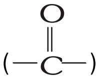
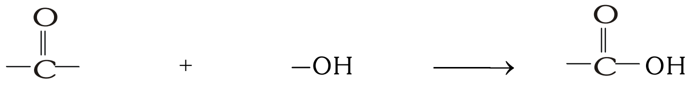
CARBOXYLIC ACID AND THEIR DERIVATIVES

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



$$-\overset{O}{\overset{\|}{C}}- \quad + \quad -OH \longrightarrow -\overset{O}{\overset{\|}{C}}-OH$$

Carbonyl group Hydroxyl group Carboxylic 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

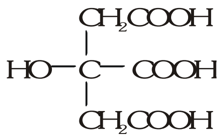
Dicarboxylic acid : Having two carboxylic groups, also called dibasic acid.

Example : 

$$\begin{array}{l} COOH \\ | \\ COOH \end{array}$$

Oxalic acid

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

Example : 

$$\begin{array}{c} CH_2COOH \\ | \\ HO-C-COOH \\ | \\ CH_2COOH \end{array}$$

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 $K_2Cr_2O_7$:**

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

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.

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

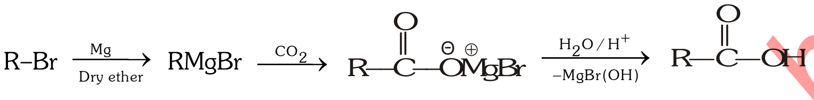
$$C_6H_5CHO + [O] \xrightarrow{\text{Tollen's Reagent}} C_6H_5COO^{\ominus} \xrightarrow{H^{\oplus}} C_6H_5COOH$$

3. **By oxidation of alkenes :**

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

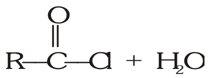
(b) $RCH = CHR' \xrightarrow[\text{(ii) } H_2O, \text{Distill}]{\text{(i) } O_3} RCOOH + R'COOH$

4. **By Carboxylation of Grignard Reagent :**

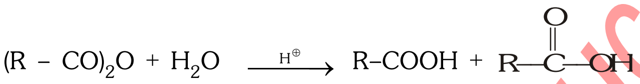


$$R\text{–}Br \xrightarrow[\text{Dry ether}]{Mg} RMgBr \xrightarrow{CO_2} R\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}\overset{\ominus}{O}\overset{\oplus}{M}gBr \xrightarrow[-MgBr(OH)]{H_2O / H^{+}} R\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}OH$$

5. **By hydrolysis of acyl derivatives of carboxylic acid :**

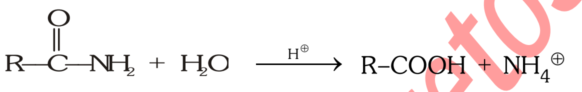


$$R\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}Cl + H_2O \xrightarrow{H^{\oplus}} R\text{–}COOH + HCl$$



$$(R - CO)_2O + H_2O \xrightarrow{H^{\oplus}} R\text{–}COOH + R\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}OH$$

$$R - COOR' + H_2O \xrightarrow{H^{\oplus}} R\text{–}COOH + ROH$$

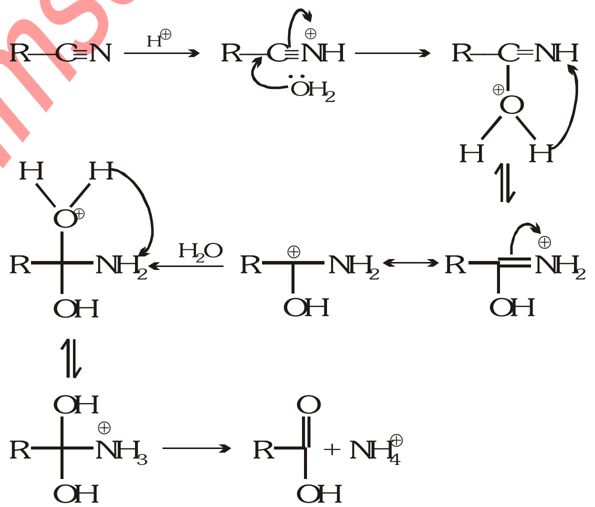


$$R\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}NH_2 + H_2O \xrightarrow{H^{\oplus}} R\text{–}COOH + NH_4^{\oplus}$$

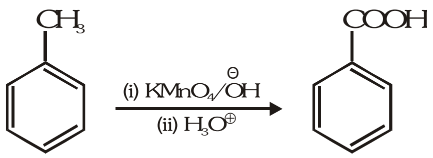
6 **Cyanide hydrolysis with dilute acids :**

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

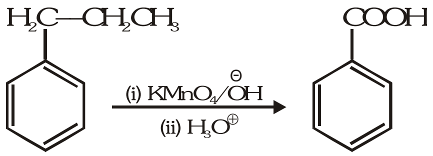
The mechanism of hydrolysis of R–CN is as follows.

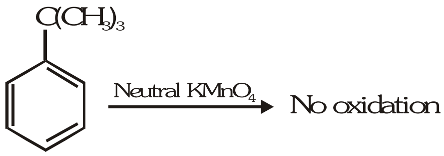


6. By oxidation of alkyl benzene :



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.



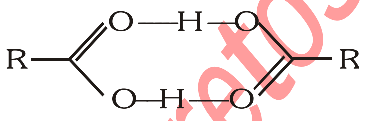


The order of benzoic acid formation by oxidation of alkyl benzene.

Methyl benzene >1 alkyl benzene >2 alkyl benzene

❑ Physical Properties of Carboxylic Acid :

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



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

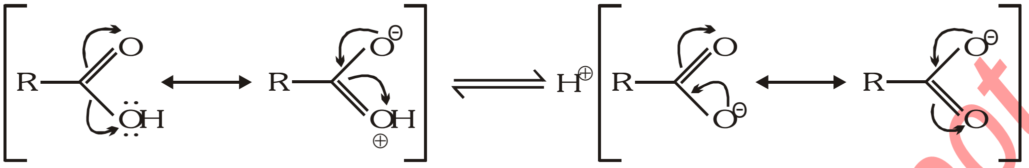
◆ **Melting Point** : Melting point of the carboxylic acid with even number of carbon atoms is higher than acid with odd number of carbon atoms. Such effect is observed in first ten members of the homologous series. This feature is based on the fact that in the carboxylic acids with even number of carbon 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.

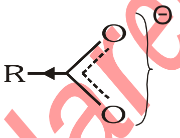
(a) An electron withdrawing substituents stabilizes the anion by dispersing the –ve charge and therefore increases the acidity of carboxylic acid.

(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.

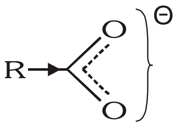
Carboxylic acids are weak acids and their carboxylate ions are strong conjugate bases. They are slightly alkaline due to the hydrolysis of carboxylate anion compared to other species. The order of acidity and basicity of corresponding conjugate bases are as follow.

Acidity––$RCOOH > HOH > ROH > CH \equiv CH > NH_3 > RH$

Basicity ––$RCOO^- < OH^- < HC \equiv C^- < NH_2^- < R^-$



Acidity increase



Acidity decrease

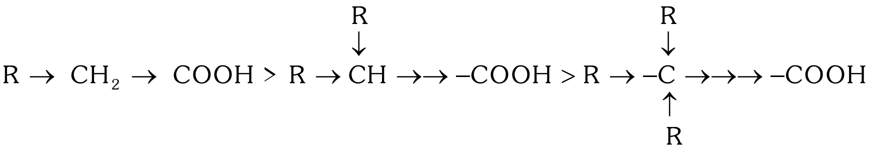
The effect of various number of the substituent and their distance from the carboxylic group has been illustrated with the help of following examples.

(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 :

$ClCH_2{-}{-}COOH < Cl_2CHCOOH < Cl_3CCOOH$

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.



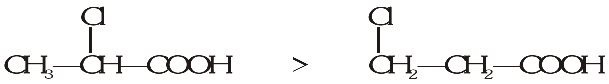
$$R \rightarrow CH_2 \rightarrow COOH > R \rightarrow \overset{\overset{R}{\downarrow}}{CH} \rightarrow\rightarrow -COOH > R \rightarrow -\underset{\underset{R}{\uparrow}}{\overset{\overset{R}{\downarrow}}{C}} \rightarrow\rightarrow\rightarrow -COOH$$

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

$ICH_2-COOH < BrCH_2COOH < ClCH_2COOH < F\ CH_2COOH$

$$CH_3-CH_2-CH_2-COOH < \underset{(sp^2)}{\underset{\uparrow}{CH_2 = CH}}-CH_2-COOH < \underset{(sp)}{\underset{\uparrow}{N{\equiv}C}}-CH_2-COOH$$

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



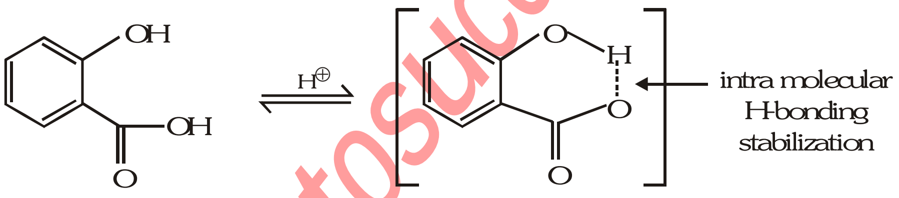
$$CH_3-\overset{Cl}{\overset{|}{CH}}-COOH > \overset{Cl}{\overset{|}{CH_2}}-CH_2-COOH$$

α-chloro propanoic acid
electron withdrawing
effect more

β-chloro propanoic acid
electron withdrawing
effect less

◆ **Ortho Effect :**

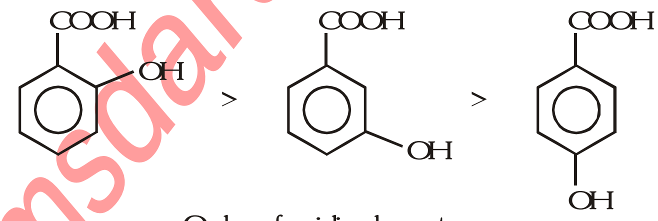
The ortho substituted benzoic acid (whether the substituent is electron withdrawing or releasing) is comparatively stronger acid than the para and meta isomers. This effect is called ortho effect. It occurs due to the joint operation of steric and intra molecular H-bonding where ever it takes chance 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.



intra molecular
H-bonding
stabilization

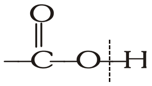
o-hydroxy benzoic acid
(Salicylic acid)

Carboxylate anion



Order of acidic character

Reaction due to cleavage of ––O––H bond as acid



$$-\overset{O}{\overset{\|}{C}}-O\,\vdots\,H$$

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

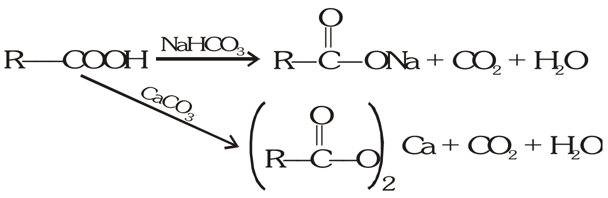
$$R-\overset{O}{\overset{\|}{C}}-OH + Na \longrightarrow R-\overset{O}{\overset{\|}{C}}-ONa + H_2(\uparrow)$$

(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



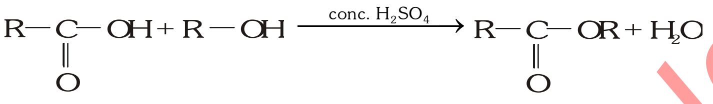
$$R{-}COOH \xrightarrow{NaHCO_3} R{-}\overset{\overset{O}{\|}}{C}{-}ONa + CO_2 + H_2O$$

$$R{-}COOH \xrightarrow{CaCO_3} \left(R{-}\overset{\overset{O}{\|}}{C}{-}O\right)_2 Ca + CO_2 + H_2O$$

❑ Reaction Involving Cleavage of –OH Group :

1. Esterification :

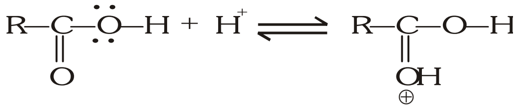
When carboxylic acid reacts with alcohol in the presence of conc. H_2SO_4 to form ester, it is known as esterification



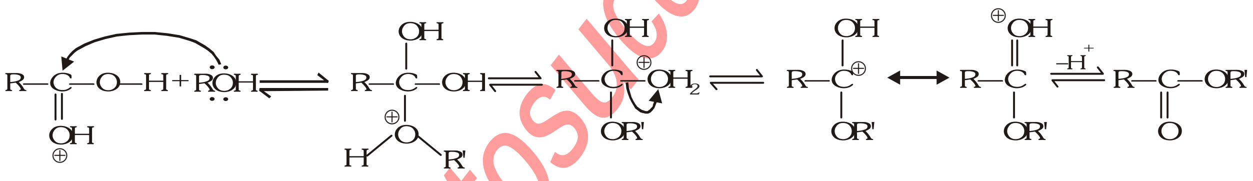
$$R{-}\underset{\underset{O}{\|}}{C}{-}OH + R{-}OH \xrightarrow{\text{conc. } H_2SO_4} R{-}\underset{\underset{O}{\|}}{C}{-}OR + H_2O$$

Mechanism :

$$H_2SO_4 \longrightarrow H^+ + HSO_4^-$$



$$R{-}\underset{\underset{O}{\|}}{C}{-}\ddot{O}{-}H + H^+ \rightleftharpoons R{-}\underset{\underset{\overset{\oplus}{O}H}{\|}}{C}{-}O{-}H$$

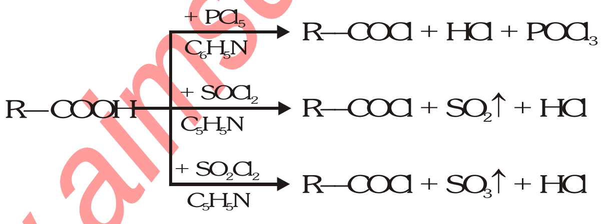


The relative reactivity of alcohol to ester formation markedly dependent on their structure. The greater the bulk of the substituents near the –OH group, the slower the reaction would be same facts is followed by acid as well

$CH_3OH > CH_3CH_2OH > (CH_3)_2\ CHOH > (CH_3)_3\ COH$

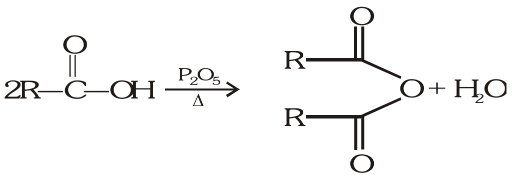
$H{-}{-}COOH > CH_3COOH > (CH_3)_2CHCOOH > (CH_3)_3CCOOH$

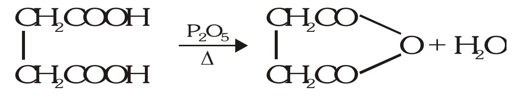
2. Formation of acid chloride :



3. Formation of Acid Anhydride :

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

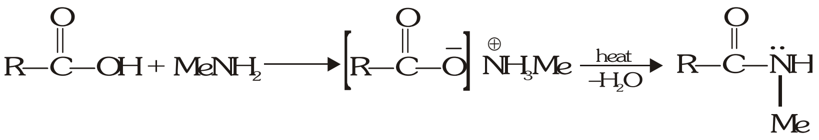




$$\begin{array}{l} CH_2COOH \\ | \\ CH_2COOH \end{array} \xrightarrow[\Delta]{P_2O_5} \begin{array}{l} CH_2CO \\ | \\ CH_2CO \end{array}\!\!>O + H_2O$$

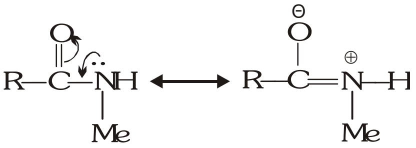
succinic acid succinic anhydride

4. **Formation of Amides :**



$$R-\overset{O}{\overset{\|}{C}}-OH + MeNH_2 \longrightarrow \left[R-\overset{O}{\overset{\|}{C}}-\bar{O}\right]\overset{\oplus}{N}H_3Me \xrightarrow[-H_2O]{heat} R-\overset{O}{\overset{\|}{C}}-\underset{Me}{\underset{|}{\ddot{N}H}}$$

The lone pair electron on N atom undergoes resonance and hence N atom carries partial +ve charge on it.



$$R-\overset{O}{\overset{\|}{C}}-\underset{Me}{\underset{|}{\ddot{N}H}} \longleftrightarrow R-\overset{\overset{\ominus}{O}}{\overset{|}{C}}=\underset{Me}{\underset{|}{\overset{\oplus}{N}}}-H$$

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

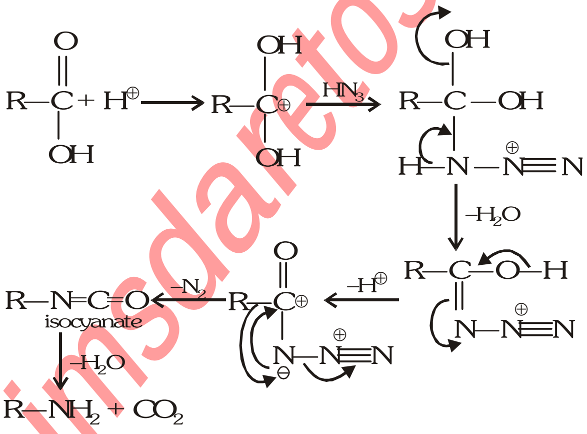
☐ **Reactions Involving –COOH Group :**

1. **Schmidt Reaction :**

Carboxylic acid reacts with hydrazoic acid in the presence of conc. H_2SO_4 at 90 C forming primary amine.

$$R-COOH + N_3H \xrightarrow{\text{Conc. } H_2SO_4} R-NH_2 + N_2 + CO_2$$

Mechanism :



2. **Soda lime Decarboxylation :**

Carboxylic acid on heating with soda lime (NaOH and CaO) give alkane with one carbon atom less than the parent acid.

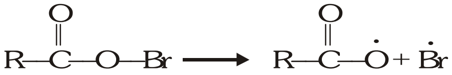
$$R{-}{-}{-}COOH \xrightarrow[\Delta]{\text{sada lime}} R{-}{-}H + CO_2$$

3. **Hunsdicker Reaction :**

$$R{-}{-}COOH \xrightarrow{Ag_2O} R{-}{-}COO^- Ag^+ \xrightarrow[\text{in } CCl_4]{Br_2} R{-}{-}Br + AgBr + CO_2$$

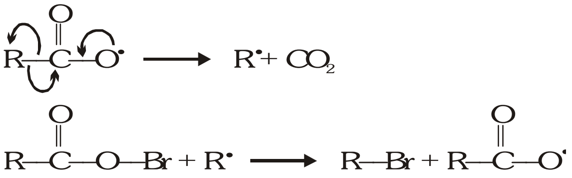
Mechanism : Reaction proceeds through free radical mechanism in various steps.

(i) Chain initiation :



$$R-\overset{\overset{O}{\|}}{C}-O-Br \longrightarrow R-\overset{\overset{O}{\|}}{C}-\dot{O} + \dot{Br}$$

(ii) Chain propagation step :

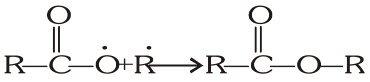


$$R-\overset{\overset{O}{\|}}{C}-O^{\bullet} \longrightarrow R^{\bullet} + CO_2$$

$$R-\overset{\overset{O}{\|}}{C}-O-Br + R^{\bullet} \longrightarrow R-Br + R-\overset{\overset{O}{\|}}{C}-O^{\bullet}$$

(iii) Chain termination :

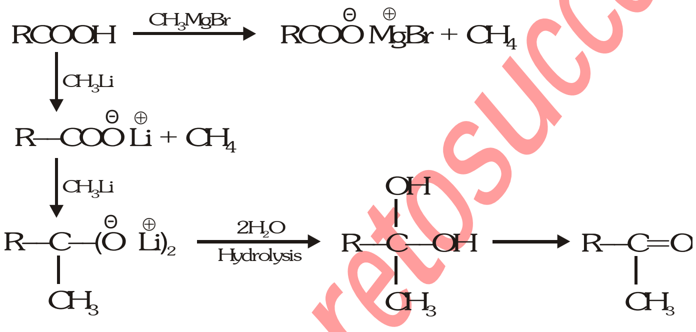
$$\dot{R} + \dot{R} \longrightarrow R-R$$



$$R-\overset{\overset{O}{\|}}{C}-\dot{O} + \dot{R} \longrightarrow R-\overset{\overset{O}{\|}}{C}-O-R$$

$$\dot{Br} + \dot{Br} \longrightarrow Br_2$$

4. With excess of organometallic compounds :



$$RCOOH \xrightarrow{CH_3MgBr} RCO\overset{\ominus}{O}\overset{\oplus}{Mg}Br + CH_4$$

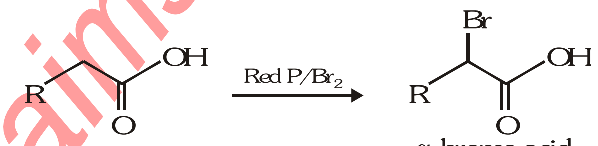
$$RCOOH \xrightarrow{CH_3Li} R-CO\overset{\ominus}{O}\overset{\oplus}{Li} + CH_4 \xrightarrow{CH_3Li} R-\underset{\underset{CH_3}{|}}{C}-(\overset{\ominus}{O}\ \overset{\oplus}{Li})_2 \xrightarrow[\text{Hydrolysis}]{2H_2O} R-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH \longrightarrow R-\underset{\underset{CH_3}{|}}{C}=O$$

acetone

2 moles of organometallic compounds are needed to form ketone.

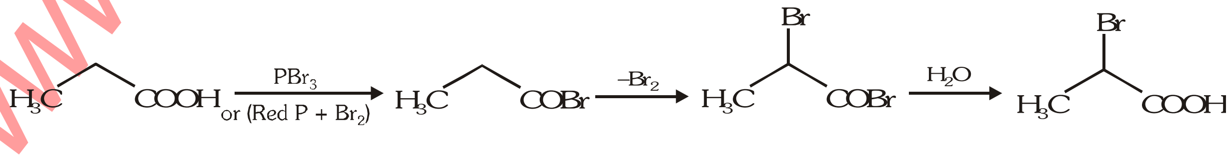
5. Hell-Volhard-Zelinsky Reaction :

This is α-halogenation of a carboxylic acid.

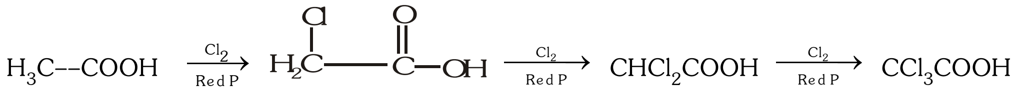


α-bromo acid

Possible Mechanism for the reaction is :

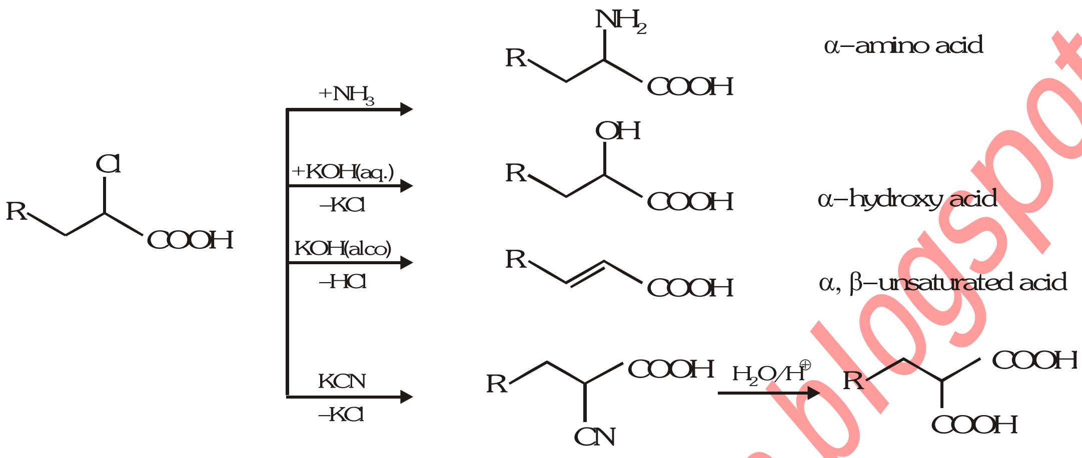


The purpose of PBr_3 is to convert –OH into –Br to make α-hydrogen atom more acidic to be replaced by Br atom of Br_2. The reaction does not stop at monosubstitution but continues till the α-hydrogen are replaced.

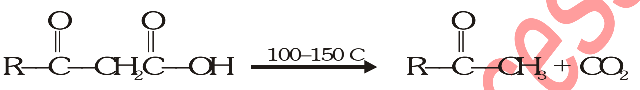


$$H_3C\text{--}COOH \xrightarrow[\text{Red P}]{Cl_2} H_2\overset{\overset{Cl}{|}}{C}\text{—}\overset{\overset{O}{\|}}{C}\text{—}OH \xrightarrow[\text{Red P}]{Cl_2} CHCl_2COOH \xrightarrow[\text{Red P}]{Cl_2} CCl_3COOH$$

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



6. Heating of β-keto acid :

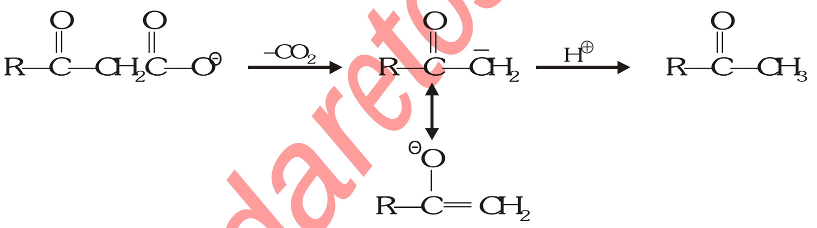


$$R\text{—}\overset{\overset{O}{\|}}{C}\text{—}CH_2\overset{\overset{O}{\|}}{C}\text{—}OH \xrightarrow{100\text{–}150\ C} R\text{—}\overset{\overset{O}{\|}}{C}\text{—}CH_3 + CO_2$$

β-keto acid

There are two facts on which ease of decarboxylation depends.

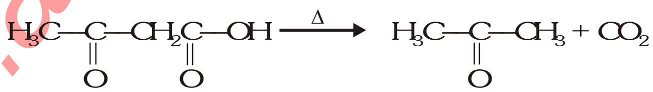
(i) When the carboxylate ion decarboxylate, it forms a resonance stabilized enolate anion.



Resonance stabilized enolate anion

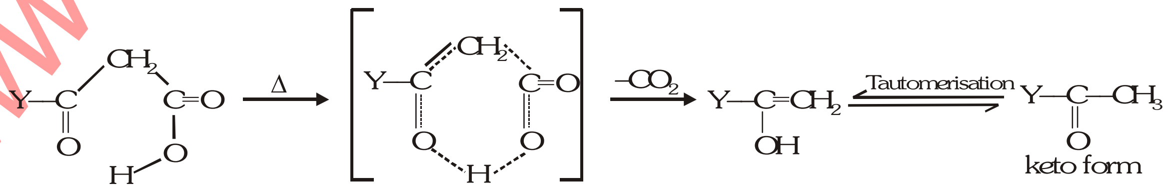
This anion is much more stable than the anion $R\bar{C}H_2$ formed by decarboxylation of an ordinary carboxylic acid anion.

(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.



$$H_3C\text{—}\underset{\underset{O}{\|}}{C}\text{—}CH_2\underset{\underset{O}{\|}}{C}\text{—}OH \xrightarrow{\Delta} H_3C\text{—}\underset{\underset{O}{\|}}{C}\text{—}CH_3 + CO_2$$

Mechanism :

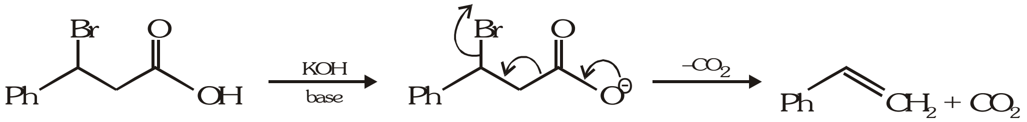


6 membered transition state

Here y can be substituents like

OH – diacid ; R – β-keto acid

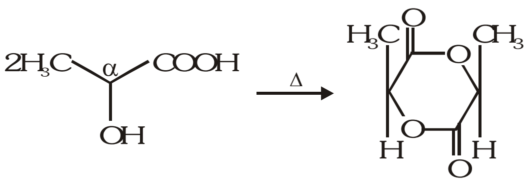
H – β aldehyde acid ; X – β halo acid



This decarboxylation proceeds through elimination.

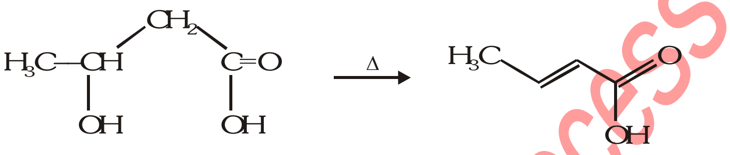
7. **Heating of α, β and γ Hydroxy Acid :**

(i)



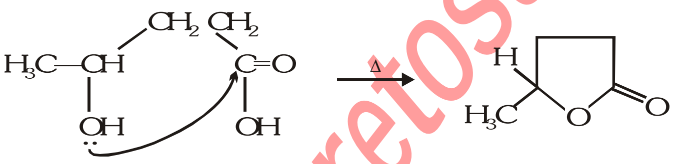
α-hydroxy Acid Lactides

(ii)



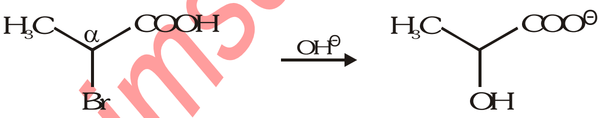
β-hydroxy Acid α, β–Unsaturatd Carboxylic Acid

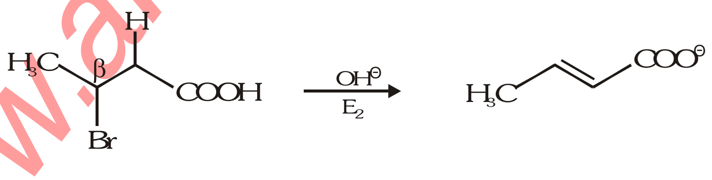
(iii)

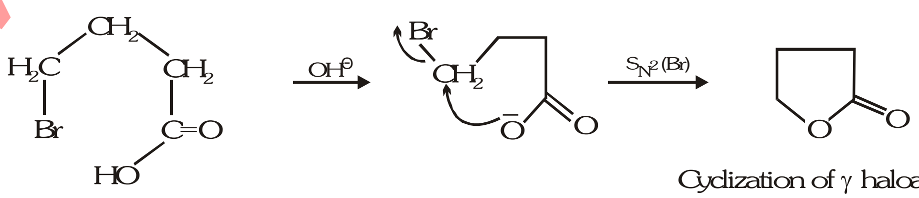


γ-hydroxy Acid 5-methyldihydrofuran-2-one

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

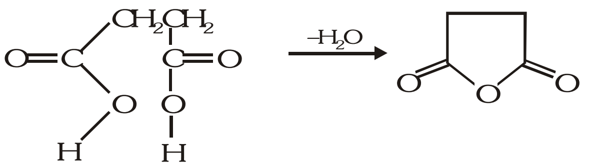






Cyclization of γ haloacid

9. Heating of Dicarboxylic Acids :



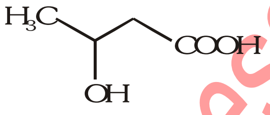
Succinic acid Succinic anhydride

Glutamic anhydride

10. Oxidation of Carboxylic acid at Alkyl Group :

Acid on treatment with mild oxidising agent such as H_2O_2, is oxidized at the β position.

$$CH_3\overset{\beta}{C}H_2-CH_2COOH+[O]\xrightarrow{H_2O_2}$$



3-hydroxybutanoic acid

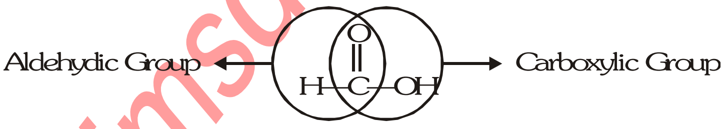
Oxidation can also occur at α carbon atom on treatment with oxidizing agent like selenium dioxide SeO_2.

$$RCH_2COOH + [O] \xrightarrow[\Delta]{SeO_2}$$

α Keto acid

❑ 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.

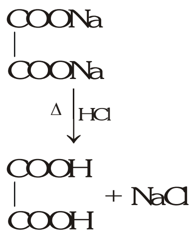
$H-COOH + Ag_2O \longrightarrow CO_2 + H_2O + 2Ag \downarrow$ Silver mirror

$H-COOH + 2CuO \longrightarrow CO_2 + H_2O + Cu_2O \downarrow$ 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.

$$2HCOOH + HgCl_2 \longrightarrow CO_2 + \underset{\text{white ppt.}}{Hg_2Cl_2 \downarrow} + 2HCl$$

Test for HCOOH and CH_3COOH

	Test	HCOOH	CH_3COOH
(i)	Reducing character		
	Reducing agents -		
	Tollen reagent	Silver mirror	–
	Fehling solution	Cu_2O red	–
	$HgCl_2$	Hg_2Cl_2	–
	Corrosive sublimate	Calomel	–
	$K_2Cr_2O_7$	Cr^{+3}	–
(ii)	Decarboxylation.	$Na_2CO_3 + H_2$	CH_4
(iii)	Heating at 160^0C	$CO_2 + H_2$	–
(iv)	Heating sodium salts of acids at 360^0C	 $\begin{array}{l} COONa \\ \vert \\ COONa \end{array} \xrightarrow[\Delta]{HCl} \begin{array}{l} COOH \\ \vert \\ COOH \end{array} + NaCl$	–
5.	Conc.H_2SO_4	$CO + H_2O$	Dissolve
6.	P_2O_5	–	Anhydride
7.	Cl_2 / P	$CO_2 + 2HCl$	Products are mono, di, tri chloro acetic acid.
8.	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.

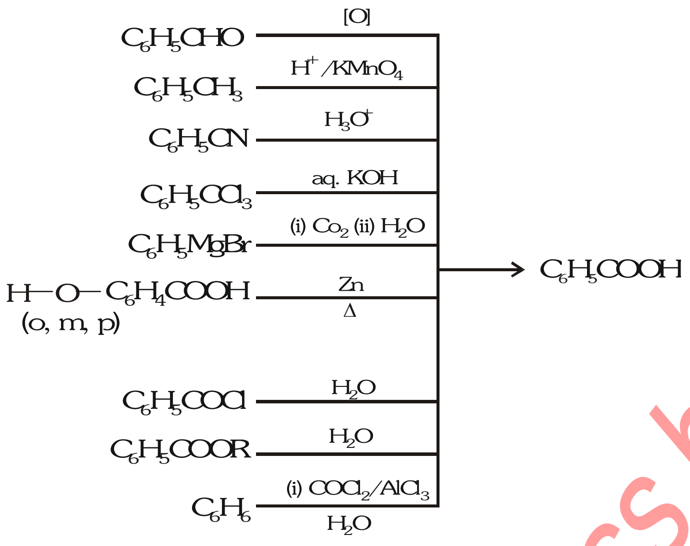
(iv) Al and Cr acetates are used as mordants.

(v) In the manufacture of dyes and perfumes.

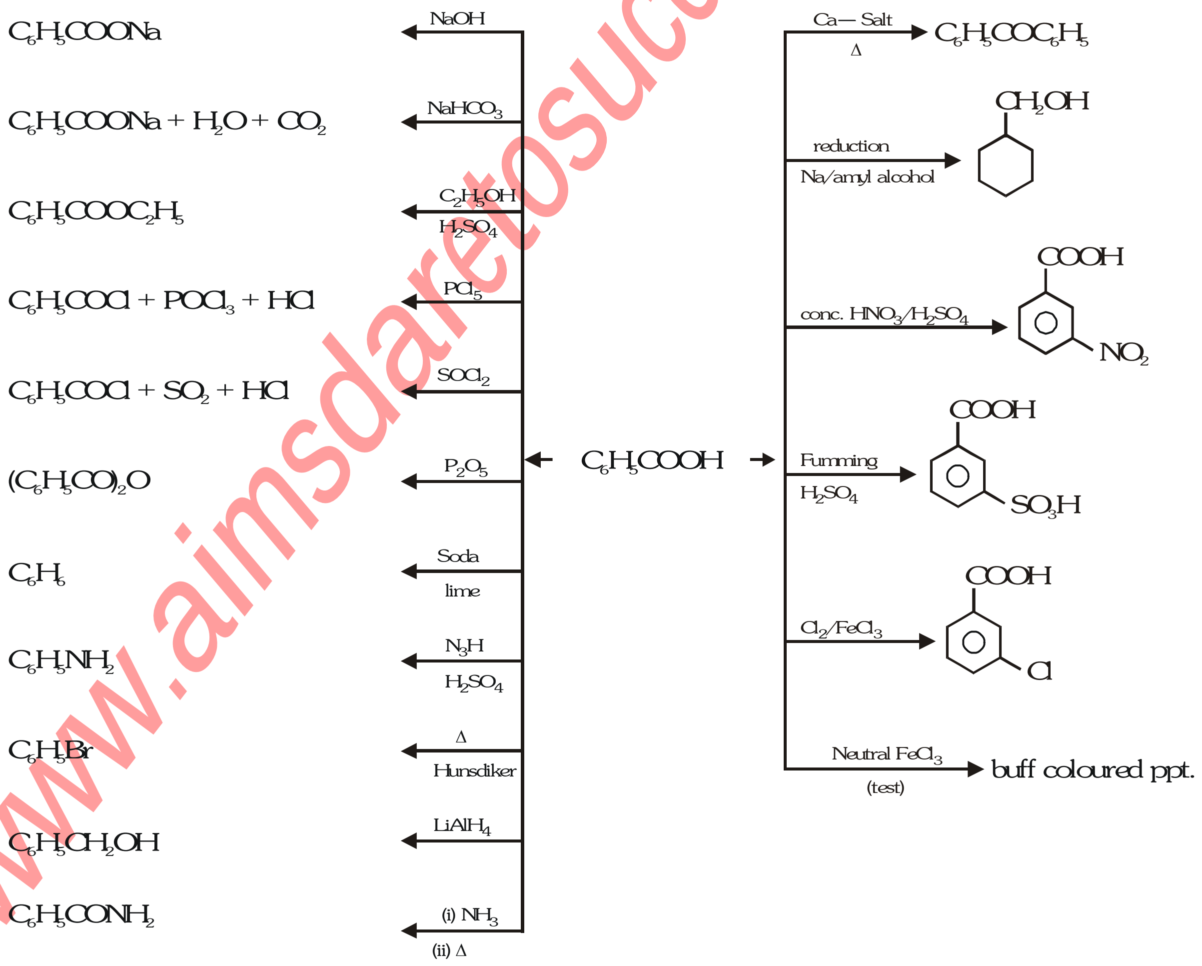
(vi) As a solvent and laboratory reagent.

BENZOIC ACID (C_6H_5COOH)

❑ General Method of Preparation :



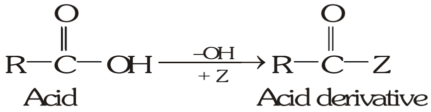
❑ Chemical properties :



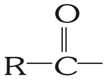
ACID DERIVATIVES

☐ Derivatives of Carboxylic Acid

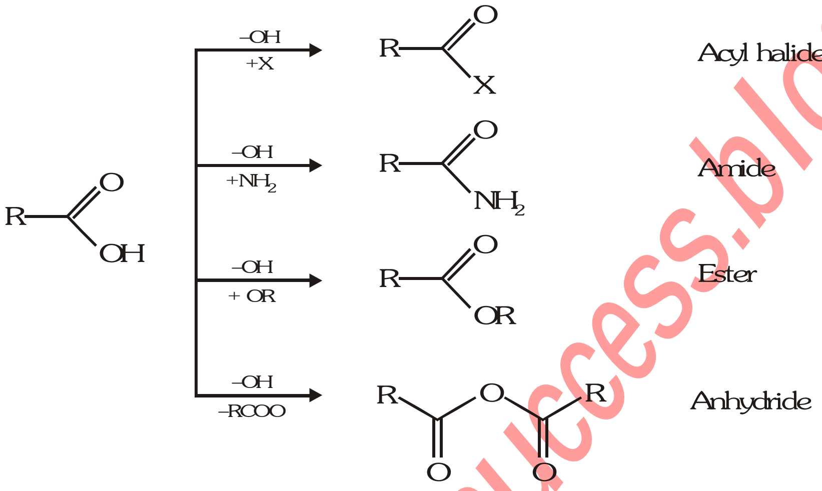
The –OH of an acid can be replaced by –Cl, –OR, or $-NH_2$ group to yield an acid chloride an ester or an amide. These compounds are called functional derivatives of acid and they all contain acyl group. The functional derivatives are all readily converted into the acid by simple hydrolysis.



$$\underset{\text{Acid}}{R-\overset{O}{\overset{\|}{C}}-OH} \xrightarrow[+Z]{-OH} \underset{\text{Acid derivative}}{R-\overset{O}{\overset{\|}{C}}-Z}$$

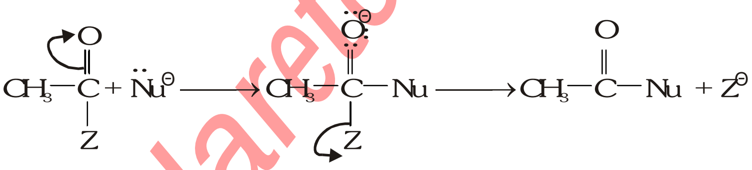


$R-\overset{O}{\overset{\|}{C}}-$ is Acyl group and Z is nucleophile $Cl^{\ominus}$, $CH_3COO^{\ominus}$, $C_2H_5O^{\ominus}$, $NH_2^{\ominus}$ etc.



☐ Characteristic reaction for acid derivatives is nucleophilic substitution reaction :

Mechanism :



$$CH_3-\overset{O}{\overset{\|}{C}}(Z)+\ddot{N}u^{\ominus}\longrightarrow CH_3-\overset{\ddot{O}^{\ominus}}{\overset{|}{C}}(Z)-Nu\longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-Nu+Z^{\ominus}$$

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

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

In the given groups Cl^- is the weakest base so it is best leaving group.

◆ **Reactivilty order** : $CH_3COCl > CH_3COOCOCH_3 > CH_2COOC_2H_5 > CH_3CONH_2$

In acid derivatives the carbonyl group > C=O is attached to highly electronegative Cl^-, CH_3COO^-, NH_2^- 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 leaves the compound and hence more is the reactivity Cl^- ion being weakest base are most reactive leaving group.

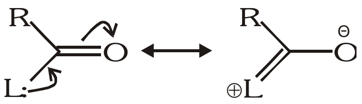
The order of basicity of the leaving group and their leaving tendency follows the order.

$H_2N^- > RO^- > RCOO^- > Cl^-$

Basicity ⟵

Ractivity ⟶

◆ **Resonance Effect :**



Resonating Structure

Due to resonance, the carbon to 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.

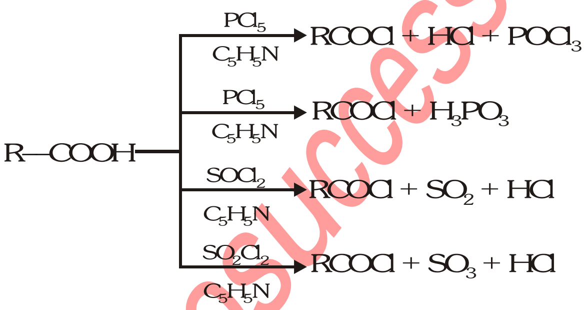
Nucleophilic acyl substitution should be catalysed by acids becasuse the protonation of the acyl compound would facillitate step (i) for nuceleophilic attack.

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.

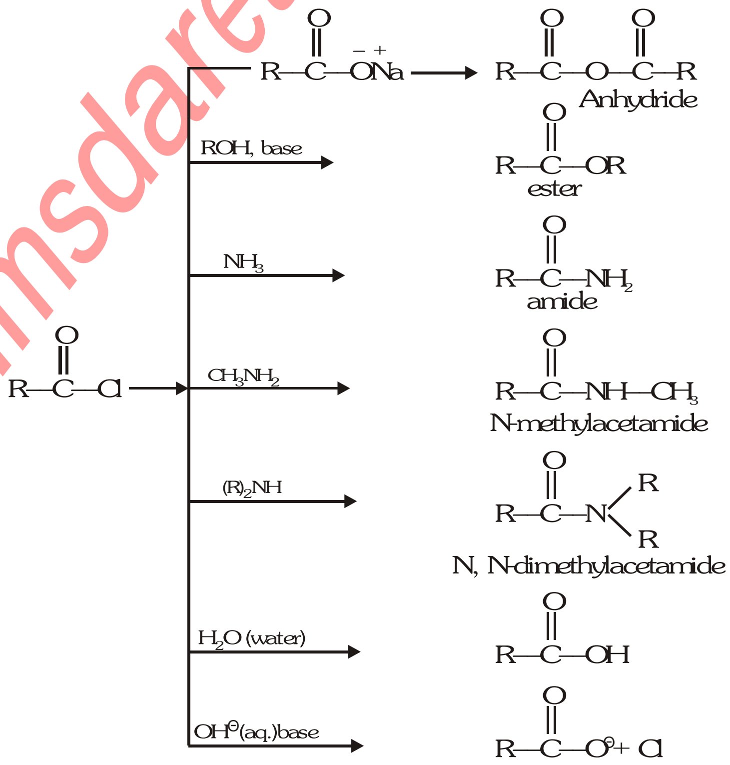
❑ **Method of Preparation :**

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.

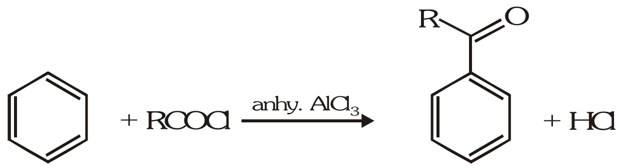


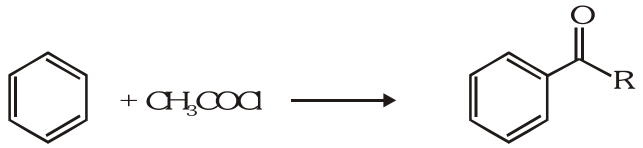
❑ **Chemical Properties :**

1. **Acylation Reaction :**

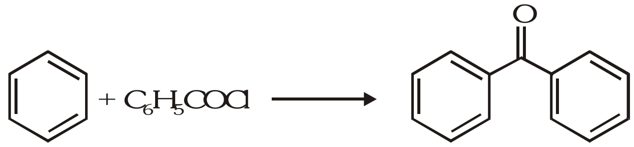


2. Acylation of aromatic compound [Friedel Craft's reaction] :



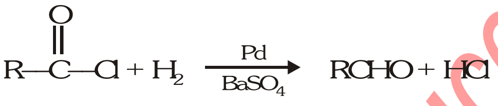


Acetophenone



benzophenone

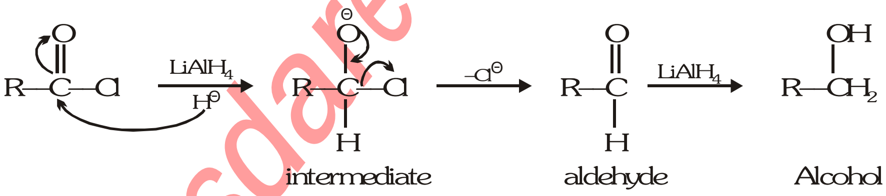
3. Catalytic hydrogenation (Rosenmund's Reaction) :



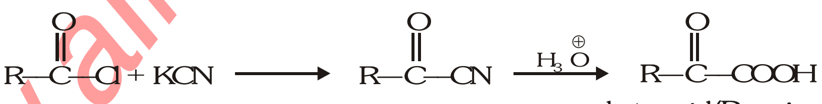
$$R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl + H_2 \xrightarrow[BaSO_4]{Pd} RCHO + HCl$$

$$RCOCl + 4H \xrightarrow[\text{or } C_2H_5OH+Na]{LiAlH_4 \text{ or } NaBH_4} R-CH_2OH + HCl$$

Mechanism :



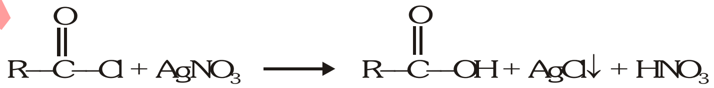
4. Reaction with KCN :



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl + KCN \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-CN \xrightarrow{H_3\overset{\oplus}{O}} R-\overset{\overset{\displaystyle O}{\|}}{C}-COOH$$

α keto acid (Pyruvic acid)

5. Reaction with $AgNO_3$:

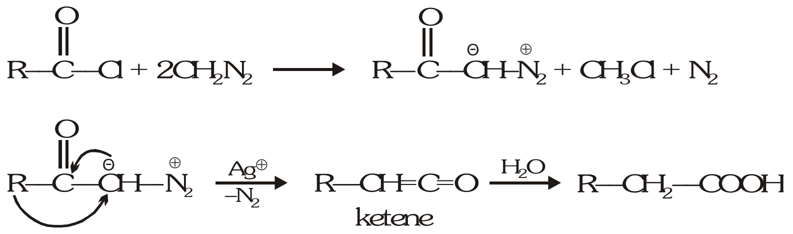


$$R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl + AgNO_3 \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-OH + AgCl\downarrow + HNO_3$$

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

6. Reaction of acyl chloride with diazomethane in presence of Ag_2O and water. (Arndt – Eistert synthesis).

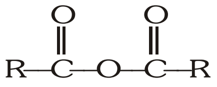
This reaction convert acyl chloride to carboxylic acid with one carbon atom more :



$$R-\overset{O}{\overset{\|}{C}}-Cl + 2CH_2N_2 \longrightarrow R-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{C}H-\overset{\oplus}{N_2} + CH_3Cl + N_2$$

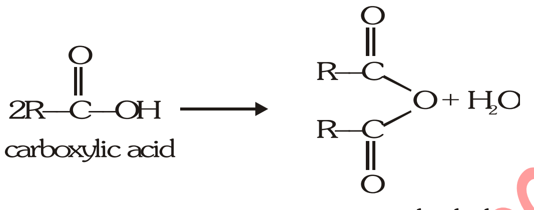
$$R-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{C}H-\overset{\oplus}{N_2} \xrightarrow[-N_2]{Ag^{\oplus}} R-CH=C=O \xrightarrow{H_2O} R-CH_2-COOH$$

ACID ANHYDRIDES (RCOOCOR)



$$R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R$$

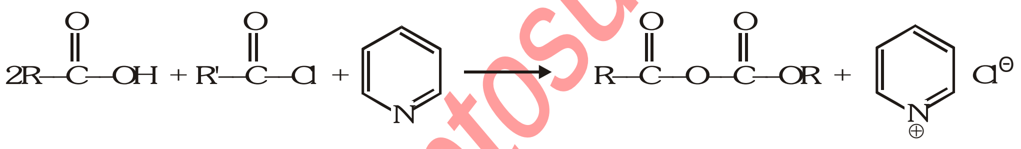
Acid anhydrides are considered to be derived from carboxylic acids by the removal of a molecule of water from two molecules of the acid.



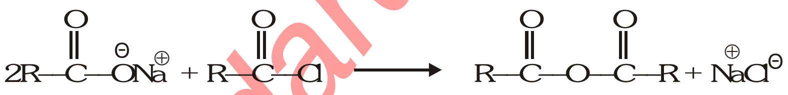
acetic anhydride

❑ **Method of preparation :**

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



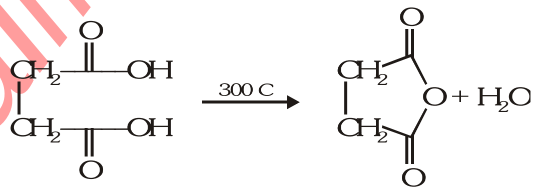
2. **Sodium salt of carboxylic acids also react with acyl chlorides to give :**



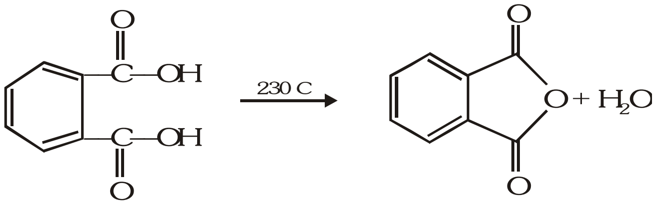
$$2R-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{O}\overset{\oplus}{Na} + R-\overset{O}{\overset{\|}{C}}-Cl \longrightarrow R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R + \overset{\oplus}{Na}\overset{\ominus}{Cl}$$

In this reaction a carboxylate ion acts as a nucleophile and brings about a nueleophilic 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.



succinic acid

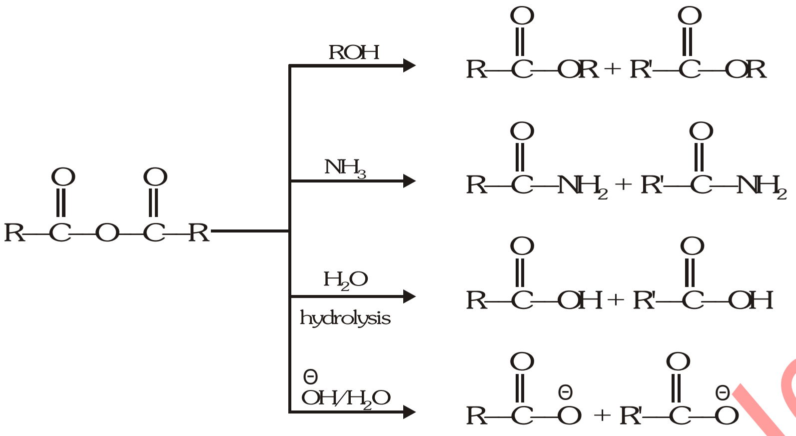


pthalic acid

pthalic anhydride

4. Chemical Properties :

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



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.

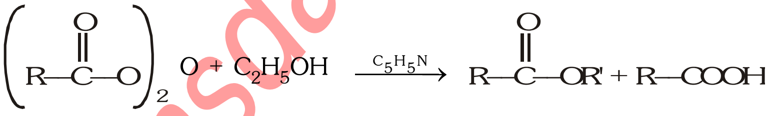
❑ Method of Preparation :

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

$$RCOOH + C_2H_5OH \xrightarrow{H^+/H_2O} R\text{--}COOC_2H_5 + H_2O$$

$$R\text{--}COOH + CH_2N_2 \xrightarrow{ether} \underset{\text{Ester}}{RCOOCH_3} + N_2$$

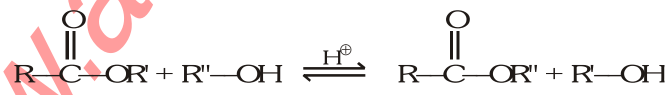
$$R\text{—}\overset{\overset{O}{\|}}{C}\text{—}Cl + C_2H_5OH \xrightarrow{C_5H_5N} R\text{—}\overset{\overset{O}{\|}}{C}\text{—}OC_2H_5 + HCl$$



$$\left(R\text{—}\overset{\overset{O}{\|}}{C}\text{—}O\right)_2 O + C_2H_5OH \xrightarrow{C_5H_5N} R\text{—}\overset{\overset{O}{\|}}{C}\text{—}OR' + R\text{—}COOH$$

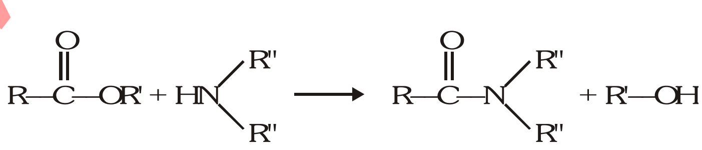
❑ Chemical Properties :

1. Conversion to other esters : Transesterifications



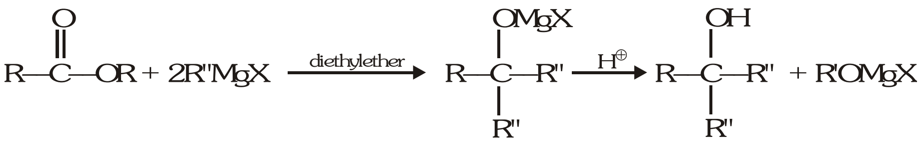
$$R\text{—}\overset{\overset{O}{\|}}{C}\text{—}OR' + R''\text{—}OH \underset{}{\overset{H^{\oplus}}{\rightleftharpoons}} R\text{—}\overset{\overset{O}{\|}}{C}\text{—}OR'' + R'\text{—}OH$$

2. Conversion to amides :



$$R\text{—}\overset{\overset{O}{\|}}{C}\text{—}OR' + HN(R'')_2 \longrightarrow R\text{—}\overset{\overset{O}{\|}}{C}\text{—}N(R'')_2 + R'\text{—}OH$$

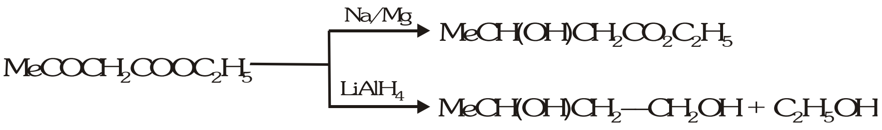
3. **Reaction with Grignard Reagent :**



$R-\overset{O}{\overset{\|}{C}}-OR + 2R''MgX \xrightarrow{\text{diethylether}} R-\underset{R''}{\overset{OMgX}{C}}-R'' \xrightarrow{H^{\oplus}} R-\underset{R''}{\overset{OH}{C}}-R'' + R'OMgX$

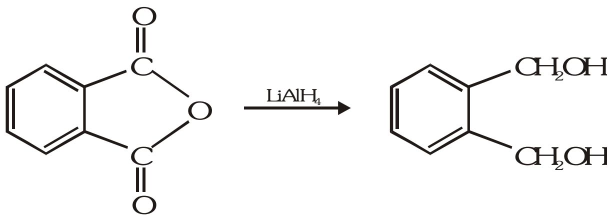
3 alcohol

4. **Reduction of ester :**



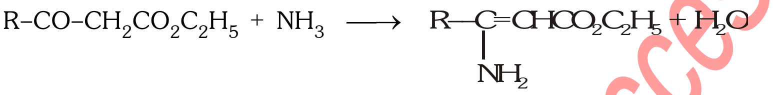
$MeCOCH_2COOC_2H_5 \xrightarrow{Na/Mg} MeCH(OH)CH_2CO_2C_2H_5$

$MeCOCH_2COOC_2H_5 \xrightarrow{LiAlH_4} MeCH(OH)CH_2-CH_2OH + C_2H_5OH$



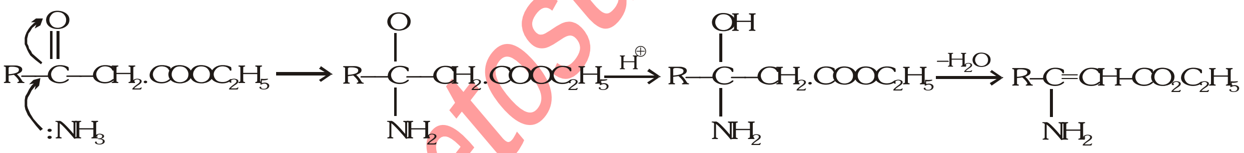
Phthalic anhydride

5. **Reaction of NH_3 with keto ester :**



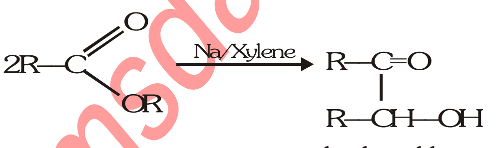
$R-CO-CH_2CO_2C_2H_5 + NH_3 \longrightarrow R-\underset{NH_2}{C}=CHCO_2C_2H_5 + H_2O$

Mechanism :



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

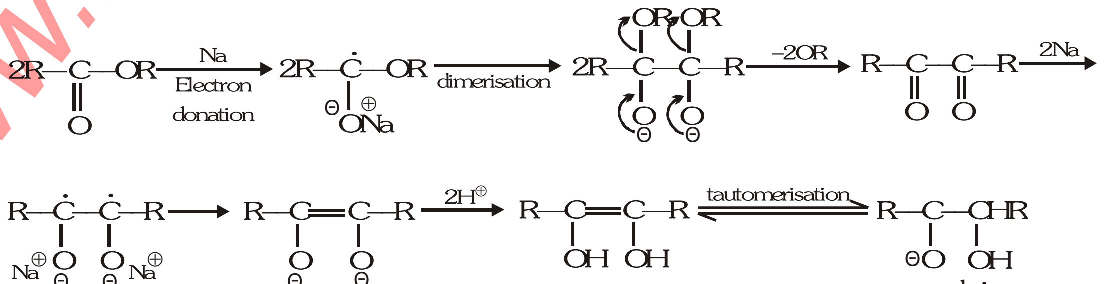
6. **Acyloin condensation :**



α-hydroxyl ketone

Mechanism :

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



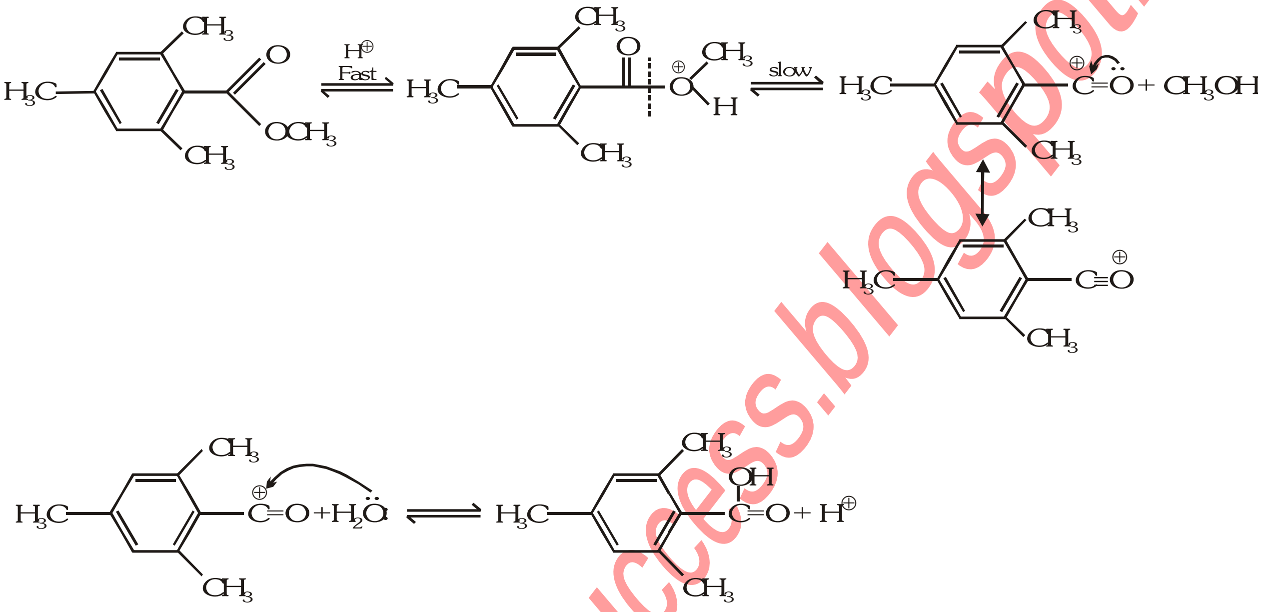
acyloin

❑ Hydrolysis of Acyl Derivatives :

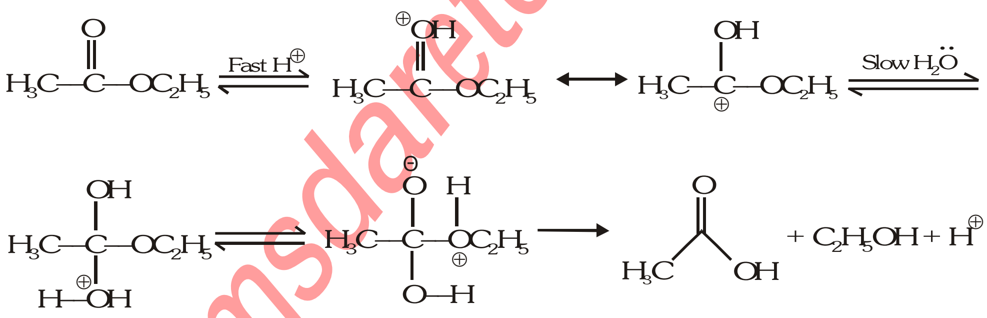
Ester hydrolysis can be carried out in mechanistic pathways $A_{AC^1}, A_{AC^2}, A_{AL^1}, B_{AC^2}$.

Here A or B stand for acid or base catalysed and Ac and Al stand for acyl oxygen and alkyl oxygen cleavage and 1 or 2 stands for unimolecular or bimolecular.

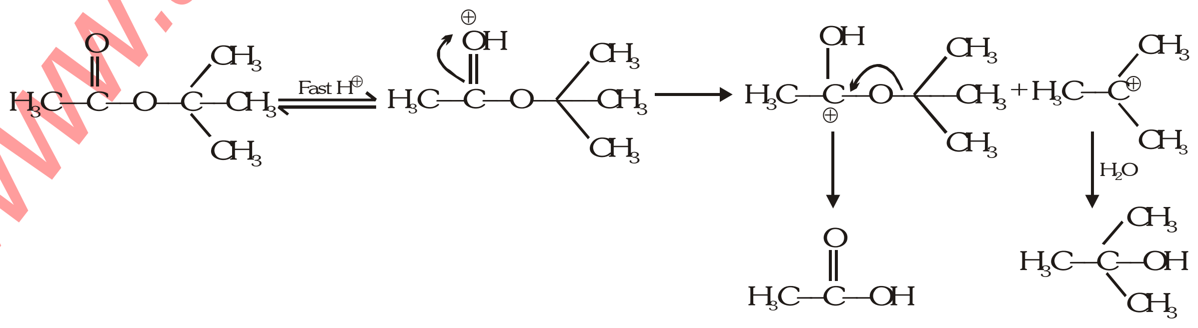
A_{AC^1} :



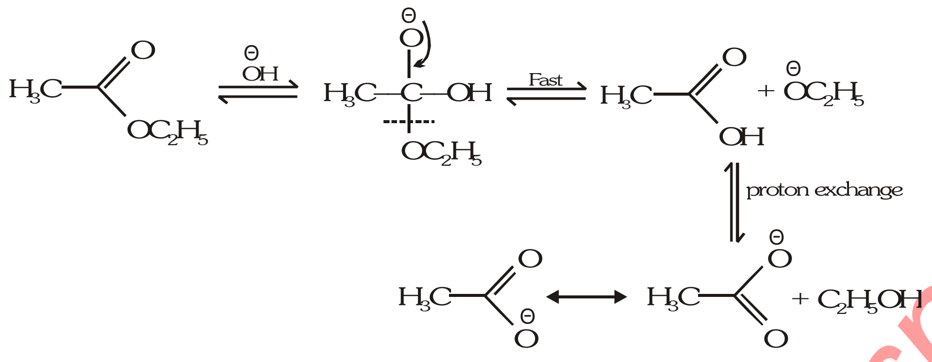
A_{AC^2} :



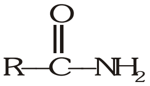
A_{AL^1} :



B_{AC^2} :



AMIDES $(RCONH_2)$

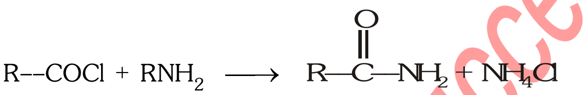


$$R-\overset{O}{\overset{\|}{C}}-NH_2$$

❑ **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.

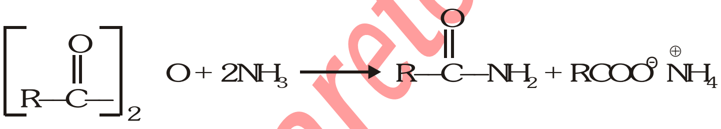


$$R\text{--}COCl + RNH_2 \longrightarrow R-\overset{O}{\overset{\|}{C}}-NH_2 + NH_4Cl$$

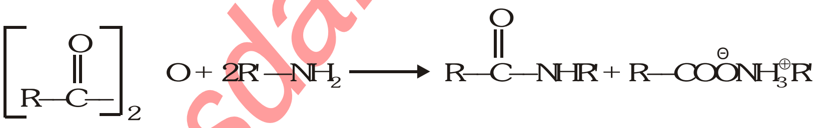
$$R\text{--}COCl + RR'NH \longrightarrow RCON(R)R' + RR'N^+H_2Cl^-$$

N, N-disubstituted amide

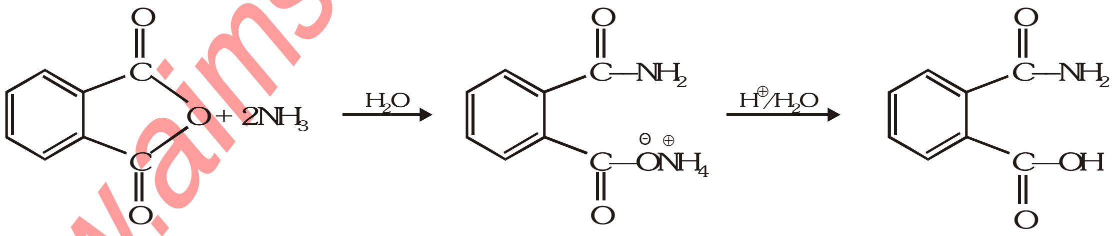
2. **Amides from acid anhydride :**



$$\left[R-\overset{O}{\overset{\|}{C}}-\right]_2 O + 2NH_3 \longrightarrow R-\overset{O}{\overset{\|}{C}}-NH_2 + RCOO^{\ominus}\overset{\oplus}{N}H_4$$



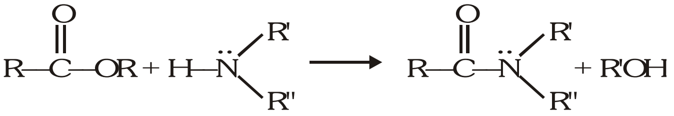
$$\left[R-\overset{O}{\overset{\|}{C}}-\right]_2 O + 2R'-NH_2 \longrightarrow R-\overset{O}{\overset{\|}{C}}-NHR' + R-COO^{\ominus}\overset{\oplus}{N}H_3R'$$



Phthalamic acid
both amide and acid

3. **From Esters (Ammonolysis) :**

Ester undergoes nucleophilic substitution at their acyl carbon by nucleophilic ammonia or its derivative

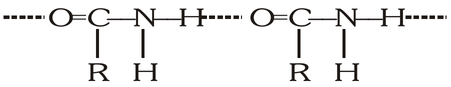


4. **By partial hydrolysis of alkyl nitriles :**

$$R\text{--}C\equiv N + H_2O \xrightarrow[OH^-]{H^+ \text{ or}} R\text{--}CO\text{--}NH_2$$

❑ **Physical Properties :**

All amides except formamide are crystalline solid at room temperature. They have relatively high melting and boiling point due to association of amide molecules by inter molecular hydrogen bonds.

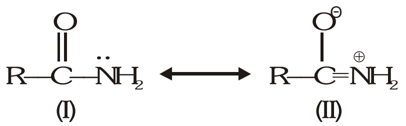


$$\cdots O{=}\underset{R}{\underset{|}{C}}{-}\underset{H}{\underset{|}{N}}{-}H\cdots O{=}\underset{R}{\underset{|}{C}}{-}\underset{H}{\underset{|}{N}}{-}H\cdots$$

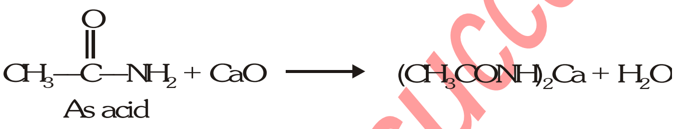
❑ **Chemical Properties :**

1. **Amphoteric character :**

Amides are very feeble bases due to involvement of pair of electron present on N atom in resonance with carboxyl groups. As a result N atom receives partial +ve charges showing feeble acidic character as well



(i) **Acidic character :** Due to structure II amide can act as acid.



$$\underset{\text{As acid}}{CH_3{-}\overset{\overset{O}{\|}}{C}{-}NH_2} + CaO \longrightarrow (CH_3CONH)_2Ca + H_2O$$

$$\underset{\text{Acid}}{CH_3CONH_2 + Na} \longrightarrow CH_3CONH^-Na^{\oplus} + \frac{1}{2}H_2$$

(ii) **Basic Character :** Due to structure I having lone pair of electrons on N atom it acts as base.

$$\underset{\text{As base}}{CH_3CONH_2} + \underset{\text{Acid}}{HCl} \longrightarrow \underset{\text{Salt}}{CH_3CONH_2^+HCl^-}$$

2. **Reaction with nitrous acid :**

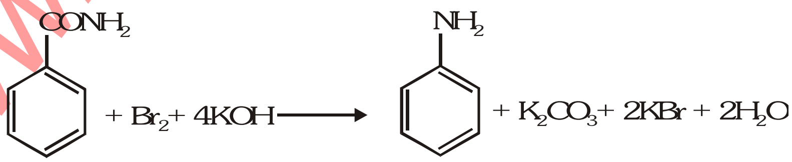
$$R\text{--}CONH_2 + HONO \longrightarrow R\text{--}COOH + N_2 + H_2O$$

The reaction proceeds via the attack of electrophilic species NO^+ generated from HNO_3.

3. **Hoffmann's Bromide Reaction :**

Amides react with bromine in the presence of alkali to form a primary amine having one carbon atom less than the parent amides.

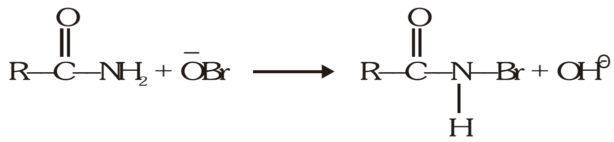
$$R\text{--}CO\text{--}NH_2 + Br_2 + KOH \longrightarrow RNH_2 + K_2CO_3 + 2KBr + 2H_2O$$



Mechanism :

$$2NaOH + Br_2 \longrightarrow NaOBr + NaBr + H_2O$$

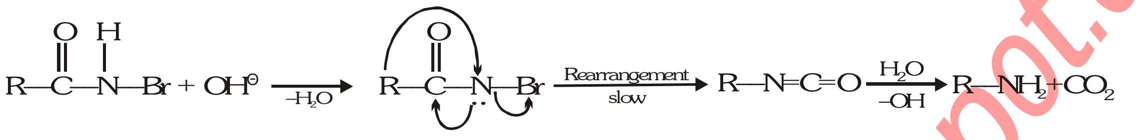
(i)



$$R-\overset{\overset{O}{\|}}{C}-NH_2 + \overline{O}Br \longrightarrow R-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-Br + OH^{\ominus}$$

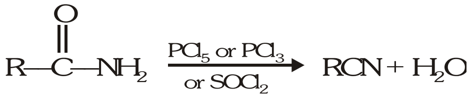
N-bromoacetamide

(ii)

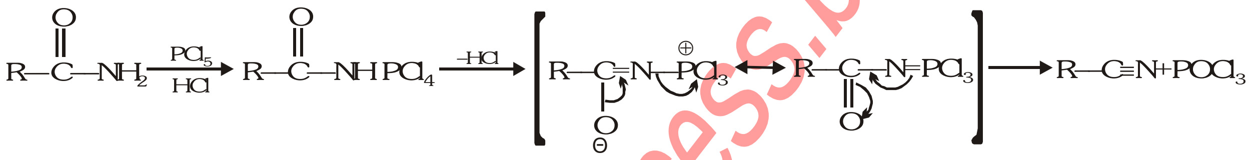


$$R-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-Br + OH^{\ominus} \xrightarrow[-H_2O]{} R-\overset{\overset{O}{\|}}{C}-\ddot{N}-Br \xrightarrow[\text{slow}]{\text{Rearrangement}} R-N=C=O \xrightarrow[-OH]{H_2O} R-NH_2+CO_2$$

4. Reaction with PCl_5 , PCl_3 or $SOCl_2$:

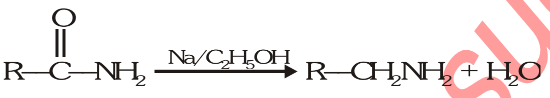


$$R-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow[\text{or } SOCl_2]{PCl_5 \text{ or } PCl_3} RCN + H_2O$$

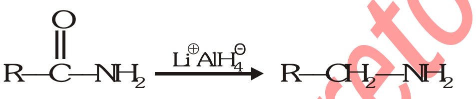


$$R-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow[HCl]{PCl_5} R-\overset{\overset{O}{\|}}{C}-NHPCl_4 \xrightarrow{-HCl} \left[R-\underset{\underset{O^{\ominus}}{|}}{C}=N-\overset{\oplus}{P}Cl_3 \longleftrightarrow R-\underset{\underset{O}{\|}}{C}-N=PCl_3 \right] \longrightarrow R-C\equiv N+POCl_3$$

5. Reduction :

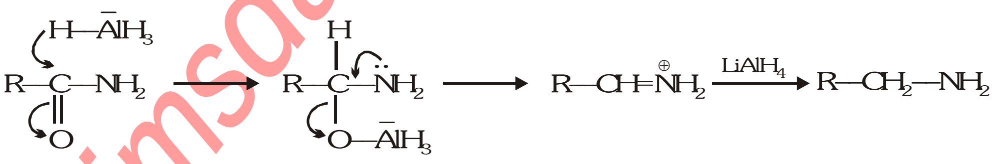


$$R-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow{Na/C_2H_5OH} R-CH_2NH_2 + H_2O$$



$$R-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow{\overset{\oplus}{Li}\,AlH_4^{\ominus}} R-CH_2-NH_2$$

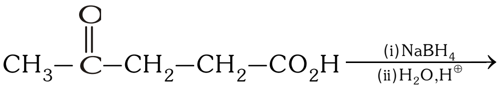
Mechanism :

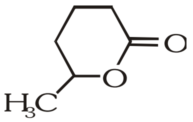


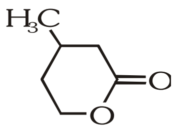
$$R-\overset{H-\overline{Al}H_3}{\underset{\underset{O}{\|}}{C}}-NH_2 \longrightarrow R-\overset{\overset{H}{|}}{\underset{\underset{O-\overline{Al}H_3}{|}}{C}}-\ddot{N}H_2 \longrightarrow R-CH=\overset{\oplus}{N}H_2 \xrightarrow{LiAlH_4} R-CH_2-NH_2$$

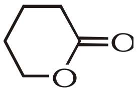
Aldehyde-ammonia state

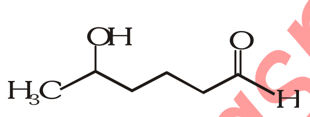
SOLVED EXAMPLES

1. End product of this conversion  $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CO_2H \xrightarrow[(ii)H_2O,H^{\oplus}]{(i)NaBH_4}$ is ?

(A) 

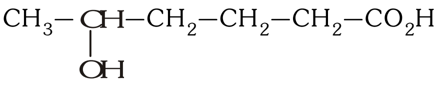
(B) 

(C) 

(D) 

Sol. (A)

$NaBH_4$ reduces reactant to



$CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-CH_2-CH_2-CO_2H$ which forms ester.

2. When acetic acid reacts with ketene, product formed is :

(A) ethyl acetate (B) aceto-acetic ester (C) acetic anhydride (D) no reaction

Sol. (C)

$CH_3COOH + \underset{\text{Ketene}}{CH_2=C=O} \longrightarrow$ acetc anhydride

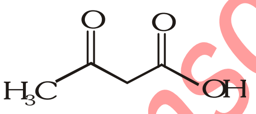
3. $R-CH_2-CH_2OH$ can be converted in $R-CH_2CH_2COOH$. The correct sequence of reagents is :

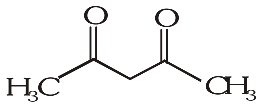
(A) PBr_3, KCN, $H^{\oplus}$ (B) PBr_3, KCN, H_2 (C) KCN, $H^{\oplus}$ (D) HCN, PBr_3, $H^{\oplus}$

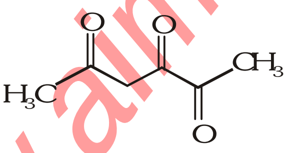
Sol. (A)

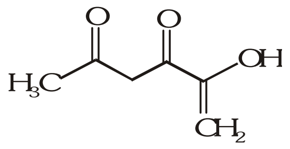
$RCH_2CH_2OH \xrightarrow{PBr_3} RCH_2CH_2Br \xrightarrow{KCN} RCH_2CH_2CN \xrightarrow{H_2O/H^{\oplus}} RCH_2CH_2COOH$

4. Which of the following compound would be expected to decarboxylate when heated :

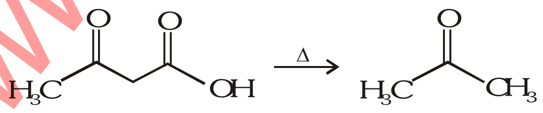
(A) 

(B) 

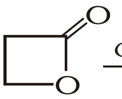
(C) 

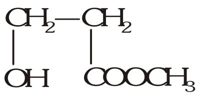
(D) 

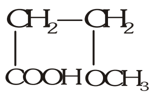
Sol. (A)



In case of β-keto acid, the decarboxylation occurs radily due to 6-membered low energy transition state formation.

5.  $\xrightarrow{CH_3OH}$ A ; A is ?

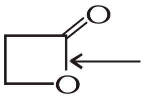
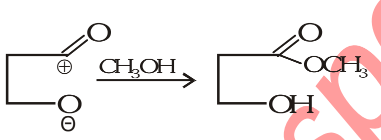
(A) 
$\underset{OH}{CH_2}-\underset{COOCH_3}{CH_2}$

(B) 
$\underset{COOH}{CH_2}-\underset{OCH_3}{CH_2}$

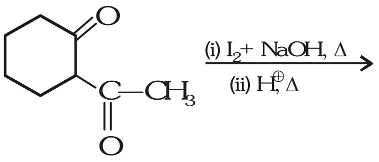
(C) both are correct

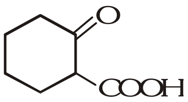
(D) None is correct

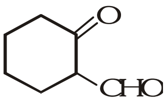
Sol. (A)

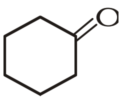

This bond breaks hence intermediate is


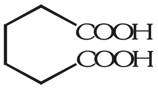
6. End product of the following sequence of reaction is :



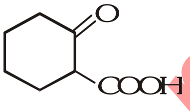
(A) Yellow ppt. of CHI_3, 

(B) Yellow ppt. of CHI_3, 

(C) Yellow ppt. of CHI_3, 

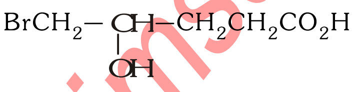
(D) Yellow ppt. of CHI_3, 

Sol. (C)

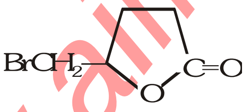
Intermediate is  ; which loses CO_2 on heating (β-keto acid)

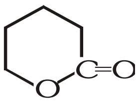
7. The final product obtained in the reaction :

$CH_2=CHCH_2CH_2CO_2H \xrightarrow{Br_2 / OH^{\ominus}}$

(A) 
$BrCH_2-\underset{OH}{CH}-CH_2CH_2CO_2H$

(B) $HOCH_2-CH_2CH_2CH_2CO_2H$

(C) 

(D) 

Sol. (C)

8. On subjecting mesityl oxide to the iodoform reaction, one of the products is the sodium salt of an organic acid. Which acid is obtained ?

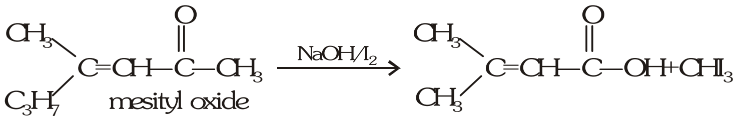
(A) $(CH_3)_2C=CH-CH_2COOH$

(B) $(CH_3)_2CH-COOH$

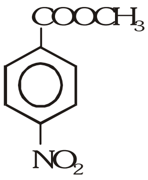
(C) $(CH_3)_2C=CH-COOH$

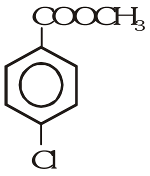
(D) $(CH_3)_2C=CH-CO-COOH$

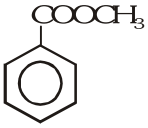
Sol. (C)

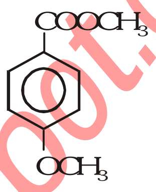


9. The ease of alkaline hydrolysis is more for :

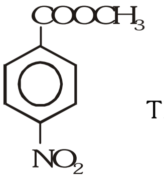
(A) 

(B) 

(C) 

(D) 

Sol. (A)



There is more electron deficiency on carbonyl carbon.

10. Which of the following does not undergo Hell-volhard Zelinsky reaction ?

(A) HCOOH (B) CCl_3COOH (C) C_6H_5COOH (D) All

Sol. (D) None of these contain alpha H-atom.
