Carboxylic Acids

Carbon compounds containing a carboxyl functional group, –COOH are called carboxylic acids. The carboxyl group, consists of a *carbonyl* group attached to a *hydroxyl* group, hence its name *carboxyl*. Carboxylic acids may be aliphatic (RCOOH) or aromatic (ArCOOH) depending on the group, alkyl or aryl, attached to carboxylic carbon. Large number of carboxylic acids are found in nature. Some higher members of aliphatic carboxylic acids (C_{12} – C_{18}) known as **fatty acids,** occur in natural fats as esters of glycerol. Carboxylic acids serve as starting material for several other important organic compounds such as anhydrides, esters, acid chlorides, amides, etc.

12.6 Nomenclature and Structure of Carboxyl Group

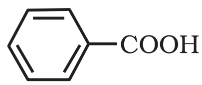
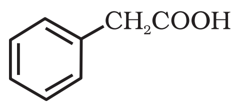
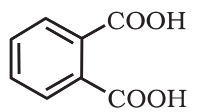
12.6.1 Nomenclature

Since carboxylic acids are amongst the earliest organic compounds to be isolated from nature, a large number of them are known by their common names. The common names end with the suffix –*ic* acid and have been derived from Latin or Greek names of their natural sources. For example, formic acid (HCOOH) was first obtained from red ants (Latin: *formica* means ant), acetic acid (CH_3COOH) from vinegar (Latin: *acetum*, means vinegar), butyric acid ($CH_3CH_2CH_2COOH$) from rancid butter (Latin: *butyrum,* means butter).

In the IUPAC system, aliphatic carboxylic acids are named by replacing the ending –*e* in the name of the corresponding alkane with –*oic acid*. In numbering the carbon chain, the carboxylic carbon is numbered one. For naming compounds containing more than one carboxyl group, the alkyl chain leaving carboxyl groups is numbered and the number of carboxyl groups is indicated by adding the multiplicative prefix, *dicarboxylic acid*, *tricarboxylic acid,* etc. to the name of parent alkyl chain. The position of –COOH groups are indicated by the arabic numeral before the multiplicative prefix. Some of the carboxylic acids along with their common and IUPAC names are listed in Table 12.3.

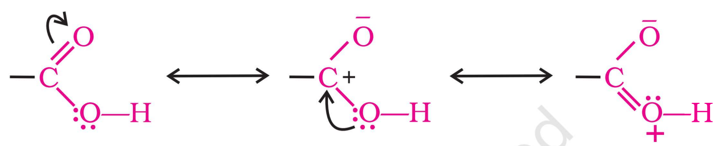
Table 12.3 Names and Structures of Some Carboxylic Acids

Structure	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
$(CH_3)_2CHCOOH$	Isobutyric 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
HOOC -CH_2-CH(COOH)-CH_2-COOH	Tricarballylic acid or carballylic acid	Propane-1, 2, 3-tricarboxylic acid

	Benzoic acid	Benzenecarboxylic acid (Benzoic acid)
	Phenylacetic acid	2-Phenylethanoic acid
	Phthalic acid	Benzene-1, 2-dicarboxylic acid

12.6.2 Structure of Carboxyl Group

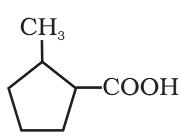
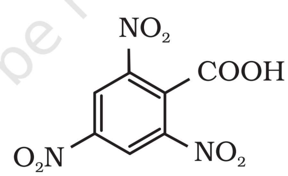
In carboxylic acids, the bonds to the carboxyl carbon lie in one plane and are separated by about 120°. The carboxylic carbon is less electrophilic than carbonyl carbon because of the possible resonance structure shown below:



Intext Question

12.6 Give the IUPAC names of the following compounds:

(i) Ph CH_2CH_2COOH (ii) $(CH_3)_2C{=}CHCOOH$

(iii)  (iv) 

12.7 *Methods of Preparation of Carboxylic Acids*

Some important methods of preparation of carboxylic acids are as follows.

1. ***From primary alcohols and aldehydes***

   Primary alcohols are readily oxidised to carboxylic acids with common oxidising agents such as potassium permanganate ($KMnO_4$) in neutral, acidic or alkaline media or by potassium dichromate ($K_2Cr_2O_7$) and chromium trioxide (CrO_3) in acidic media (Jones reagent).

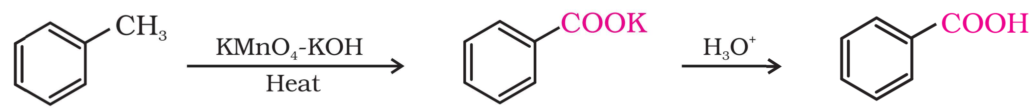
$$RCH_2OH \xrightarrow[2.\ H_3\overset{+}{O}]{1.\ \text{alkaline } KMnO_4} RCOOH$$

$$\underset{\text{1-Decanol}}{CH_3(CH_2)_8CH_2OH} \xrightarrow[\text{Jones reagent}]{CrO_3\text{-}H_2SO_4} \underset{\text{Decanoic acid}}{CH_3(CH_2)_8COOH}$$

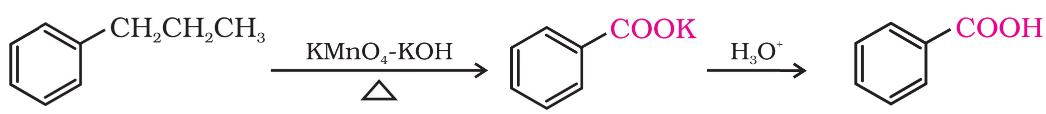
Carboxylic acids are also prepared from aldehydes by the use of mild oxidising agents (Section 12.4).

2. *From alkylbenzenes*

Aromatic carboxylic acids can be prepared by vigorous oxidation of alkyl benzenes with chromic acid or acidic or alkaline potassium permanganate. The entire side chain is oxidised to the carboxyl group irrespective of length of the side chain. Primary and secondary alkyl groups are oxidised in this manner while tertiary group is not affected. Suitably substituted alkenes are also oxidised to carboxylic acids with these oxidising reagents (refer Unit 13, Class XI).



Benzoic acid



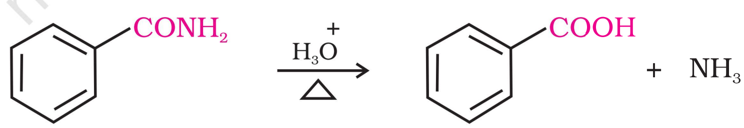
Benzoic acid

3. *From nitriles and amides*

Nitriles are hydrolysed to amides and then to acids in the presence of H^+ or $\overset{-}{O}H$ as catalyst. Mild reaction conditions are used to stop the reaction at the amide stage.

$$\text{R-CN} \xrightarrow[\text{H}_2\text{O}]{\overset{+}{\text{H}}\text{ or }\overset{-}{\text{O}}\text{H}} \text{R}-\overset{\overset{\displaystyle \text{O}}{\|}}{\text{C}}-\text{NH}_2 \xrightarrow[\Delta]{\overset{+}{\text{H}}\text{ or }\overset{-}{\text{O}}\text{H}} \text{RCOOH}$$

$$\underset{\text{Ethanamide}}{\text{CH}_3\text{CONH}_2} \xrightarrow[\Delta]{\text{H}_3\overset{+}{\text{O}}} \underset{\text{Ethanoic acid}}{\text{CH}_3\text{COOH}} + \text{NH}_3$$



Benzamide Benzoic acid

4. *From Grignard reagents*

Grignard reagents react with carbon dioxide (dry ice) to form salts of carboxylic acids which in turn give corresponding carboxylic acids after acidification with mineral acid.

$$\text{R-Mg-X} + \text{O=C=O} \xrightarrow{\text{Dry ether}} \text{R}-\text{C}\begin{smallmatrix}\nearrow\!\!\!\!\!=\text{O} \\ \searrow \text{O}^-\text{MgX}^+\end{smallmatrix} \xrightarrow{\text{H}_3\text{O}^+} \text{RCOOH}$$

As we know, the Grignard reagents and nitriles can be prepared from alkyl halides (refer Unit 10, Class XII). The above methods

(3 and 4) are useful for converting alkyl halides into corresponding carboxylic acids having one carbon atom more than that present in alkyl halides (ascending the series).

5. *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. Anhydrides on the other hand are hydrolysed to corresponding acid(s) with water.

$$RCOCl \xrightarrow{H_2O} RCOOH + \bar{C}l$$

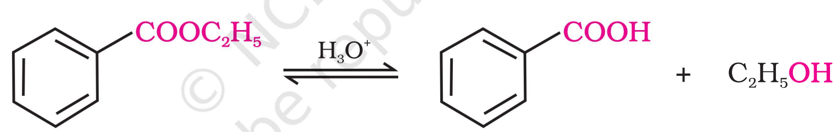
$$RCOCl \xrightarrow{\bar{O}H/H_2O} RCOO^- + \bar{C}l \xrightarrow{H_3O^+} RCOOH$$

$$\underset{\text{Benzoic anhydride}}{(C_6H_5CO)_2O} \xrightarrow{H_2O} \underset{\text{Benzoic acid}}{2\ C_6H_5COOH}$$

$$\underset{\text{Benzoic ethanoic anhydride}}{C_6H_5COOCOCH_3} \xrightarrow{H_2O} \underset{\text{Benzoic acid}}{C_6H_5COOH} + \underset{\text{Ethanoic acid}}{CH_3COOH}$$

6. *From esters*

Acidic hydrolysis of esters gives directly carboxylic acids while basic hydrolysis gives carboxylates, which on acidification give corresponding carboxylic acids.



Ethyl benzoate   Benzoic acid

$$\underset{\text{Ethyl butanoate}}{CH_3CH_2CH_2COOC_2H_5} \overset{NaOH}{\rightleftharpoons} CH_3CH_2CH_2COONa + C_2H_5OH$$

$$CH_3CH_2CH_2COONa \xrightarrow{H_3O^+} \underset{\text{Butanoic acid}}{CH_3CH_2CH_2COOH}$$

Example 12.5

Write chemical reactions to affect the following transformations:

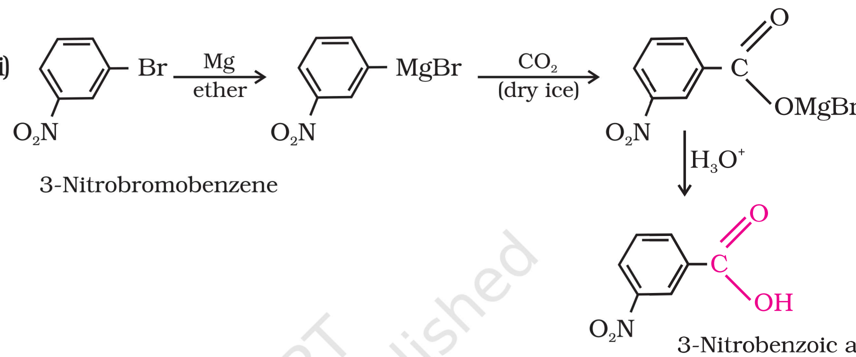
(i) Butan-1-ol to butanoic acid
(ii) Benzyl alcohol to phenylethanoic acid
(iii) 3-Nitrobromobenzene to 3-nitrobenzoic acid
(iv) 4-Methylacetophenone to benzene-1,4-dicarboxylic acid
(v) Cyclohexene to hexane-1,6-dioic acid
(vi) Butanal to butanoic acid.

Solution (i) $CH_3CH_2CH_2CH_2OH \xrightarrow[\text{Jones reagent}]{CrO_3\text{-}H_2SO_4} CH_3CH_2CH_2COOH$

Butan-1-ol → Butanoic acid

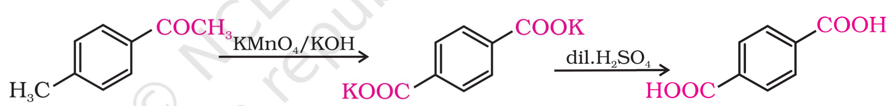
(ii) $C_6H_5CH_2OH \xrightarrow{HBr} C_6H_5CH_2Br \xrightarrow{KCN} C_6H_5CH_2CN \xrightarrow[\Delta]{H_3O^+} C_6H_5CH_2COOH$

Benzyl alcohol → Benzyl bromide → Benzyl cyanide → Phenylethanoic acid

(iii) 

3-Nitrobromobenzene

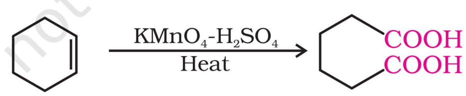
3-Nitrobenzoic acid

(iv) 

4-Methylacetophenone

Dipotassium benzene-1, 4-dicarboxylate

Benzene-1, 4-dicarboxylic acid (Terephthalic acid)

(v) 

Cyclohexene

Hexane-1, 6-dioic acid (Adipic acid)

(vi) $CH_3CH_2CH_2CHO \xrightarrow[\text{(Tollens' reagent)}]{\text{Ammoniacal } AgNO_3} CH_3CH_2CH_2COOH$

Butanal → Butanoic acid

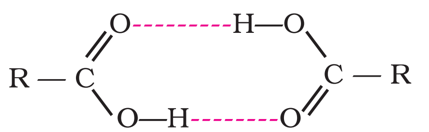
Intext Question

12.7 Show how each of the following compounds can be converted to benzoic acid.

(i) Ethylbenzene (ii) Acetophenone

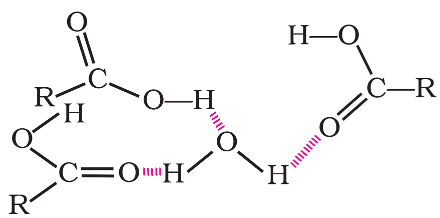
(iii) Bromobenzene (iv) Phenylethene (Styrene)

12.8 Physical Properties



dimer

In vapour state or in aprotic solvent



Hydrogen bonding of RCOOH with H_2O

Aliphatic carboxylic acids upto nine carbon atoms are colourless liquids at room temperature with unpleasant odours. The higher acids are wax like solids and are practically odourless due to their low volatility. Carboxylic acids are higher boiling liquids than aldehydes, ketones and even alcohols of comparable molecular masses. This is due to more extensive association of carboxylic acid molecules through intermolecular hydrogen bonding. The hydrogen bonds are not broken completely even in the vapour phase. In fact, most carboxylic acids exist as dimer in the vapour phase or in the aprotic solvents.

Simple aliphatic carboxylic acids having upto four carbon atoms are miscible in water due to the formation of hydrogen bonds with water. The solubility decreases with increasing number of carbon atoms. Higher carboxylic acids are practically insoluble in water due to the increased hydrophobic interaction of hydrocarbon part. Benzoic acid, the simplest aromatic carboxylic acid is nearly insoluble in cold water. Carboxylic acids are also soluble in less polar organic solvents like benzene, ether, alcohol, chloroform, etc.

12.9 Chemical Reactions

The reaction of carboxylic acids are classified as follows:

12.9.1 Reactions Involving Cleavage of O–H Bond

Acidity

Reactions with metals and alkalies

The carboxylic acids like alcohols evolve hydrogen with electropositive metals and form salts with alkalies similar to phenols. However, unlike phenols they react with weaker bases such as carbonates and hydrogencarbonates to evolve carbon dioxide. This reaction is used to detect the presence of carboxyl group in an organic compound.

$$2R\text{-}COOH + 2Na \longrightarrow \underset{\text{Sodium carboxylate}}{2R\text{-}CO\bar{O}Na^+} + H_2$$

$$R\text{-}COOH + NaOH \longrightarrow R\text{-}CO\bar{O}Na^+ + H_2O$$

$$R\text{-}COOH + NaHCO_3 \longrightarrow R\text{-}CO\bar{O}Na^+ + H_2O + CO_2$$

Carboxylic acids dissociate in water to give resonance stabilised carboxylate anions and hydronium ion.