CHAPTER / 19

Carboxylic Acids

Topics Covered

Classification, Structure, Nomenclature, Isomerism and Methods of Preparation
- Classification
- Structure
- Nomenclature
- Isomerism
- Methods of Preparation

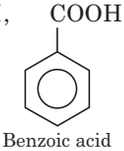
Physical and Chemical Properties
- Physical Properties
- Acidic Nature of Carboxylic Acids
- Chemical Properties
- Tests
- Uses

Organic compounds containing —COOH as the functional group are called **carboxylic acid**. The —COOH group which itself is made up of a carbonyl group ($>C=O$) and a hydroxyl group (—OH) is called **carboxyl group**. The general formula of carboxylic acid is $C_nH_{2n+1}COOH$, where $n = 0, 1, 2 \ldots\ldots$.

TOPIC ~01 Classification, Structure, Nomenclature, Isomerism and Methods of Preparation

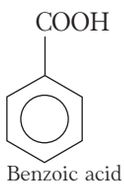
Classification

Carboxylic acids may be aliphatic (RCOOH) or aromatic (ArCOOH) depending on the groups, alkyl or aryl, attached to carboxylic carbon,

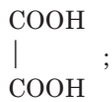
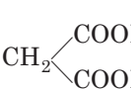
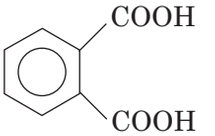
e.g. $\underset{\text{Ethanoic acid}}{CH_3COOH}$, $\underset{\text{Butanoic acid}}{CH_3CH_2CH_2COOH}$, 
Benzoic acid

where, ethanoic and butanoic acid are aliphatic acids and benzoic acid is an aromatic acid. Depending upon the number of carboxylic groups present in a molecule, carboxylic acids are classified as monocarboxylic acids, dicarboxylic acids or tricarboxylic acids.

(i) **Monocarboxylic Acids**

$\underset{\text{Formic acid}}{HCOOH}$; $\underset{\text{Acetic acid}}{CH_3COOH}$; 
Benzoic acid

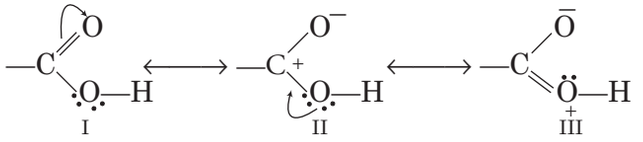
(ii) **Dicarboxylic Acids**


Oxalic acid ; 
Malonic acid ; 
Phthalic acid

Structure

In carboxylic acids, the bonds attached to the carboxyl carbon are co-planar and are separated by about 120°.

The carboxylic carbon is less electrophilic than carbonyl carbon because of the following possible resonance structures:



In structures (I) and (III), carboxyl carbon is electrically neutral. As a result, the carboxyl carbon of resonance hybrid is less positive. However, like carbonyl group, carboxyl group is also polar due to the resonance structures (II) and (III).

Nomenclature

Carboxylic acids are named by the following two systems.

I. Common System

The common names end with the suffix, i.e. acid and have been derived from Latin or Greek names of their natural sources.

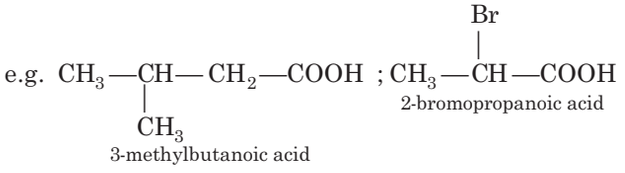
II. IUPAC System

(i) The IUPAC name of carboxylic acid is alkanoic acid.

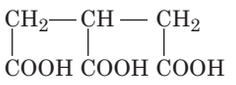
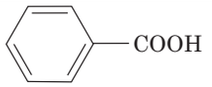
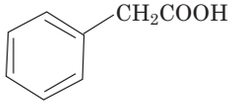
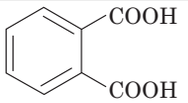
(ii) Their names are derived by replacing the terminal 'e' from the name of corresponding straight chain alkane by suffix 'oic' acid'.

(iii) Their suitable numbers are assigned to the substituents.

(iv) The prefix di, tri, tetra are added before the 'oic' acid form acids containing 2, 3, 4 carboxylic groups, respectively.



Common and IUPAC names of some carboxylic acids

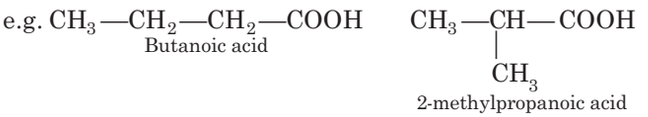
Structural formula	Common name	IUPAC name
HCOOH	Formic acid	Methanoic acid
CH_3COOH	Acetic acid	Ethanoic acid
CH_3CH_2COOH	Propionic acid	Propanoic acid
$CH_3CH_2CH_2COOH$	Butyric acid	Butanoic acid
$(CH_3)_2CHCOOH$	*iso*-butyric acid	2-methylpropanoic acid
HOOC— COOH	Oxalic acid	Ethanedioic acid
HOOC— CH_2— COOH	Malonic acid	Propanedioic acid
HOOC— $(CH_2)_2$— COOH	Succinic acid	Butanedioic acid
HOOC— $(CH_2)_3$— COOH	Glutaric acid	Pentanedioic acid
HOOC — $(CH_2)_4$ — COOH	Adipic acid	Hexanedioic acid
	—	Propan-1,2,3-tricarboxylic acid
	Benzoic acid	Benzene carboxylic acid (benzoic acid)
	Phenylacetic acid	2-phenylethanoic acid
	Phthalic acid	Benzene-1, 2-dicarboxylic acid

Isomerism

Carboxylic acids show the following types of isomerism.

1. Chain Isomerism

When the compounds have same molecular formula but exhibit different carbon chain then they show chain isomerism.

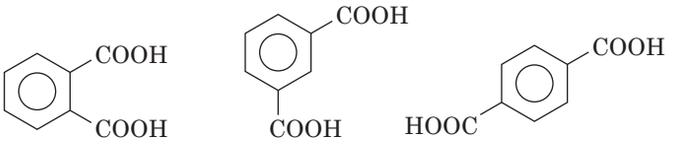


2. Functional Isomerism

When the same molecular formula represents two or more compounds which carry different functional groups, then such isomers are called functional isomers. The acid having three or more carbon atoms may show functional isomerism.

3. Position Isomerism

This type of isomerisem is exhibited by aromatic acids. For example: Position isomers of benzene dicarboxylic acids are:



1, 2-benzene dicarboxylic acid (phthalic acid)

1, 3-benzene dicarboxylic acid (isophthalic acid)

1, 4-benzene dicarboxylic acid (terephthalic acid)

Methods of Preparation

(i) By the Oxidation of Primary Alcohol

Primary alcohol can easily be oxidised to the corresponding carboxylic acid with oxidising agents such as potassium permanganate (in acidic or alkaline medium), potassium dichromate (in acidic medium).

$$\underset{\text{Primary alcohol}}{R\text{CH}_2\text{OH}} + [\text{O}] \xrightarrow[\text{H}_2\text{SO}_4]{\text{K}_2\text{Cr}_2\text{O}_7} \underset{\text{Aldehyde}}{R\text{CHO}} \xrightarrow[\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4]{[\text{O}]} \underset{\text{Carboxylic acid}}{R\text{COOH}}$$

(ii) By the Oxidation of Aldehydes and Ketones

Aldehydes and ketones can easily be oxidised to the corresponding carboxylic acids with oxidising agents such as acidified potassium dichromate or potassium permanganate.

$$\underset{\text{Aldehyde}}{R\text{CHO}} + [\text{O}] \xrightarrow{\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+} \underset{\text{Carboxylic acid}}{R\text{COOH}}$$

(iii) Hydrolysis of Nitriles or Cyanides

Compounds containing cyanide ($-\text{C} \equiv \text{N}$) group are called nitriles. Nitriles yield carboxylic acids, when subjected to hydrolysis with an acid or alkali.

$$\underset{\text{Alkyl cyanide}}{R-\text{C} \equiv \text{N}} + \text{H}_2\text{O} \xrightarrow{\text{HCl}} \underset{\text{Acid amide}}{R\text{CONH}_2} \xrightarrow[\text{HCl}]{\text{H}_2\text{O}} \underset{\text{Carboxylic acid}}{R\text{COOH}} + \text{NH}_4\text{Cl}$$

(iv) From Acyl Halides and Anhydrides

Acid chlorides when hydrolysed with water give carboxylic acids or more readily hydrolysed with aqueous base to give carboxylate ions which on acidification provide corresponding carboxylic acids. Anhydride(s) on the other hand are hydrolysed to corresponding acid(s) with water.

$$R\text{COCl} \longrightarrow \begin{cases} \xrightarrow{\text{H}_2\text{O}} R\text{COOH} + \text{HCl} \\ \xrightarrow[\text{OH}/\text{H}_2\text{O}]{-} R\text{COO}^- + \text{Cl} \xrightarrow{\text{H}_3\text{O}^+} R\text{COOH} \end{cases}$$

(v) Hydrolysis of Esters

Esters on hydrolysis with dilute mineral acids yield corresponding carboxylic acids. Hydrolysis of esters can also be carried out with an alkali. The alkaline hydrolysis of esters is termed as saponification and yields a salt of the carboxylic acid (soap). The carboxylic acid can be obtained by treating the salt with a dilute mineral acid.

$$\underset{\text{Ester}}{R\text{COO}R} + \text{HOH} \xrightarrow{\text{HCl}} \underset{\text{Carboxylic acid}}{R\text{COOH}} + R\text{OH}$$

(vi) By the Carboxylation of Grignard's Reagent

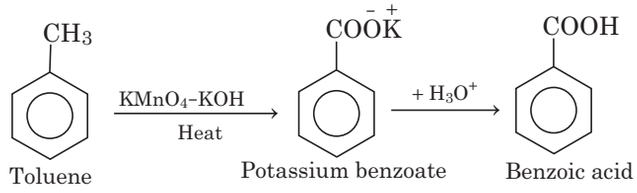
A Grignard reagent on treatment with carbon dioxide in an ethereal solution followed by hydrolysis of the addition product by a dilute mineral acid yields a carboxylic acid.

$$\underset{\substack{\text{Alkyl magnesium}\\ \text{halide}}}{R\text{Mg}X} + \text{O}=\text{C}=\text{O} \longrightarrow \underset{\text{Addition product}}{R-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{OMg}X} \xrightarrow{\text{H}_2\text{O}/\text{H}^+} \underset{\text{Carboxylic acid}}{R-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{OH}} + \text{Mg(OH)}X$$

Formic acid cannot be prepared by this method.

(vii) By Oxidation of Alkylbenzenes (Arenes)

Aromatic acids are obtained by vigorous oxidation of alkyl benzene with chromic acids or acidic or alkaline $KMnO_4$.



(viii) By the Hydrolysis of Trichloroalkanes

Hydrolysis of trihalogen compounds produce carboxylic acids in presence of alkali.

$$R-\text{C}\begin{matrix}\diagup X \\ -X \\ \diagdown X\end{matrix} + 3\,\text{NaOH} \longrightarrow \left[R-\text{C}\begin{matrix}\diagup \text{OH} \\ -\text{OH} \\ \diagdown \text{OH}\end{matrix}\right] + 3\text{Na}^+X^- \xrightarrow[-\text{H}_2\text{O}]{} R-\overset{\overset{\text{O}}{\|}}{\text{C}}-\bar{\text{O}}\overset{+}{\text{Na}}$$

PRACTICE QUESTIONS

Exams', Textbook's Other Imp. Questions

1 MARK *Questions*

Exams' Questions

Q.1 The product formed during hydrolysis of methyl nitrile in acidic medium is **[2018, Textbook]**

(a) $CH_3—\overset{\overset{O}{\|}}{C}—NH_2$ (b) $CH_3—\overset{\overset{O}{\|}}{C}—OH$

(c) $CH_3—\overset{\overset{O}{\|}}{C}—H$ (d) $CH_3—CH_2—\overset{\overset{O}{\|}}{C}—OH$

Sol (*b*) The product formed during hydrolysis of methyl nitrile in acidic medium is acetic acid (CH_3COOH).

$$\underset{\text{Methyl nitrile}}{CH_3—CN} \xrightarrow{H_3O^+} \underset{\text{Acetic acid}}{CH_3\overset{\overset{O}{\|}}{C}OH} + NH_3 \uparrow$$

Q.2 What is the functional isomer of monocarboxylic acid? **[2011 Instant]**

Sol The functional isomer of monocarboxylic acid is an ester.

e.g. $\underset{\text{Propanoic acid}}{CH_3CH_2COOH}$; $\underset{\text{Methyl ethanoate}}{CH_3COOCH_3}$

Q.3 Name the following compound in IUPAC system. **[2011]**

$$CH_3—\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}—CH_2—COOH$$

Sol $\overset{4}{C}H_3—\overset{3}{\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}}—\overset{2}{C}H_2—\overset{1}{C}OOH$

3, 3-dimethyl butanoic acid

Q.4 Write the IUPAC name of the following compound.

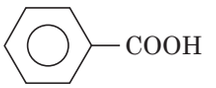
$$(CH_3)_2CH—\underset{\underset{Br}{|}}{CH}—COOH$$ **[2003]**

Sol $CH_3—\underset{\underset{CH_3}{|}}{CH}—\underset{\underset{Br}{|}}{CH}—COOH$ is

2-bromo-3-methylbutanoic acid

Q.5 Write the structural formula of benzoic acid.

Sol The structure of benzoic acid is **[2002]**



Important Questions

Q.6 The end product in the sequence of reaction

$$R—X \xrightarrow{KCN} A \xrightarrow{NaOH} B \text{ is}$$ **[Textbook]**

(a) an alkane
(b) a carboxylic acid
(c) sodium salt of carboxylic acid
(d) saponification

Sol (*c*) The reaction product is as follows:

$$R—X \xrightarrow{KCN} \underset{(A)}{RCN} \xrightarrow{NaOH} \underset{(B)}{R—CO\overset{-}{O}\overset{+}{N}a}$$

Q.7 Vinegar contains **[Textbook]**

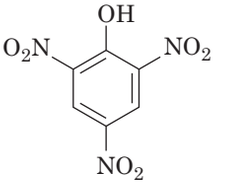
(a) 10 to 20% acetic acid (b) 10% acetic acid
(c) 6 to 10% acetic acid (d) 100% acetic acid

Sol (*c*) Vinegar is an aqueous solution of acetic acid, it contains 6 to 10% acetic acid.

Q.8 The acid which does not contain —COOH group is **[Textbook]**

(a) ethanoic acid (b) picric acid
(c) lactic acid (d) palmitic acid

Sol (*b*) The acid that does not contain —COOH group is picric acid. Its structural formula is



Q.9 Acids are obtained as a result of reaction between a Grignard reagent and **[Textbook]**

(a) oxygen (b) CO_2
(c) CH_3COCl (d) CH_3CHO

Sol (*b*) Acids are obtained as a result of reaction between a Grignard reagent and CO_2.

The reaction is as follows:

$$R\text{Mg}X + O=C=O \longrightarrow R—\overset{\overset{O}{\|}}{C}\overset{-}{O}\overset{+}{\text{Mg}}X \xrightarrow{H_2O/H^+} R\text{COOH} + \text{Mg(OH)}X$$

Q.10 Formic acid is obtained by the hydrolysis of
(a) HCN (b) CH_3CN **[Textbook]**
(c) $(COONa)_2$ (d) $CO + CO_2$

Sol (*a*) Formic acid is obtained by the hydrolysis of HCN. The reaction is as follows:

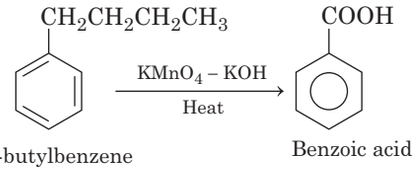
$$HCN + H_2O \xrightarrow{HCl} HCONH_2 \xrightarrow{H_3O^+H} HCOOH + NH_4Cl$$

Q.11 Stings of bees and wasps contain **[Textbook]**
(a) formalin (b) formaldehyde
(c) acetic acid (d) formic acid

Sol (*d*) Stings of bees and wasps contain formic acid (HCOOH).

Q.12 *n*-butylbenzene on oxidation will give **[Textbook]**
(a) benzyl alcohol (b) butanoic acid
(c) benzoic acid (d) benzaldehyde

Sol (*c*) *n*- butylbenzene on oxidation will give benzoic acid

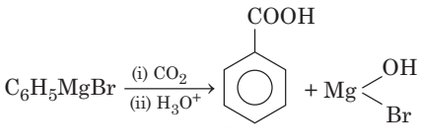


n-butylbenzene Benzoic acid

Q.13 $C_6H_5MgBr \xrightarrow[(ii)\ H_3O^+]{(i)\ CO_2} P$ **[Textbook]**

In the above equation, product '*P*' is
(a) benzaldehyde (b) benzoic acid
(c) phenol (d) benzophenone

Sol (*b*)



Benzoic acid

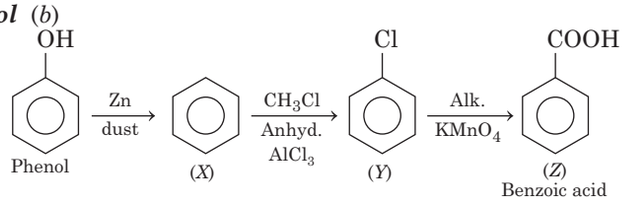
Q.14 Which of the following does not give benzoic acid on hydrolysis? **[Textbook]**
(a) Phenyl cyanide (b) Benzoyl chloride
(c) Benzyl chloride (d) Methyl benzoate

Sol (*c*) Benzyl chloride does not give benzoic acid on hydrolysis

Q.15 Phenol $\xrightarrow[dust]{Zn} X \xrightarrow[Anhyd.AlCl_3]{CH_3Cl} Y \xrightarrow[KMnO_4]{Alk.} Z$,

the product '*Z*' is **[Textbook]**
(a) benzaldehyde (b) benzoic acid
(c) benzene (d) toluene

Sol (*b*)



Phenol (*X*) (*Y*) (*Z*) Benzoic acid

Q.16 Methyl cyanide on hydrolysis yields ..... . **[Textbook]**

Sol Methyl cyanide on hydrolysis yields acetic acid as shown below:

$$CH_3CN + 2H_2O \xrightarrow[Boil]{H^+} CH_3COOH + NH_3$$

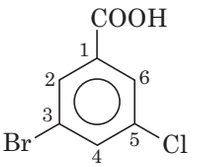
Q.17 Write the structural formula of 3-hydroxy butanoic acid.

Sol $CH_3-\underset{\underset{OH}{|}}{C}H-CH_2-COOH$

Q.18 Write the IUPAC name of the following compounds: **[Textbook]**
(i) $CH_3-CH_2-COOC_2H_5$
(ii) $HOOC-CH_2-CH_2-CH_2-COOH$

Sol (i) Ethyl propanoate (ii) Pentanedioic acid

Q.19 Write the IUPAC name of the following compound.



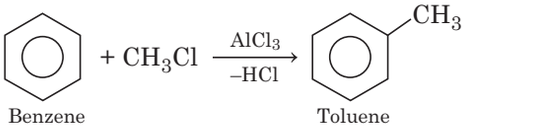
Sol 3-bromo-5-chlorobenzoic acid.

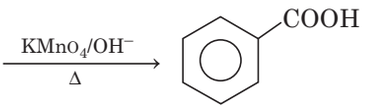
2 MARK *Questions*

Exams' Questions

Q.20 How can you convert benzene to benzoic acid? **[2014, 2011, 2003]**

Sol





Benzoic acid **(2)**

Q.21 Give the IUPAC name of the following compounds. **[2013]**
(i) $PhCH_2CH_2COOH$ (ii) $(CH_3)_2C = CHCOOH$

Sol (i) $Ph-\overset{3}{C}H_2-\overset{2}{C}H_2-\overset{1}{C}OOH$
3-phenylpropanoic acid **(1)**

(ii) $\overset{4}{C}H_3-\underset{\underset{CH_3}{|}}{\overset{3}{C}}=\overset{2}{C}H-\overset{1}{C}OOH$
3-methyl but-2- en-1-oic acid **(1)**

Q.22 How is phenyl magnesium bromide converted into benzoic acid ? **[2012 Instant]**

Sol $\underset{\text{Phenyl magnesium bromide}}{C_6H_5MgBr} + CO_2 \xrightarrow{\text{Dry ether}} C_6H_5-\overset{\overset{O}{\|}}{C}-OMgBr$

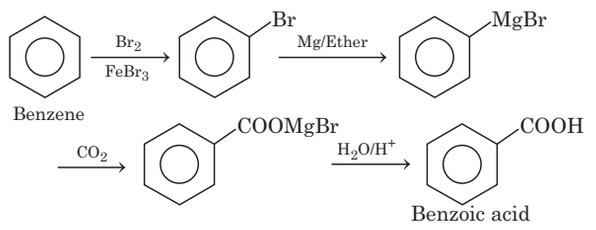
$\xrightarrow{H^+/H_2O} \underset{\text{Benzoic acid}}{C_6H_5COOH} + Mg\begin{matrix}OH\\Br\end{matrix}$ **(2)**

Q.23 How will you convert formic acid to acetic acid? **[2008, Textbook]**

Sol $\underset{\text{Formic acid}}{HCOOH} \xrightarrow{Ca(OH)_2} (HCOO)_2Ca \xrightarrow{\Delta} HCHO \xrightarrow{Na/alc.} CH_3OH \xrightarrow{PCl_5} CH_3Cl \xrightarrow{KCN} CH_3CN \xrightarrow[\Delta]{H_3O^+} \underset{\text{Acetic acid}}{CH_3COOH}$ **(2)**

Q.24 How can benzoic acid be prepared from benzene using Grignard's reagent ? **[2008, 2000]**

Sol



(2)

Important Questions

Q.25 What happens, when acetamide is boiled with NaOH solution? **[Textbook]**

Sol Ethanoic acid is formed, when acetamide is boiled with NaOH.

$CH_3-\overset{\overset{O}{\|}}{C}NH_2 \xrightarrow[NaOH]{H_2O/\text{boil}} CH_3COOH$ **(2)**

Q.26 Explain, why the bond length of C—O in carboxylic acid is slightly larger than that aldehydes and ketones. **[Textbook]**

Sol The bond length of C — O in carboxylic acid is slightly larger than that aldehydes and ketones because of resonance. **(2)**

Q.27 How acetic acid is prepared from methyl cyanide? **[Textbook]**

Sol $CH_3C \equiv N + H_2O \xrightarrow{HCl} CH_3CONH_2$

$CH_3CONH_2 + H_2O \xrightarrow[HCl]{Boil} CH_3COOH$ **(2)**

3 MARK *Questions*

Exams' Questions

Q.28 Write the structural formulae of the three derivatives of monocarboxylic acid. Identify the functional group present in them. **[2016, Textbook]**

Sol The three derivatives of monocarboxylic acids are:

Amides $R-\overset{\overset{O}{\|}}{C}-\underset{\text{Primary amide}}{NH_2}$, $R-\overset{\overset{O}{\|}}{C}-\underset{\text{Secondary amide}}{NHR'}$, $R-\overset{\overset{O}{\|}}{C}-\underset{\text{Tertiary amide}}{NR'_2}$

Acid chlorides $R-\overset{\overset{O}{\|}}{C}-Cl$

Esters $R-\overset{\overset{O}{\|}}{C}-OR'$

where, R, R' are alkyl groups.

The functional group present in these derivatives are:

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

Acid chlorides $-\overset{\overset{O}{\|}}{C}-Cl$

Esters $-\overset{\overset{O}{\|}}{C}-OR'$ **(3)**

Q.29 Phenyl magnesium bromide in ether is treated with carbon dioxide and the product is hydrolysed with dilute acid. **[2014 Annual]**

Sol $C_6H_5MgBr + CO_2 \longrightarrow C_6H_5COO^-MgBr^+$

$C_6H_5COO^-MgBr^+ + H_3O^+ \longrightarrow C_6H_5COOH + H_2O + MgBr_2$ **(3)**

Important Questions

Q.30 Convert methyl iodide to acetic acid. **[Textbook]**

Sol $CH_3I \xrightarrow[\text{Heat}]{KCN} CH_3CN \xrightarrow[\text{Boil}]{H_2O/H^+} CH_3COOH$ **(3)**

Q.31 Identify A, B and C from the following ,

$C_2H_5OH \xrightarrow{PCl_5} A \xrightarrow{KCN} B \xrightarrow{H_3O^+} C$

Sol $C_2H_5OH \xrightarrow{PCl_5} \underset{(A)}{C_2H_5Cl} \xrightarrow{KCN} \underset{(B)}{C_2H_5CN} \xrightarrow{H_3O^+} C_2H_5COOH$ **(3)**

Q.32 Give the IUPAC name of **[Textbook]**

(i) CH_3COCH_2COOH

(ii) $CH_3CH = CHCOOH$

(iii) $HO-CH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}H-COCH$

Sol (i) 3 - oxobutanoic acid

(ii) but-2-enoic acid

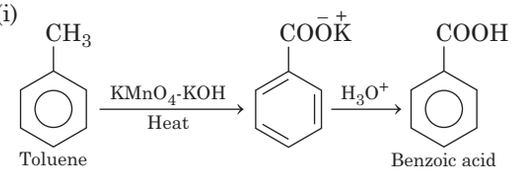
(iii) 4-hydroxy - 2- methyl butanoic acid **(3)**

7 MARK *Questions*

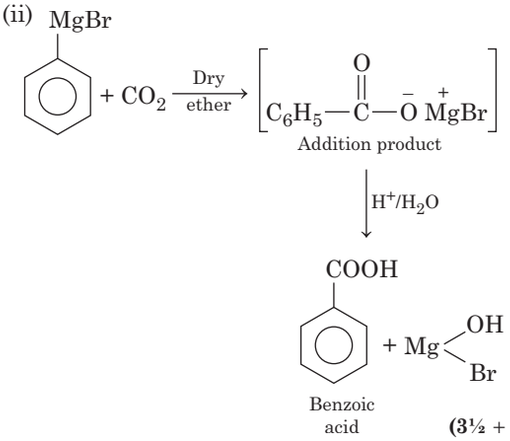
Exams' Questions

Q.33 Show the preparation of benzoic acid from
(i) toluene and
(ii) carboxylation of Grignard's reagent with equation.
[2013]

Sol (i)



(ii)

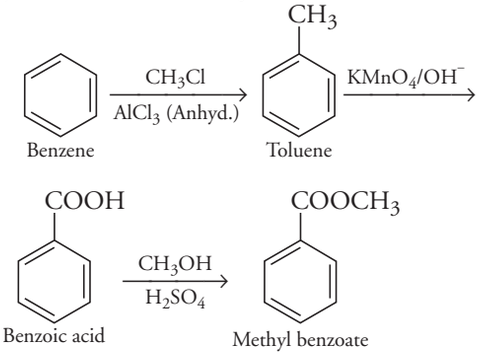


(3½ + 3½ = 7)

Important Questions

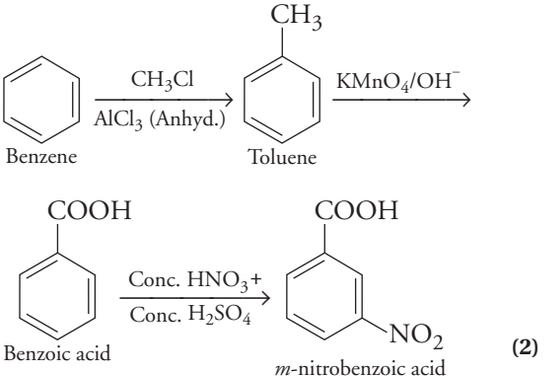
Q.34 How will you prepare the following compounds from benzene? You may use any inorganic reagent and any organic reagent having not more than one carbon atom.
(i) Methyl benzoate (ii) *m*-nitrobenzoic acid
(iii) *p*-nitrobenzoic acid (iv) Phenylacetic acid

Sol. (i) **Benzene to methyl benzoate**



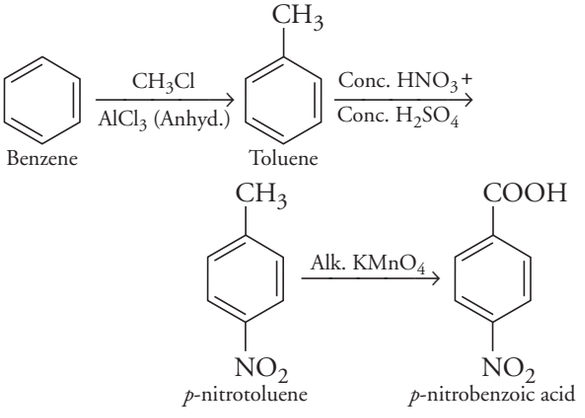
(1)

(ii) **Benzene to *m*-nitrobenzoic acid**



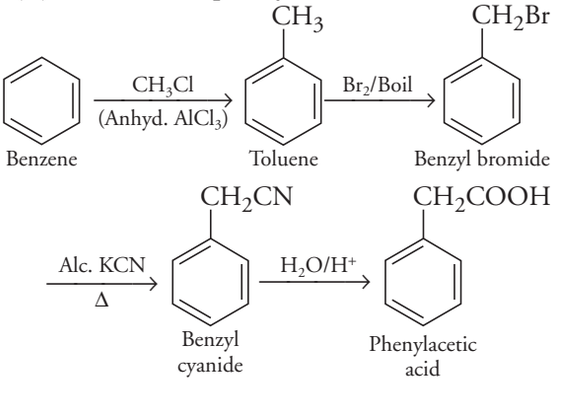
(2)

(iii) **Benzene to *p*-nitrobenzoic acid**



(2)

(iv) **Benzene to phenylacetic acid**



(2)

TOPIC TEST 1

- *Choose the correct option.*

1. The correct IUPAC name of the following structure $CH_3CH_2CH_2COOH$ is

(a) propanoic acid (b) ethanoic acid

(c) butanoic acid (d) pentanoic acid

[***Ans.*** (c)]

- *Fill in the blanks.*

2. ..... on hydrolysis with dil.mineral acids give carboxylic acids. [*Ans.* Alkyl cyanides]

3. ..... is formed when benzoic acid is treated with $LiAlH_4$. [*Ans.* Benzyl alcohol]

- *Correct the sentence, if required by the changing of underlined words. (Q.Nos. 4 to 5)*

4. C_3H_7COOH has <u>three</u> structural isomers. [*Ans.* two]

5. Hydrolysis of nitriles produces <u>aldehydes</u>. [*Ans.* carboxylic]

- *Complete the following:*

6. $CH_3CH_2OH \xrightarrow[\Delta]{K_2Cr_2O_7/H_2SO_4}$ **7.** $CH_3CH_2I \xrightarrow[\text{Heat}]{KCN}$

- *Name the following structures:*

8. $CH_3CH_2CH(CH_2CH_3)—COOH$ **9.** $CH_3CH(CH_3)—CH(CH_3)—COOH$

10. $HOOC—(CH_2)_3COOH$

- *Explain the following:*

11. Hydrolysis of nitriles

12. Oxidation of alcohols

13. Carboxylation of Grignard reagent.

TOPIC ~02 Physical and Chemical Properties

Physical Properties

(i) **Physical state** Aliphatic carboxylic acids upto nine carbon atoms are colourless liquids at room temperature while higher carboxylic acids are wax like solids.

(ii) **Solubility** Simple aliphatic carboxylic acids having upto four carbon atoms are miscible in water because of hydrogen bonds.

Solubility decreases with increase in the number of carbon atoms which is due to increased hydrophobic interaction of hydrocarbon part.

Carboxylic acids are also soluble in less polar organic solvents like benzene, ether, alcohol, chloroform, etc.

(iii) **Boiling points** As compared to hydrocarbons, aldehydes and ketones, carboxylic acids have higher boiling points because they have high extent of hydrogen bonding with water, due to which they exists as associated molecules.

(iv) **Melting points** The melting point of an acid containing even number of carbon atoms is higher than the next member containing odd number of carbon atoms.

Acidic Nature of Carboxylic Acids

In aqueous solution, carboxylic acids ionise and exist in dynamic equilibrium between carboxylate ion and the hydronium ion.

$$R—C(=O)—OH + H_2O \rightleftharpoons H_3O^+ + [R—C(=O)—O^-] \equiv R$$

$$K_{eq} = \frac{[H_3O^+][RCOO^-]}{[H_2O][RCOOH]}$$

$$K_a = K_{eq}\,[H_2O] = \frac{[H_3O^+][RCOO^-]}{[RCOOH]}$$

where, K_{eq} is equilibrium constant and K_a is the acid dissociation constant.

The strength of an acid is usually indicated by its pK_a value rather than its K_a value.

$$pK_a = -\log K_a$$

Smaller the value of pK_a, the stronger is the acid. Trifluoroacetic acid is the strongest organic acid (pK_a of CF_3COOH = 0.23). pK_a of hydrochloric acid, benzoic and acetic acid are –7.0, 4.19 and 4.76, respectively.

Stronger acids have pK_a values < 1, the acids with pK_a values between 1 and 5 are considered to be moderately strong acids, weak acids have pK_a values between 5 and 15 and extremely weak acids have pK_a values >15.

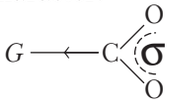
Carboxylic acids are weaker than mineral acids but they are stronger acids than alcohols and many simple phenols.

Effect of Substituents on Acidity

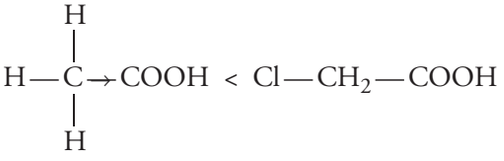
Substituents may affect the stability of the conjugate base and thus also affect the acidity of the carboxylic acids.

(i) Effect of Electron Withdrawing Groups (EWG)

Effect of Electron Withdrawing Group (– *I* effect)
An electron withdrawing group (EWG) stabilises the carboxylate ion by dispersal of negative charge. Thus, increases the acidic character.



e.g. Acetic acid is weaker acid than chloroacetic acid

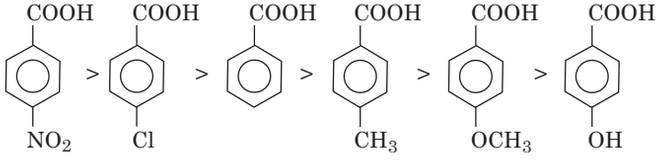


(ii) Acidity of Benzoic Acid

Benzoic acid is stronger acid than acrylic acid (CH_2═ CHCOOH) because delocalisation destroys the aromatic character of the benzene ring.

Electron releasing substituents (—OH, —CH_3) decreases the strength of acid, whereas electron withdrawing groups (—NO_2,—CN) increases the strength of the acid.

Acidic strength of some substituted aromatic acids are:



Comparison of Acidic Strength of Aliphatic and Aromatic Acids (Unsubstituted)

Generally, electron releasing group decreases the acids strength. On comparing the acidic strength of HCOOH, CH_3COOH and C_6H_5COOH, it is found that CH_3COOH has least acidic strength due to +*I* effect of alkyl group (CH_3).

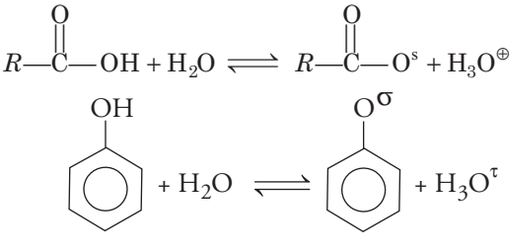
In benzoic acid —C_6H_5 attached to —COOH group has an overall electron donating effect but it is weaker than +*I* effect of —CH_3 group. So, the correct order is

$$HCOOH > C_6H_5COOH > CH_3COOH$$

Similarly, $C_6H_5CH_2COOH > C_6H_5COOH$

Comparison of Acid Strength of Carboxylic Acid and Phenols

Due to resonance stabilisation, phenols are acidic but less acidic than carboxylic acids.



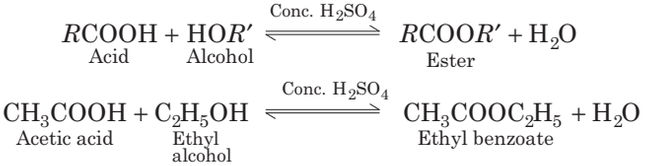
As we have already discussed that carboxylate ion have two equivalent resonating structures because of the presence of two electronegative oxygen atoms whereas phenoxide ion have more resonating structures. Hence, resonance stabilised.

Chemical Properties

Important chemical properties are as follows:

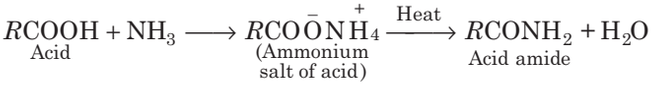
(i) Formation of Esters (Reaction with Alcohols)

When carboxylic acids are heated with alcohols in the presence of concentrated H_2SO_4 or dry HCl gas, esters are formed. The reaction is reversible in nature and is called **esterification**.



(ii) Formation of Amides (Reaction with Ammonia)

All acids react with ammonia to form corresponding ammonium salts. These ammonium salts lose a molecule of water when subjected to heating and form corresponding acid amides.



(iii) Formation of Acid Halide (Action with PCl_5)

When a carboxylic acid is treated with phosphorus pentachloride (PCl_5), the —OH part of the carboxyl group gets replaced by Cl-atom and the corresponding acid chloride is obtained.

$$\underset{\text{Acid}}{R\text{COOH}} + PCl_5 \longrightarrow \underset{\text{Acid chloride}}{R\text{COCl}} + \underset{\substack{\text{Phosphorus}\\ \text{oxy chloride}}}{POCl_3} + HCl$$

(iv) Action with P_2O_5

Acetic acid on heating with P_2O_5 gives acetic anhydride

$$\underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow[\text{Heat}]{P_2O_5} \underset{\text{Acetic anhydride}}{(CH_3CO)_2O} + H_2O$$

(v) Action with Thionyl Chloride ($SOCl_2$)

Carboxylic acids reacts with thionyl chloride ($SOCl_2$) to give acid chlorides.

$$\underset{\text{Carboxylic acid}}{R\text{—}\overset{\overset{O}{\|}}{C}\text{—OH}} + SOCl_2 \longrightarrow R\text{—}\overset{\overset{O}{\|}}{C}\text{—Cl} + SO_2 + HCl$$

e.g. $CH_3COOH + SOCl_2 \longrightarrow \underset{\text{Acetyl chloride}}{CH_3COCl} + SO_2 + HCl$

(vi) Formation of Alkane (Reaction with Soda lime, Decarboxylation)

When the sodium salt of a carboxylic acid is heated with soda lime (NaOH + CaO) the acid undergoes decarboxylation to give an alkane, which contains one carbon atom less than the parent acid.

$$R\text{COONa} + \text{NaOH} \xrightarrow{\text{CaO}} R\text{H} + Na_2CO_3$$

$$\underset{\text{Sodium acetate}}{CH_3COONa} \xrightarrow[\Delta]{\text{CaO}} CH_4 + Na_2CO_3$$

$$\underset{\text{Sodium formate}}{HCOONa} + \text{NaOH} \xrightarrow[\Delta]{\text{CaO}} H_2 + Na_2CO_3$$

(vii) Electrolytic Decarboxylation (Kolbe's electrolysis)

Aqueous solution of sodium or potassium salt of a fatty acid on electrolysis gives alkane.

$$2R\text{COO}^-\text{Na}^+ \longrightarrow 2R\text{CO}\bar{\text{O}} + 2\overset{+}{\text{N}}\text{a}$$

$$2H_2O \longrightarrow 2\bar{O}H + 2\overset{+}{H}$$

At anode $2R\text{CO}\bar{\text{O}} \xrightarrow{-2e} \underset{\text{Unstable}}{2R\text{COO}} \longrightarrow \underset{\text{Alkane}}{R\text{—}R} + 2CO_2$

At cathode $2H^+ + 2e^- \longrightarrow H_2\uparrow$

(viii) Reaction with Metals

Carboxylic acids react with strong electropositive metals like Na, Zn, etc. to liberate hydrogen gas with the formation of salts.

$$2R\text{COOH} + 2\text{Na} \longrightarrow 2R\text{COO}^-\overset{+}{\text{N}}\text{a} + H_2$$

$$2CH_3COOH + Zn \longrightarrow (CH_3COO)_2Zn + H_2$$

(ix) Reaction with Alkali

Carboxylic acids react with alkali to form salts and water.

$$R\text{COOH} + \text{NaOH} \longrightarrow R\text{COO}^-\overset{+}{\text{N}}\text{a} + H_2O$$

$$CH_3COOH + \text{NaOH} \longrightarrow CH_3CO\bar{O}\overset{+}{\text{N}}\text{a} + H_2O$$

(x) Reaction with Carbonates and Bicarbonates.

Carboxylic acids react with carbonates or bicarbonates to liberate CO_2.

$$2R\text{COOH} + Na_2CO_3 \longrightarrow 2R\text{COO}^-\text{Na}^+ + CO_2 + H_2O$$

$$CH_3COOH + NaHCO_3 \longrightarrow CH_3COO^-\ \text{Na}^+ + CO_2 + H_2O$$

(xi) Reduction of Carboxylic Acids

Carboxylic acids get reduced to primary alcohols, when heated with $LiAlH_4$ or with hydrogen and copper chromite ($CuCr_2O_4$).

$$R\text{COOH} \xrightarrow[\text{or } CuCr_2O_4 + H_2]{LiAlH_4} \underset{\text{Primary alcohol}}{R\text{CH}_2\text{OH}}$$

(xii) Reaction with HI

Carboxylic acids when heated with red P and HI at 500 K are reduced to alkanes.

$$R\text{COOH} + 6\text{HI} \xrightarrow[\text{at } 500\text{ K}]{\text{Red P}} R\text{CH}_3 + 2H_2O + 3I_2$$

(xiii) Decomposition of Calcium Salts of Carboxylic Acids

Dry distillation of calcium salts of fatty acids results in the formation of carbonyl compounds.

$$\begin{matrix}\text{HCOO}\\ \text{HCOO}\end{matrix}\!\!>\!\text{Ca} \xrightarrow{\Delta} CaCO_3 + \underset{\text{Formaldehyde}}{\text{HCHO}}$$

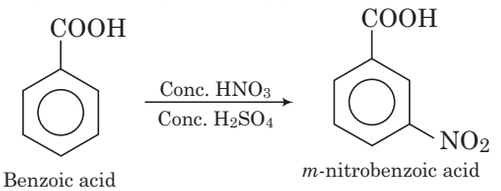
(xiv) Reaction with Halogen

Carboxylic acids having an α- hydrogen atom react with chlorine or bromine in the presence of small amount of red phosphorus to form α- halocarboxylic acids. This reaction is called HVZ (Hell-Volhard Zelinsky reaction).

$$R\text{—}CH_2COOH \xrightarrow{X_2/\text{P}} R\text{—}\underset{\displaystyle X}{\underset{|}{\text{CH}}}\text{—COOH}$$

(xv) Electrophilic Substitution Reactions

- **Nitration** Benzoic acid reacts with concentrated nitric acid in the presence of concentrated sulphuric acid to form *m*-nitrobenzoic acid.



Benzoic acid — *m*-nitrobenzoic acid

- **Halogenation** Carboxylic acids having an α-hydrogen are halogenated at the α-position in the presence of small amount of red phosphorus to give α-halocarboxylic acids. This reaction is known as **Hell-Volhard-Zelinsky reaction.**

$$R-CH_2-COOH \xrightarrow[(ii)\ H_2O]{(i)\ X_2/\text{Red phosphorus}} R-\underset{\underset{X}{|}}{CH}-COOH$$

α – halocarboxylic acid

(where, $X = Cl,\ Br$)

Unique Characteristic Reactions of Formic Acid

Reducing Nature

Formic acid is a strong reducing agent as it gets oxidised to CO_2 and H_2O and hence can be distinguished from other carboxylic acids.

$$HCOOH \xrightarrow{[O]} CO_2 + H_2O$$

(i) It oxidises ammoniacal solution of silver nitrate (Tollen's reagent) to metallic silver.

$$HCOOH + \underset{\text{(From Tollen's reagent)}}{Ag_2O} \longrightarrow 2Ag + CO_2 + H_2O$$

(ii) It oxidises Fehling's solution to red cuprous oxide.

$$HCOOH + \underset{\text{From Fehling's solution}}{2CuO} \longrightarrow \underset{\substack{\text{Cuprous oxide}\\(\text{Red})}}{Cu_2O} + CO_2 + H_2O$$

(iii) It oxidises mercuric chloride to mercurous chloride.

$$HCOOH + 2HgCl_2 \longrightarrow \underset{\text{Mercurous chloride}}{2HgCl} + CO_2 + HCl$$

Also it decolourises acidified $KMnO_4$ solution.

$$2MnO_4^- + 6H^+ + 5HCOOH \longrightarrow 2Mn^{2+} + 8H_2O + 5CO_2$$

Tests

(i) Aqueous sodium bicarbonate ($NaHCO_3$) reacts with carboxylic acid to give CO_2 gas with effervescence that turns lime water milky.

(ii) In presence of conc. H_2SO_4, carboxylic acid reacts with alcohol to form ester with fruity smell.

Uses

Some important uses of carboxylic acids are:

(i) Ethanoic acid is widely used as a solvent and it is also used as vinegar in food industry.

(ii) In the manufacture of nylon-6,6, hexanedioic acid (adipic acid) is used.

(iii) In perfume industry, esters of benzoic acid are used.

PRACTICE QUESTIONS

Exams', Textbook's Other Imp. Questions

1 MARK *Questions*

Exams' Questions

Q.1 Which of the following reagents produces pure acid-chloride from monocarboxylic acid?

(a) PCl_3 (b) PCl_5

(c) SO_2Cl_2 (d) $SOCl_2$ **[2016, Textbook]**

Sol (*b*) Monocarboxylic acids on treatment with PCl_5 produces acid chloride.

Example

$$\underset{\text{Carboxylic acid}}{RCOOH} + \underset{\substack{\text{Phosphorus}\\\text{pentachloride}}}{PCl_5} \longrightarrow \underset{\substack{\text{Acid}\\\text{chloride}}}{RCOCl} + \underset{\substack{\text{Phosphorus}\\\text{oxychloride}}}{POCl_3} + HCl$$

Q.2 How will you convert benzoic acid to benzene ? **[2014, 2012, 2009, 2006]**

Sol Benzoic acid is heated with sodalime to get C_6H_6.

$$\underset{\text{Benzoic acid}}{C_6H_5COOH} \xrightarrow{NaOH} C_6H_5COONa \xrightarrow[CaO/\Delta]{NaOH} \underset{\text{Benzene}}{C_6H_6} + Na_2CO_3$$

Q.3 Alkaline hydrolysis of an ester is called **[2013]**

(a) neutralisation (b) esterification

(c) polymerisation (d) saponification

Sol (*d*) Alkaline hydrolysis of an ester is termed as saponification and yield a salt of the carboxylic acid (soap).

Q.4 How formic acid reacts with Tollen's reagent? **[2012 Instant, 2003]**

Sol $\underset{\text{Formic acid}}{HCOOH} + 2\underset{\text{Tollen's reagent}}{[Ag(NH_3)_2]^+}\ OH^- \longrightarrow HCO\bar{O}NH_4^+ + 3NH_3 + 2H_2O + 2Ag$ (Silver mirror)

Q.5 What happens, when propionic acid is treated with thionyl chloride? **[2012]**

Sol Propionic acid reacts with thionyl chloride ($SOCl_2$) to give propyl chloride.

$$CH_3CH_2COOH + SOCl_2 \longrightarrow CH_3CH_2COCl + SO_2 + HCl$$

Q.6 How can you convert acetic acid to methyl amine? **[2011 Instant, 2008]**

Sol $\underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{NH_3} CH_3CO\bar{O}NH_4^+ \xrightarrow{\Delta}$

$$\underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow{Br_2/KOH} \underset{\text{Methylamine}}{CH_3NH_2}$$

Q.7 Suggest tests to distinguish between acetic acid and formic acid. Give equation. **[2011 Instant, 2009,2007]**

Sol Formic acid on warming with Tollen's reagent forms silver mirror, whereas acetic acid does not.

$$\underset{\text{Formic acid}}{HCOOH} + 2\ \underset{\text{Tollen's reagent}}{[Ag(NH_3)_2]^+} + 2OH^- \longrightarrow CO_2 + \underset{\text{Mirror}}{2Ag\downarrow} + 4NH_3 + 2H_2O$$

Q.8 The correct order of acidic strength is

(a) $HCOOH > C_6H_5COOH > CH_3COOH$
(b) $HCOOH > CH_3COOH > C_6H_5COOH$
(c) $C_6H_5COOH > HCOOH > CH_3COOH$
(d) $CH_3COOH > C_6H_5COOH > HCOOH$ **[2010]**

Sol (*c*) $C_6H_5COOH > HCOOH > CH_3COOH$

Electron donating groups decrease the stability of the carboxylate ion by intensifying the negative charge.

Q.9 Name the products formed, when ethanamide is allowed to react with sodium nitrite and dilute hydrochloric acid at low temperature. **[2008]**

Sol $\underset{\text{Ethanamide}}{CH_3CONH_2} + HONO \xrightarrow{NaNO_2/HCl} \underset{\text{Acetic acid}}{CH_3COOH} + N_2 + H_2O$

Important Questions

Q.10 Formic acid and acetic acid may be distinguished by reaction with **[Textbook]**

(a) sodium
(b) dilute acidified $KMnO_4$
(c) 2, 4-dinitrophenyl hydrazine
(d) sodium ethoxide

Sol (*b*) Formic acid and acetic and may be distinguished by reaction with dil. acidified $KMnO_4$.

$$5HCOOH + 2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 5CO_2\uparrow + 8H_2O$$

$CH_3COOH \xrightarrow[H_2SO_4]{KMnO_4}$ does not discharge pink colour of $KMnO_4$.

Q.11 Acetic acid can be halogenated in presence of red P and halogen, but formic acid cannot be halogenated in the same way due to **[Textbook]**

(a) presence of α-hydrogen atom in acetic acid
(b) presence of —COOH group in formic acid
(c) presence of carbonyl group in acetic acid
(d) None of the above

Sol (*a*) Acetic acid can be halogenated in presence of red P and halogen, but formic acid cannot be halogenated in the same way, due to presence of α-hydrogen atom in acetic acid. Reactions involved are as follows:

$$CH_3COOH \xrightarrow[\Delta]{RedP/Cl_2} \underset{\displaystyle Cl}{\overset{\displaystyle |}{CH_2}}\!\!-COOH$$

Q.12 Among acetic acid, phenol and *n*-hexanol, which of the compound reacts with $NaHCO_3$ solution to give sodium salt and carbon dioxide? **[Textbook]**

(a) Acetic acid
(b) *n*-hexanol
(c) Acetic acid and phenol
(d) Phenol

Sol (*a*) Among acetic acid, phenol and n hexanol, the compound that reacts with $NaHCO_3$ solution to give sodium salt and carbon dioxide is acetic acid Reaction is as follows:

$$CH_3COOH + NaHCO_3 \longrightarrow CH_3CO\bar{O}\overset{+}{N}a + CO_2 + H_2O$$

Q.13 Which acid is strongest?

(a) CCl_3COOH (b) $Cl_2CHCOOH$
(c) $ClCH_2COOH$ (d) CH_3COOH

Sol (*a*) CCl_3COOH is the strongest acid.

Q.14 Which of the following cannot reduce Fehling's solution? **[Textbook]**

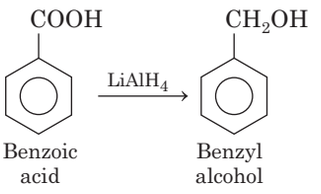
(a) Formic acid (b) Acetic acid
(c) Formaldehyde (d) Acetaldehyde

Sol (*b*) Acetic acid cannot reduce Fehling's solution, while formic acid, formaldehyde and acetaldehyde reduce Fehling solution due to the presence of CHO group.

Q.15 When benzoic acid is reacted with $LiAlH_4$, it forms

(a) benzene (b) benzaldehyde
(c) toluene (d) benzyl alcohol

Sol (*d*) When benzoic acid is reacted with $LiAlH_4$, if forms benzyl alcohol. Reaction is as follows:



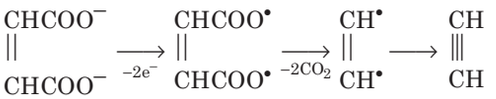
Q.16 Electrolysis of sodium salt of maleic acid to ethyne is known as
(a) Wurtz's reaction
(b) Clemmensen's reduction
(c) Kolbe's reaction
(d) Sabatier-Senderen's reaction

Sol (*c*) Electrolysis of sodium salt of maleic acid to ethyne is known as **Kolbe's reaction**.

Sodium moleate

At cathode $2Na^+ + 2e^- \longrightarrow 2Na$

At anode



Q.17 Which of the following reactions is expected to readily give a hydrocarbon product in good yield ? **[Textbook]**

(a) $R\text{COO}\overset{-+}{K} \xrightarrow[\text{oxidation}]{\text{Electrolysis}}$ (b) $R\text{COOAg} \xrightarrow{I_2}$

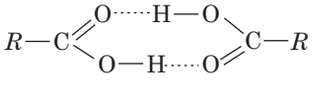
(c) $CH_3CH_3 \xrightarrow[h\nu]{Cl_2}$ (d) $(CH_3)_3CCl \xrightarrow{C_2H_5OH}$

Sol (*a*) Electrolytic oxidation of $R\text{COO}^-\text{K}^+$ yield hydrocarbon. Reactions are as follows:

$$R\text{COO}^-\text{K}^+ \xrightarrow[\text{oxidation}]{\text{Electrolysis}} \underset{\text{Alkane}}{R\text{—}R} + 2CO_2$$

Q.18 The boiling point of acetic acid is higher than expected from its molecular weight, because of **[Textbook]**
(a) solubility in water
(b) non-polar character
(c) strong oxidising character
(d) association through hydrogen bonding

Sol (*d*) The boiling point of acetic acid is higher than expected from its molecular weight because of association through hydrogen bonding.



Q.19 Carboxylic acids are more soluble in **[Textbook]**
(a) ether (b) C_6H_6
(c) Na_2CO_3 solution (d) $CHCl_3$

Sol (*c*) Carboxylic acids are more soluble in Na_2CO_3 solution because of its acidic character.

Q.20 Which acid is weaker than benzoic acid? **[Textbook]**
(a) *p* - methylbenzoic acid (b) *p* - chlorobenzoic acid
(c) *p* - nitrobenzoic acid (d) *o* - chlorobenzoic acid

Sol (*a*) *p* - methyl benzoic acid is weaker than benzoic acid. Due to the electron releasing effect of —CH_3 group, *p* - methyl benzoic acid is less acid than benzoic acid.

Q.21 What is the main reason for the fact that carboxylic acids can undergo ionisation? **[Textbook]**
(a) Absence of α-hydrogen
(b) Resonance stabilisation of the carboxylate ion
(c) High reactivity of α-hydrogen
(d) Hydrogen bonding

Sol (*b*) The main reason for the fact that carboxylic acids can undergo ionisation is the resonance stabilisation of the carboxylate ion.

Q.22 $R\text{COOH} \longrightarrow R\text{CH}_2\text{OH}$. This mode of reduction of an acid to alcohol can be affected by **[Textbook]**
(a) Zn/HCl (b) Na/alcohol
(c) aluminium isopropoxide and isopropyl alcohol
(d) $LiAlH_4$

Sol (*d*) The given reaction $R\text{COOH} \longrightarrow R\text{CH}_2\text{OH}$, i.e. mode of reduction of an acid to alcohol can be affected by $LiAlH_4$.

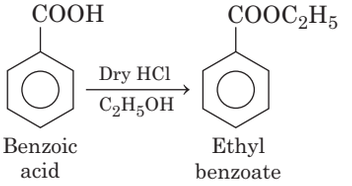
Q.23 Calcium acetate on heating yields **[Textbook]**
(a) CaO, CO_2 and H_2O
(b) $CaCO_3$ and H_2O
(c) acetaldehyde and $CaCO_3$
(d) $CaCO_3$ and acetone

Sol (*d*) Calcium acetate on heating yields $CaCO_3$ and acetone.

$$(CH_3COO)_2Ca \xrightarrow{\Delta} CaCO_3 + CH_3\overset{\overset{O}{\|}}{C}CH_3$$

Q.24 Benzoic acid may be converted into ethyl benzoate by reaction with **[Textbook]**
(a) ethyl chloride (b) dry HCl, C_2H_5OH
(c) ethyl alcohol (d) sodium ethoxide

Sol (*b*) Benzoic acid may be converted into ethylbenzoate by reaction with dry HCl and C_2H_5OH.



Q.25 Which of the following is the strongest acid ? **[Textbook]**
(a) *o* -nitrobenzoic acid (b) *p* -nitrobenzoic acid
(c) *p* -chlorobenzoic acid (d) Benzoic acid

Sol (*a*) Among the given options, *o*- nitrobenzoic acid is the strongest acid because —NO_2 group at *ortho* position has higher inductive effect compared to the nitro group on *para* position.

Q.26 Which has the highest pK_a value? **[Textbook]**

(a) Benzoic acid (b) *p* -nitrobenzoic acid
(c) *m*-nitrobenzoic acid (d) *o*-nitrobenzoic acid

Sol (*a*) Benzoic acid has the highest pK_a value.

p -nitrobenzoic acid, *m*-nitrobenzoic acid and *o* nitro benzoic acid possess —NO_2 group that decreases the pK_a value.

Q.27 Among the following compounds, most acidic is **[Textbook]**

(a) *p* -nitrophenol
(b) *p* -hydroxybenzoic acid
(c) *o* -hydroxybenzoic acid
(d) *p* -toluic acid

Sol (*c*) At *ortho* position strong hydrogen bonding is formed between the phenolic —OH and the carboxylate ion in *o*-hydroxybenzoic acid. Therefore, it is most acidic.

Q.28 How will you prepare acetamide from acetic acid? **[Textbook]**

Sol $CH_3COOH + NH_3 \longrightarrow CH_3COO^{-}\overset{+}{N}H_4 \xrightarrow{\text{Heat}} CH_3CONH_2 + H_2O$

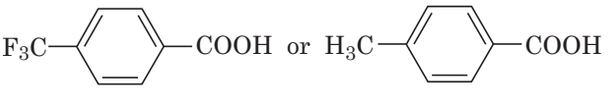
Q.29 Benzoyl chloride is formed by the action of PCl_5 on ..... . **[Textbook]**

Sol Benzoyl chloride is formed by the action of PCl_5 on benzoic acid.

Reaction is as follows:

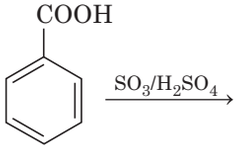
$\underset{\text{Benzoic acid}}{C_6H_5COOH} + \underset{\text{Phosphorus pentachloride}}{PCl_5} \longrightarrow \underset{\text{Benzoyl chloride}}{C_6H_5COCl} + POCl_3 + HCl$

Q.30 Which acid of given pair here would you expect to be stronger ?

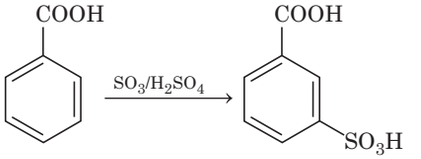


Sol

Q.31 Complete the following equation.



Sol



Benzoic acid — *m*-carboxy benzene sulphonic acid

2 MARK *Questions*

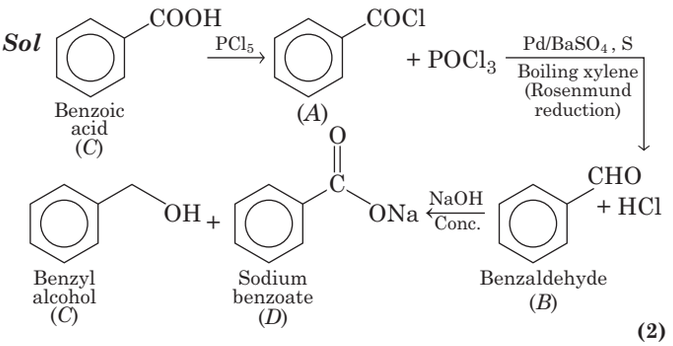
Exams' Questions

Q.32 Identify *A*, *B*, *C* and *D*.

$$C_6H_5COOH \xrightarrow{PCl_5} A \xrightarrow[H_2,\ \text{boiling xylene}]{Pd/BaSO_4,\ S} B \xrightarrow[NaOH]{\text{Conc.}} C + D$$

[2015]

Sol



(2)

Q.33 Suggest a chemical test to distinguish between acetic acid and formic acid. Give equation. **[2015]**

Sol Formic acid acts as a reducing agent, while acetic acid is not. Formic acid reduces Tollen's reagent forming silver mirror, while acetic acid does not.

$$\underset{\text{Formic acid}}{HCOOH} + 2\underset{\text{Tollen's reagent}}{[Ag(NH_3)_2]OH} \longrightarrow HCOONH_4 + 3NH_3 + \underset{\text{(Mirror)}}{2Ag\downarrow} + H_2O$$

Acetic acid does not reduce Tollen's reagent. **(2)**

Q.34 Identify *A*, *B*, *C* and *D*. **[2009]**

$$CH_3COOH \xrightarrow{NH_3} A \xrightarrow{\Delta} B \xrightarrow[KOH]{Br_2} C \xrightarrow[\text{with } CH_3I\text{(Excess)}]{\text{Heat}} D$$

Sol $A = CH_3COONH_4$ (Ammonium acetate)

$B = CH_3CONH_2$ (Ethanamide)

$C = CH_3NH_2$ (Methanamine)

$D = (CH_3)_3N$ or CH_3I **(2)**

Q.35 How will you obtain acetyl chloride from acetic acid? Give equation. **[2004,2003]**

Sol Acetic acid is treated with PCl_5 to get acetyl chloride.

$\underset{\text{Acetic acid}}{CH_3COOH} + PCl_5 \longrightarrow \underset{\text{Acetyl chloride}}{CH_3COCl} + HCl + POCl_3$ **(2)**

Q.36 How can a carboxylic acid be converted to acetaldehyde in two steps? **[2002]**

Sol Acetic acid is first converted into its calcium salt. Then calcium acetate is mixed with calcium formate and mixture is distilled. Acetaldehyde results.

$$\begin{matrix} CH_3COO \\ CH_3COO \end{matrix}\!\!\diagdown\!\!\diagup Ca + \begin{matrix} HCOO \\ HCOO \end{matrix}\!\!\diagdown\!\!\diagup Ca \xrightarrow{\text{Distillation}} 2CaCO_3 + \underset{\text{Acetaldehyde}}{2CH_3CHO}$$

(2)

Q.37 Identify *A*, *B*, *C* and *D*.

$$CH_3C{\equiv}N \xrightarrow{H_3O^+} A \xrightarrow{SOCl_2} B \xrightarrow{H_2\text{-}Pd/BaSO_4} C \xrightarrow{HCN} D$$ **[2002]**

Sol *A* is CH_3COOH, *B* is CH_3COCl **(1)**

C is CH_3CHO, *D* is $CH_3CH(OH)CN$ **(1)**

Important Questions

Q.38 What happens, when acetic acid reacts with ethyl alcohol in presence of conc.H_2SO_4? **[Textbook]**

Sol Refer to text (formation of esters) on page 287. **(2)**

Q.39 Arrange the following in the increasing order of acidic strength. **[Textbook]**

(i) $ClCH_2COOH$ (ii) $ClCH_2CH_2COOH$

(iii) FCH_2COOH (iv) CH_3COOH

Sol The correct increasing order of acidic strength is (iv) < (ii) < (i) < (iii)

The electron withdrawing inductive effect of the halogens decreases in the order F > Cl > Br > I and also acidic strength decreases with increase in distance of halogen atom from — COOH group. **(2)**

Q.40 How can you distinguish acetic acid from acetone? **[Textbook]**

Sol Acetic acid react with sodium bicarbonate, while acetone does not. Reaction is as follows:

$$CH_3COOH + NaHCO_3 \longrightarrow CH_3COO^-Na^+ + CO_2 + H_2O$$ **(2)**

Q.41 What is the reaction of formic acid with Tollen's reagent and also with sodium? **[Textbook]**

Sol Formic acid oxidises ammoniacal solution of silver nitrate (Tollen's reagent) to metallic silver.

$$HCOOH + \underset{\text{(From Tollen's reagent)}}{Ag_2O} \longrightarrow 2Ag + CO_2 + H_2O$$ **(1)**

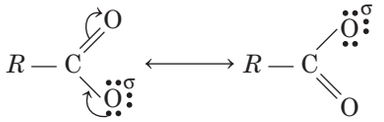
From sodium Formic acids react with strong electrostatic metals like Na, to liberate H_2 gas with formation of sodium formate.

$$2HCOOH + 2Na \longrightarrow 2HCOO^-Na^+ + H_2$$ **(1)**

Q.42 What do you say about the acidic character of carboxylic acid?

Sol The acidic character is due to the greater resonance stabilisation of carboxylate ion. More the stability of carboxylate ion, stronger is the acid.

$$RCOOH \rightleftharpoons RCOO^- + H^+$$



The presence of electron releasing groups makes the acid weak, whereas the presence of electron attracting groups make the acid strong. **(2)**

Q.43 How can a carboxylic acid be converted to an aldehyde in two steps? **[Textbook]**

Sol **Step 1** $RCOOH \xrightarrow{LiAlH_4} RCH_2OH$ **(1)**

Step 2 $RCH_2OH \xrightarrow[K_2Cr_2O_7]{[O]} RCH_2CHO$ **(1)**

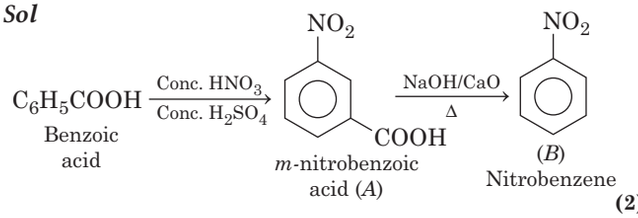
Q.44 Why *m*-nitrobenzoic acid is a stronger acid than benzoic acid? **[Textbook]**

Sol *m* - nitrobenzoic acid is a stronger acid than benzoic acid. Presence of —NO_2 (EWG) group on benzene decreases its electron density and increase the acidity. **(2)**

Q.45 Identify *A* and *B*. **[Textbook]**

$$C_6H_5COOH \xrightarrow[Conc.H_2SO_4]{Conc.HNO_3} A \xrightarrow[\Delta]{NaOH/CaO} B$$

Sol



(2)

Q.46 Give possible explanation for each of the following:

During the preparation of esters from a carboxylic acid and an alcohol in the presence of an acid catalyst, the water or the ester should be removed as soon as it is formed.

Sol Esterification is a reversible reaction.

$$RCOOH + R'OH \overset{H_2SO_4}{\rightleftharpoons} \underset{\text{Ester}}{RCOOR'} + H_2O$$

When the sufficient amount of products is formed, the rate of forward reaction decreases and the reverse reaction begins.

To avoid this condition, i.e. in order to shift the equilibrium in forward direction, the concentration of products (ester and/or water) should be decreased (Le-Chatelier's principle). So, water should be removed from time to time. **(2)**

Q.47 What happens, when acetic acid reacts with ethyl alcohol in the presence of concentrated H_2SO_4 ?

Sol Ethyl acetate is formed. **(1)**

$$\underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Ethyl alcohol}}{C_2H_5OH} \xrightarrow{Conc.\ H_2SO_4}$$

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + H_2O$$ **(1)**

Q.48 Identify the compounds *A* and *B* in the following reaction.

$$CH_3—Br \xrightarrow{Mg/\text{Ether}} CH_3—MgBr \xrightarrow[\text{(ii) Water}]{\text{(i) } CO_2} A \xrightarrow[\Delta]{CH_3OH/H^+} B$$

Sol $CH_3—Br \xrightarrow{Mg/\text{Ether}} CH_3—MgBr \xrightarrow[\text{(ii) } H_2O]{\text{(i) } CO_2}$

$CH_3—\overset{\overset{O}{\|}}{C}—OCH_3 \xleftarrow[\text{Esterification}]{CH_3OH/H^+,\ \Delta} CH_3—\overset{\overset{O}{\|}}{C}—OH \leftarrow$

Methyl ethanoate (*B*) — Ethanoic acid (*A*) **(2)**

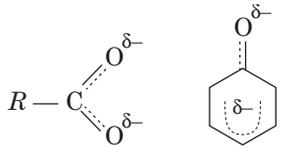
3 MARK *Questions*

Exams' Questions

Q.49 Although phenoxide ion has more number of resonating structures than carboxylate ion, carboxylic acid is a stronger acid than phenol. Why? **[2017]**

Sol Phenoxide ion has non-equivalent resonanting structures in which the negative charge is at the less electronegative carbon atom. **(1)**

The negative charge is delocalised over two electronegative oxygen atoms in carboxylate ion, whereas in phenoxide ion the negative charge is less effectively delocalised over one oxygen atom and less electronegative carbon atoms. **(1)**



Carboxylate ion — Phenoxide ion

Therefore, carboxylic acid is a stronger acid than phenol. **(1)**

Q.50 Which acid of each pair shown here would you expect to be stronger?

(i) CH_3COOH or CH_2FCOOH

(ii) CH_2FCOOH or $CH_2ClCOOH$

(iii) $CH_2FCH_2CH_2COOH$ or CH_3CHFCH_2COOH **[2012]**

Sol (i) CH_2FCOOH is stronger acid. **(1)**

(ii) CH_2FCOOH is a stronger acid. **(1)**

(iii) CH_3CHFCH_2COOH is a stronger acid. **(1)**

Q.51 An organic compound *A* molecular formula ($C_8H_{16}O_2$) was hydrolysed with dilute sulphuric acid to give a carboxylic acid *B* and alcohol of *C*. Oxidation of *C* with chromic acid produces *B*. *C* on dehydration gives but-1-ene. Write equations for the reactions involved. **[2010, 2009, 2008]**

Sol (i) Since, *A* produces carboxylic acid *B* and an alcohol *C* on hydrolysis, compound *A* is an ester. **(1)**

(ii) Alcohol *C* on oxidation produces acid *B*. It means both *B* and *C* have same number of carbon atoms, i.e. four each. **(1)**

(iii) The equations for all the above reactions are.

$$CH_3CH_2CH_2—\overset{\overset{O}{\|}}{C}—OCH_2CH_2CH_2CH_3$$

Butyl butanoate (*A*)

$$\xrightarrow[\text{Hydrolysis}]{\text{Dil. } H_2SO_4} CH_3CH_2CH_2—\overset{\overset{O}{\|}}{C}—OH + CH_3CH_2CH_2CH_2OH$$

Butanoic acid (*B*) + Butan-1-ol (*C*) **(1)**

Important Questions

Q.52 What happens when CH_3COONa is electrolysed? Explain with, mechanism. **[Textbook]**

Sol Sodium acetate undergoes decarboxylation on electrolysis of its aqueous solution and forms hydrocarbon having twice the number of carbon atoms present in the alkyl group of acid. This reaction is known as **Kolbe electrolysis**.

$$2CH_3COO^-Na^+ \rightleftharpoons 2CH_3COO^- + 2Na^+$$

$$2H_2O \rightleftharpoons 2OH^- + 2H^+$$

At anode

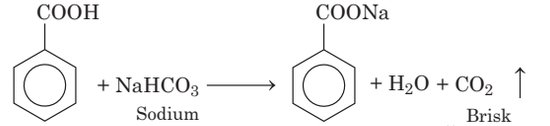
$$2CH_3COO^- \xrightarrow{-2e^-} \underset{\text{(Unstable)}}{2CH_3COO} \longrightarrow \underset{\text{Ethane}}{CH_3—CH_3} + 2CO_2$$

At cathode $2H^+ + 2e^- \longrightarrow H_2\uparrow$ **(3)**

Q.53 How will you distinguish between benzoic acid and phenol? **[Textbook]**

Sol **Sodium bicarbonate** ($NaHCO_3$) **test**

Benzoic acid when treated with $NaHCO_3$ gives effervescence due to the evolution of CO_2 gas, whereas phenol being weak acid does not give this reaction. **(1½)**

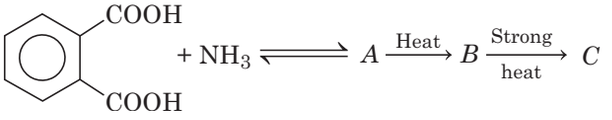


Benzoic acid — Sodium benzoate **(1½)**

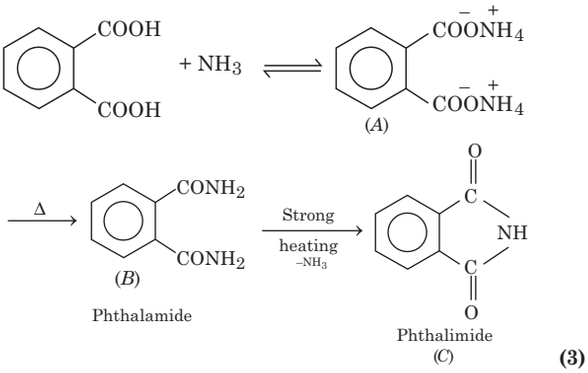
Q.54 CH_3COOH gives HVZ reaction, whereas HCOOH does not. Explain. **[Textbook]**

Sol CH_3COOH gives HVZ reaction because it has an α-hydrogen atom that gives α-halocarboxylic acid on reaction with red P- whereas HCOOH does not have α-H atom. Thus, does not give this reaction. **(3)**

Q.55 Identify *A*, *B* and *C* in the sequence.



Sol



(3)

Q.56 A compound *A* (C_2H_6O) on oxidation by PCC give *B*, which on treatment with aqueous alkali and subsequent heating furnished *C*. *B* on oxidation by $KMnO_4$, forms a monobasic carboxylic acid with molar mass 60 g mol^{-1}. Deduce the structures of *A*, *B* and *C*.

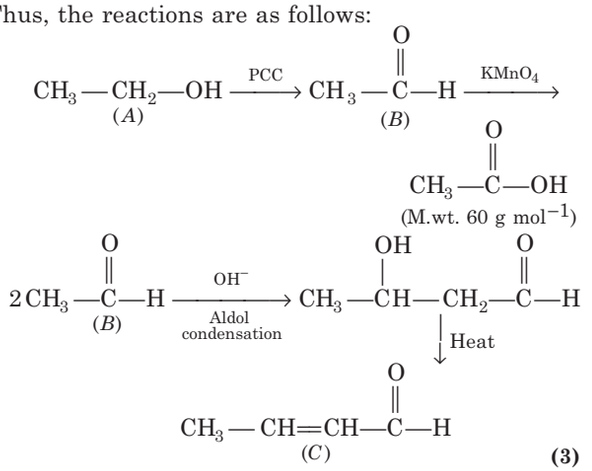
Sol Monobasic carboxylic acid = *R*COOH

Given that, molar mass of *R*COOH = 60 g mol^{-1}

i.e. $x + 12 + 16 + 16 + 1 = 60 \Rightarrow x = 15$

Thus, $R = -CH_3$ (molar mass 15) and the acid is CH_3COOH. Since, the acid is obtained by the oxidation of aldehyde, so *B* is an aldehyde, i.e. CH_3CHO and *A* is CH_3CH_2OH.

Thus, the reactions are as follows:



(3)

7 MARK *Questions*

Exams' Questions

Q.57 How is acetic acid prepared from methyl magnesium bromide? What happens, when acetic acid is

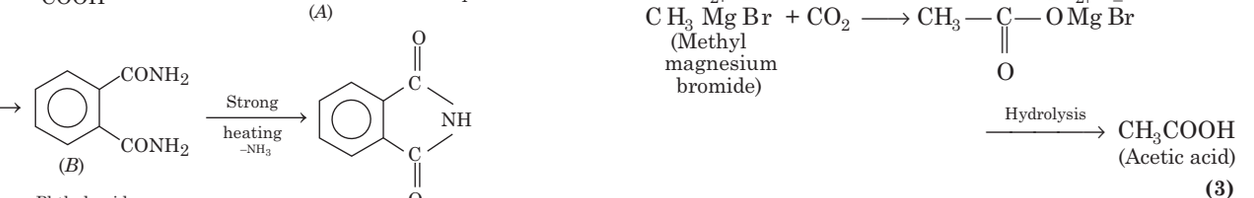
(i) reduced by lithium aluminium hydride and

(ii) treated with ammonium hydroxide and the resulting product is heated at high temperature?

[2019, Textbook]

Sol Acetic Acid from Methyl Magnesium Bromide

Methyl magnesium bromide when reacts with dry ice (solid CO_2) in etheral solution produce salts of carboxylic acid, which on acidification with mineral acids give corresponding carboxylic acids.



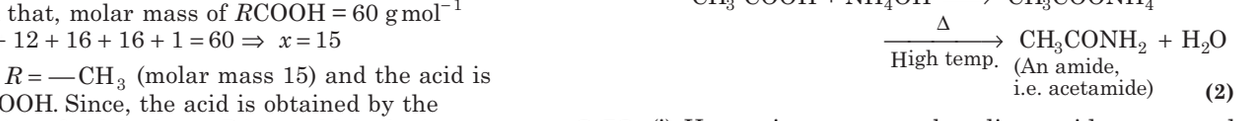
(3)

(i) **Reaction of CH_3COOH with $LiAlH_4$**

On reaction of CH_3COOH with lithium aluminium hydride ($LiAlH_4$), it reduces to give an alcohol :

(2)

(ii) Reaction of CH_3COOH with NH_4OH, followed by heating at high temperature give amides :



(2)

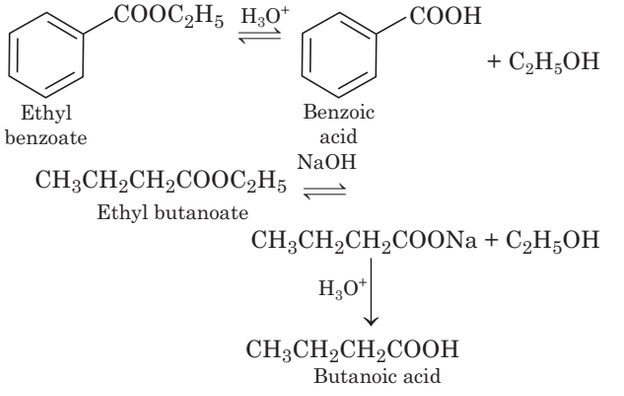
Q.58 (i) How is mono-carboxylic acid prepared from ester?

How does it react with sodium bicarbonate?

(ii) Arrange the following acids in the order of their increasing acidity with reason.

HCOOH, CH_3COOH, C_6H_5COOH **[2015]**

Sol. (i) **From Esters** Acidic hydrolysis of esters gives directly carboxylic acids while basic hydrolysis gives carboxylates, which on acidification give corresponding carboxylic acids.



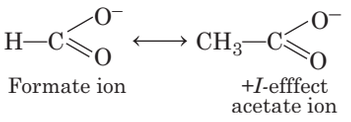
Reaction with sodium bicarbonate

$$\underset{\text{Acetic acid}}{CH_3COOH} + NaHCO_3 \longrightarrow \underset{\text{Sodium acetate}}{CH_3COONa} + CO_2 + H_2O$$

(3)

(ii) **Order of increasing acidity**

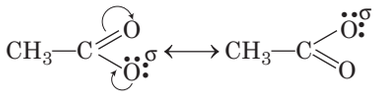
$HCOOH > C_6H_5COOH > CH_3COOH$ Acetic acid is weaker acid than formic acid because methyl group being electron releasing causes $+I$-effect decreasing the ionisation of acetic acid and destabilises the acetate ion by negative charge.



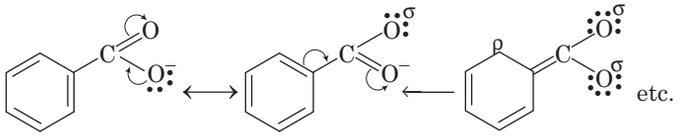
Formate ion +*I*-efffect acetate ion

As a result, acetic acid dissociates to a lesser extent than formic acid.

Benzoic acid C_6H_5COOH is a weak acid but slightly stronger than acetic acid. The reason for this is that benzoate ion is more stable than acetate ion. Acetate ion and benzoate ion can be written in the following resonating structures.



Negative charge is dispersed on two oxygen atoms and there are two resonating structures.



etc.

The negative charge is dispersed on two oxygen atoms in both the cases but the number of resonating structures in benzoate ion are more than those in acetate ion.

Hence, benzoate ion is more stable than acetate ion and benzoic acid is more acidic. **(4)**

Q.59 (i) Compare the acid characters of formic acid and acetic acid.

(ii) Compound A ($C_6H_{12}O_2$) on reduction with $LiAlH_4$ yields two compounds B and C. The compound B on oxidation gives D which on treatment with aqueous alkali and subsequent heating furnishes E. The latter on catalytic hydrogenation gives C. The compound D on further oxidation gives CH_3COOH. Deduce the structures of A, B, C, D and E. **[2009]**

Sol (i) Refer to text on page 289. **(2)**

(ii) D gives CH_3COOH on oxidation, so it must be CH_3CHO and it is obtained by the oxidation of B, so B is CH_3CH_2OH.

Further, D being an aldehyde having α-H undergoes aldol condensation. The α,β-unsaturated aldehyde formed gives C on hydrogenation. Thus, compound A is $CH_3CO(CH_2)_3CH_2OH$ and the reactions involved are as follows:

$$CH_3\overset{\underset{O}{\|}}{C}—O\underset{(A)}{CH_2CH_2CH_2CH_3} \xrightarrow{LiAlH_4} \underset{(C)}{CH_3CH_2CH_2CH_2OH} + \underset{(B)}{CH_3CH_2OH}$$

(5)

Important Questions

Q.60 (i) How is acetic acid prepared? Give any two method.

(ii) Identify A to E in the following sequence.

$$CH_3CH_2COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow{Br_2/KOH} B \xrightarrow{HONO} C \xrightarrow{[O]} CH_3COOH \xrightarrow[\text{Dil. HCl}]{Ca(OH)_2} D \xrightarrow{LiAlH_4} E$$

Sol (i) Refer to the text on page 183, 184 . (oxidation of primary alcohol, hydrolysis of nitriles).

(ii) $CH_3CH_2COOH \xrightarrow[\Delta]{NH_3} \underset{\text{Ethanamide}\ (A)}{CH_3CH_2CONH_2}$

$$\xrightarrow{Br_2/KOH} \underset{\text{Ethanamine}\ (B)}{CH_3CH_2NH_2} \xrightarrow{HNO_2} \underset{\text{Ethanol}\ (C)}{CH_3CH_2OH}$$

$$\xrightarrow{[O]} \underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow[\text{dil. HCl}]{Ca(OH)_2} \underset{\text{Acetone}\ (D)}{CH_3COCH_3}$$

$$\xrightarrow{LiAlH_4} CH_3\overset{\underset{OH}{|}}{C}HCH_3$$

Propan-2-ol (E)

(7)

Q.61 How do you prepare the following from acetic acid?

(i) Acetaldehyde (ii) Methyl amine

(iii) Methyl cyanide (iv) Acetone

Sol (i) $CH_3COOH \xrightarrow{LiAlH_4} CH_3CH_2OH \xrightarrow[K_2Cr_2O_7]{[O]} CH_3CHO$

(ii) $CH_3COOH \xrightarrow{SOCl_2} CH_3COCl \xrightarrow[\text{excess}]{NH_3} CH_3CONH_2 \xrightarrow{Br_2/NaOH} CH_3NH_2$

(iii) $CH_3COOH \xrightarrow[\Delta]{NH_3} CH_3CONH_2 \xrightarrow[\Delta]{P_2O_5} CH_3CN + H_2O$

(iv) $CH_3COOH \xrightarrow{Ca(OH_2)} (CH_3COO)_2O \xrightarrow[\text{distillation}]{\text{Dry}} CH_3\overset{\underset{O}{\|}}{C}CH_3 + CaCO_3$

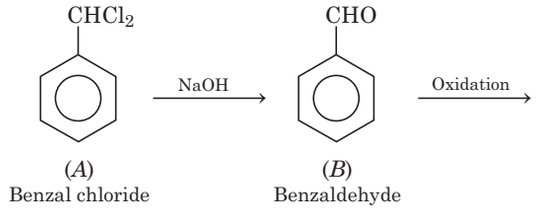
(7)

Q.62 An organic compound A ($C_7H_6Cl_2$) on treatment with NaOH solution gives another compound B (C_7H_6O). B on oxidation gives an acid

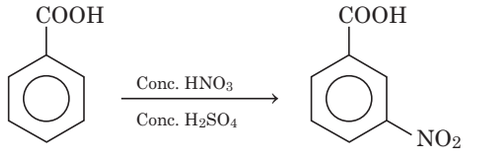
($C_7H_5O_2$) which on treatment with a mixture of conc. HNO_3 and H_2SO_4 gives a compound *D* ($C_7H_5NO_2$). *B* on treatment with conc. NaOH gives compound *E* (C_7H_8O) and C_6H_5COONa. Deduce the structures of *A*, *B*, *C*, *D* and *E*.

Sol Since, compound *A* on treatment with NaOH gives C_7H_6O, i.e. only one O-atom is introduced, both the Cl atoms must be present on the same carbon atom.

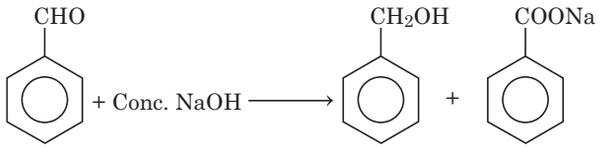
The molecular formula C_7H_6O suggest the structure of *B* is C_6H_5CHO. Thus, *A* must be $C_6H_5CHCl_2$. The relevant equations are: **(1)**



(*A*) Benzal chloride (*B*) Benzaldehyde



(*C*) Benzoic acid (*D*) *m*-nitrobenzoic acid **(1 × 4 = 4)**



(*B*) Benzaldehyde (*E*) Benzyl alcohol Sodium benzoate **(2)**

Q.63 (i) Write the reactions involved in the following:

(a) Hell-Volhard-Zelinsky reaction

(b) Decarboxylation reaction

(ii) State reasons for

(a) monochloroethanoic acid is a weaker acid than dichloroethanoic acid.

(b) benzoic acid is a stronger acid than ethanoic acid.

Sol (i) (a) **Hell-Volhard-Zelinsky reaction**

Carboxylic acids having α-hydrogen are halogenated at the α-position. On treatment with chlorine or bromine in the presence of small amount of red phosphorus it give α-halocarboxylic acids. The reaction is known as Hell-Volhard-Zelinsky reaction. **(1)**

$$R\text{—}CH_2\text{—}COOH \xrightarrow[(ii)\ H_2O]{(i)\ X_2/\text{Red phosphorus}} R\text{—}\underset{\displaystyle X}{\underset{|}{C}}H\text{—}COOH$$

α-halocarboxylic acid

(where, *X* = Cl, Br) **(2)**

(b) **Decarboxylation reaction**

Decarboxylation is a chemical reaction that take place in carboxylic acid *via* the release of carbon dioxide (CO_2). It is an example of the cleavage of a carbon-carbon single bond.

Using sodalime

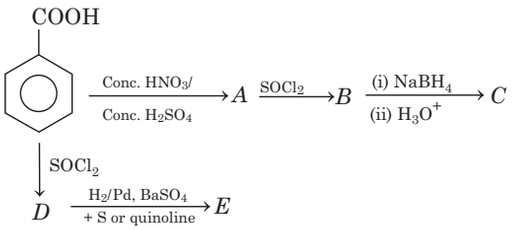
$$R\text{—}CO\bar{O}\overset{+}{N}a \xrightarrow[\text{Heat}]{\text{NaOH and CaO}} \underset{\text{Alkane}}{R\text{—}H} + Na_2CO_3$$

(In sodalime, the ratio of NaOH and CaO is 3 : 1.) **(1)**

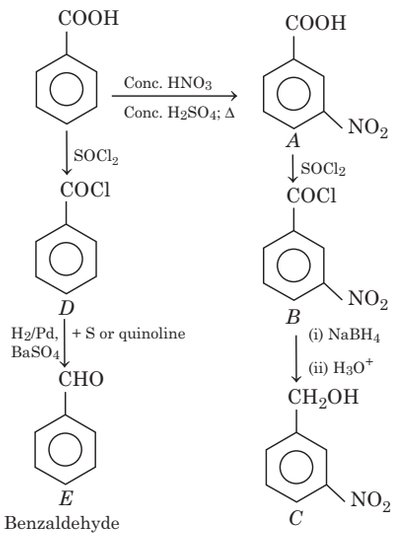
(ii) (a) It is because, dichloroethanoic acid has two — Cl groups that exhibit more – *I*-effect and thus make the carboxylate ion more stable than monochloroethanoic acid which has only one — Cl group. **(1½)**

(b) In benzoic acid, the carboxylate ion is resonance stabilised while in case of ethanoic acid, it is destabilised due to the presence of electron releasing — CH_3 group. Higher be the stability of carboxylate ion, easier is the removal of a proton from the carboxylic acid and stronger is the acid. Thus, benzoic acid is a stronger acid than ethanoic acid. **(1½)**

Q.64 Identify *A* to *E* in the following reaction.



Sol



(2) **(2)** **(3)**

TOPIC TEST 2

- *Choose the correct option*

1. Which of the following is most acidic?

(a) Cl_2CHCH_2COOH (b) $BrCH_2COOH$

(c) $HCOOH$ (d) $ClCH_2CH_2COOH$

2. Consider the following reaction.

$$R\text{COOH} + R'\text{OH} \overset{H^+}{\rightleftharpoons} R\text{COO}R' + H_2O$$

The name of reaction is

(a) esterification

(b) carboxylation

(c) ammonification

(d) None of these [***Ans.*** **1.** (a), **2.** (a)]

- *Fill in the blanks*

3. ..... are reduced to 1° alcohols by $LiAlH_4$.

[***Ans.*** Carboxylic acids]

4. $R\text{COONa} \xrightarrow{\text{NaOH/CaO}} \ldots\ldots + Na_2CO_3$. [***Ans.*** RH]

- *Correct the sentence, if required by the changing of underlined words.*

5. $\underline{PCl_5}$ is preferred for the synthesis of RCOCl from RCOOH. [***Ans.*** Sentence is correct]

6. Carboxylic acids react with NH_4Cl to give ammonium salt. [***Ans.*** NH_3]

7. What is decarboxylation? Give example.

8. What is HVZ reaction?

9. Complete the following:

(i) $R\text{CH}_2\text{COOH} \xrightarrow[\text{(ii) } H_2O]{\text{(i) } X_2/\text{Red P}}$

(ii) $C_6H_5COOH + NH_3 \rightleftharpoons$

10. Explain the acidic character of carboxylic acids? And also, write the products of the following:

(i) $R\text{COOH} + PCl_5 \longrightarrow$

(ii) $R\text{COOH} + HI \xrightarrow[\text{At 500 K}]{\text{Red P}}$

Chapter Test

1 MARK *Questions*

1 Benzoic acid can be obtained by hydrolysis of propyl benzene. (State True/False) [***Ans.*** True]

2 What is esterification reaction. Give an example.

3 When chlorine is passed through acetic acid in the presence of red P, it forms

(i) 2-chloro ethanoic acid

(ii) trichloro acetaldehyde

(iii) trichloro acetic acid

(iv) methyl chloride [***Ans.*** (i)]

4 Ammonium salt of carboxylic acid on heating lose a ..... molecule and form ..... .

[***Ans.*** Water amide]

5 Carboxylic acid on treatment with Br_2 and red phosphorus gives ..... .

[***Ans.*** α-bromocarboxylic acid]

6 Complete the following reaction

$C_2H_5COOH \xrightarrow{Br_2/P}$

7 Write the IUPAC name of

$$CH_3—C\equiv C—CH=CH—\underset{\underset{O}{\|}}{C}—OH.$$

2 MARK *Questions*

8 Although phenoxide ion has more number of resonating structures than carboxylate ion, carboxylic acid is a stronger acid than phenol. Give two reasons.

9 Arrange the following compounds in an increasing order of their property as indicated

$CH_3CH_2CH(Br)COOH$, $CH_3CH(Br)CH_2COOH$, $(CH_3)_2CHCOOH$ (acidic strength).

10 Write the reaction of acetic acid with

(i) PCl_5 (ii) $SOCl_2$

11 What is meant by decarboxylation reaction? Explain with examples.

12 Carboxylic acids do not give the characteristic reactions of carboxyl group. Explain.

3 MARK *Questions*

13 Complete the following.

$CH_3CH_2OH \xrightarrow{PCl_5} A \xrightarrow{KCN} B \xrightarrow{H_2O/H^+} C.$

14 How can you form acetic acid from methanol? Write the equations involved.

15 Highly branched carboxylic acid are less acidic than unbranched acids. Why?

7 MARK *Questions*

16 Explain the following:

(i) (a) Why pK_a of methanoic acid is lower than that of ethanoic acid?

(b) Boiling point of benzoic acid is higher than that of *n*-propanol.

(c) Acetic acid is a stronger acid than alkanes.

(ii) Starting from methyl magnesium bromide, how will you synthesise acetic acid?

(iii) How is methanol converted into ethanoic acid?

17 (i) An organic compound *X* undergoes acid hydrolysis to form two compounds *Y* and *Z*. *Y* reacts with sodium carbonate to form *A*. *A* is heated with soda lime to form $B(CH_4)$. *Y* on reduction with $LiAlH_4$ gives *Z*. Identify *X*, *Y*, *Z*, *A* and also write the reactions involved.

(ii) Discuss some important uses of carboxylic acids.

(iii) Discuss briefly the effect of electron donating and electron withdrawing substituents on the acidity of aliphatic carboxylic acids.

18 Carry out the following conversions.

(i) Acetylene to acetic acid

(ii) Propionic acid to acetic acid

(iii) Ethanoic acid to propanoic acid

(iv) Acetic acid to methylamine

(v) Acetic acid to acetaldehyde

(vi) Propionic acid to isopropyl alcohol

(vii) Propionic acid to ethyl amine