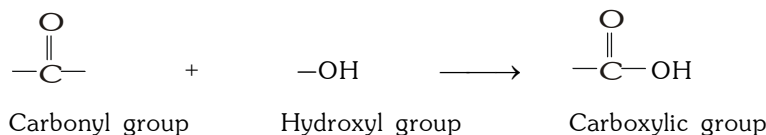


CARBOXYLIC ACID AND THEIR DERIVATIVES

Organic compounds having $-\text{COOH}$ group called Carboxylic group. This functional group is composed of

Carbonyl ($-\overset{\text{O}}{\parallel}{\text{C}}-$) and hydroxyl ($-\text{OH}$) 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 $\text{C}_n\text{H}_{2n}\text{O}_2$.

Classification :

Monocarboxylic acid (RCOOH) :

Having one carboxylic group, also called monobasic acid. General formula - $\text{C}_n\text{H}_{2n}\text{O}_2$ ($n = 1, 2, 3, \dots$). Higher mono carboxylic acids are called **fatty acids**.

Example : CH_3COOH acetic acid

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

Example : $\begin{array}{c} \text{COOH} \\ | \\ \text{COOH} \end{array}$ Oxalic acid

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

Example : $\begin{array}{c} \text{CH}_2\text{COOH} \\ | \\ \text{HO}-\text{C}-\text{COOH} \\ | \\ \text{CH}_2\text{COOH} \end{array}$ Citric acid

NOMENCLATURE

Acid	Common name	IUPAC name
HCOOH	Formic acid (formica-red ants)	Methanoic acid
CH_3COOH	Acetic acid (acetum-vinegar)	Ethanoic acid
$\text{CH}_3\text{CH}_2\text{COOH}$	Propionic acid (Propan-first pion-fat)	Propanoic acid
$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$	Butyric acid (Butter-butyrums)	Butanoic acid
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}$	Valeric acid (valerian-plant root)	Pentanoic acid
$\text{C}_5\text{H}_{11}\text{COOH}$	Caproic acid	Hexanoic acid
$\text{C}_7\text{H}_{15}\text{COOH}$	Caprylic acid	Octanoic acid
$\text{C}_9\text{H}_{19}\text{COOH}$	Capric acid	Decanoic acid

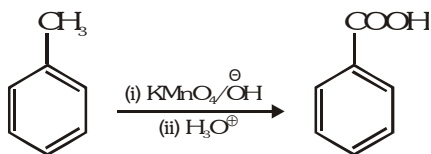
Last three acids are found in goat fat word - (Caper-Goat).

General Method of Preparation

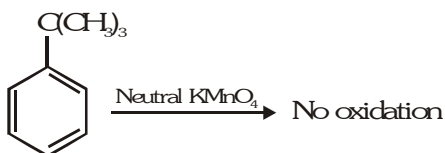
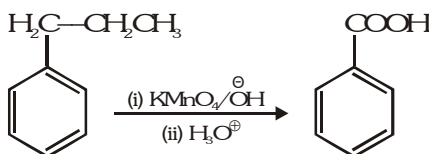
1. By oxidation of primary alcohol with acidic KMnO_4 or acidic $\text{K}_2\text{Cr}_2\text{O}_7$:



6. By oxidation of alkyl benzene :



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

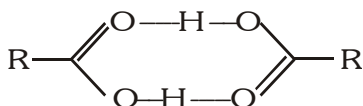


The order of benzoic acid formation by oxidation of alkyl benzene.

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 dimer 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.

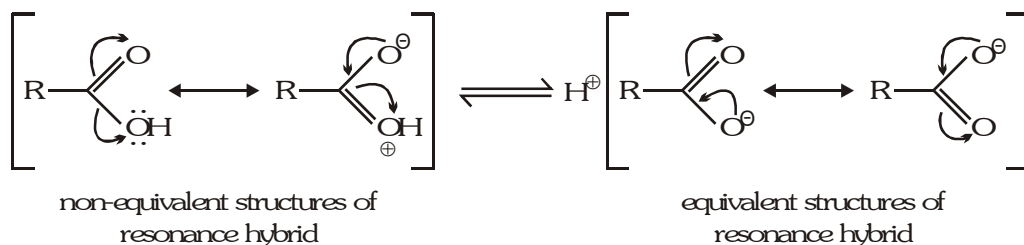
◆ **Melting Point** : Melting point of the carboxylic acid with even number of carbon atoms is higher than acid with odd number of carbon atoms. Such effect is observed in first ten members of the homologous series. This feature is based on the fact that in the carboxylic acids with even number of carbon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



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

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



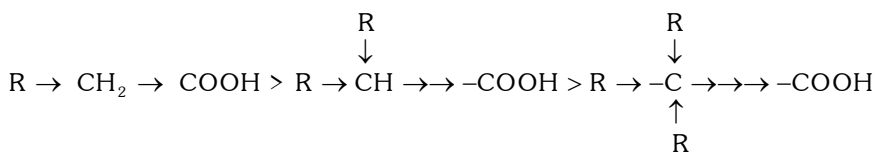
The effect of various number of the substituent and their distance from the carboxylic group has been illustrated with the help of following examples.

- (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 :

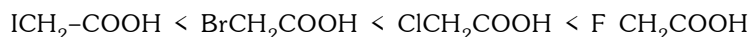


The increase in the no. of chloro substituent on α -carbon atom of acetic acid make the electron withdrawing effect more pronounced and hence make carboxylate ion more stable.

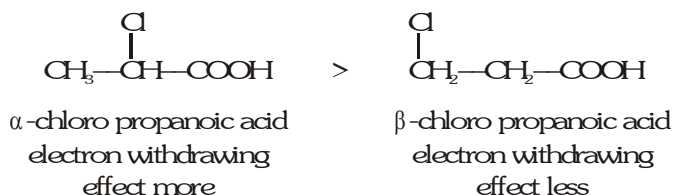
When electron releasing substituent is attached to the carboxylic group then acid strength decreases as the electron releasing power increases.



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

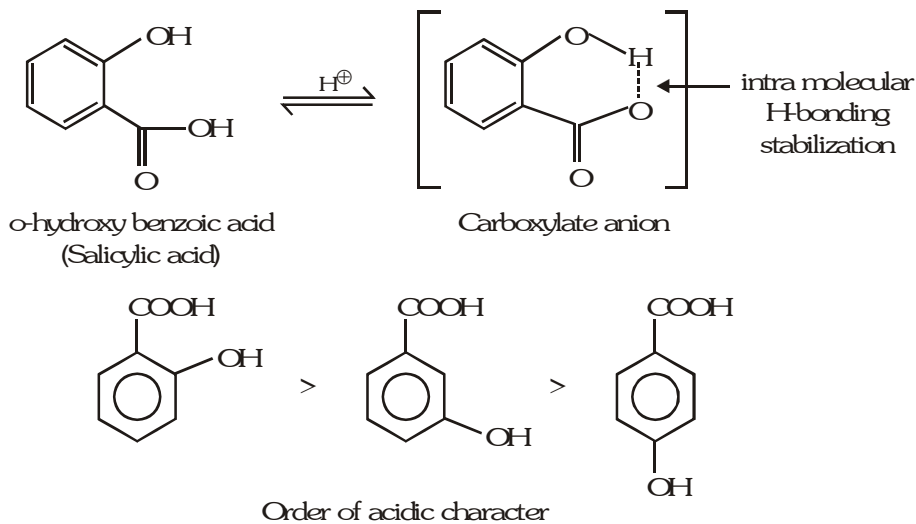


(iii) Effect of the position of the substituent : The effect of the substituent decreases as its distance from $-\text{COOH}$ group increases.

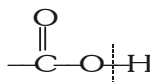


◆ Ortho Effect :

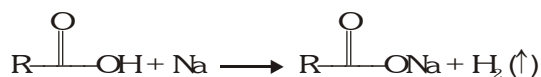
The ortho substituted benzoic acid (whether the substituent is electron withdrawing or releasing) is comparatively stronger acid than the para and meta isomers. This effect is called ortho effect. It occurs due to the joint operation of steric and intra molecular H-bonding where ever it takes chance to stabilize the carboxylate anion due to nearness of the substituent. Groups like $-\text{OH}$, $-\text{Cl}$, $-\text{NO}_2$ will cause more stabilization to anion due to direct interaction through intra molecular H-bonding.



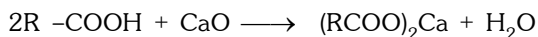
Reaction due to cleavage of $-\text{O}-\text{H}$ bond as acid

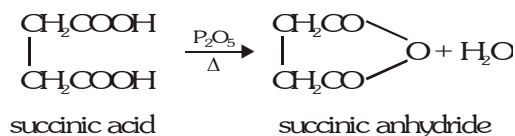


(i) Reaction with active metals [alkali and alkaline metal] :

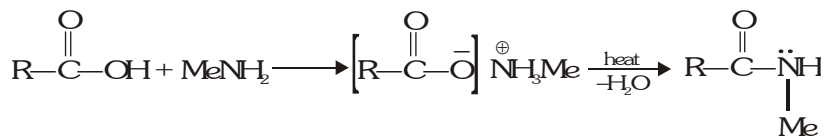


(ii) Reaction with CaO :

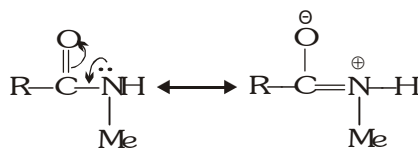




4. Formation of Amides :



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

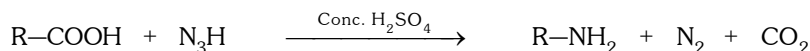


Thus extent of H-bonding increases which makes the boiling and melting points of amides higher than other acid derivatives.

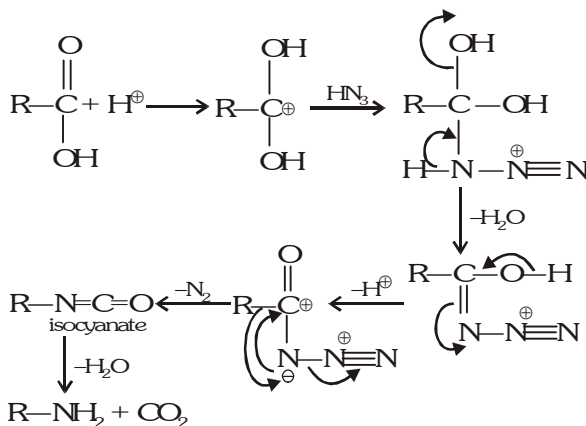
☐ Reactions Involving -COOH Group :

1. Schmidt Reaction :

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

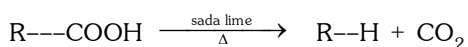


Mechanism :

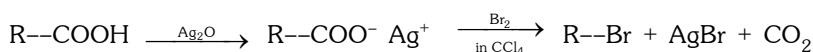


2. Soda lime Decarboxylation :

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



3. Hunsdicker Reaction :

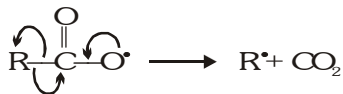


Mechanism : Reaction proceeds through free radical mechanism in various steps.

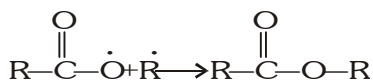
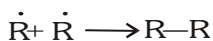
(i) Chain initiation :



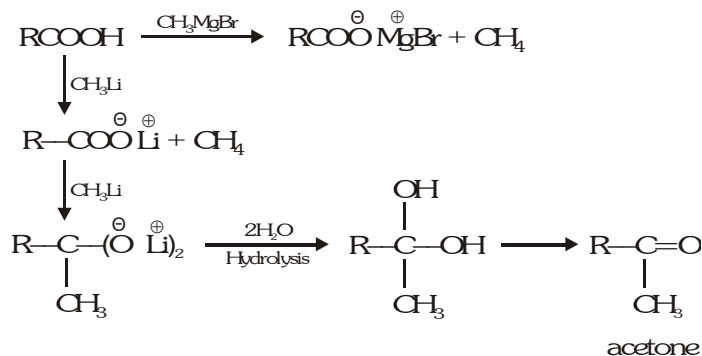
(ii) Chain propagation step :



(iii) Chain termination :



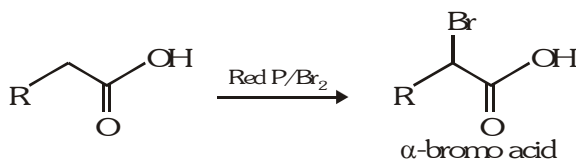
4. With excess of organometallic compounds :



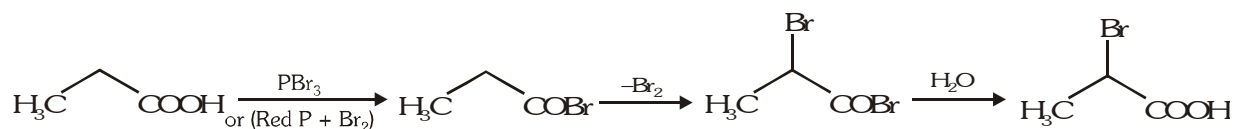
2 moles of organometallic compounds are needed to form ketone.

5. Hell-Volhard-Zelinsky Reaction :

This is α -halogenation of a carboxylic acid.



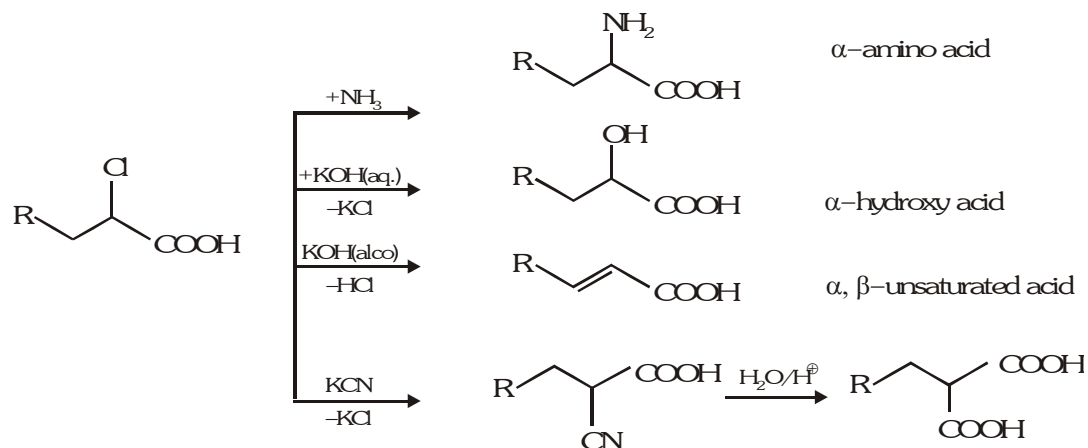
Possible Mechanism for the reaction is :



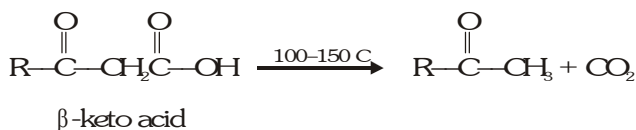
The purpose of PBr_3 is to convert $-\text{OH}$ into $-\text{Br}$ to make α -hydrogen atom more acidic to be replaced by Br atom of Br_2 . The reaction does not stop at monosubstitution but continues till the α -hydrogen are replaced.



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

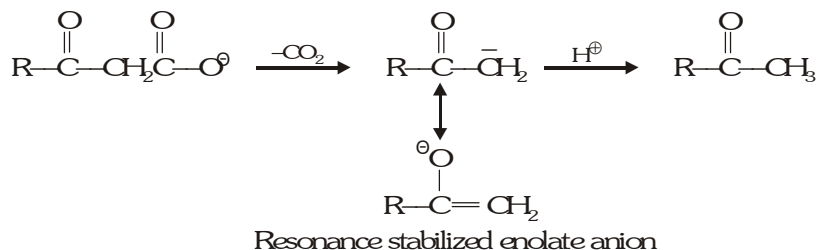


6. Heating of β -keto acid :



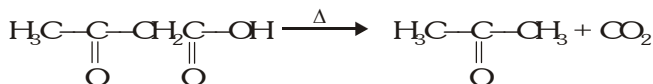
There are two facts on which ease of decarboxylation depends.

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

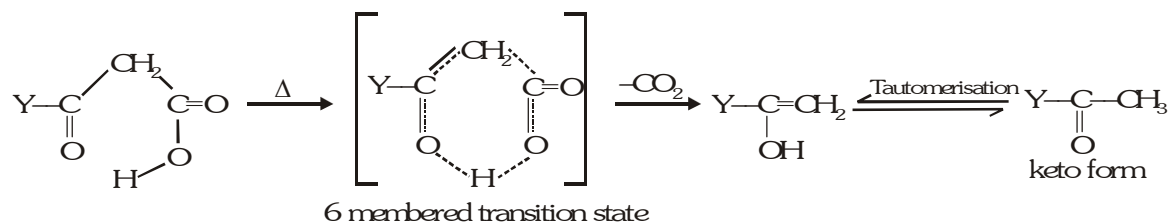


This anion is much more stable than the anion $\text{R}\overset{\ominus}{\text{C}}\text{H}_2$ formed by decarboxylation of an ordinary carboxylic acid anion.

(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 .



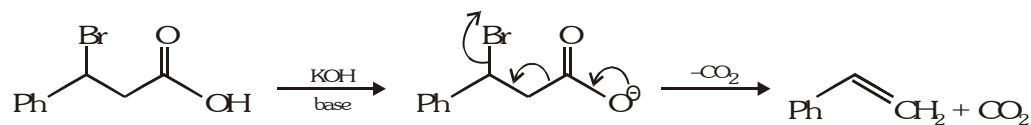
Mechanism :



Here y can be substituents like

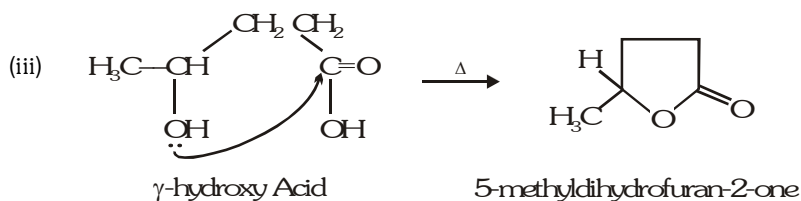
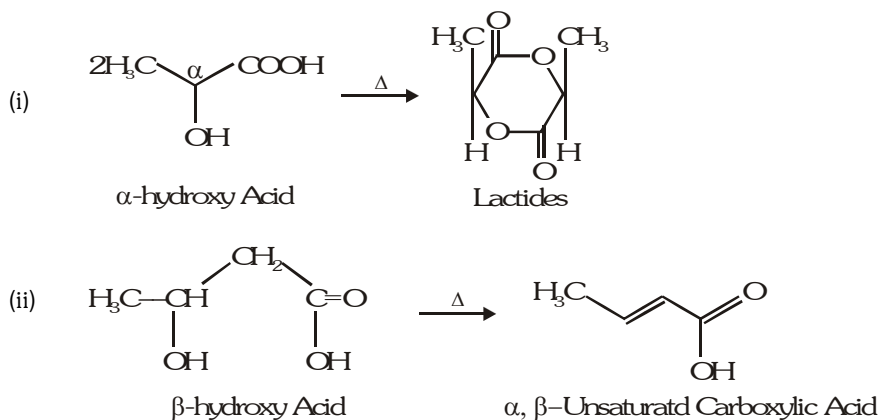
OH - diacid ; R - β -keto acid

H - β aldehyde acid ; X - β halo acid

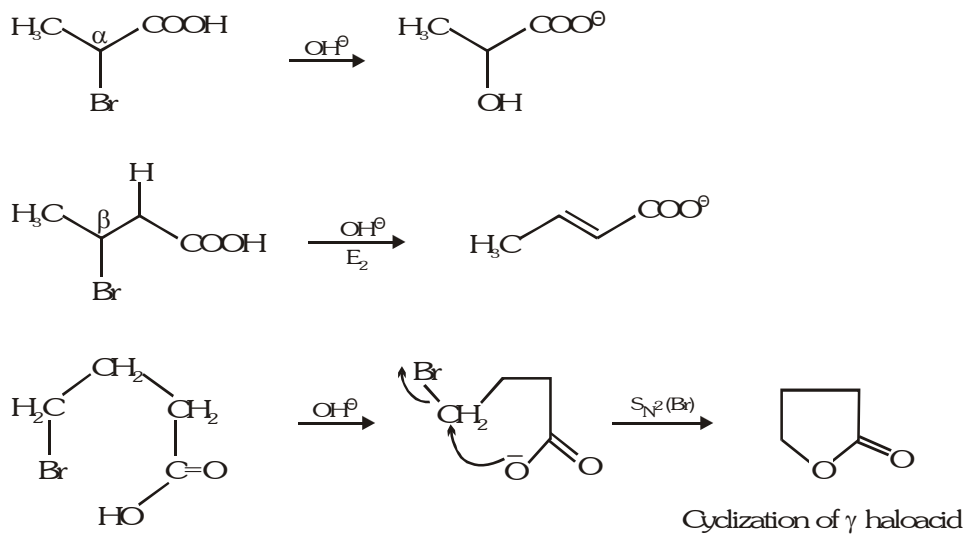


This decarboxylation proceeds through elimination.

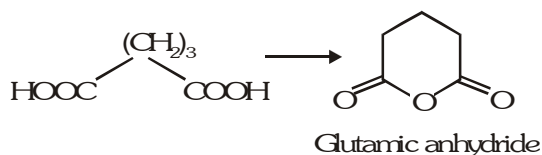
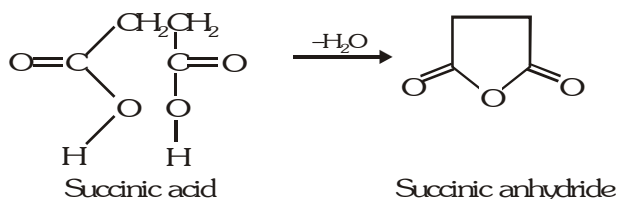
7. Heating of α , β and γ Hydroxy Acid :



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

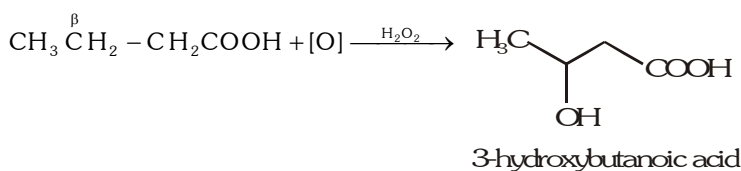


9. Heating of Dicarboxylic Acids :

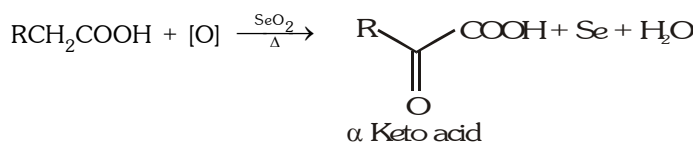


10. Oxidation of Carboxylic acid at Alkyl Group :

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

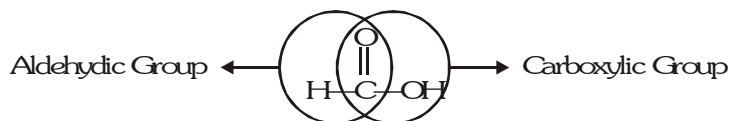


Oxidation can also occur at α carbon atom on treatment with oxidizing agent like selenium dioxide SeO_2 .



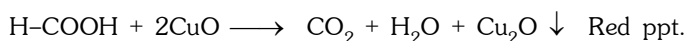
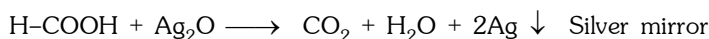
❑ Abnormal Behaviour of Formic Acid :

The behaviour of formic acid is different from other carboxylic acid due to presence of aldehydic group.

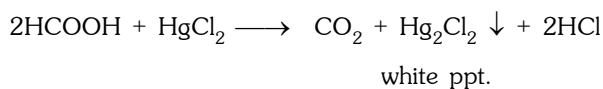


❑ Reaction with :

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



- (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.



Test for HCOOH and CH₃COOH

	Test	HCOOH	CH ₃ COOH
(i)	Reducing character Reducing agents - Tollen reagent Fehling solution HgCl ₂ Corrosive sublimate K ₂ Cr ₂ O ₇	Silver mirror Cu ₂ O red Hg ₂ Cl ₂ Calomel Cr ⁺³	- - - - -
(ii)	Decarboxylation.	Na ₂ CO ₃ + H ₂	CH ₄
(iii)	Heating at 160 ⁰ C	CO ₂ + H ₂	-
(iv)	Heating sodium salts of acids at 360 ⁰ C	$\begin{array}{c} \text{COONa} \\ \\ \text{COONa} \\ \Delta \downarrow \text{HCl} \\ \text{COOH} \\ \\ \text{COOH} \end{array} + \text{NaCl}$	-
5.	Conc. H ₂ SO ₄	CO + H ₂ O	Dissolve
6.	P ₂ O ₅	-	Anhydride
7.	Cl ₂ / P	CO ₂ + 2HCl	Products are mono, di, tri chloro acetic acid.
8.	Ca salt heat	HCHO	CH ₃ COCH ₃

❑ Uses of Formic Acid :

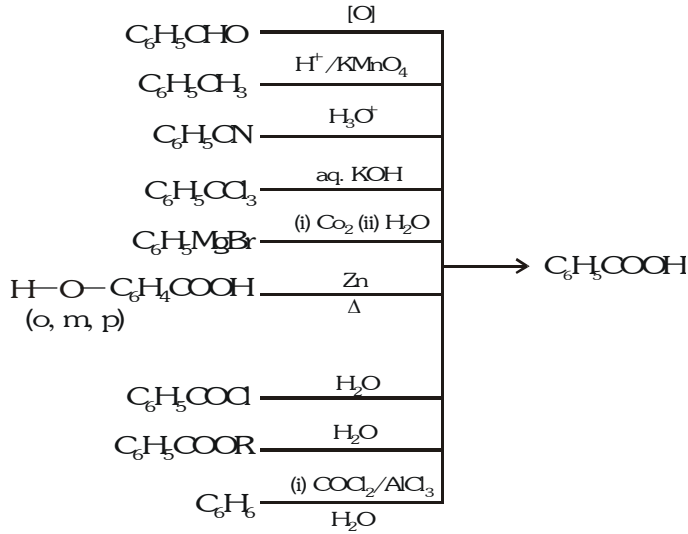
- (i) As an antiseptic
- (ii) For preservation of fruits.
- (iii) For leather tanning.
- (iv) In dyeing wool and cotton fabrics.
- (v) As a coagulating agent for rubber.
- (vi) For hydrogenation of oil as Ni-formate.

❑ Uses of Acetic Acid :

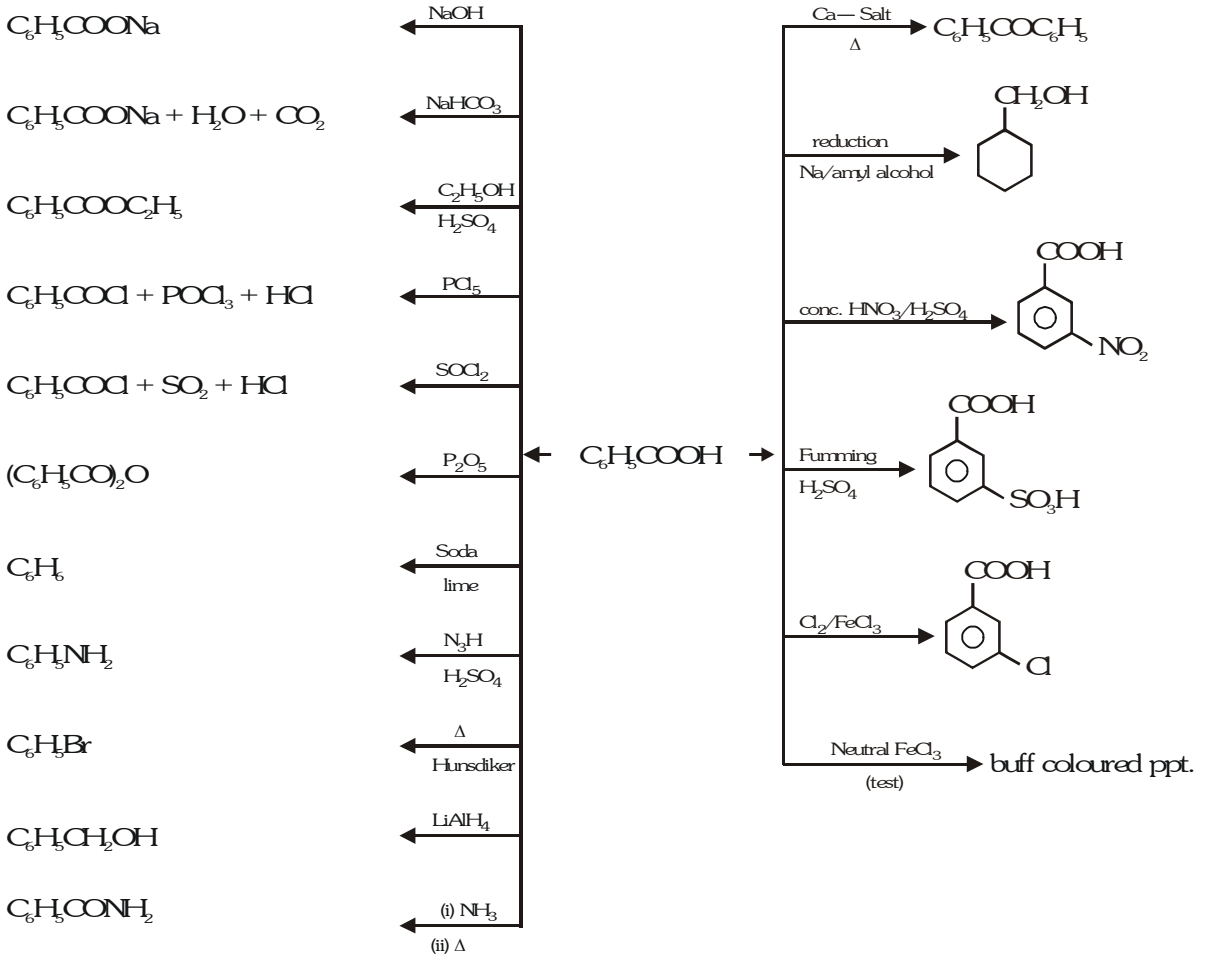
- (i) Vinegar (6 - 10% solution) used as **table acid** and manufacture of pickles.
- (ii) In the form of salts, it is used in medicine and paints.
- (iii) For manufacture of rubber from latex and casein from milk CH₃COOH is used as coagulant.
- (iv) Al and Cr acetates are used as mordants.
- (v) In the manufacture of dyes and perfumes.
- (vi) As a solvent and laboratory reagent.

BENZOIC ACID (C₆H₅COOH)

General Method of Preparation :



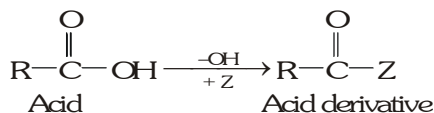
Chemical properties :



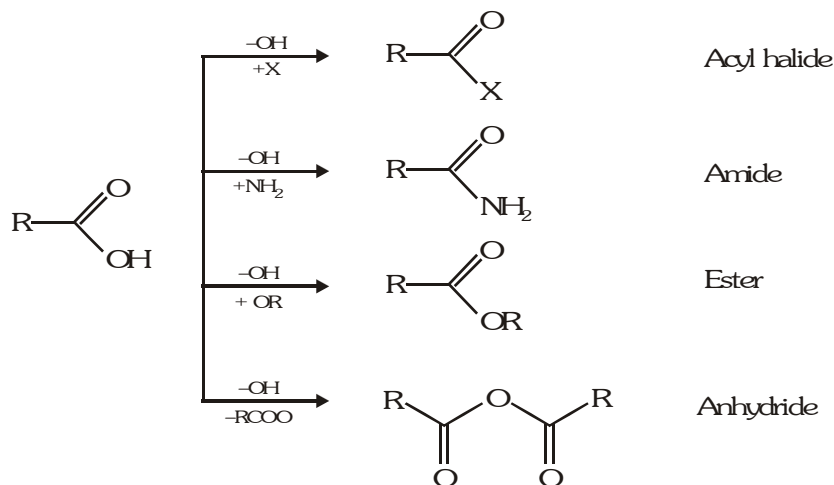
ACID DERIVATIVES

Derivatives of Carboxylic Acid

The -OH of an acid can be replaced by -Cl, -OR, or -NH₂ group to yield an acid chloride, an ester, or an amide. These compounds are called functional derivatives of acid and they all contain an acyl group. The functional derivatives are all readily converted into the acid by simple hydrolysis.

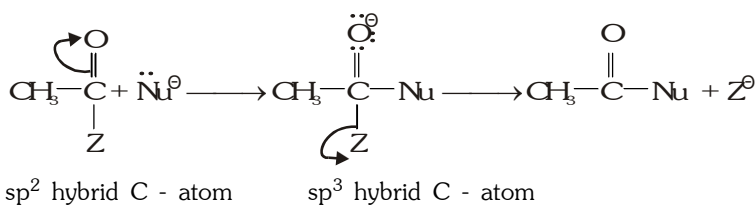


$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-$ is Acyl group and Z is nucleophile Cl^\ominus , $\text{CH}_3\text{COO}^\ominus$, $\text{C}_2\text{H}_5\text{O}^\ominus$, NH_2^\ominus etc.



Characteristic reaction for acid derivatives is nucleophilic substitution reaction :

Mechanism :



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

Reactivity order - depends on the basic character of Z



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

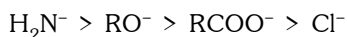
Reactivity order : $\text{CH}_3\text{COCl} > \text{CH}_3\text{COOCOCH}_3 > \text{CH}_2\text{COOC}_2\text{H}_5 > \text{CH}_3\text{CONH}_2$

In acid derivatives the carbonyl group $\text{C}=\text{O}$ is attached to highly electronegative Cl^- , CH_3COO^- , NH_2^- etc. group due to the electron withdrawing effect of these groups, the electron density on the carbonyl carbon is reduced further. Thus the acetyl group is readily attacked by $\ddot{\text{Nu}}$ showing 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 the weakest base is the most reactive leaving group.

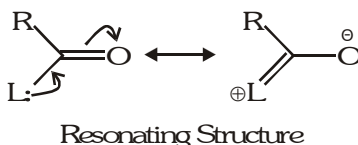
The order of basicity of the leaving group and their leaving tendency follows the order.



Basicity ←

Reactivity →

◆ **Resonance Effect :**



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.

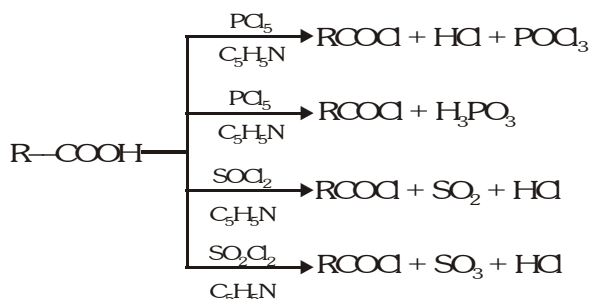
Nucleophilic acyl substitution should be catalysed by acids because the protonation of the acyl compound would facilitate step (i) for nucleophilic attack.

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.

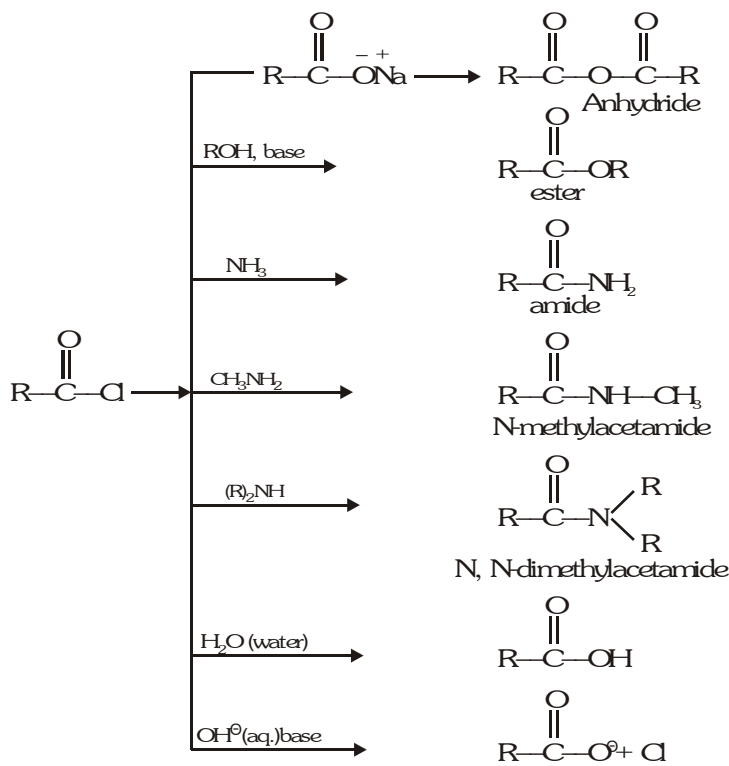
□ **Method of Preparation :**

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 .



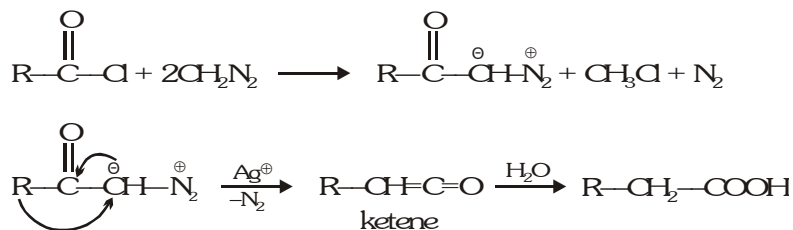
□ **Chemical Properties :**

1. **Acylation Reaction :**

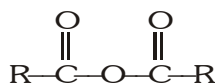


6. Reaction of acyl chloride with diazomethane in presence of Ag_2O and water. (Arndt - Eistert synthesis).

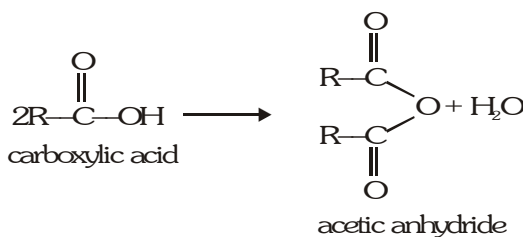
This reaction convert acyl chloride to carboxylic acid with one carbon atom more :



ACID ANHYDRIDES (RCOOCOR)

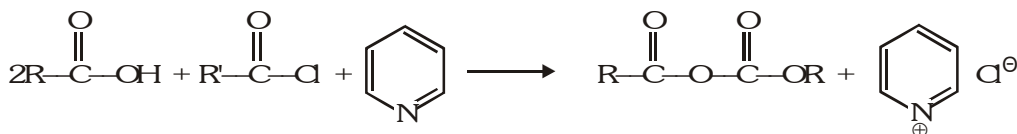


Acid anhydrides are considered to be derived from carboxylic acids by the removal of a molecule of water from two molecules of the acid.

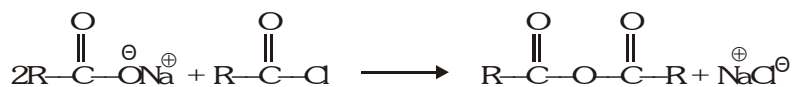


Method of preparation :

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

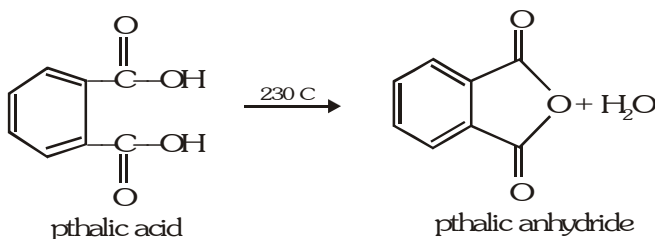
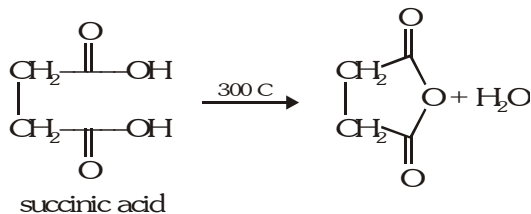


2. Sodium salt of carboxylic acids also react with acyl chlorides to give :



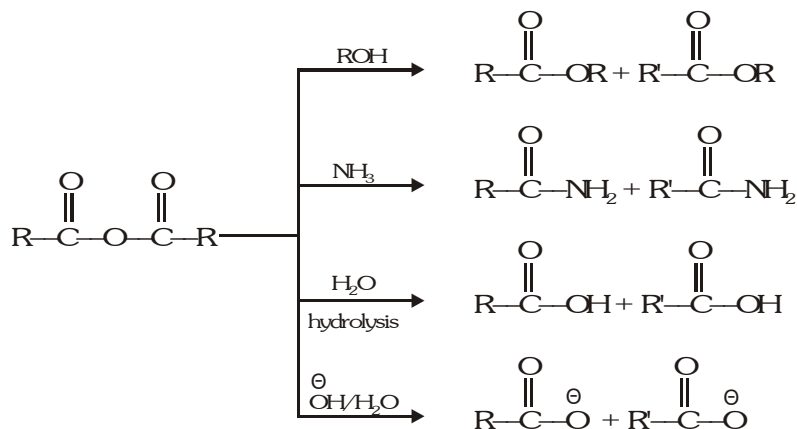
In this reaction a carboxylate ion acts as a nucleophile and brings about a nucleophilic substitution reaction at the acyl carbon of acyl chloride.

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



4. Chemical Properties :

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

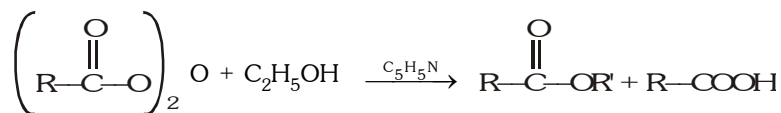
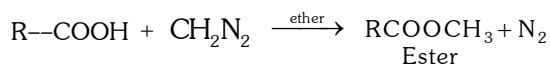
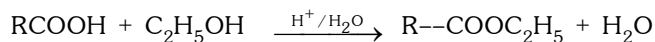


ESTERS (RCOOR)

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.

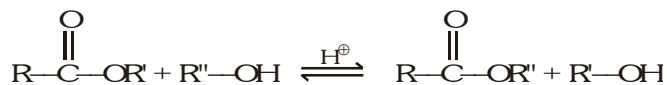
Method of Preparation :

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

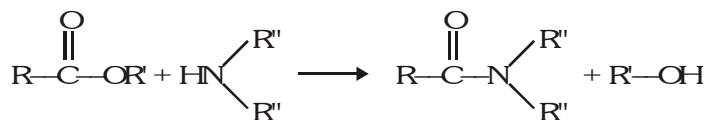


Chemical Properties :

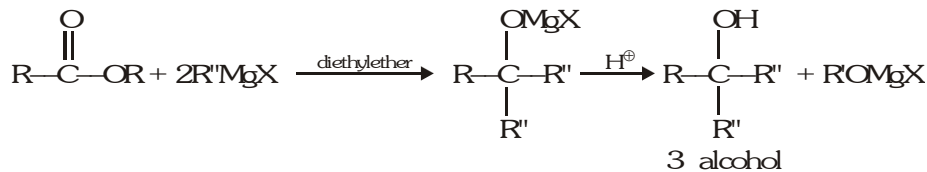
1. Conversion to other esters : Transesterifications



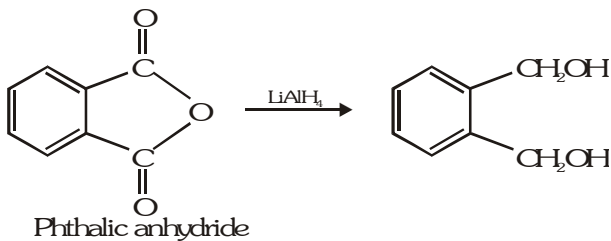
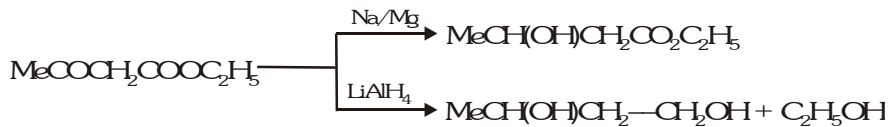
2. Conversion to amides :



3. Reaction with Grignard Reagent :



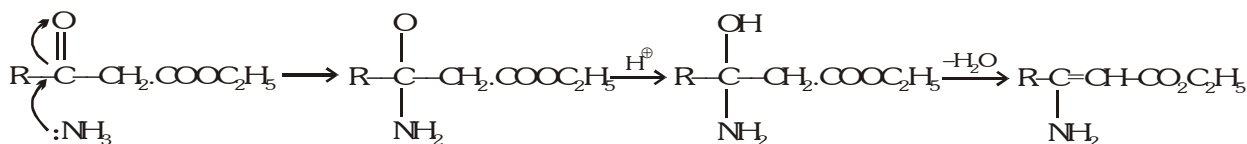
4. Reduction of ester :



5. Reaction of NH₃ with keto ester :

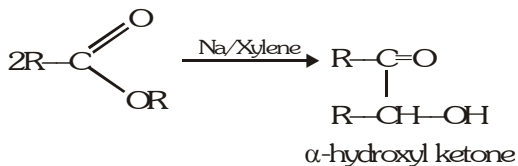


Mechanism :



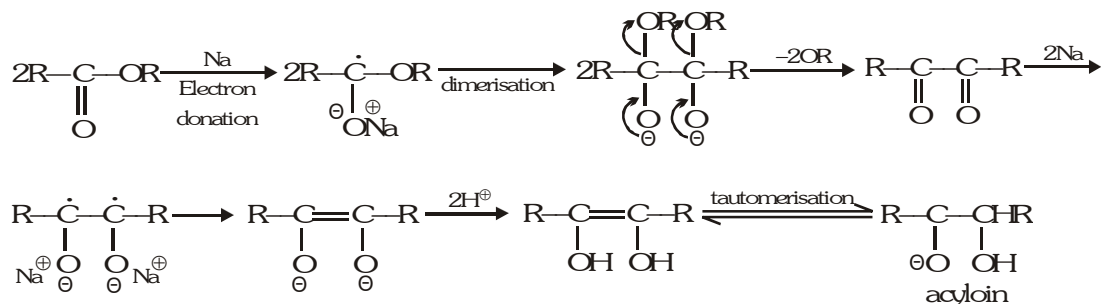
Attack will occur at carbonyl group first because of high degree of +ve charge on carbonyl carbon atom.

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 α-hydroxy ketone (acyloin).

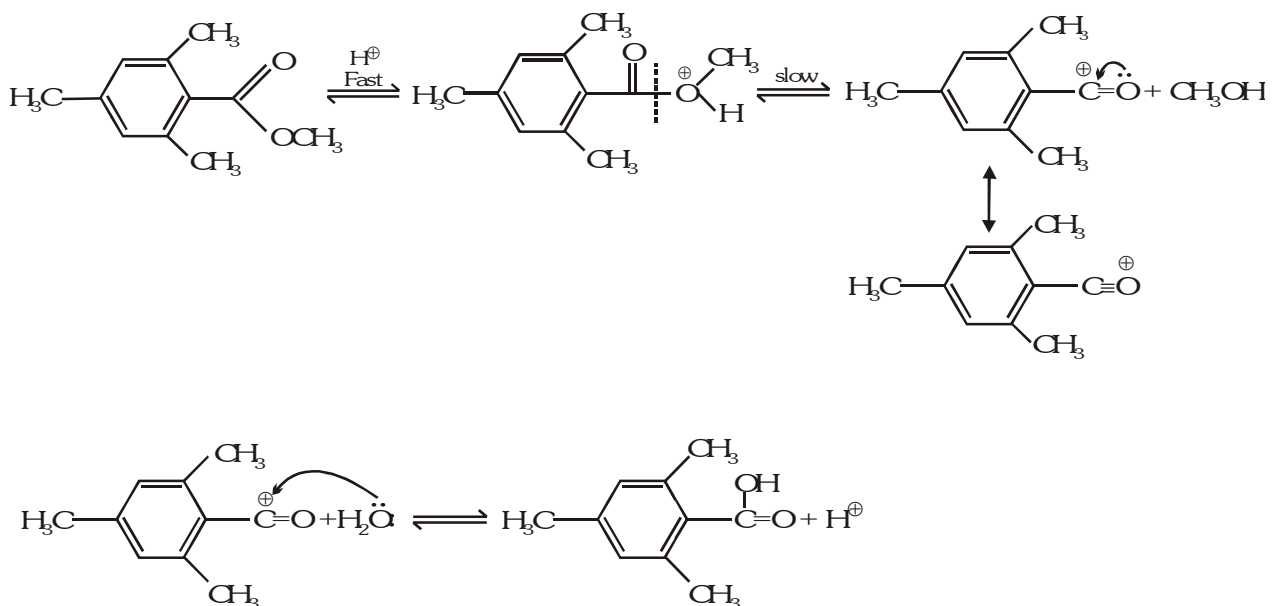


Hydrolysis of Acyl Derivatives :

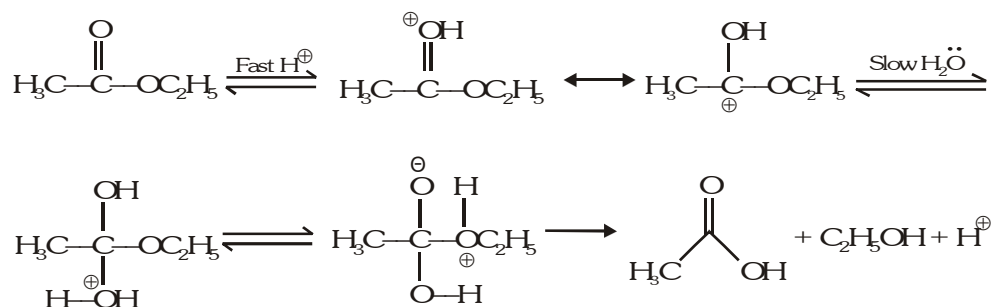
Ester hydrolysis can be carried out in mechanistic pathways $A_{AC^1}, A_{AC^2}, A_{AL^1}, B_{AC^2}$.

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.

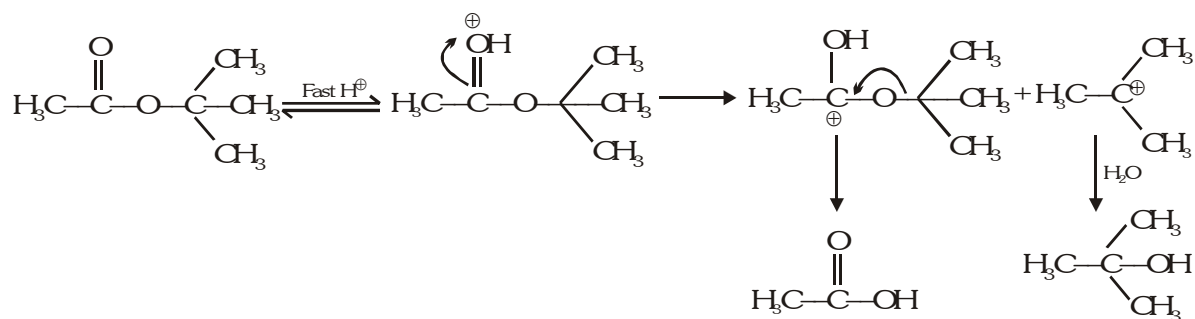
A_{AC^1} :



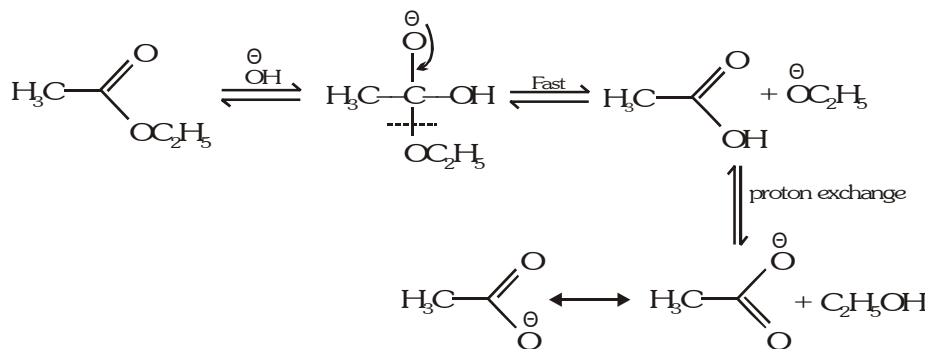
A_{AC^2} :



A_{AL^1} :



B_{AC2} :



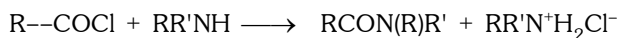
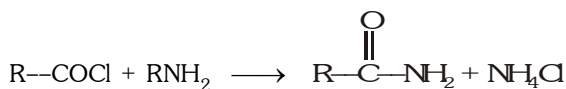
AMIDES (RCONH₂)



Method of Preparation :

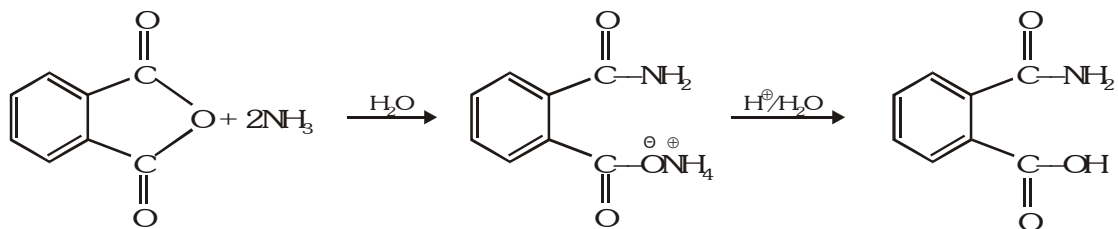
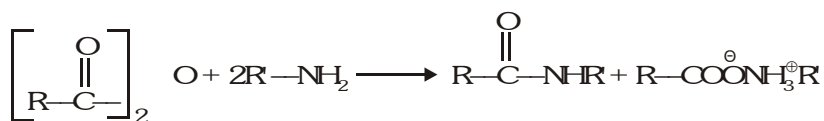
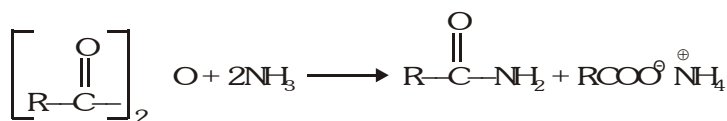
1. Amides from Acyl chloride :

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

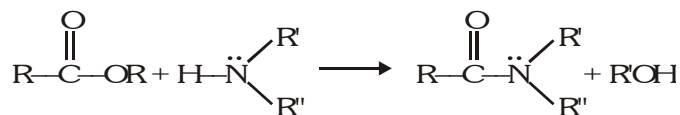
2. Amides from acid anhydride :



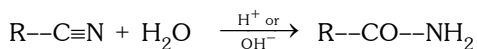
Phthalamic acid
both amide and acid

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 :



Physical Properties :

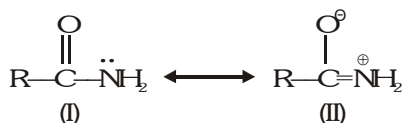
All amides except formamide are crystalline solid at room temperature. They have relatively high melting and boiling point due to association of amide molecules by inter molecular hydrogen bonds.



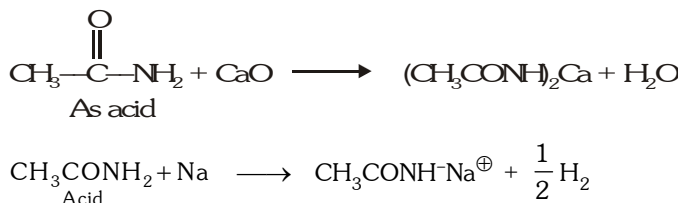
Chemical Properties :

1. Amphoteric character :

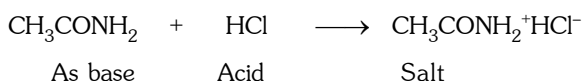
Amides are very feeble bases due to involvement of pair of electron present on N atom in resonance with carboxyl groups. As a result N atom receives partial +ve charges showing feeble acidic character as well



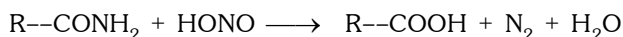
(i) **Acidic character** : Due to structure II amide can act as acid.



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



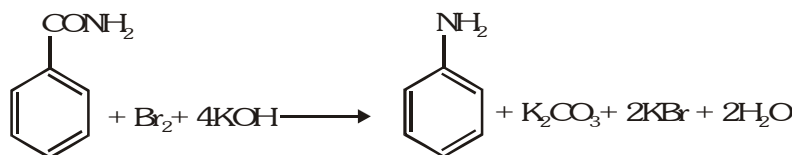
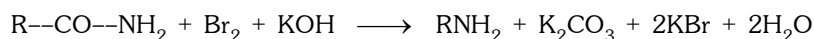
2. Reaction with nitrous acid :



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

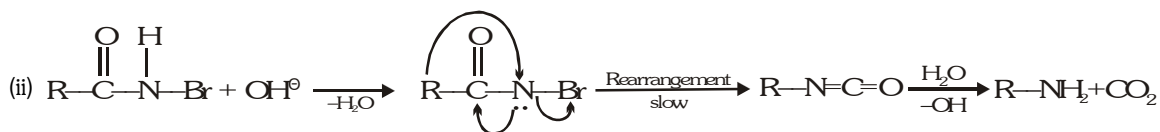
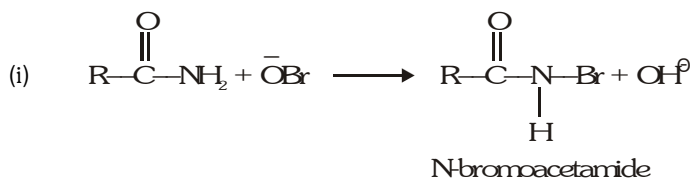
3. Hoffmann's Bromide Reaction :

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

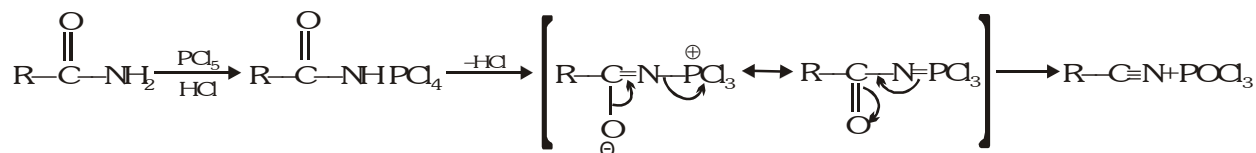
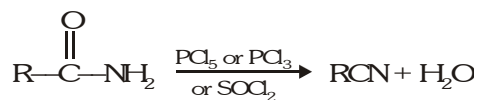


Mechanism :

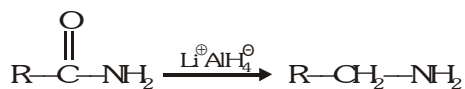
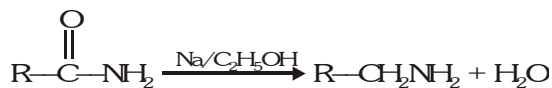




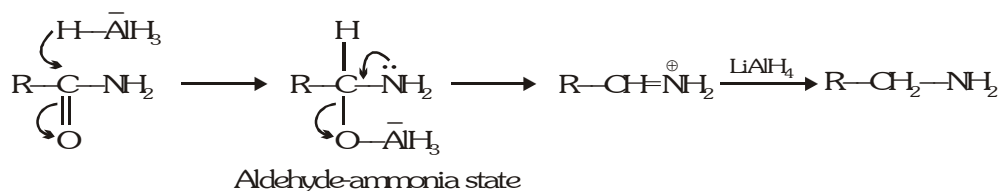
4. Reaction with PCl_5 , PCl_3 or SOCl_2 :



5. Reduction :

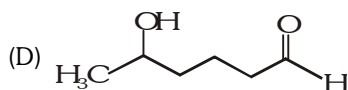
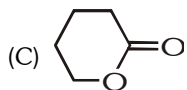
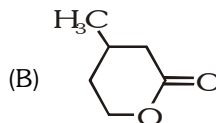
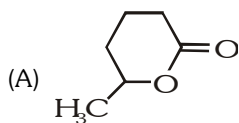


Mechanism :



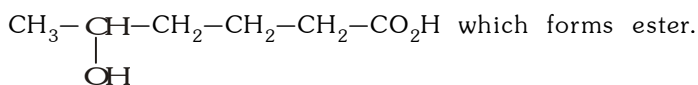
SOLVED EXAMPLES

1. End product of this conversion $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\text{CH}_2-\text{CO}_2\text{H} \xrightarrow[\text{(ii)H}_2\text{O,H}^\oplus]{\text{(i)NaBH}_4} \text{ is ?}$



Sol. (A)

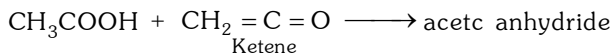
NaBH_4 reduces reactant to



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

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

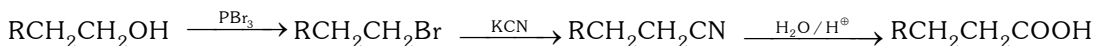
Sol. (C)



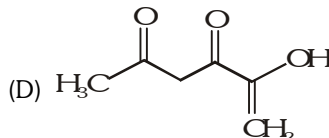
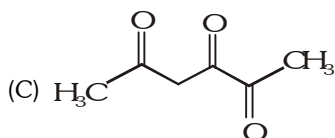
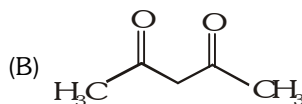
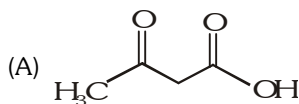
3. $\text{R}-\text{CH}_2-\text{CH}_2\text{OH}$ can be converted in $\text{R}-\text{CH}_2\text{CH}_2\text{COOH}$. The correct sequence of reagents is :

(A) $\text{PBr}_3, \text{KCN}, \text{H}^\oplus$ (B) $\text{PBr}_3, \text{KCN}, \text{H}_2$ (C) $\text{KCN}, \text{H}^\oplus$ (D) $\text{HCN}, \text{PBr}_3, \text{H}^\oplus$

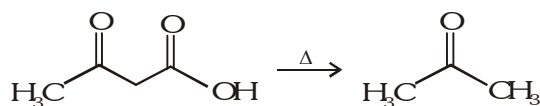
Sol. (A)



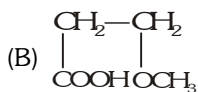
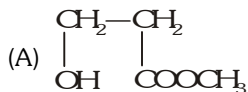
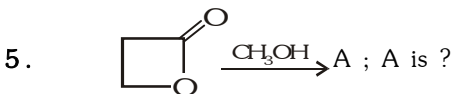
4. Which of the following compound would be expected to decarboxylate when heated :



Sol. (A)

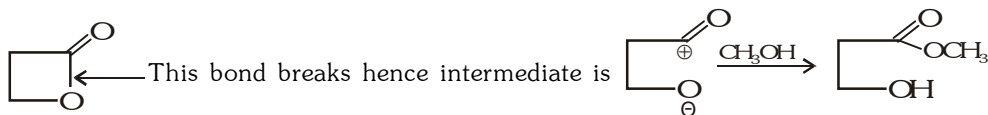


In case of β -keto acid, the decarboxylation occurs readily due to 6-membered low energy transition state formation.

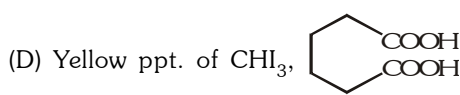
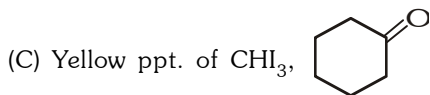
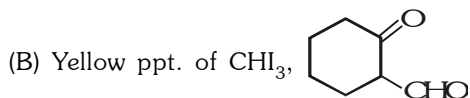
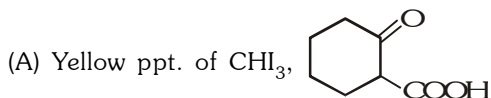
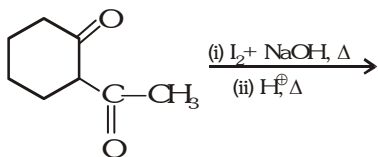


(C) both are correct (D) None is correct

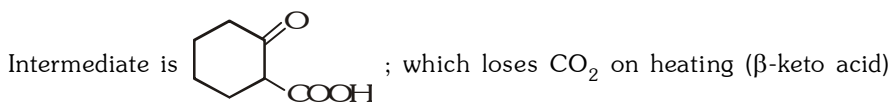
Sol. (A)



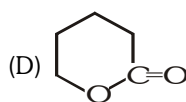
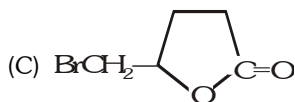
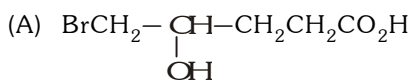
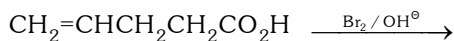
6. End product of the following sequence of reaction is :



Sol. (C)

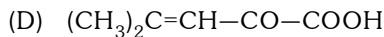
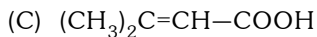
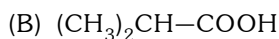
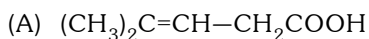


7. The final product obtained in the reaction :

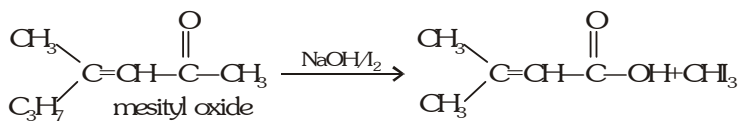


Sol. (C)

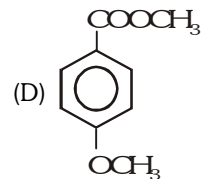
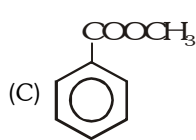
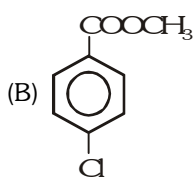
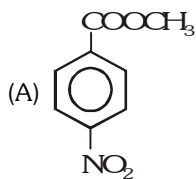
8. On subjecting mesityl oxide to the iodoform reaction, one of the products is the sodium salt of an organic acid. Which acid is obtained ?



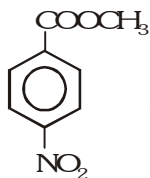
Sol. (C)



9. The ease of alkaline hydrolysis is more for :

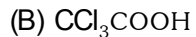
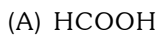


Sol. (A)



There is more electron deficiency on carbonyl carbon.

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



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