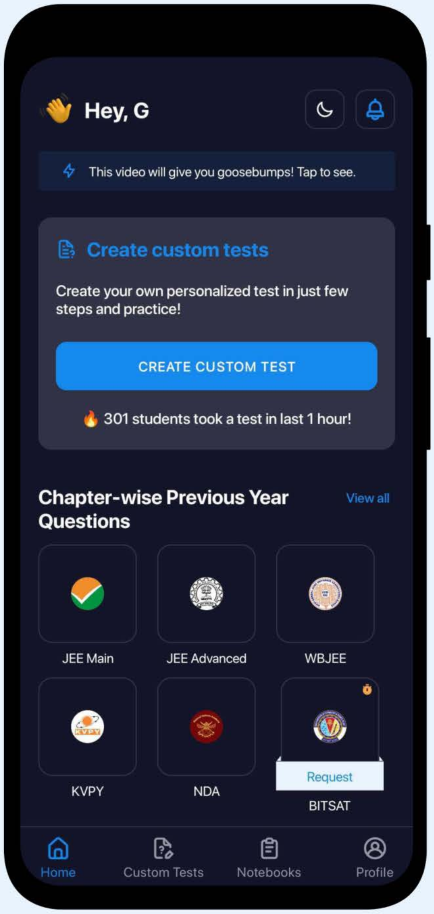

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Carboxylic Acid & Derivative

CARBOXYLIC ACIDS (–COOH)

When a carbonyl carbon also bears a hydroxyl group (– COOH), then these compounds are appreciably acidic, and are called **carboxylic acid.**

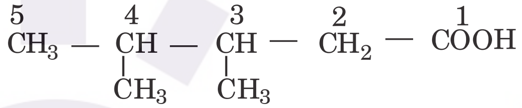
NOMENCLATURE

The aliphatic carboxylic acids are commonly known by their initial names.

Example {Common names}

• $HCOOH$	Formic acid
• CH_3COOH	Acetic acid
• $CH_3\ CH_2\ COOH$	Propionic acid

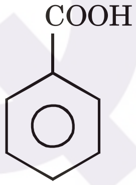
IUPAC naming : These are normally suffixed as "oic acid", when COOH is the principal functional group and its carbon is counted while numbering longest chain. The carboxyl carbon is assigned number 1 in the IUPAC nomenclature. For example,

1. 

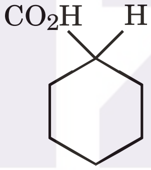
$$\overset{5}{CH_3}-\underset{\displaystyle CH_3}{\overset{4}{CH}}-\underset{\displaystyle CH_3}{\overset{3}{CH}}-\overset{2}{CH_2}-\overset{1}{COOH}$$

3, 4,-dimethyl pentanoic acid

2. $HCOOH$ Methanoic acid

3. 

Benzene Carboxylic acid
(or Benzoic acid)

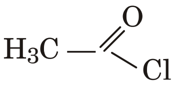
4. 

Cyclohexane
Carboxylic acid

Dicarboxylic acids are named as "alkanedioic acids". For example,  $\begin{array}{c}COOH\\|\\COOH\end{array}$ is named as ethanedioic acid.

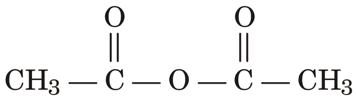
Naming Acid Chlorides & Anhydrides

Acids chlorides are named systematically as acyl chlorides.



Acetyl Chloride

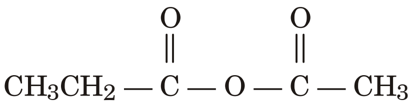
An acid anhydride is named by substituting anhydride for acid in the name of acid from which it is derived.



$$CH_3-\overset{O}{\overset{\parallel}{C}}-O-\overset{O}{\overset{\parallel}{C}}-CH_3$$

Ethanoic Anhydride

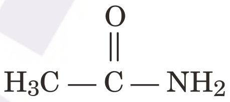
If two different alkyl groups are present, then alkanoic are named in alphabetical order



$$CH_3CH_2-\overset{O}{\overset{\parallel}{C}}-O-\overset{O}{\overset{\parallel}{C}}-CH_3$$

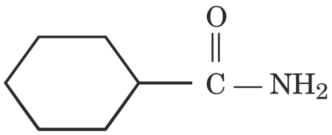
Ethanoic propionic anhydride

Naming Amides and Imides : The names of amides are formed by replacing – oic acid by amide or – carboxylic acid by carboxamide.



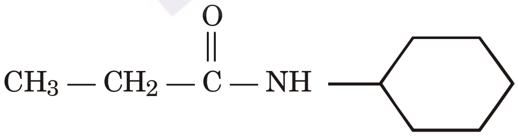
$$H_3C-\overset{O}{\overset{\parallel}{C}}-NH_2$$

Acetamide

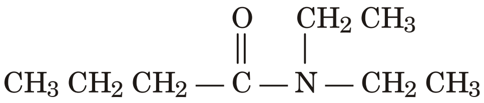


Cyclohexane Carboxamide

If the nitrogen atom of amide has any alkyl groups as substituents, the name of the amide is prefixed by the capital letter N i to indicate substitution on nitrogen, followed by name(s) of alkyl group(s).



N–cyclohexyl propanamide



$$CH_3\,CH_2\,CH_2-\overset{O}{\overset{\parallel}{C}}-\overset{CH_2\,CH_3}{\overset{|}{N}}-CH_2\,CH_3$$

N, N–diethyl butanamide

Physical Properties

(a) Physical state and smell

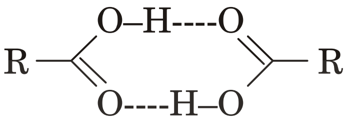
The first three members are colourless liquids and have pungent smell. The next six members are oily liquids with a faint unpleasant odour.

Still higher acids are colourless waxy solids.

Benzoic acids and its homologues are colourless solids.

(b) Boiling points : They have higher boiling points than the corresponding alcohols of comparable molecular masses.

Carboxylic acids have higher boiling points due to the presence of intramolecular hydrogen bonding. Due to the hydrogen bonding, carboxylic acids exists as dimers.



(c) Melting point : In the case of first ten carboxylic acids, the melting points of acids containing even number of carbon atoms is higher than the next lower and higher member containing odd number of carbon atoms.

The melting and boiling points of aromatic acids are usually higher than those of aliphatic acids of comparable molecular masses.

(d) Solubility in water : The first four members of aliphatic carboxylic acids are very soluble in water. The solubility in water decreases gradually with rise in molecular mass. All are soluble in alcohol or ether.

Benzoic acid is sparingly soluble in cold water but is soluble in hot water, alcohol and ether.

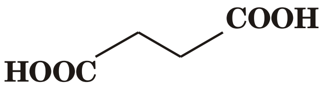
Example 1

Give the IUPAC names of the following compounds :

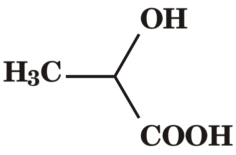
(i)

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

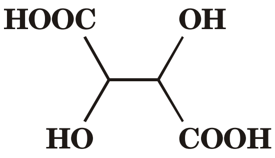
(ii)



(iii)



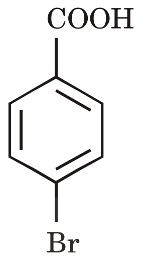
(iv)



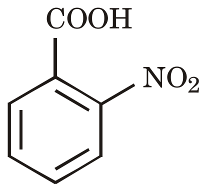
Solution :

	IUPAC name	**General name**
(i)	Ethanedioic acid	Oxalic acid
(ii)	Butanedioic acid	Succinic acid
(iii)	2-Hydroxy propanoic acid	Lactic acid
(iv)	2, 3 Dihydroxybutanedioic acid	Tartaric acid

Aromatic acids Ar – COOH are usually named as derivatives of the parent acid i.e. benzoic acid, C_6H_5COOH.



4–bromobenzoic acid



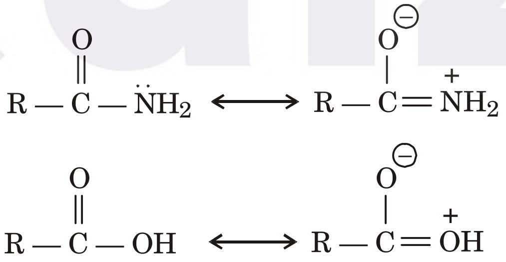
2–nitrobenzoic acid

Example 2

Acid and acid derivatives although contain > C = O group, do not undergo the usual properties of carbonyl group explain.

Solution :

It is because of the possibility of resonance which compensates the electron deficiency of carbonyl carbon to some extent for example.



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-\ddot{N}H_2 \longleftrightarrow R-\overset{\overset{\displaystyle O^{\ominus}}{|}}{C}=\overset{+}{N}H_2$$

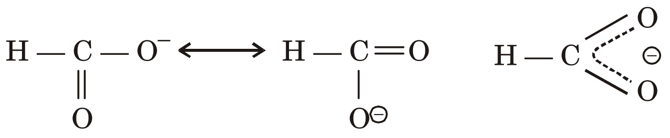
$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH \longleftrightarrow R-\overset{\overset{\displaystyle O^{\ominus}}{|}}{C}=\overset{+}{O}H$$

Example 3

Carbon-oxygen bond length in formic acid are 1.24 Å and 1.36 Å but in sodium formate both the carbon-oxygen bonds have same value i.e. 1.27 Å.

Solution :

In formate ion resonance gives rise to identical bond lengths.



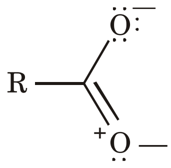
$$H-\underset{\underset{\displaystyle O}{\|}}{C}-O^- \longleftrightarrow H-\underset{\underset{\displaystyle O^{\ominus}}{|}}{C}=O$$

Whereas no such resonance is noticed in formic acid (H — COOH) and thus C — O bonds are different in HCOOH.

Example 4

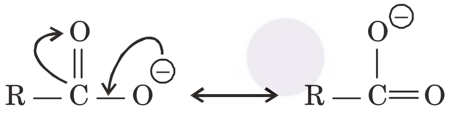
Why the bond length of C = O in carboxylic acids is bit longer than in aldehydes ?

Solution :

Due to resonance, there is considerable contribution of the resonance from  to the hybrid from, i.e., there is some single bond character in C = O bond which makes it some what longer than in aldehydes.

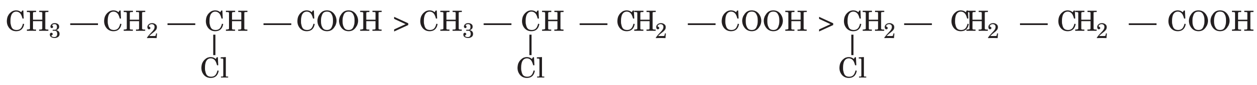
Acidity of Carboxylic Acids

The acidity of a carboxylic acid is due to the resonance stabilization of its anion.



The acidity of carboxylic acid depends very much on the substituent attached to – COOH group. Since acidity is due to the resonance stabilization of anion, substituents causing stabilization of anion increases acidity whereas substituent causing destabilization of anion decreases acidity. For example, electron withdrawing group disperses the negative charge of the anion and hence makes it more stable causing the increase in the acidity of the corresponding acid. On the other hand, electron releasing group increases the negative charge on the anion and hence makes it less stable causing the decrease in acidity.

- Increase in the number of halogen atoms on α-position increases the acidity, e.g.
  $CCl_3\ COOH > CHCl_2COOH > ClCH_2\ COOH > CH_3COOH$.
- Increase in the distance of halogen from COOH decrease the acidity, e.g.



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

Example 5

Arrange the following in increasing order of acidic strength :

Benzoic acid, 4-nitrobenzoic acid, 3, 4-dinitrobenzoic acid, 4-methoxybenzoic acid

Solution :

Since electro-donating groups decrease the acid strength, therefore, 4-methoxybenzoic acid is a weaker acid than benzoic acid.

Further since electron-withdrawing groups increase the acid strength, therefore, both 4-nitrobenzoic acid and 3, 4-dinitrobenzoic acids are stronger acids than benzoic acid. Further due to presence of an additional NO_2 at m-position w.r.t. COOH group, 3, 4-dinitrobenzoic acid is a little stronger acid than 4-nitrobenzoic acid. Thus the overall acid strength increases in the order :

4-methoxybenzoic acid < benzoic acid < 4-nitrobenzoic acid < 3, 4-dinitrobenzoic acid

---

Example 6

(a) Why are both p–Me and m–Me substituted acids weaker than $PhCO_2H$ with the p–acid being the weakest one ?

(b) Why is the p–OH acid weaker than $PhCO_2H$ while the m–OH acid is stronger ?

Solution :

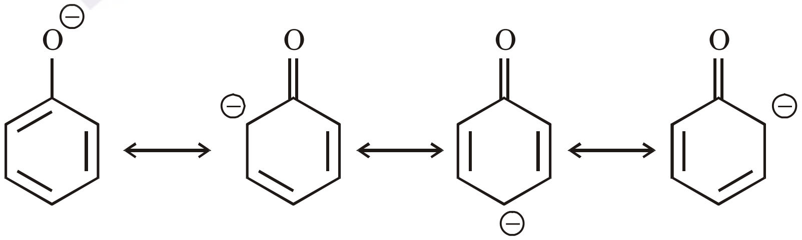
(a) Both p–Me and m–Me are electron–donating and acid weakening. m–Me is electron donating by induction while p–Me is electron–donating by induction as well as hyperconjugation. p–Me being more electron releasing is more acid weakening and p–Me and m–Me substituted acids both are weaker than $PhCO_2H$.

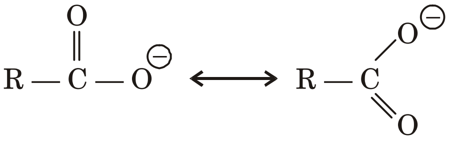
(b) OH group shows – I effect from m–position while from p–position it shows –I and + R effects. Electron–donation by resonance (+ R) is more prominent than electron withdrawal by induction (– I) for OH group. So m–OH is electron–withdrawing and acid strengthening, thus m–OH acid is stronger than $PhCO_2H$. p–OH is electron–donating and acid weakening, thus p–OH acid is weaker than $PhCO_2H$.

Example 7

Though phenoxide ions ($C_6H_5O^-$) has more resonating structure than carboxylate ion, but carboxylic acid is stronger acid than phenol, explain.

Solution :





Acquisition of negative charge on more electropositive carbon atom, drives the phenoxide towards lesser stability.

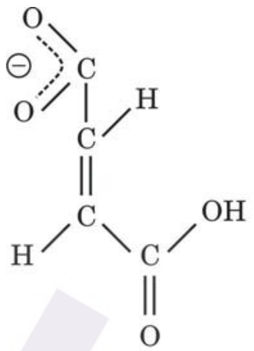
Example 8

On the basis of H-bonding explain that the second ionization constant K_2 for fumaric acid is greater than for maleic acid.

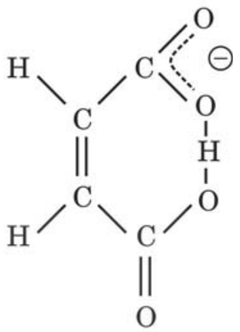
Solution :

We know that H-bonding involving acidic H has an acid weakening effect and H-bonding in conjugate base has an acid strengthening effect.

Both dicarboxylic acids have two ionisable hydrogen atoms. Considering second ionization step.



Fumarate monoanion
(no H-bonding)



Maleate monoanion
(H-bonding)

Since the second ionisable H of the Maleate ion participates in H-bonding more energy is needed to remove this H because the H-bond must be broken. The maleate mono anion is, therefore, the weaker acid.

General Methods of Preparation

1. By oxidation of primary alcohols or aldehydes oxidation of primary alcohols can be achieved by acidified $K_2Cr_2O_7$ or acidified/alkaline $KMnO_4$.

$$RCH_2OH \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } KMnO_4/OH^-} RCOOH$$

Aldehydes can be oxidized to carboxylic acids with mild oxidizing agents such as

$Ag\,(NH_3)_2^+\ \overset{-}{O}H$

$$R - CHO \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } Ag_2O \text{ or } Ag(NH_3)_2^+} R - COOH$$

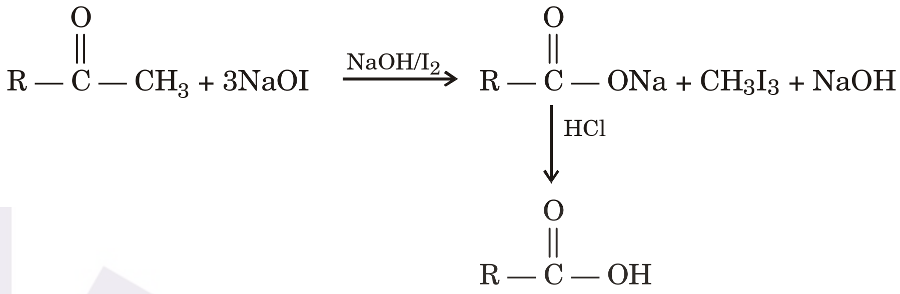
2. By oxidation of alkenes when alkenes are treated with an oxidizing agent such as $KMnO_4$ or on oxidative ozonlysis, it forms carboxylic acids.

$$RCH = CHR' \xrightarrow[\text{(ii) Heat, } H_2O]{\text{(i) } KMnO_4,\ \overline{O}H} RCOOH + R'COOH$$

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

3. By haloform reaction

- This method involves oxidation of methyl ketones with hypohalite ion, $XO^{\ominus}$ ($NaOH + X_2$)

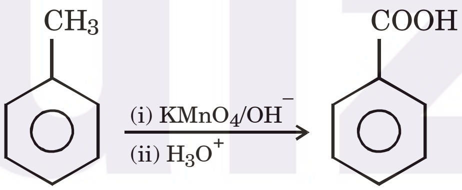


$$R-\overset{O}{\overset{\|}{C}}-CH_3 + 3NaOI \xrightarrow{NaOH/I_2} R-\overset{O}{\overset{\|}{C}}-ONa + CH_3I_3 + NaOH \xrightarrow{HCl} R-\overset{O}{\overset{\|}{C}}-OH$$

Note : In this method, the acid produced has one C atom less than parent ketone.

4. By oxidation of alkyl benzene

When the arenes containing an α-**hydrogen atom** are reacted with a strong oxidizing agent like alkaline $KMnO_4$, it forms benzoic acid.



5. Formation and Hydrolysis of Nitriles

Nitriles can be hydrolyzed by dilute acid to generate carboxylic acids.

E.g. $$R-C \equiv N \xrightarrow[\text{or } ^{-}OH]{H_3O^+} R-CO_2H$$

Nitriles are easily made by the action of cyanide ion as a nucleophile on alkyl halides (or tosylates).

$$R-CH_2-Br \xrightarrow{NaCN} R-CH_2-C \equiv N \xrightarrow{H_3O^+} R-CH_2-CO_2H$$

Again the overall transformation is from alkyl halide to a carboxylic acid with **an extra carbon atom.**

6. Using Grignard Reagent

Grignard Reagents react with carbon dioxide to yield magnesium carboxylate acidification produces carboxylic acids.

$$\begin{tikzcd}
R - X + Mg \arrow[r, "\text{dry ether}"] & R - MgX \arrow[d, "CO_2"] \\
R\,COOH & R\text{-}COOMgX \arrow[l, "H_3O^+"']
\end{tikzcd}$$

Note : The acid thus formed has one carbon more than the alkyl group of the Grignard reagent.

7. By hydrolysis of 1, 1, 1-Trihalogen Derivatives

$$\begin{tikzcd}
R\,CX_3 \arrow[r, "KOH"] & {[\,R - C(OH)_3]} \arrow[d, "\text{unstable}"', phantom, shift right=3] \arrow[d, "-H_2O"] \\
 & R - COOH + H_2O
\end{tikzcd}$$

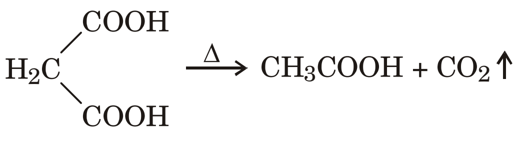
8. By alkenes (Koch Reaction)

A recent method for manufacturing fatty acids is to heat an olefin with carbon monoxide and steam under pressure at 300-400 C in the pressure of catalyst. e.g. phosphoric acid.

$$CH_2 = CH_2 + CO + H_2O \xrightarrow[\text{steam } 300\text{-}400°C]{H_3PO_4} CH_3 - CH_2 - COOH$$

9. Decarboxylation of gemdicarboxylic acid

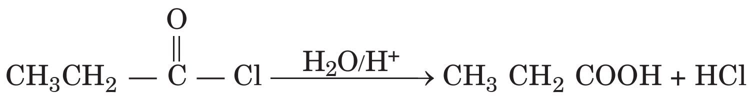
Monocarboxylic acids may also result from the decarboxylation of dicarboxylic acids (when the two CO_2H groups are present on same carbon). Acetic acid is thus obtained by heating/ warming malonic acid.



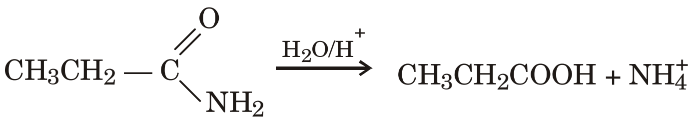
$$H_2C(COOH)_2 \xrightarrow{\Delta} CH_3COOH + CO_2\uparrow$$

10. Hydrolysis of acid derivatives

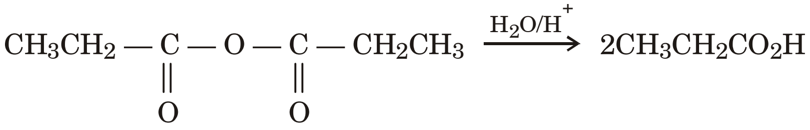
Another useful method constitutes the hydrolysis of carboxylic acid derivatives such as acyl halides, acid amides, acid anhydrides or esters.



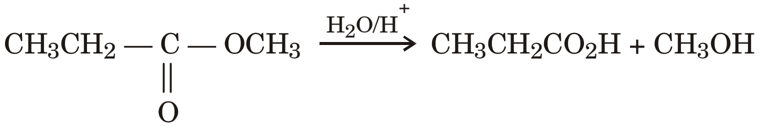
$$CH_3CH_2 - \overset{\overset{\large O}{\|}}{C} - Cl \xrightarrow{H_2O/H^+} CH_3\,CH_2\,COOH + HCl$$



$$CH_3CH_2-C(=O)NH_2 \xrightarrow{H_2O/H^+} CH_3CH_2COOH + NH_4^+$$



$$CH_3CH_2-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-CH_2CH_3 \xrightarrow{H_2O/H^+} 2CH_3CH_2CO_2H$$



$$CH_3CH_2-\underset{\underset{O}{\|}}{C}-OCH_3 \xrightarrow{H_2O/H^+} CH_3CH_2CO_2H + CH_3OH$$

Example 9

How will you synthesize ?

- **(i) Acetic acid from methyl iodide**
- **(ii) Acetic acid from propionic acid**
- **(iii) Acetic acid from acetamide**

Solution :

(i) $CH_3I + KCN \longrightarrow CH_3\ CN \xrightarrow{H_2O\ /\ H^+} CH_3COOH$

(ii)

$$\begin{tikzcd} CH_3CH_2COOH \arrow[r, "NH_3"] & CH_3CH_2COONH_4 \arrow[r, "\Delta"] & CH_3CH_2CONH_2 \arrow[r, "Br_2/KOH"] & CH_3CH_2NH_2 \arrow[d, "HNO_2"] \\ & CH_3COOH & CH_3CHO \arrow[l, "{[O]}"'] & CH_3CH_2OH \arrow[l, "Na_2Cr_2O_7"', "H_2SO_4"] \end{tikzcd}$$

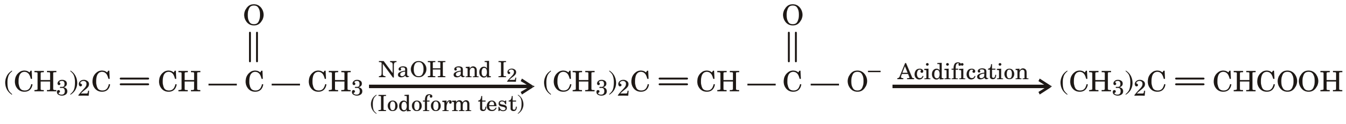
(iii) $CH_3CONH_2 + HNO_2 \longrightarrow CH_3COOH + N_2 + H_2O$

Example 10

$(CH_3)_2C = CHCOCH_3$ can be oxidised $(CH_3)_2C = CHCOOH$ by

- **(a) Chromic acid**
- **(b) NaOH and I_2**
- **(c) Cu at 300 C**
- **(d) $KMnO_4$**

Solution :

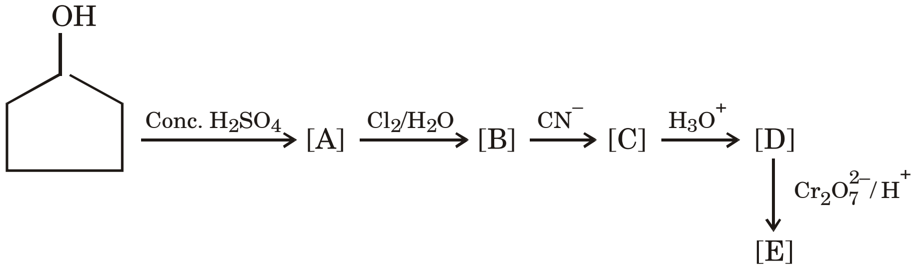


$$(CH_3)_2C=CH-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow[\text{(Iodoform test)}]{\text{NaOH and } I_2} (CH_3)_2C=CH-\overset{\overset{O}{\|}}{C}-O^- \xrightarrow{\text{Acidification}} (CH_3)_2C=CHCOOH$$

$\therefore$ (b)

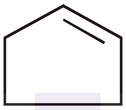
Example 11

Identify A to E

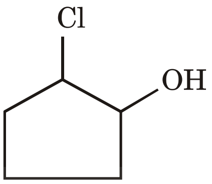


Solution :

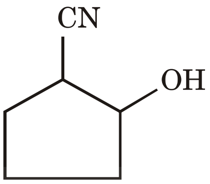
A :



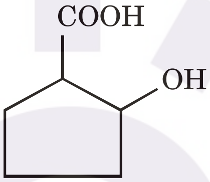
B :



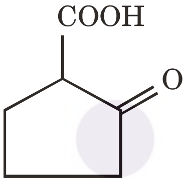
C :



D :



E :



CHEMICAL PROPERTIES :

Reactions of carboxylic acids can be discussed under four heads :

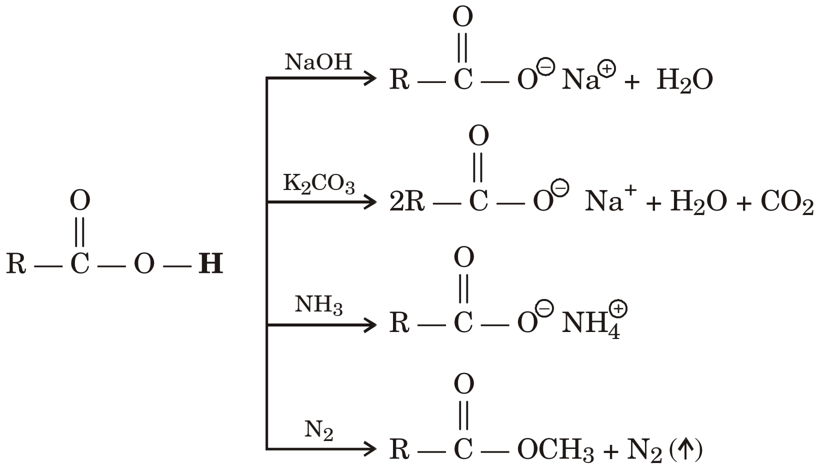
(1) Reactions due to H atom of – COOH group

(2) Reactions due to – OH part

(3) Reactions due to – COOH group

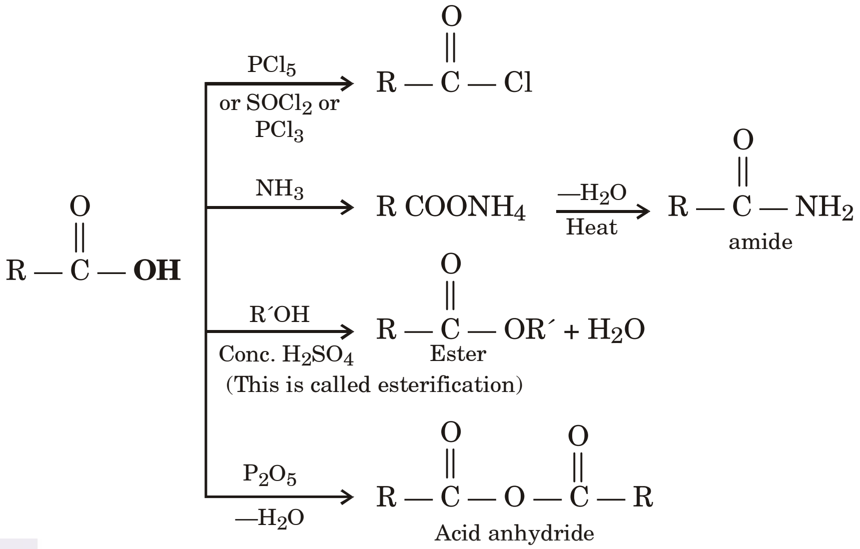
(4) Reactions due to R-part

I. Reactions due to H atom of – COOH part



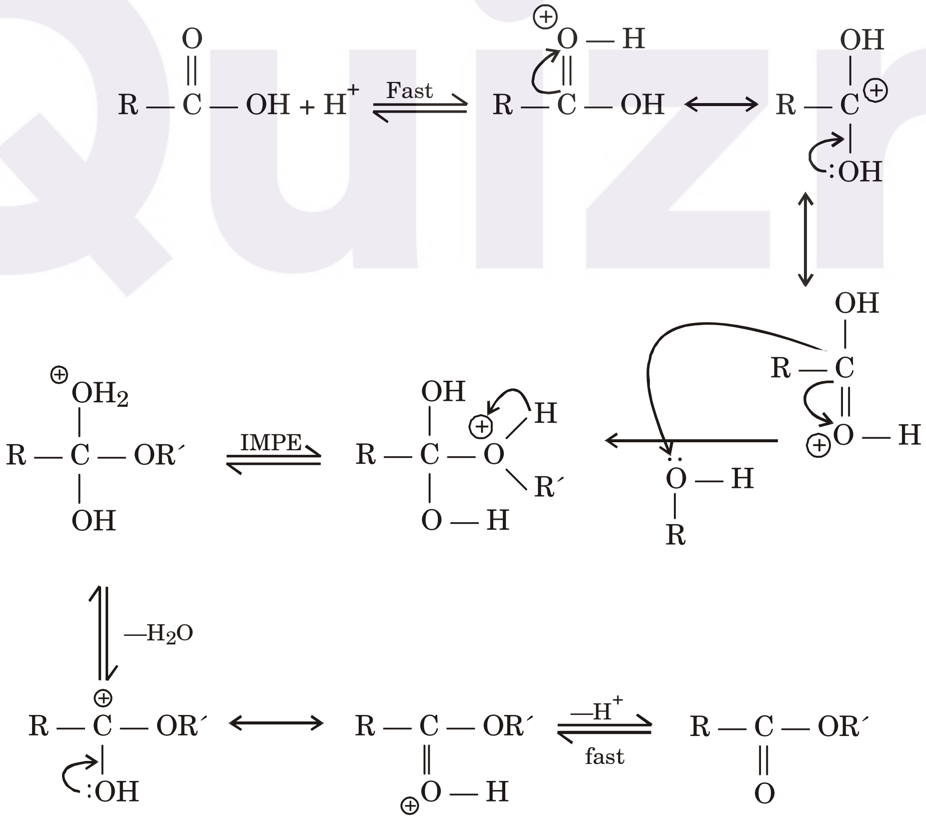
$$R-\overset{\overset{\displaystyle O}{\|}}{C}-O-\mathbf{H}\ \begin{cases}\xrightarrow{NaOH} R-\overset{\overset{\displaystyle O}{\|}}{C}-O^{\ominus}Na^{\oplus}+H_2O\\ \xrightarrow{K_2CO_3} 2R-\overset{\overset{\displaystyle O}{\|}}{C}-O^{\ominus}\ Na^{+}+H_2O+CO_2\\ \xrightarrow{NH_3} R-\overset{\overset{\displaystyle O}{\|}}{C}-O^{\ominus}NH_4^{\oplus}\\ \xrightarrow{N_2} R-\overset{\overset{\displaystyle O}{\|}}{C}-OCH_3+N_2(\uparrow)\end{cases}$$

II. Reaction due to – OH group



Mechanism of esterification by acid catalysis

A direct reaction between a carboxylic acid and alcohol under the catalytic effect of sulphuric acid yields an ester. This is a reversible reaction.



- The reactivity of esterification decreases with increase in crowding of alkyl groups around – OH among alcohols and around – COOH among acids. For example,

$$CH_3\ OH > C_2H_5OH > (CH_3)_2\ CHOH > (CH_3)\ COH$$

Also, $$HCOOH > CH_3COOH > (CH_3)\ CHCOOH$$

- The reactivity of aromatic acids towards esterification decreases with increase in the number of alkyl substituents at ortho position.

III. Reaction involving complete – COOH group

(1) **Soda lime decarboxylation :** Sodium or potassium salts of carboxylic acids on heating with soda lime (NaOH and CaO) give alkanes with one carbon less than the parent acids.

$$\underset{\text{Sodium salt of acid}}{RCOONa} + NaOH \xrightarrow{CaO} \underset{\text{alkane}}{R - H} + Na_2CO_3$$

(2) Reduction

$$R\ COOH \xrightarrow{LiAlH_4} R\ CH_2OH$$

(3) Reaction with hydrazoic acid (HN_3)

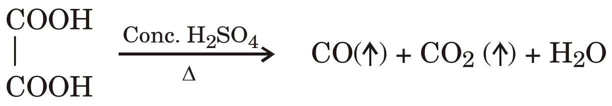
$$R - \overset{\overset{O}{||}}{C} - OH + HN_3 \xrightarrow{H_2SO_4} R - NH_2 + CO_2 + N_2$$

(4) Brominative decarboxylation (Hunsdicker reaction)

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

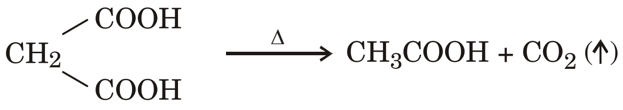
(5) Heating of dicarboxylic acids :

(a)



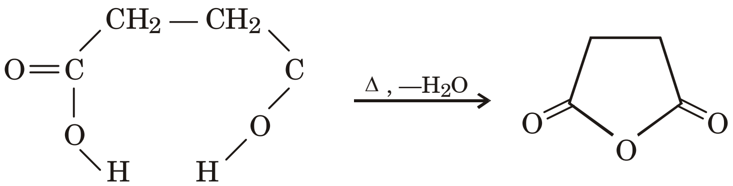
$$\begin{matrix} COOH \\ | \\ COOH \end{matrix} \xrightarrow[\Delta]{\text{Conc. } H_2SO_4} CO(\uparrow) + CO_2\ (\uparrow) + H_2O$$

(b)



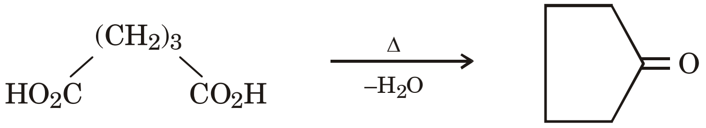
$$CH_2\begin{matrix} \diagup COOH \\ \diagdown COOH \end{matrix} \xrightarrow{\Delta} CH_3COOH + CO_2\ (\uparrow)$$

(c)



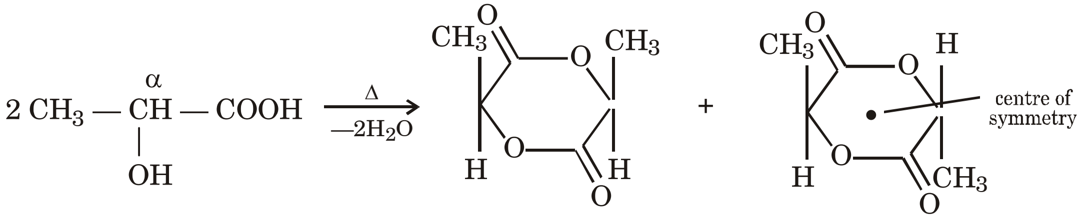
Succinic acid

Succinic anhydride

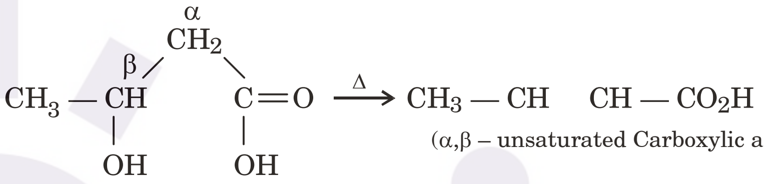
(d) 

Cyclopentanone

(6) Heating of α, β and γ-hydroxy Carboxylic acids

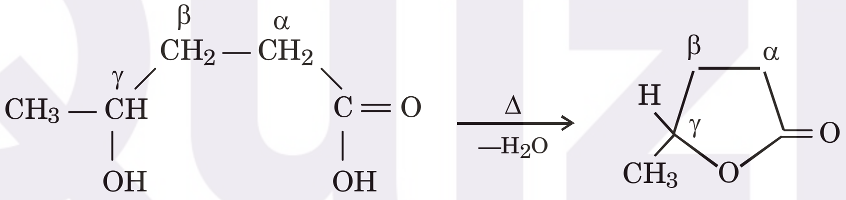
(i) 

Cis — Lactide (racemic)   trans – lactide (Meso)

(ii) 

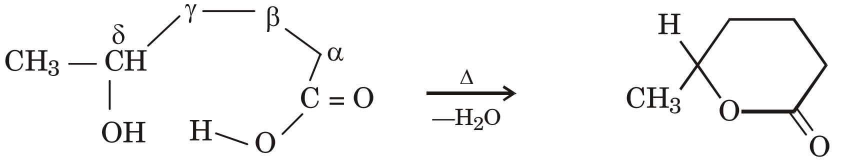
(β–hydroxy acid)

(α,β – unsaturated Carboxylic acid)

(iii) 

γ – hydroxy acid

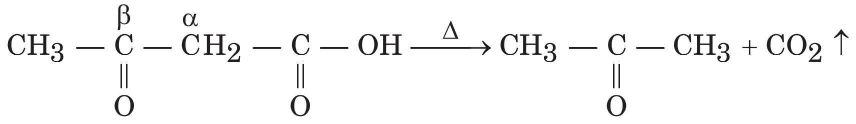
5 – Methyl – γ – butyrolactone
or pentano – 4 – Lactone

(iv) 

δ – hyrdroxy acid

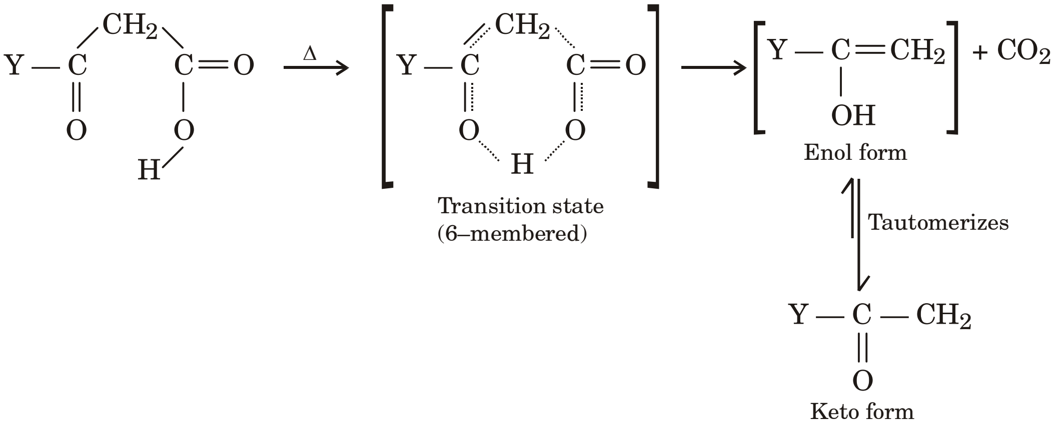
6 – methyl – δ – valero lactone
or Hexano – 5 – Lactone

7. **Decarboxylation :** β-keto acids on slightest warming alone or in presence of a base undergoes ready loss of CO_2. The process of loss of CO_2 is called "decarboxylation". For example,

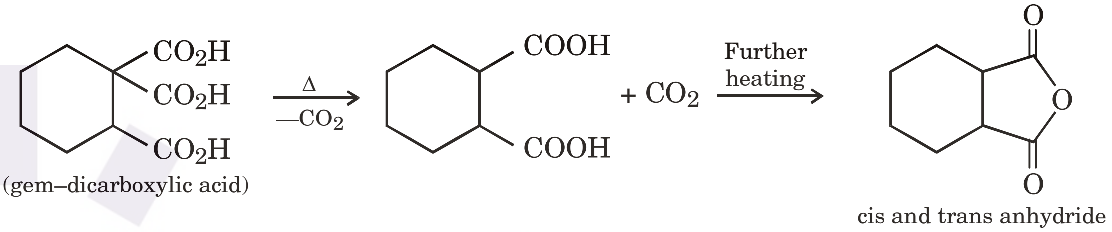


$$CH_3-\overset{\beta}{\underset{\underset{O}{\|}}{C}}-\overset{\alpha}{C}H_2-\underset{\underset{O}{\|}}{C}-OH\xrightarrow{\Delta}CH_3-\underset{\underset{O}{\|}}{C}-CH_3+CO_2\uparrow$$

Mechanism :



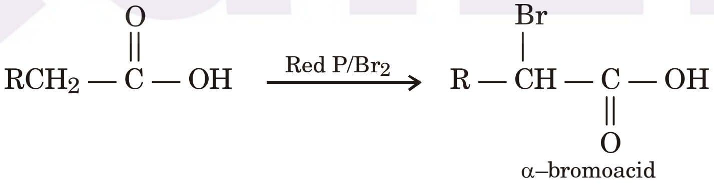
Here Y can be substituents like CH_3, OH etc.



IV. Reactions involving R-Part

(1) Hell-Volhard Zelinsky (HVZ) reaction

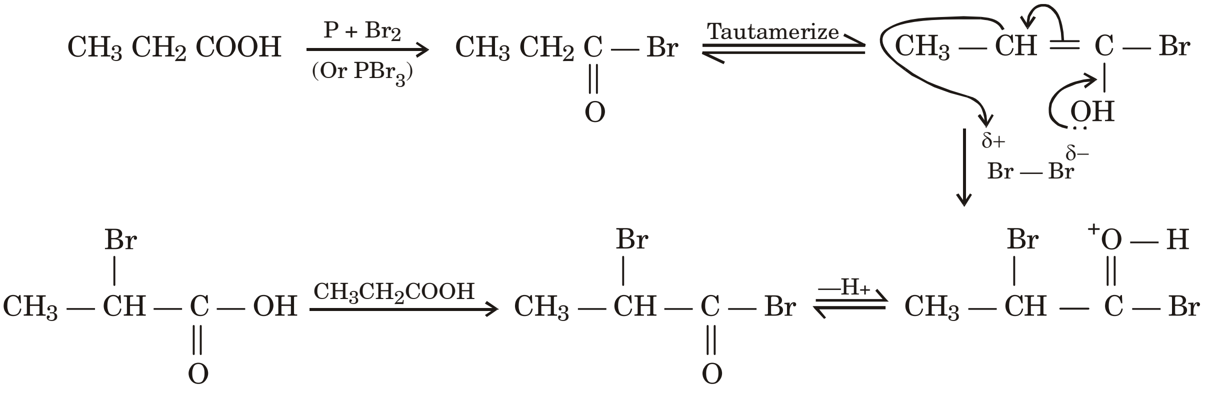
It is also the α-Halogenation of aliphatic acids. When carboxylic acids are treated with Cl_2 or Br_2 in presence of red phosphorus, the α-hydrogen atoms of carboxylic acids are replaced by chlorine or bromine.



$$RCH_2-\overset{\overset{O}{\|}}{C}-OH \xrightarrow{\text{Red P/Br}_2} R-\overset{\overset{Br}{|}}{CH}-\underset{\underset{O}{\|}}{C}-OH$$

α–bromoacid

Mechanism :



Example 13

Acetic acid can be halogenated in presence of phosphorus and chlorine but formic acid cannot be halogenated in the same way.

Solution :

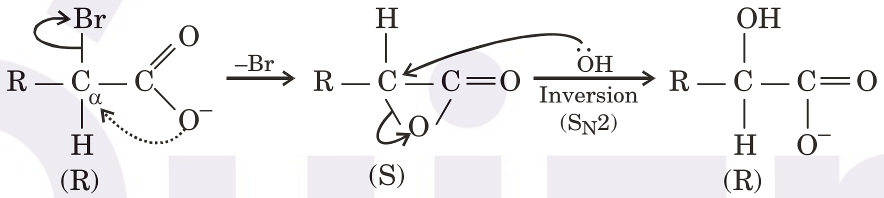
This is HVZ reaction. It occurs only in those carboxylic acids which have α-hydrogen atoms. Acetic acid possesses three α-hydrogen atoms but formic acid does not have even a single α-hydrogen atom. Thus, formic acid does not undergo this reaction.

Example 14

Predict the stereochemistry at α–C for β–bromo acid (optically active) when treated with NaOH.

Solution :

The configuration (if chiral carbon) at α–carbon remains same i.e. reaction proceeds with retenition of configuration.

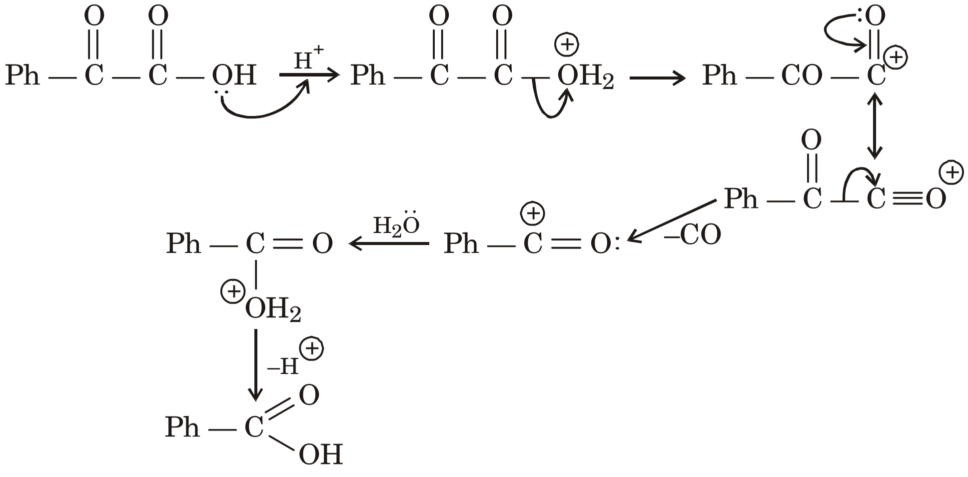


Example 15

Write possible mechanism for the given reaction.

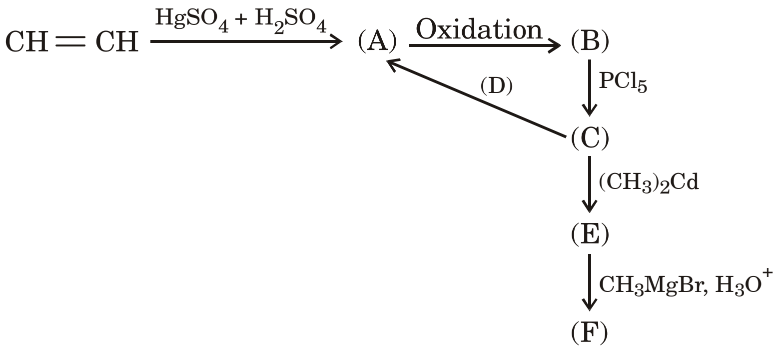
$$\text{Ph — COCOOH} \xrightarrow{H^+} \text{PhCOOH + CO}$$

Solution :



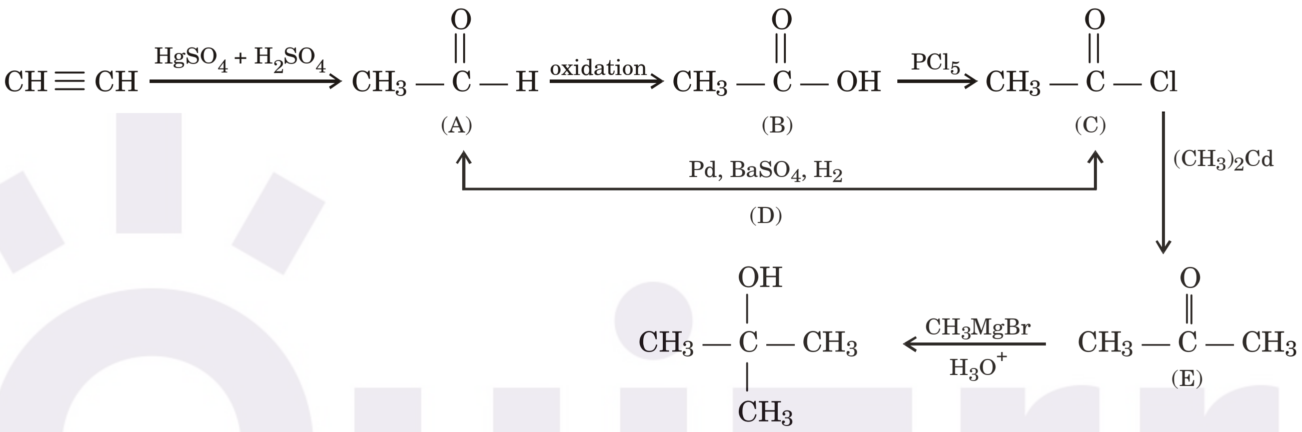
Example 16

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



$$\begin{tikzcd} CH = CH \arrow[r, "HgSO_4 + H_2SO_4"] & (A) \arrow[r, "Oxidation"] & (B) \arrow[d, "PCl_5"] \\ & & (C) \arrow[ul, "(D)"] \arrow[d, "(CH_3)_2Cd"] \\ & & (E) \arrow[d, "CH_3MgBr,\ H_3O^+"] \\ & & (F) \end{tikzcd}$$

Solution :



$$CH \equiv CH \xrightarrow{HgSO_4 + H_2SO_4} \underset{(A)}{CH_3 - \overset{\overset{O}{\|}}{C} - H} \xrightarrow{oxidation} \underset{(B)}{CH_3 - \overset{\overset{O}{\|}}{C} - OH} \xrightarrow{PCl_5} \underset{(C)}{CH_3 - \overset{\overset{O}{\|}}{C} - Cl}$$

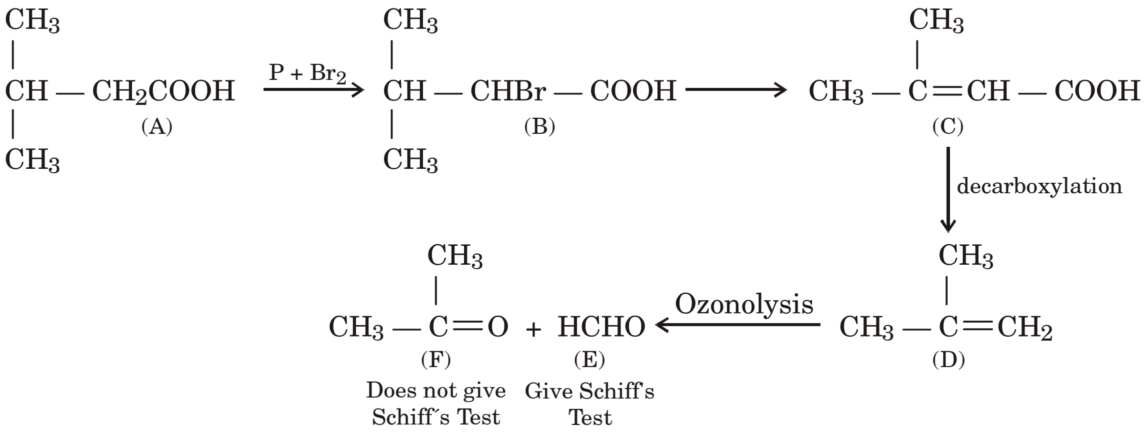
$$(C) \xrightarrow[(D)]{Pd,\ BaSO_4,\ H_2} (A)$$

$$(C) \xrightarrow{(CH_3)_2Cd} \underset{(E)}{CH_3 - \overset{\overset{O}{\|}}{C} - CH_3} \xrightarrow[H_3O^+]{CH_3MgBr} CH_3 - \overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}} - CH_3$$

Example 17

An organic acid (A), $C_5H_{10}O_2$ reacts with Br_2 in the presence of phosphorus to give (B). Compound (B) contains an asymmetric carbon atom and yields (C) on dehydrobromination. Compound (C) does not show geometric isomerism and on decarboxylation gives as alkene (D) which on ozonolysis gives (E) and (F). Compound (E) gives a positive Schiffs test but (F) does not. Give structures of (A) to (F) with reasons.

Solution :



$$\underset{(A)}{\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{CH}} - CH_2COOH} \xrightarrow{P + Br_2} \underset{(B)}{\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{CH}} - CHBr - COOH} \longrightarrow \underset{(C)}{CH_3 - \overset{\overset{CH_3}{|}}{C} = CH - COOH}$$

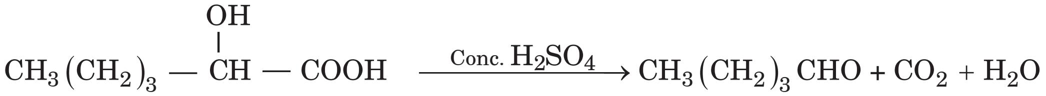
$$(C) \xrightarrow{decarboxylation} \underset{(D)}{CH_3 - \overset{\overset{CH_3}{|}}{C} = CH_2} \xrightarrow{Ozonolysis} \underset{(F)}{CH_3 - \overset{\overset{CH_3}{|}}{C} = O} + \underset{(E)}{HCHO}$$

Example 18

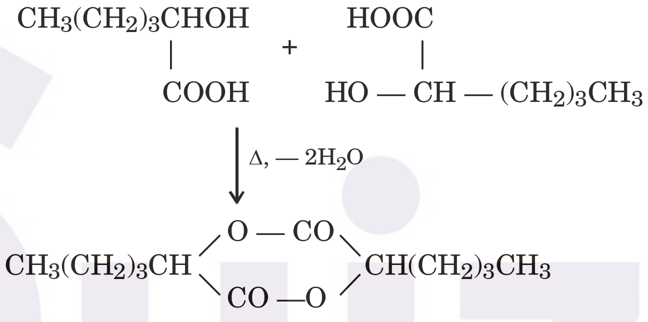
An organic compound (A) $C_6H_{12}O_3$ on treatment with concentrated H_2SO_4 gives CO, H_2O and (B). Compound (B) can be prepared by passing vapours of 1–pentanol over heated copper at 570 K. Compound (A) on heating gives (C) $C_{12}H_{20}O_4$. Give structures of (A) to (C) with proper reasoning.

Solution :

$$CH_3(CH_2)_3\ CH_2OH \xrightarrow[570\text{ K}]{\text{Cu}} CH_3(CH_2)_3-CHO + H_2O$$



$$CH_3(CH_2)_3-\overset{\displaystyle OH}{\overset{|}{CH}}-COOH \xrightarrow{\text{Conc. } H_2SO_4} CH_3(CH_2)_3CHO + CO_2 + H_2O$$

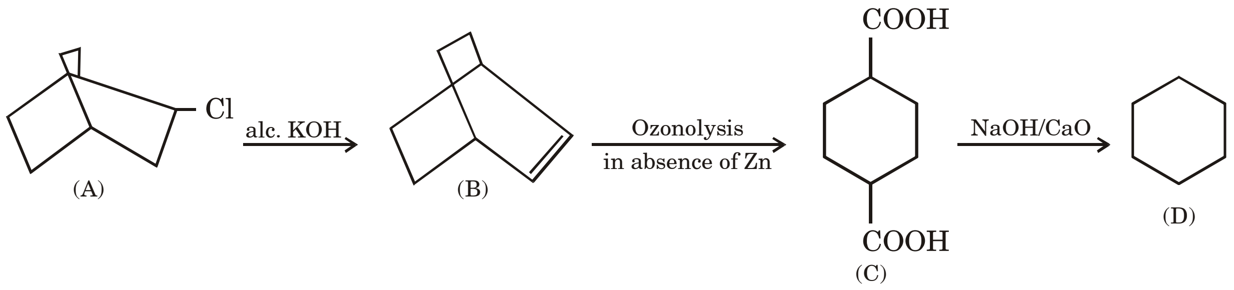


Lactide

Example 19

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

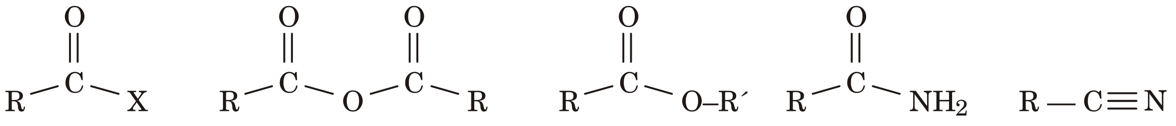
Solution :



CARBOXYLIC ACID DERIVATIVES

Carboxylic derivatives are described as compounds that can be converted to carboxylic acids via simple acidic or basic hydrolysis.

The most important acid derivatives are esters, amides and nitriles, although acid halides and anhydrides are also derivatives (really activated forms of a carboxylic acid).



acid halide $RCOX$

anhydride $(RCO)_2O$

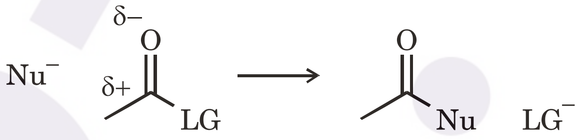
ester RCO_2R''

amide $RCONH_2$

nitrile RCN

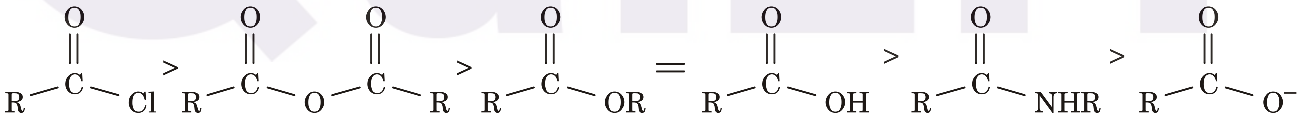
Reactivity of Carboxylic Acid Derivatives

Carboxylic acid derivatives react tend to react via Nucleophilic Acyl substitution where the group on the acyl unit, R-C=O undergoes substitution :



Study Tip : Note that unlike aldehydes and ketones, this reactivity of carboxylic acids retains the carbonyl group, C=O.

The observed reactivity order is shown below :



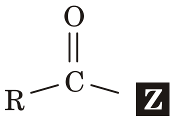
$$RCOCl > (RCO)_2O > RCOOR = RCOOH > RCONHR > RCOO^-$$

This reactivity order is important. You should be able to understand, rationalise and use it.

It is useful to view the carboxylic acid derivatives as an acyl group, R-C=O, with a different substituent attached.

The important features of the carboxylic acid derivatives that influences their reactivity are governed by this substituent in the following ways :

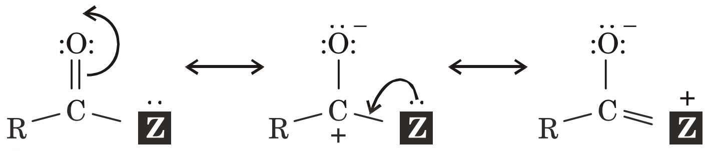
- the effect the substituent has on the electrophilicity of the carbonyl C



   - * if the substituent is electron donating, then the electrophilicity is reduced, ∴ less reactive.
   - * if the substituent is electron withdrawing, the electrophilicity is increased, ∴ more reactive.
- the ability of the substituent to function as a leaving group.

There are 3 resonance structures to consider for carboxylic acid derivatives.

I and **II** are similar to those of aldehydes and ketones, but there is also a third possibility **III** where a lone pair on the heteroatom Z is able to donate electrons to the adjacent positive center. The stronger this electron donation from Z the less positive the carbonyl C and the less electrophilic the carbonyl group. The ability of Z to donate electrons is linked to its electronegativity... the more electronegative Z is, the less the stabilising effect.



I II III

It is also useful to appreciate where aldehydes and ketones fit into the reactivity scale towards nucleophiles.

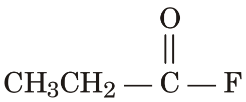
acyl halides > anhydrides > aldehydes > ketones > esters = carboxylic acids > amides

Acid Halides

Nomenclature

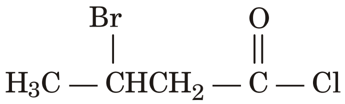
Acid halides are named by taking the -ic acid suffix of the related carboxylic acid, replacing it with -yl, and adding the halide name.

E.g.



$$CH_3CH_2-\overset{\overset{\large O}{\|}}{C}-F$$

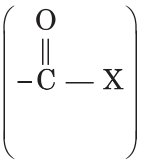
propanoyl fluoride



$$H_3C-\overset{\overset{\large Br}{|}}{C}HCH_2-\overset{\overset{\large O}{\|}}{C}-Cl$$

3–bromobutanoyl chloride

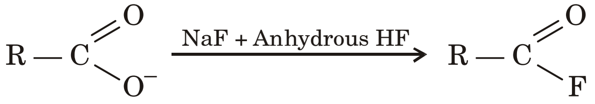
(a) Preparation of acid halides



$$\left(-\overset{\overset{\large O}{\|}}{C}-X\right)$$

(i) $R-COOH + SOCl_2 \longrightarrow RCOCl + SO_2\uparrow + HCl\uparrow$

(ii) $3R-COOH + PBr_3 \longrightarrow 3RCOBr + H_3PO_3$

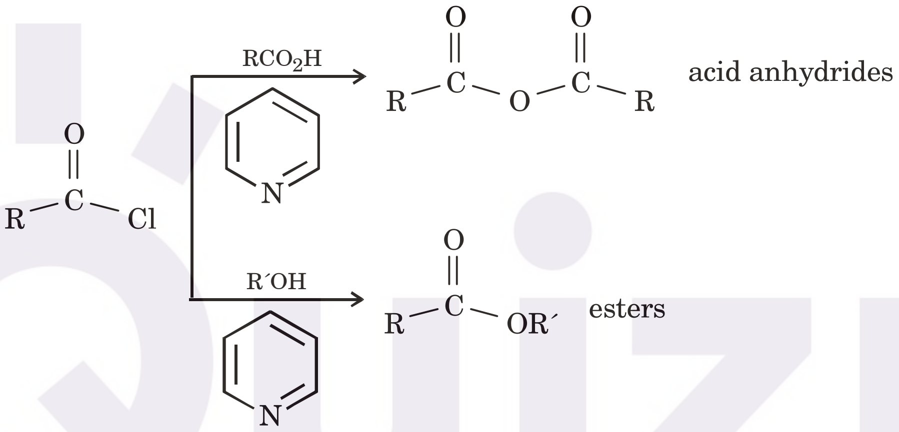
(iii)

$$R-C(=O)O^- \xrightarrow{NaF + \text{Anhydrous } HF} R-C(=O)F$$

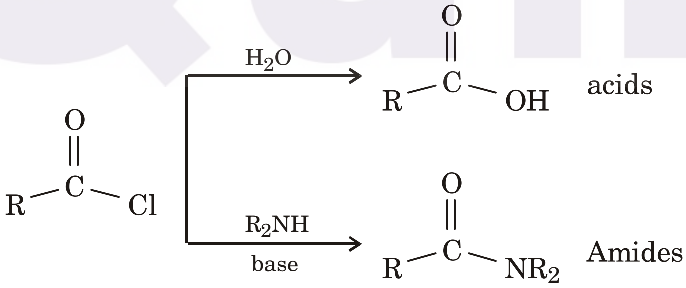
(iv) $RCOOH + PCl_5 \longrightarrow RCOCl + POCl_3 + HCl$

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

(b) Reactions of acid halides

(i) Interconversion Reactions of Acyl Chlorides



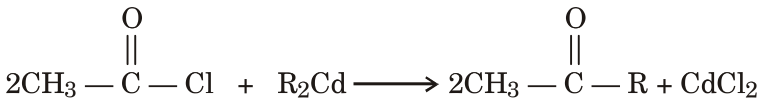


All are nucleophilic acyl substitution reaction

- Acyl chlolrides are the most reactive of the carboxylic acid derivatives and therefore can be readily converted into other carboxylic acid derivatives (see above).
- They are sufficiently reactive that they react quite readily with cold water and hydrolyse to the carboxylic acid.
- The HCl by-product is usually removed by adding a base such as pyridine or triethyl amine.

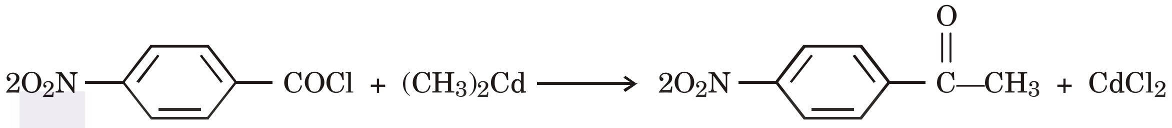
(ii) **Formation of ketones :** Alkyl Grignard reagent react with anhydrous cadmium chloride, $CdCl_2$ to form a dialkylcadmium compound, R_2Cd. This intermediate, on reaction with an acyl chloride, yields a ketone. Organo cadmium compounds are less reactive than Grignard reagents and are thus more selective in their attack as nucleophiles.

$$2R - MgX + CdCl_2 \longrightarrow R_2Cd + 2MgXCl$$



$$2CH_3 - \overset{\overset{\displaystyle O}{\|}}{C} - Cl + R_2Cd \longrightarrow 2CH_3 - \overset{\overset{\displaystyle O}{\|}}{C} - R + CdCl_2$$

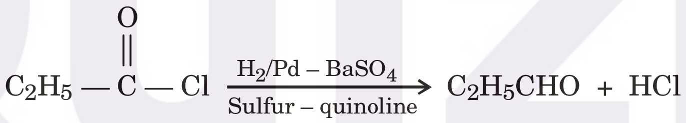
Both aliphatic and aromatic ketones can be prepared in this matter.



p–Nitrobenzoyl chloride

p–Nitroacetophenone

(iii) **Rosenmund Reduction :** This reaction requires hydrogen and Pd, which is a catalyst, adsorbed on $BaSO_4$ and a catalytic poison like quinoline to slow down the reaction. The result is the formation of an aldehyde. If the given catalytic poison is not employed the product would have been a primary alcohol.



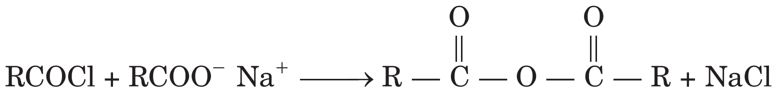
$$C_2H_5 - \overset{\overset{\displaystyle O}{\|}}{C} - Cl \xrightarrow[\text{Sulfur – quinoline}]{H_2/Pd - BaSO_4} C_2H_5CHO + HCl$$

Acid Hydrazides

ROCl on treatment with hydrazine yields acid hydrazides.

$$RCOCl + 2NH_2 - NH_2 \longrightarrow RCONH\,NH_2 + NH_2\,NH_3^+\,Cl^-$$

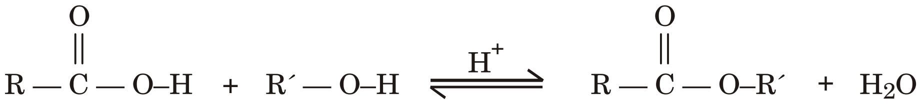
The acid halide, on treating with the salt of corresponding acid, yields an anhydride.



$$RCOCl + RCOO^-\,Na^+ \longrightarrow R - \overset{\overset{\displaystyle O}{\|}}{C} - O - \overset{\overset{\displaystyle O}{\|}}{C} - R + NaCl$$

Esters

These are derivatives of carboxylic acids where the hydroxyl group is replaced by an alkoxy group.



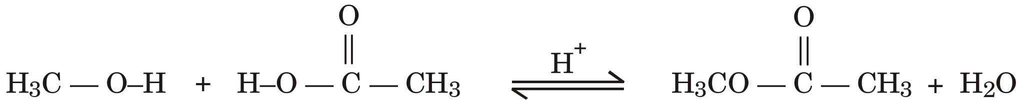
$$R-\overset{\overset{\displaystyle O}{\|}}{C}-O\text{–}H + R'-O\text{–}H \overset{H^+}{\rightleftharpoons} R-\overset{\overset{\displaystyle O}{\|}}{C}-O\text{–}R' + H_2O$$

Nomenclature

The names of esters are derived from the names of the compounds that are used to create them.

The first word of the name comes from the alkyl group of the alcohol, and the second part comes from the carboxylate group of the acid used.

E.g.

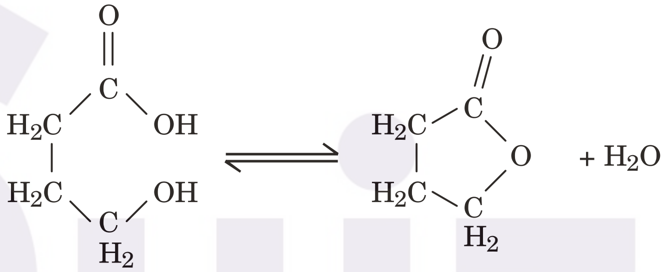


$$H_3C-O\text{–}H + H\text{–}O-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \overset{H^+}{\rightleftharpoons} H_3CO-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + H_2O$$

methanol ethnoic acid methyl ethanoate

A cyclic ester is called a lactone, and IUPAC names of lactones are derived by adding the term lactone at the end of the name of the parent carboxylic acid it came from.

E.g.

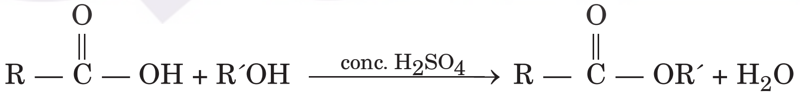


4–hydroxybutanoic acid

4–hydroxybutanoic acid lactone

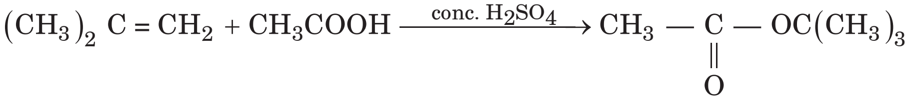
Preparation :

(i)



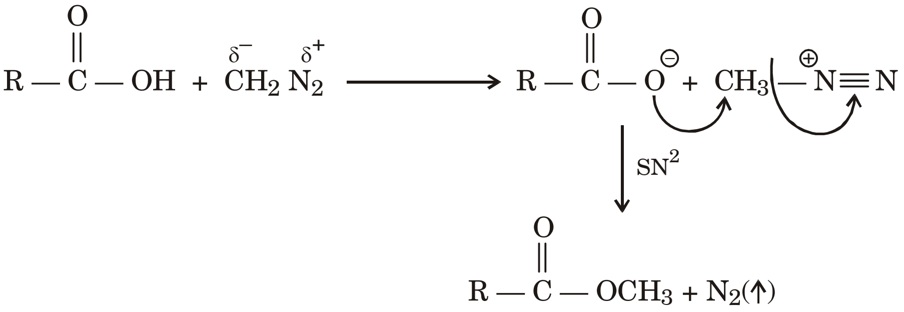
$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH + R'OH \xrightarrow{\text{conc. } H_2SO_4} R-\overset{\overset{\displaystyle O}{\|}}{C}-OR' + H_2O$$

(ii)



$$(CH_3)_2\,C=CH_2 + CH_3COOH \xrightarrow{\text{conc. } H_2SO_4} CH_3-\underset{\underset{\displaystyle O}{\|}}{C}-OC(CH_3)_3$$

(iii)



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH + \overset{\delta^-}{CH_2}\,\overset{\delta^+}{N_2} \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\ominus}{O} + CH_3-\overset{\oplus}{N}\equiv N \xrightarrow{SN^2} R-\overset{\overset{\displaystyle O}{\|}}{C}-OCH_3 + N_2(\uparrow)$$

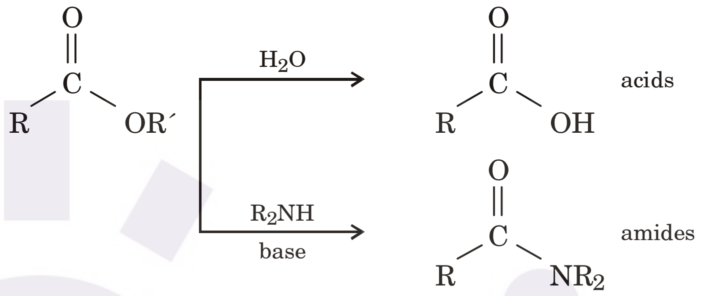
(iv) **Transesterification :** This is basically a process called as “alcoholysis”. This is carried out by refluxing the ester with large excess of alcohol, preferably in the presence of small amount of acid or sodium alkoxide as catalyst.

$$CH_3\ COO\ C_4H_9 + C_2H_5OH \xrightleftharpoons{C_2H_5O^{\ominus}\ NO^{\oplus}} CH_3CO_2C_2H_5 + C_4H_9OH$$

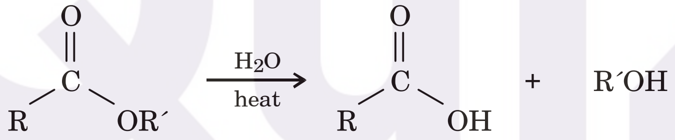
This is usually effective in replacing a higher alcohol by a lower one.

REACTIONS :

(1) Interconversion Reactions of Esters



(2) Hydrolysis of Ester



- Carboxylic esters hydrolyse to the parent carboxylic acid and an alcohol.
- Reagents : aqueous acid (e.g. H_2SO_4) / heat, or aqueous NaOH/heat (known as “saponification”).
- Both are based on the formation of a tetrahedral intermediate which then dissociates.
- In both cases it is the C-O bond between the acyl group and the oxygen that is cleaved.

Reaction under Basic conditions :

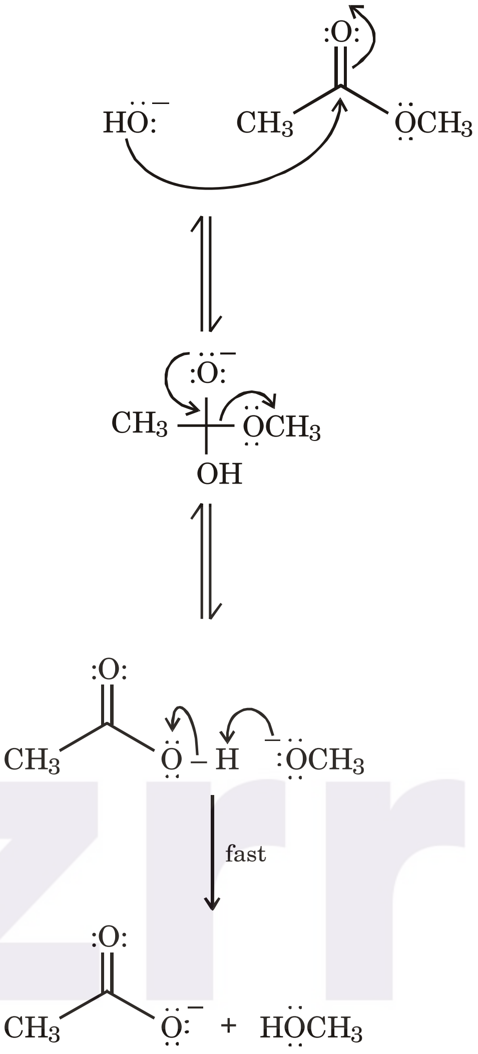
- The mechanism shown below leads to acyl-oxygen cleavage
- This reaction is known as “saponification” because it is the basis of making soap from glycerol triestsers in fats.

Mechanism of the base hydrolysis of Esters

Step 1 : The hydroxide nucleophiles attacks at the electrophilic C of the ester C = O, breaking the π bond and creating the tetrahedral intermediate.

Step 2 : The intermediate collapses, reforming the C = O results in the loss of the leaving group the alkoxide, leading to the carboxylic acid.

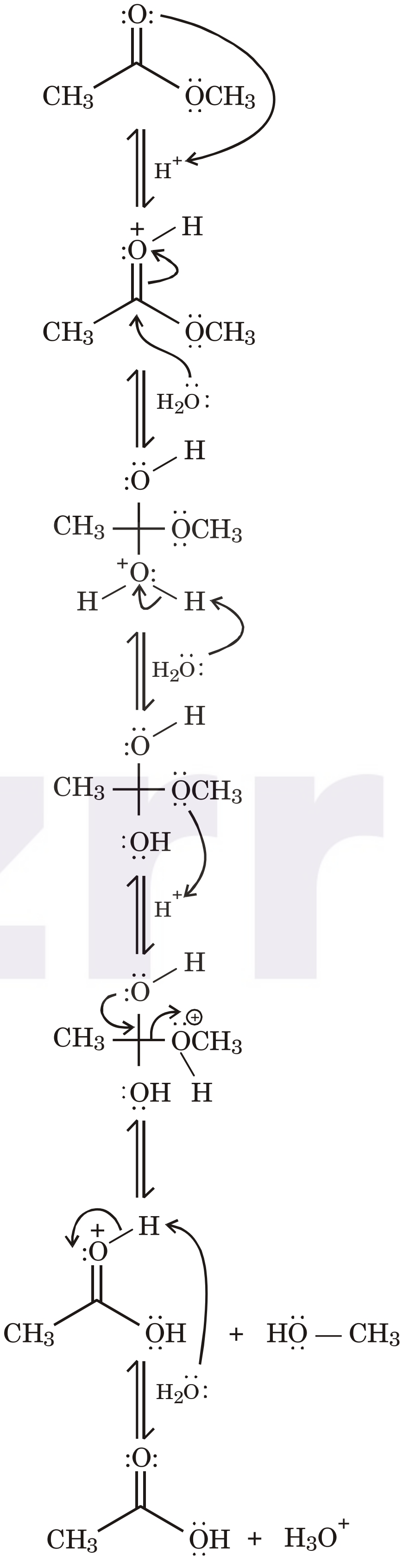
Step 3 : An acid/base reaction. A very rapid equilibrium where the alkoxide functions as a base deprotonating the carboxylic acid (an acidic work up would allow the carboxylic acid to be obtained from the reaction).



Reaction under Acidic conditions :

- Note that the acid catalysed mechanism is the reverse of the Fischer esterification.
- The mechanism shown below also leads to acyl-oxygen cleavage

Mechanism of the Acid Catalysed Hydrolysis of Esters



Step 1 **:** An acid/base reaction. Since we only have a weak nucleophile and a poor electrophile we need to activate the ester. Protonation of the ester carbonyl makes it more electrophilic.

Step 2 **:** The water O functions as the nucleophile attacking the electrophilic C in the C = O, with the electrons moving towards the oxonium ion, creating the tetrahedral intermediate.

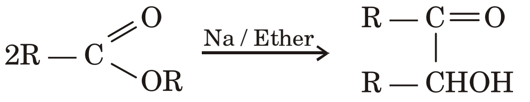
Step 3 **:** An acid/base reaction. Deprotonate the oxygen that came from the water molecule.

Step 4 **:** An acid/base reaction. Need to make the $-OCH_3$ leave, but need to convert it into a good leaving group first by protonation.

Step 5 **:** Use the electrons of an adjacent oxygen to help "push out" the leaving group, a neutral methanol molecule.

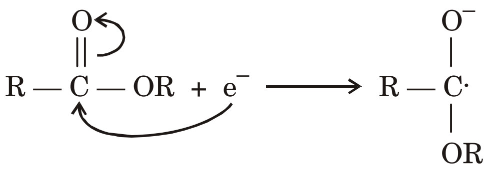
Step 6 **:** An acid/base reaction. Deprotonation of the oxonium ion reveals the carbonyl in the carboxylic acid product and regenerates the acid catalyst.

(3) Acyloin condensation

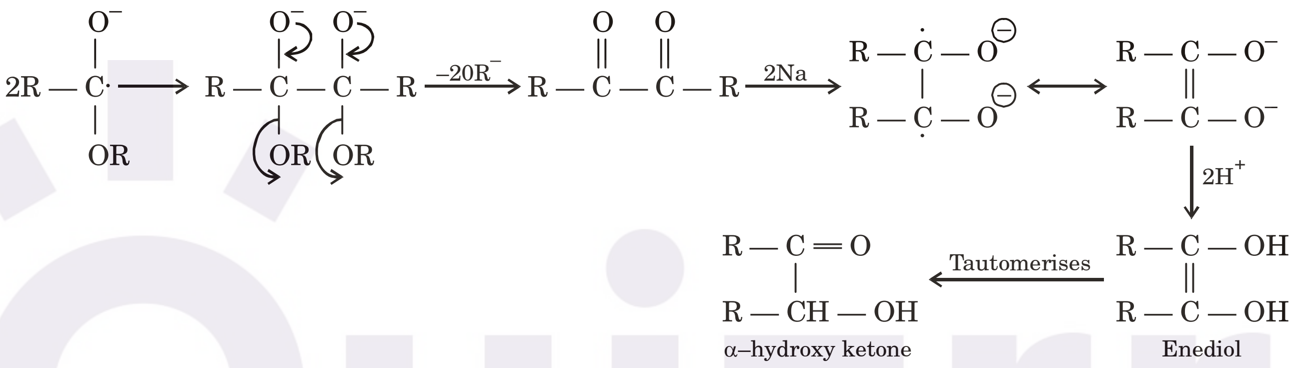


(α – hydroxy ketone)

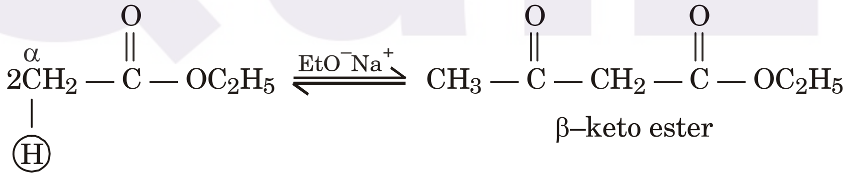
$$Na \longrightarrow Na^+ + e^-$$



(Radical anion)



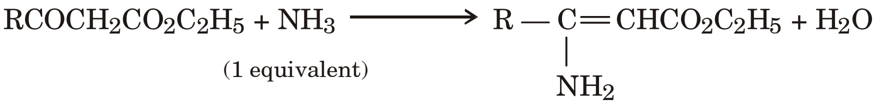
(4) Claisen ester condensation



$$2\overset{\alpha}{C}H_2-\overset{O}{\overset{\|}{C}}-OC_2H_5 \xrightleftharpoons{EtO^-Na^+} CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OC_2H_5$$

β–keto ester

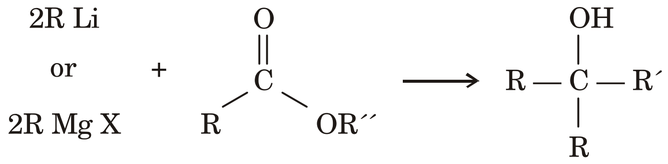
(5) Reaction of NH_3 with ester and keto ester



$$RCOCH_2CO_2C_2H_5 + NH_3 \longrightarrow \underset{NH_2}{\underset{|}{R-C}}=CHCO_2C_2H_5 + H_2O$$

(1 equivalent)

(6) Reactions of RLi and RMgX with Esters



Reaction usually in Et_2O followed by H_3O^+ work-up

- Carboxylic esters, $R'CO_2R''$, react with 2 equivalents of organolithium or Grignard reagents to give tertiary alcohols.
- The tertiary alcohol that results contains 2 identical alkyl groups (from R in the scheme)
- The reaction proceeds via a ketone intermediate which then reacts with the second equivalent of the organometallic
- Since the ketone is more reactive than the ester, the reaction cannot be used as a preparation of ketones
- The mechanism is an example of the reactive system type.

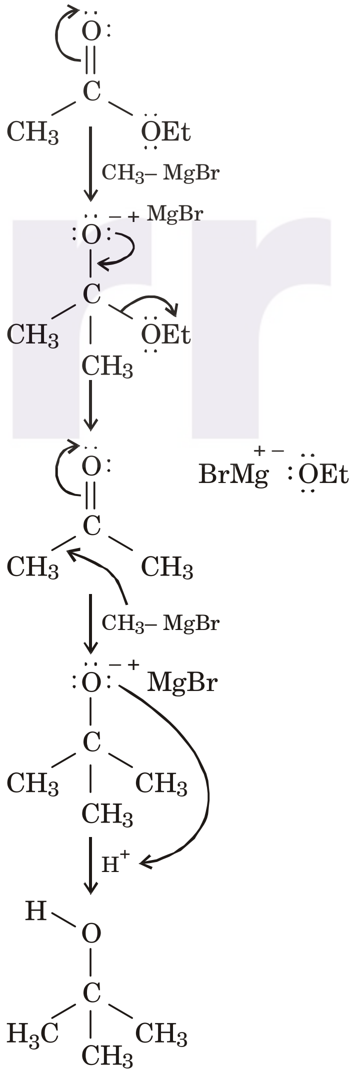
Reaction of RMgX with Ester

Step 1 : The nucleophilic C in the organometallic reagent adds to the electrophilic C in the polar carbonyl group of the ester. Electrons from the C = O move to the electronegative O creating an intermediate metal alkoxide complex.

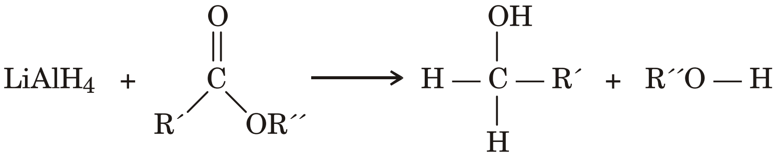
Step 2 : The tetrahedral intermediate collapses and displaces the alcohol portion of the ester as a leaving group, this produces a ketone as an intermediate.

Step 3 : The nucleophilic C in the organometallic reagent adds to the electrophilic C in the polar carbonyl group of the ketone. Electrons from the C = O move to the electronegative O creating an intermediate metal alkoxide complex.

Step 4 : This is the work-up step, a simple acid/base reaction. Protonation of the alkoxide oxygen creates the alcohol product from the intermediate complex.

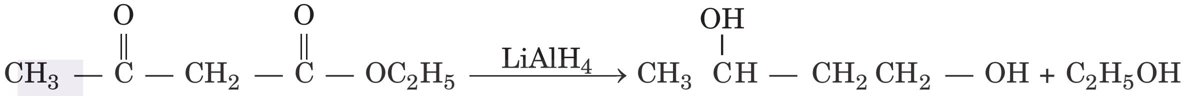


(7) Reduction of Esters



- Carboxylic esters are reduced give 2 alcohols, one from the alcohol portion of the ester and a 1 alcohol from the reduction of the carboxylate portion.
- Esters are less reactive towards Nu than aldehydes or ketones.
- They can only be reduced by $LiAlH_4$ and **Not** by the less reactive $NaBH_4$.

For example :

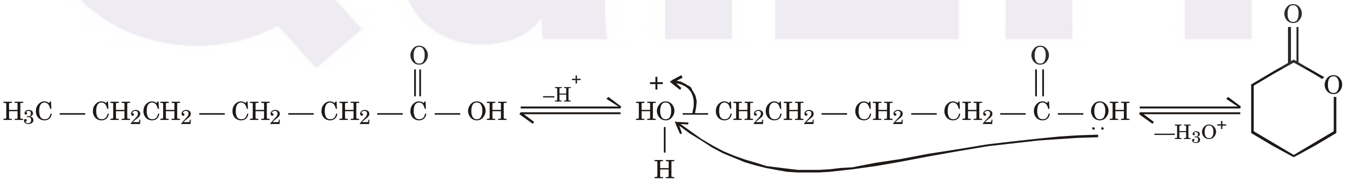


$$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OC_2H_5 \xrightarrow{LiAlH_4} CH_3\ \overset{OH}{\overset{|}{C}}H-CH_2\,CH_2-OH+C_2H_5OH$$

Example 20

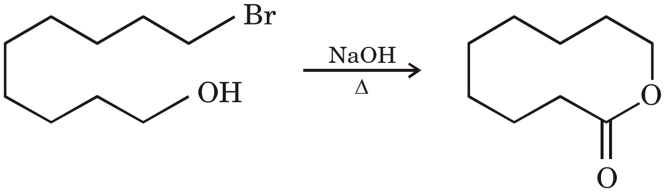
Propose mechanism of the following esterfication reaction :

Solution :



Example 21

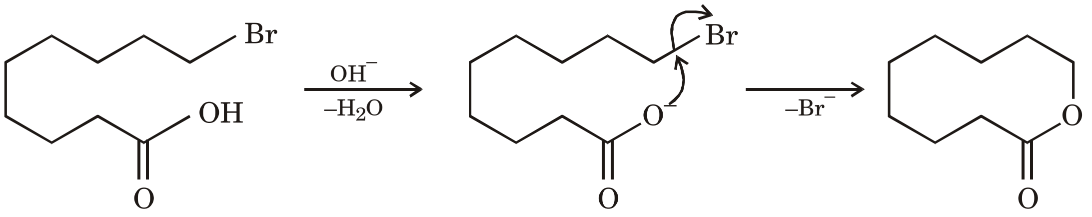
(a) Write a mechanism of the following reaction.



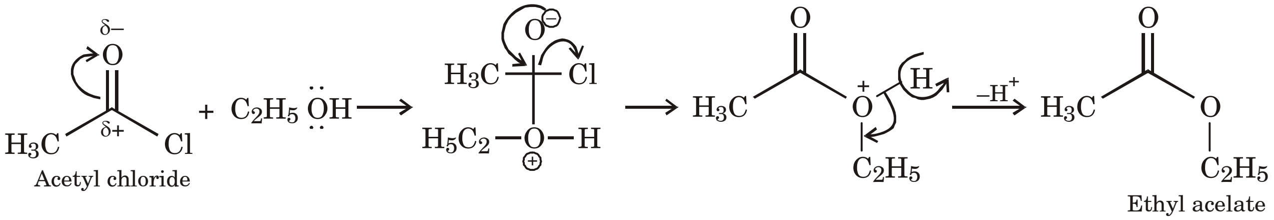
(b) Give the mechanism for the reaction of acetyl chloride with ethyl alcohol.

Solution :

(a)

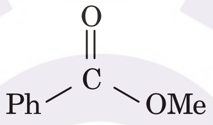


(b)

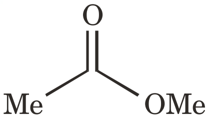


Example 22

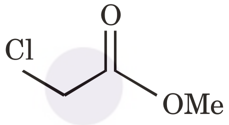
The order of reactivity of the following esters towards hydrolysis is



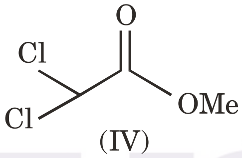
(I)



(II)



(III)



(IV)

(a) **(I) > (II) > (III) > (IV)**

(b) **(III) > (I) > (III) > (IV)**

(c) **(IV) > (III) > (II) > (I)**

(d) **(IV) > (III) > (I) > (II)**

Solution :

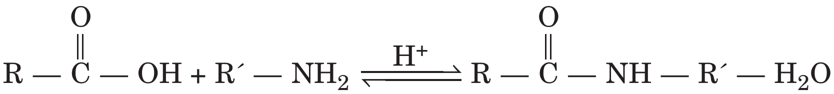
More are the electron withdrawing groups, more is the positive charge density on 'C' and more readily the attack can occur.

∴ (c)

Acid Amides

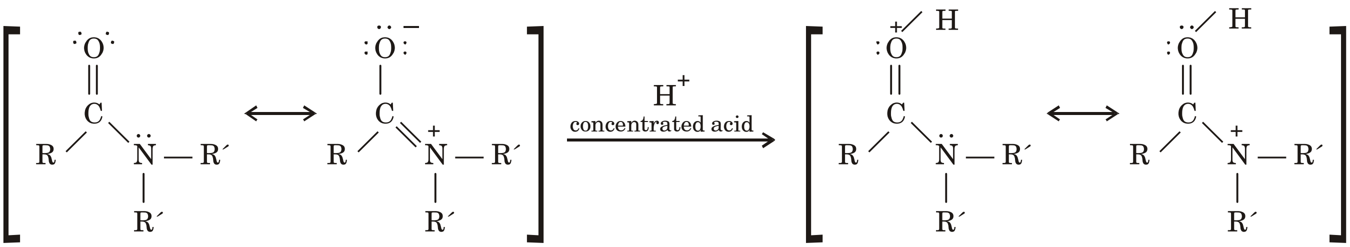
An amide is a composite of a carboxylic acid and an amine (or ammonia).

Heating the salt formed when an amine and carboxylic acid react drives off the water produced, and an amide is formed.



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH + R'-NH_2 \underset{}{\overset{H^+}{\rightleftharpoons}} R-\overset{\overset{\displaystyle O}{\|}}{C}-NH-R'-H_2O$$

Amides are much less basic than their parent amines since the lone pair of electrons on Nitrogen are delocalized onto the carbonyl oxygen.



very weakly basic

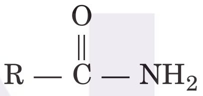
protonation on oxygen

In fact in strong acid, it is the oxygen that gets protonated first!

The C-N bond has partial double bond character, and the rotational barrier is 18 kcal/mol.

Amides of the form R-CO-NH_2 are called primary amides since the nitrogen is only bound to one carbon atom (like R-NH_2 is primary).

Amides that are of the form R-CO-NHR´ are called secondary amides, or N-substituted amides.

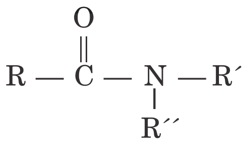


$R-\overset{O}{\overset{\|}{C}}-NH_2$

primary

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

secondary



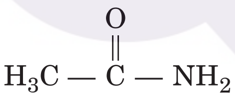
$R-\overset{O}{\overset{\|}{C}}-\underset{R''}{\underset{|}{N}}-R'$

tertiary

Amides of the form R-CO-NR_2 are tertiary amides, or N, N-disubstituted amides.

Nomenclature of Amides

To name a primary amide, identify the acid part and remove the -oic acid suffix and add amide. E.g.



$H_3C-\overset{O}{\overset{\|}{C}}-NH_2$

ethanamide

$H_3C-\overset{O}{\overset{\|}{C}}-NH-CH_2CH_3$

N-ethylethanamide

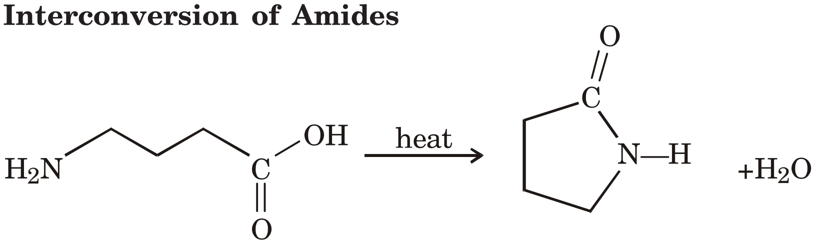
$H-\overset{O}{\overset{\|}{C}}-N(CH_3)_2$

N, N-dimethylmethanamide

To name a secondary or tertiary amide, the alkyl groups on nitrogen are treated as substituents, and are given the prefix N (since they are the nitrogen).

Reactions :

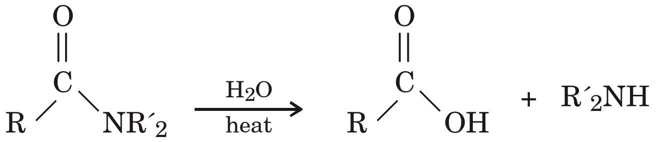
(1) Interconversion of Amides



4-aminobutanoic acid

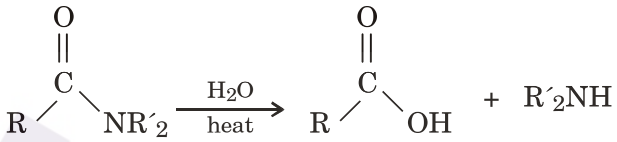
4-aminobutanoic acid lactam

They are named by adding the word lactam to the correct IUPAC name of the parent acid.

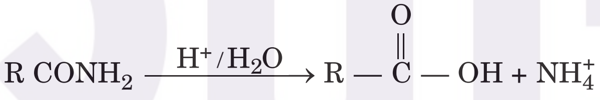


- Amides are the least reactive of the neutral carboxylic acid derivatives.
- The only interconversion reaction that amides undergo is hydrolysis back to the parent carboxylic acid and the amine.
- Reagents : Strong acid (e.g. H_2SO_4) or strong base (e.g. NaOH) / heat

(2) Hydrolysis of Amides



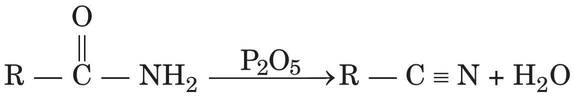
- Amides hydrolyse to the parent carboxylic acid and the appropriate amine.
- The mechanisms are similar to those of esters.
- Reagents : Strong acid (e.g. H_2SO_4)/heat (preferred) or strong base (e.g. NaOH)/heat.



$$R\,CONH_2 \xrightarrow{H^+/H_2O} R-\overset{\overset{\displaystyle O}{\|}}{C}-OH + NH_4^+$$

$$R\,CONH_2 \xrightarrow{OH^-/H_2O} R-COO^- + NH_3$$

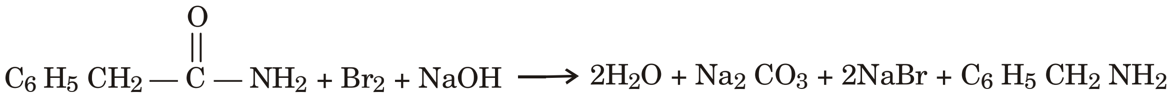
(3) Dehydration



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 \xrightarrow{P_2O_5} R-C\equiv N + H_2O$$

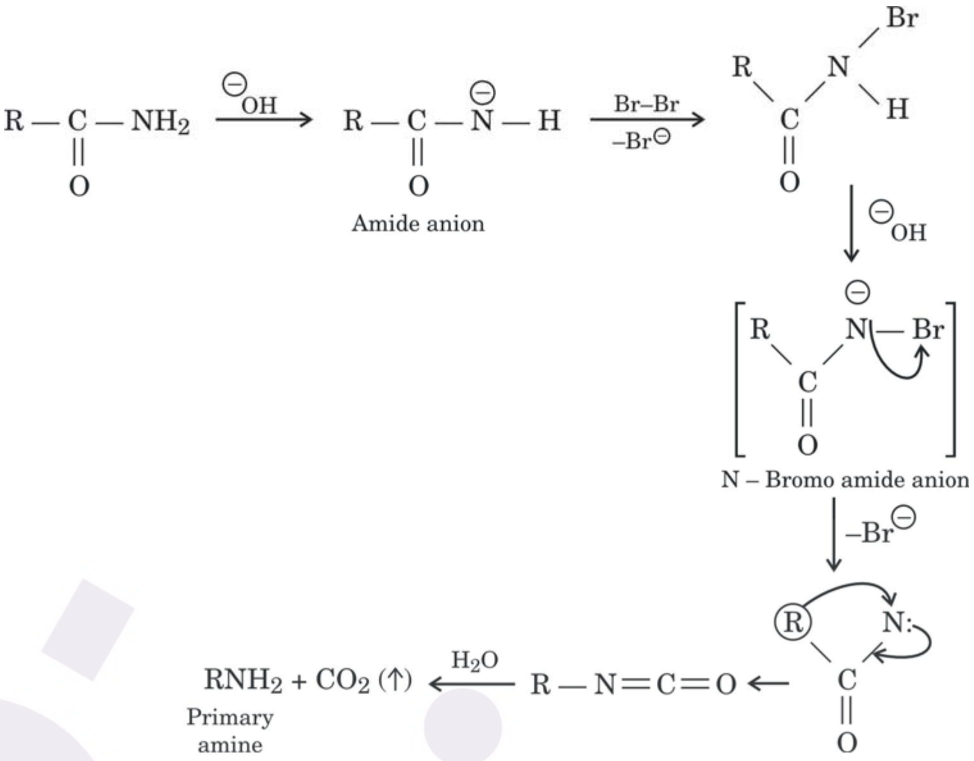
(4) Hoffmann Degradation Reaction

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



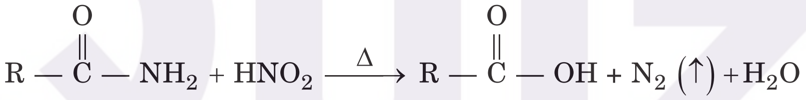
$$C_6H_5CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 + Br_2 + NaOH \longrightarrow 2H_2O + Na_2CO_3 + 2NaBr + C_6H_5CH_2NH_2$$

Mechanism :



$$R-C(=O)-NH_2 \xrightarrow{\overset{\ominus}{O}H} R-C(=O)-\overset{\ominus}{N}-H \xrightarrow[-Br^{\ominus}]{Br-Br} RC(=O)NHBr \xrightarrow{\overset{\ominus}{O}H} \left[RC(=O)\overset{\ominus}{N}-Br\right] \xrightarrow{-Br^{\ominus}} RC(=O)\ddot{N} \longrightarrow R-N=C=O \xrightarrow{H_2O} RNH_2 + CO_2(\uparrow)$$

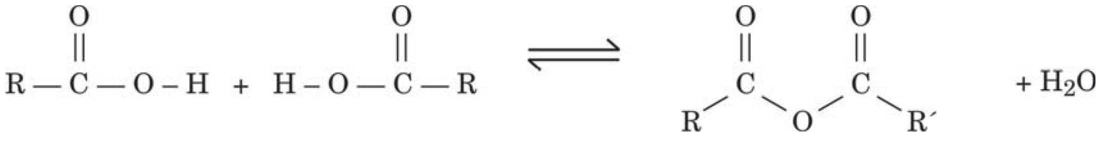
(5)



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 + HNO_2 \xrightarrow{\Delta} R-\overset{\overset{\displaystyle O}{\|}}{C}-OH + N_2(\uparrow) + H_2O$$

Acid Anhydrides

The word anhydride literally means without water, and an acid anhydride is the combination of two molecules of carboxylic acid with the elimination of one molecule of water.



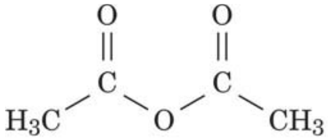
Anhydrides are also considered as activated forms of carboxylic acids, although anhydrides are not as reactive as acid halides.

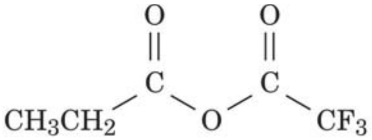
The anhydride group also inductively withdraws electron density from the carbonyl carbon, and the carboxylate anion serves as a good leaving group.

Half of the anhydride is ‘lost’ as the leaving group, and if the carboxylic acid is very precious (expensive or limited quantity) then this is an undesirable way of making an activated carboxylic acid, and the acid chloride route would be more desirable.

Nomenclature

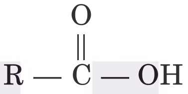
(Simple) anhydrides are simply named by replacing the acid suffix of the parent carboxylic acids with the word anhydride. E.g.

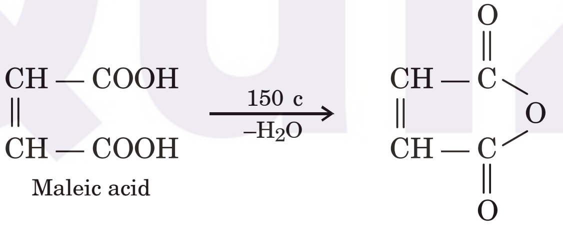

ethanoic anhydride


trifluoroethanoic propanoic anyhydride

Mixed anhydrides that consist of two different acid derived parts are named using the names of the two individual acids, with the highest priority acid being the first name.

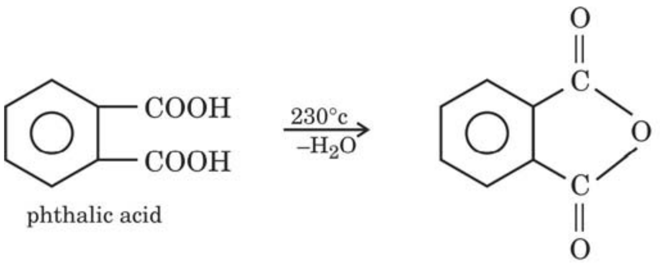
Preparation

(1) Heating of 2 moles of  $R-\overset{\overset{O}{\|}}{C}-OH$ with dehydrating agents also produces $(RCO)_2O$



Maleic acid

Maleic anhydride

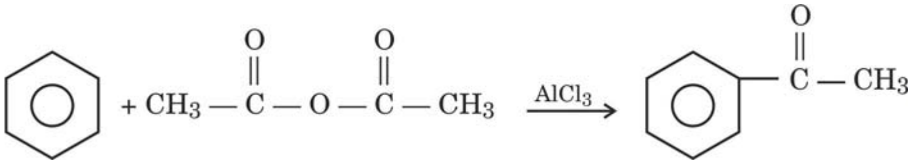


phthalic acid

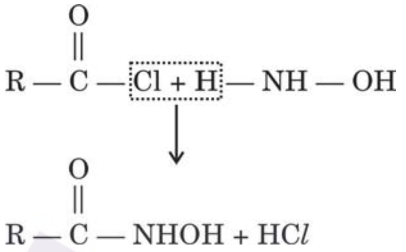
phthalic anhydride

Reactions :

(1) Friedel Crafts acylation

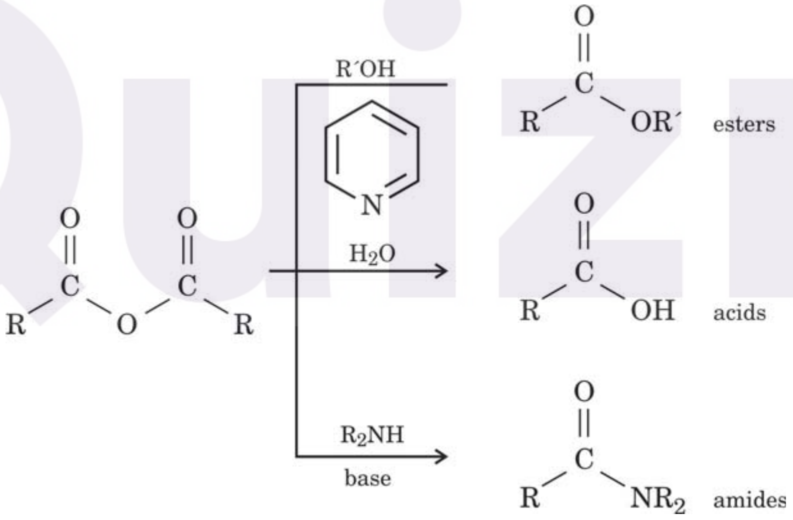


(2) Reaction with hydroxylamine



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-\boxed{Cl + H}-NH-OH \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-NHOH + HCl$$

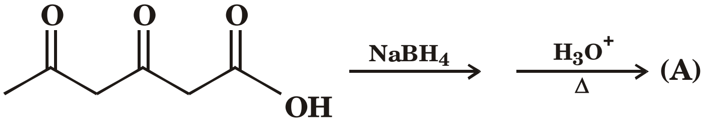
(3) Interconversion Reactions of Acid Anhydrides



- Acid anhydrides are the second most reactive of the carboxylic acid derivatives and can therefore, be fairly readily converted into the other less reactive carboxylic acid derivatives.
- A base in often added to neutralise the carboxylic acid by product that is formed.

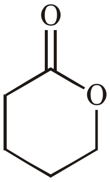
SOLVED EXAMPLES

Example 1

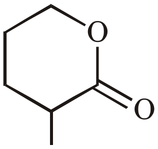


The compound (A) would be

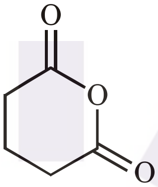
(a)



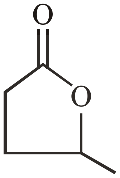
(b)



(c)

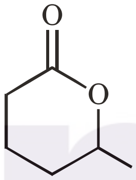


(d)



Solution :

$CH_3CO(CH_2)_3COOH \xrightarrow[(2)\ H_3O^+]{(1)\ NaBH_4} \underset{\delta\text{-hydroxy acid}}{CH_3CH(OH)(CH_2)_3COOH} \xrightarrow{\Delta}$

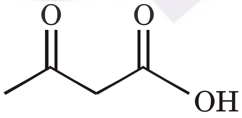


(A)
δ-lactone

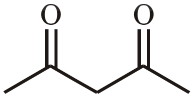
Example 2

Which of the following compound would be expected to decarboxylate when heated ?

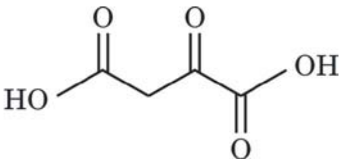
(a)



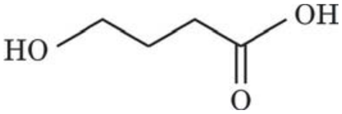
(b)



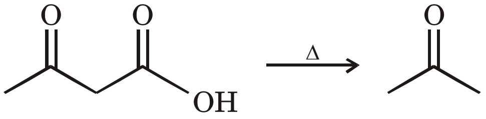
(c)



(d)



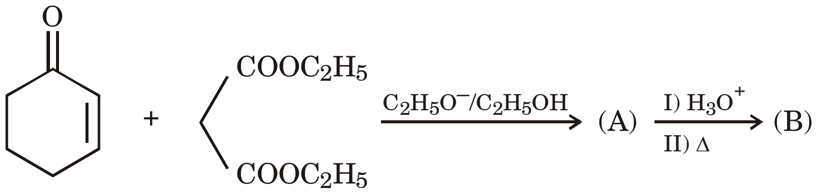
Solution :



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

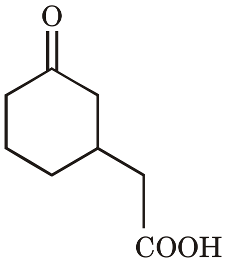
∴ (a)

Example 3

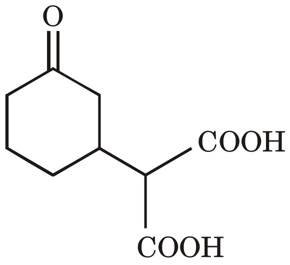


The compound B is

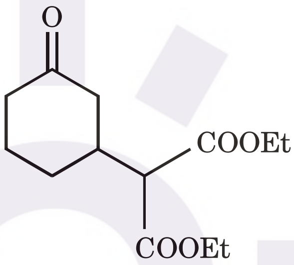
(a)



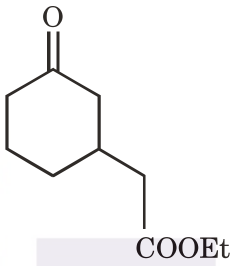
(b)



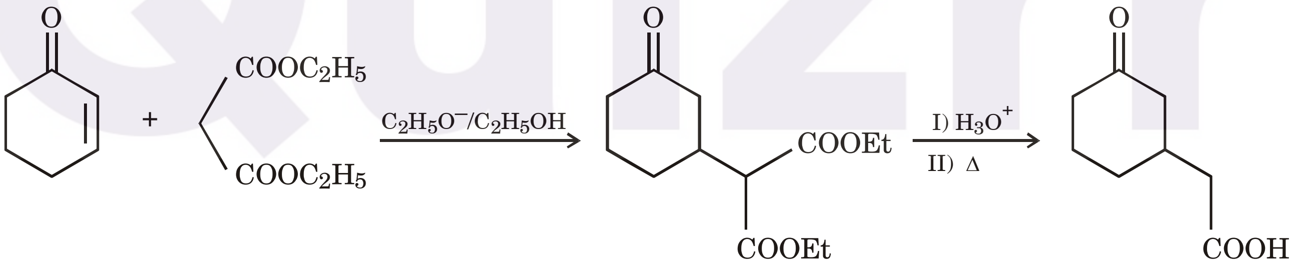
(c)



(d)



Solution :

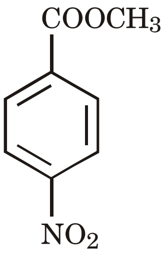


Hence, (A) is correct.

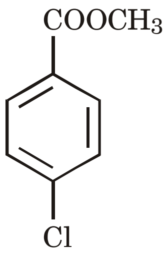
Example 4

The case of alkaline hydrolysis is more for

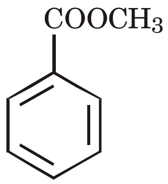
(a)



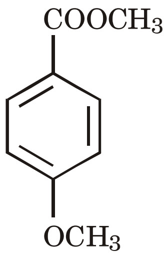
(b)



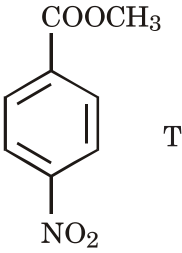
(c)



(d)



Solution :

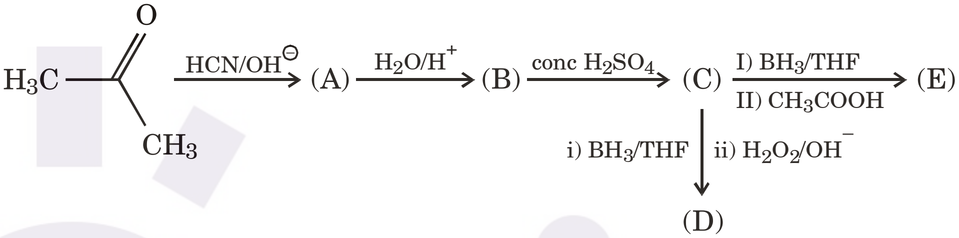


There is more electron deficiency on carbonyl carbon.

Hence, (A) is correct.

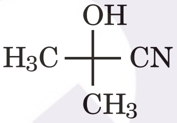
Example 5

Identify the missing reagents or products.



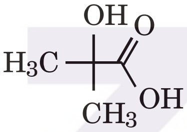
Solution :

A =

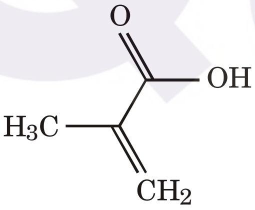


$H_3C-C(OH)(CH_3)-CN$

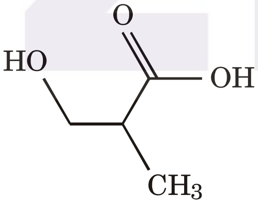
B =



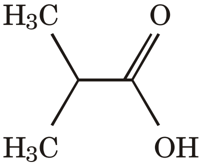
C =



D =



E =



Example 6

R — CH_2 — CH_2OH can be converted to R—CH_2CH_2COOH. The correct sequence of reagents is

(A) PBr_3, KCN, H^+
(B) PBr_3, KCN, H_2
(C) KCN, H^+
(D) HCN, PBr_3, H^+

Solution :

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

Hence, (A) is correct.

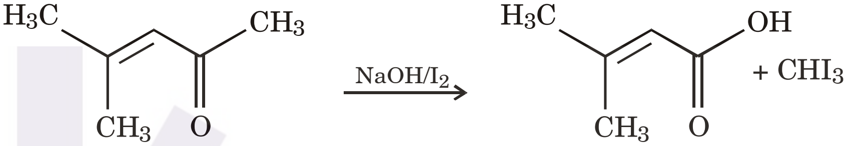
Example 7

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)** $(CH_3)_2C = CH — CO — COOH$

Solution :



Mesityl oxide

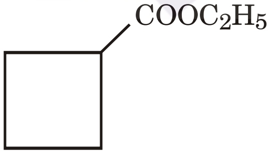
Hence, (C) is correct.

Example 8

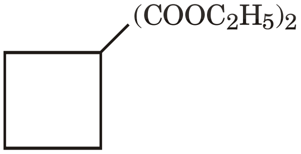
What is the most likely product form the following reaction ?

$$CH_2(COOC_2H_5)_2 + Br(CH_2)_3Br \xrightarrow[EtOH]{EtONa} \xrightarrow{H^+, H_2O}$$

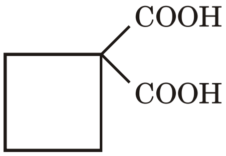
(a)



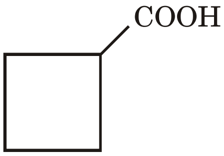
(b)



(c)

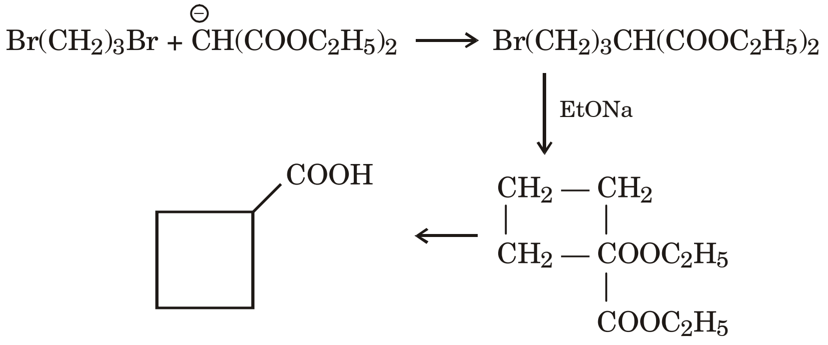


(d)



Solution :

$$CH_2(COOC_2H_5)_2 \xrightarrow[EtOH]{EtONa} \overset{\ominus}{C}H(COOC_2H_5)_2$$



∴ (d)

Example 9

What happens when :

(i) Dry chlorine is passed through acetic acid in presence of sunlight.

(ii) Formic acid is reacted with ammonical silver nitrate solution.

Solution :

(i) $CH_3COOH \xrightarrow[\text{sunlight}]{Cl} CH_2ClCOOH$

(ii) $HCOOH + Ag(NH_3)_2NO_3 \longrightarrow Ag + 2NH_4NO_3 + CO_2$

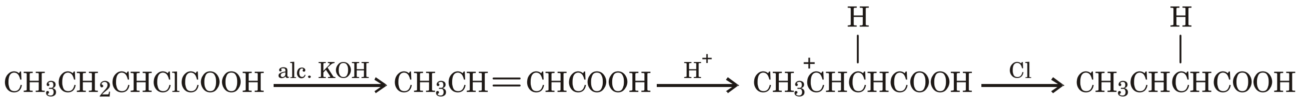
Example 10

(a) Convert 2-chlorobutanoic acid into 3-chlorobutanoic acid

(b) Prepare malonic acid from acetic acid

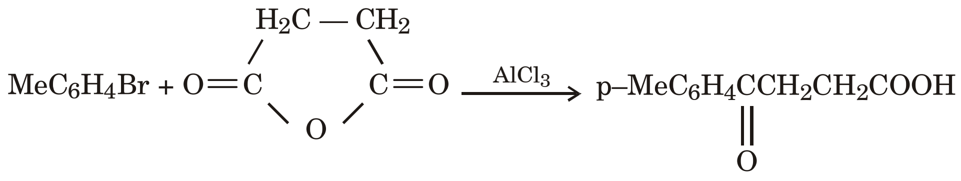
(c) Prepare 4-p tolylbutanoic acid from toluene and succinic anhydride.

Solution :

(a) 

$$CH_3CH_2CHClCOOH \xrightarrow{\text{alc. KOH}} CH_3CH{=}CHCOOH \xrightarrow{H^+} CH_3\overset{+}{C}H\overset{\overset{H}{|}}{C}HCOOH \xrightarrow{Cl} CH_3CH\overset{\overset{H}{|}}{C}HCOOH$$

(b) $CH_3COOH \xrightarrow{Br_2/PBr_3} BrCH_2COOH \xrightarrow{CN} NCCH_2COOH \xrightarrow{H_2O} CH_2(COOH)_2$

(c) 

$$\xrightarrow{\text{Zn/Hg, HCl}} p\text{–}MeC_6H_4CH_2CH_2CH_2COOH$$

Example 11

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

Solution :

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