ketene on photolysis give carbene



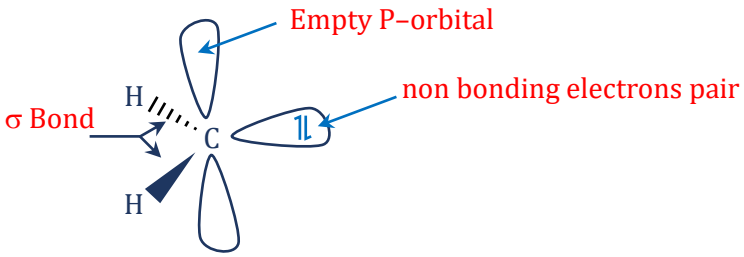
(4) From CBr_4

Type of carbene

1. Single

(1) Two electrons are present in one orbital
(2) One empty P–orbital is present
(3) Two sigma bond (σ) are present
(4) Singlet carbene is diamagnetic
(5) Singlet carbene work as Lewis Acid & Base
(6) Carbon is sp^2 hybridized
(7) Singlet carbene contain more repulsion
(8) Spin (s) $\Rightarrow \frac{1}{2}-\frac{1}{2}=0$

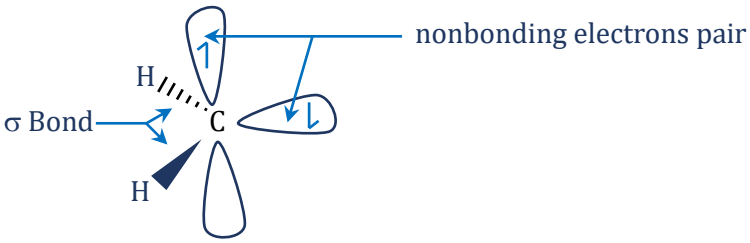
Total spin = 2 |s| +1
$\Rightarrow 2 \times 0 + 1 = 1$



2. Triple

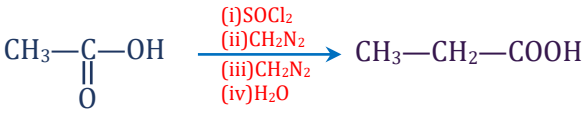
(1) One electron is present in one orbital
(2) Two unpaired electron are present
(3) Two sigma bond (σ) are present
(4) Triplet carbene is paramagnetic
(5) Triplet carbene work as Lewis Acid
(6) Carbon is sp/sp^2 hybridized
(7) Triplet carbene contain less repulsion
(8) Spin (s) $\Rightarrow \frac{1}{2}+\frac{1}{2}=1$

Total spin = 2 |s| +1
$\Rightarrow 2 \times 1 + 1 = 3$

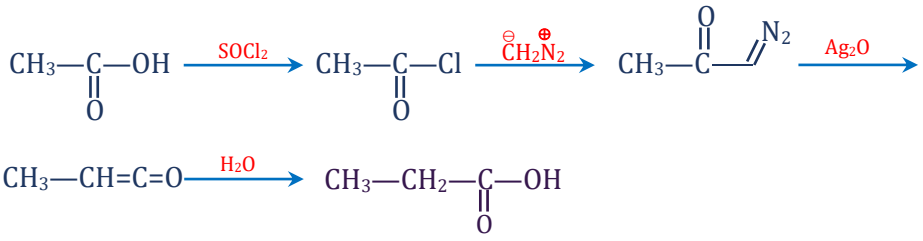


Arndt-Eistert Synthesis (AES) Homologation

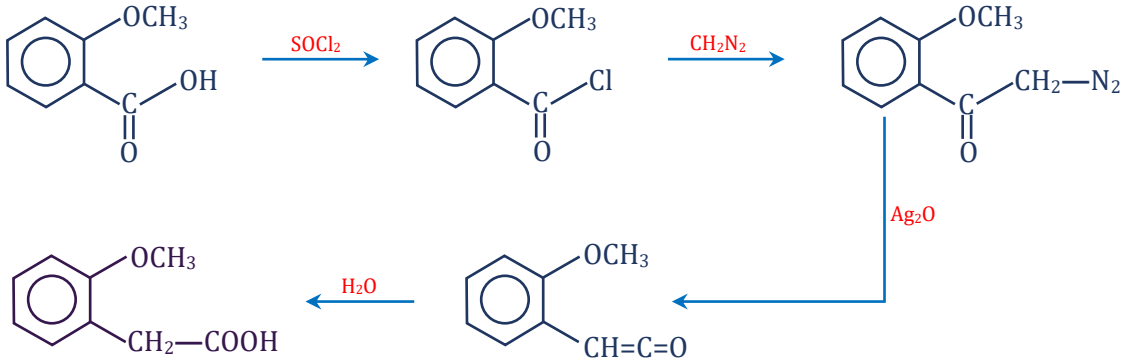
In this reaction, next homologus of carboxylic acid is obtained as product.

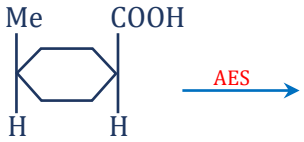


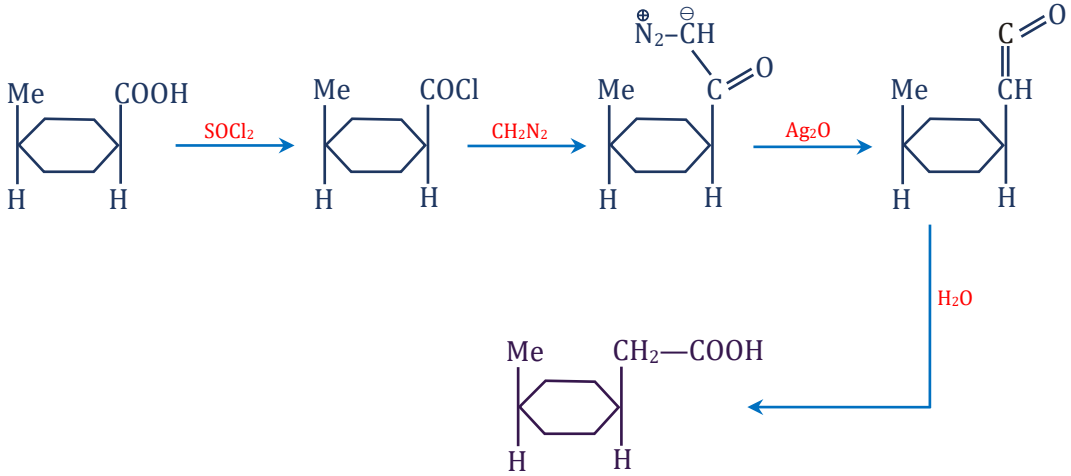
Mechanism :



1. 

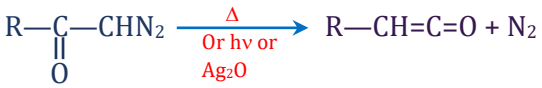
Sol. 

2. 

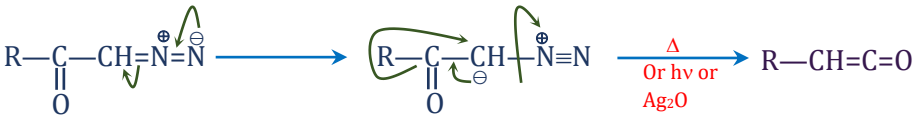
Sol. 

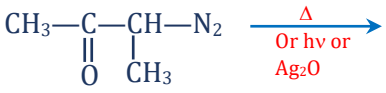
WOLF REARRANGEMENT :

In this reaction, a-diazocarbonyl compound is treated with thermally,photochemically or catalytically so that ketene is obtained.

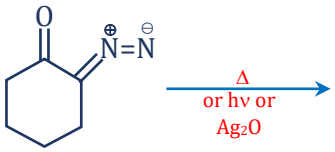


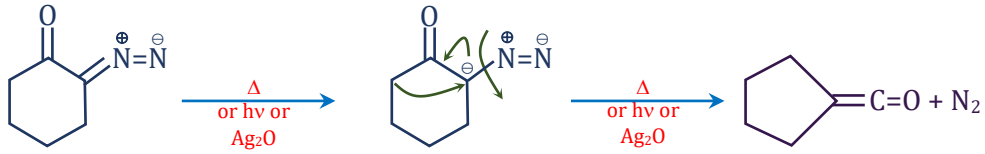
Mechanism :



1. 

Sol. 

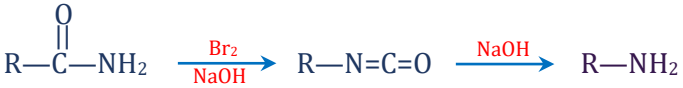
2. 

Sol. 

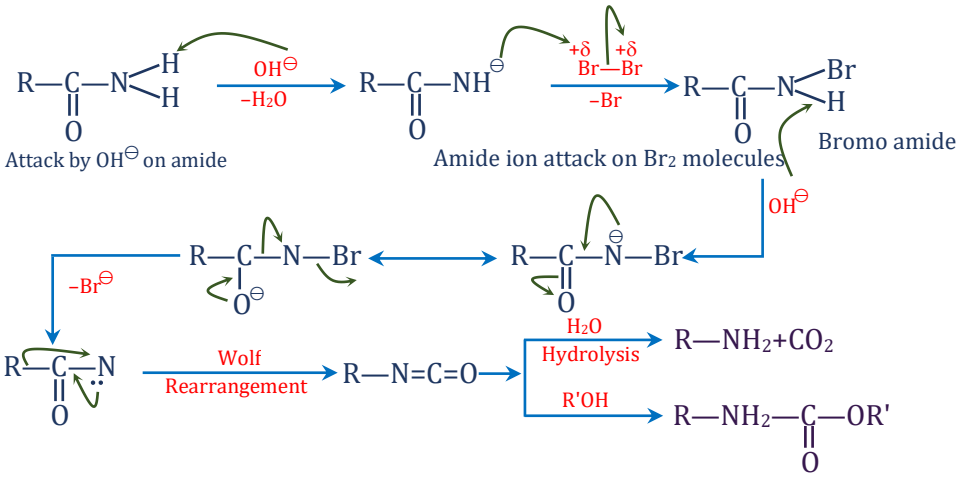
HOFFMANN'S BROMAMIDE & Schmidt reaction

HOFFMANN'S BROMAMIDE

Amide on reaction with Br_2 Or Cl_2 in alkali give 1° amine with one C–atom less than present amide known as Hoffmann bromamide reaction



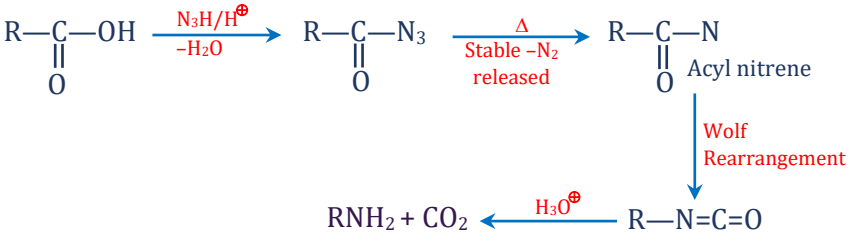
Mechanism



Schmidt reaction

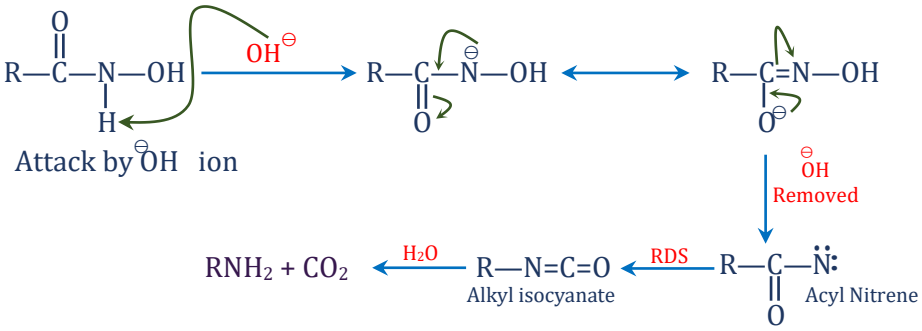
Carboxylic acid on reaction with hydrazoic acid (N_3H) in acidic medium give acyl azide.

Acyl azide on heating rearrange into alkyl isocyanate and alkyl isocyanate on hydrolysis give 1° amine.



LOSSEN REACTION

Hydroxamic acid in basic medium give alkyl nitrene which on rearrangement converted into alkyl isocyanate and alkyl isocyanate on hydrolysis give 1° amine.

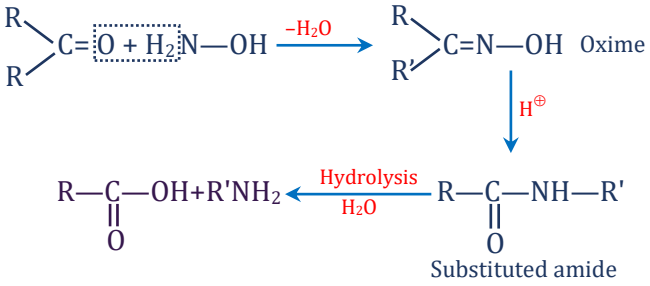


BECKMANN REARRANGEMENT

Beckmann reaction

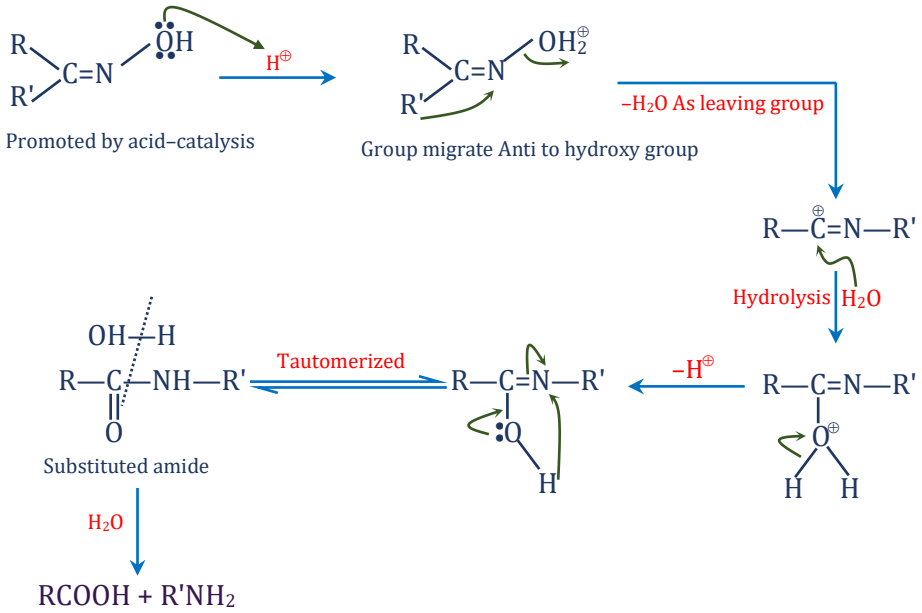
In Beckmann rearrangement an oxime functional group converted into substituted amide and amide on hydrolysis give carboxylic acid and amine.

Beckmann rearrangement promoted by acid catalyzed like – H_2SO_4, HCl or Lewis acid, PCl_5, $POCl_3$, $PhSO_2Cl$.



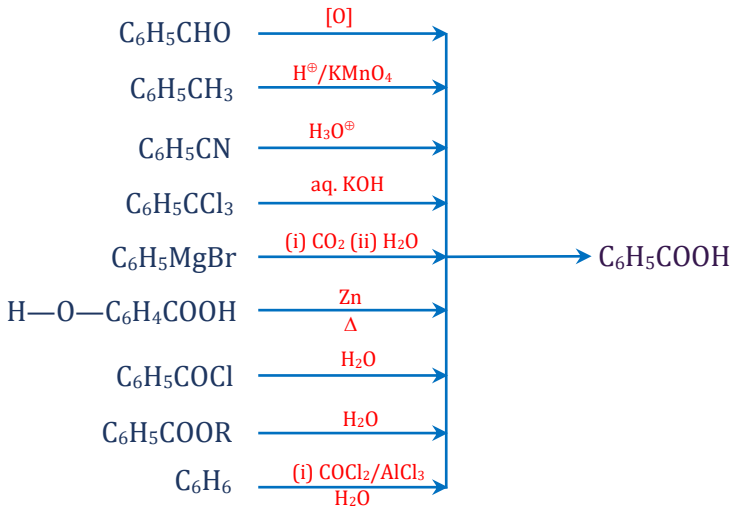
Mechanism

It is called anti– elimination, alkyl/aryl group which is anti to the hydroxy group migrate C to N– atom.

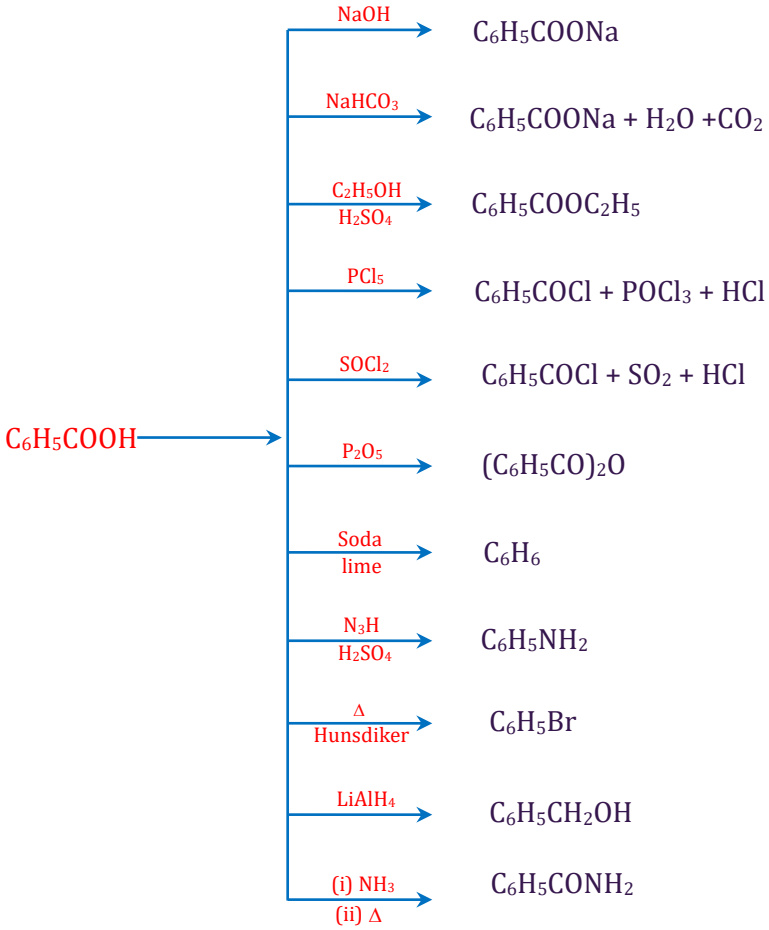


BENZOIC ACID (C_6H_5COOH)

General Method of Preparation :

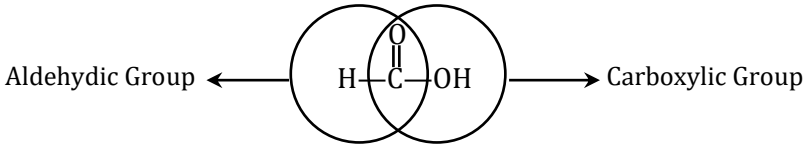


Chemical properties :



EXTRA

- **Abnormal Behaviour of Formic Acid :**
  The behaviour of formic acid is different from other carboxylic acid due to presence of aldehydic group.



- **Reaction with :**
  (a) **Tollen's reagents** : formic acid behaves as a reducing agent and reduces Tollen's reagent or Felhing solution. But others acid fail to do so.

$H—COOH + Ag_2O \longrightarrow CO_2 + H_2O + 2Ag\downarrow$ silver mirror

$H—COOH + 2CuO \longrightarrow CO_2 + H_2O + Cu_2O\downarrow$ Red ppt.

  (b) **Reaction with $HgCl_2$** : Formic acid forms white ppt. of Hg_2Cl_2 with $HgCl_2$ which is converted to Grey ppt of mercury.

$2HCOOH + HgCl_2 \longrightarrow CO_2 + Hg_2Cl_2\downarrow + 2HCl$
white ppt.

Test for HCOOH and CH_3COOH

	Test	HCOOH	CH_3COOH
1.	Reducing character		
	Reducing agents -		
	Tollen reagent	Silver mirror	–
	Fehling solution	Cu_2O red	–
	$HgCl_2$	Hg_2Cl_2	–
	Corrosive sublimate	Calomel	–
	$K_2Cr_2O_2$	Cr^{+3}	–
2.	Decarboxylation.	$Na_2CO_3 + H_2$	CH_4
3.	Heating at 160°C	$CO_2 + H_2$	–
4.	Conc.H_2SO_4	$CO + H_2O$	Dissolve
5.	P_2O_5	–	Anhydride
6.	Ca salt heat	HCHO	CH_3COCH_3

- **Uses of Formic Acid :**
  (i) As an antiseptic
  (ii) For preservation of fruits.
  (iii) For leather tanning.
  (iv) In dying wool and cotton fabrics.
  (v) As a coagulating agent for rubber.
  (vi) For hydrogenation of oil as Ni-formate.
- **Uses of Acetic Acid :**
  (i) Vinegar (6 - 10% solution) used as **table acid** and manufacture of pickles.
  (ii) In the form of salts, it is used in medicine and paints.
  (iii) For manufacture of rubber from latex and casein from milk CH_3COOH is used as coagulant.
  (iv) Al and Cr acetates are used as mordants.
  (v) In the manufacture of dyes and perfumes.
  (vi) As a solvent and laboratory reagent.