Unit

12

Aldehydes, Ketones and Carboxylic Acids

Objectives

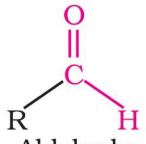
After studying this Unit, you will be able to

- write the common and IUPAC names of aldehydes, ketones and carboxylic acids;
- write the structures of the compounds containing functional groups namely carbonyl and carboxyl groups;
- describe the important methods of preparation and reactions of these classes of compounds;
- correlate physical properties and chemical reactions of aldehydes, ketones and carboxylic acids, with their structures;
- explain the mechanism of a few selected reactions of aldehydes and ketones;
- understand various factors affecting the acidity of carboxylic acids and their reactions;
- describe the uses of aldehydes, ketones and carboxylic acids.

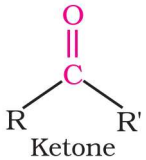
Carbonyl compounds are of utmost importance to organic chemistry. They are constituents of fabrics, flavourings, plastics and drugs.

In the previous Unit, you have studied organic compounds with functional groups containing carbon-oxygen single bond. In this Unit, we will study about the organic compounds containing carbon-oxygen double bond (>C=O) called carbonyl group, which is one of the most important functional groups in organic chemistry.

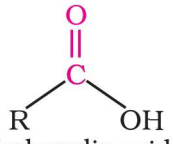
In aldehydes, the carbonyl group is bonded to a carbon and hydrogen while in the ketones, it is bonded to two carbon atoms. The carbonyl compounds in which carbonyl group is bonded to oxygen are known as carboxylic acids, and their derivatives (e.g. esters, anhydrides) while in compounds where carbon is attached to nitrogen and to halogens are called amides and acyl halides respectively. The general formulas of these classes of compounds are given below:



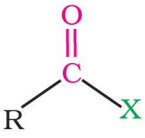
Aldehyde



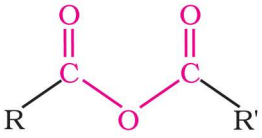
Ketone



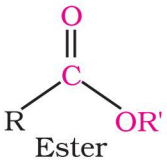
Carboxylic acid



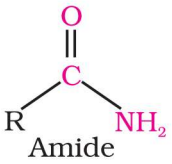
Acyl halide; X = (Halogen)



Acid anhydride

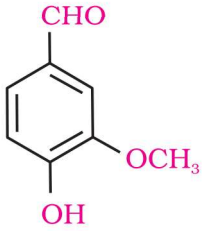


Ester

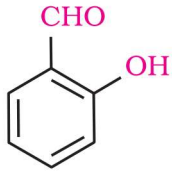


Amide

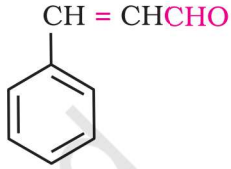
Aldehydes, ketones and carboxylic acids are widespread in plants and animal kingdom. They play an important role in biochemical processes of life. They add fragrance and flavour to nature, for example, vanillin (from vanilla beans), salicylaldehyde (from meadow sweet) and cinnamaldehyde (from cinnamon) have very pleasant fragrances.



Vanillin



Salicylaldehyde



Cinnamaldehyde

They are used in many food products and pharmaceuticals to add flavours. Some of these families are manufactured for use as solvents (i.e., acetone) and for preparing materials like adhesives, paints, resins, perfumes, plastics, fabrics, etc.

12.1 Nomenclature and Structure of Carbonyl Group

12.1.1 Nomenclature

I. Aldehydes and ketones

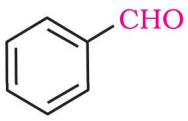
Aldehydes and ketones are the simplest and most important carbonyl compounds.

There are two systems of nomenclature of aldehydes and ketones.

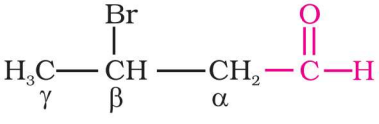
(a) Common names

Aldehydes and ketones are often called by their common names instead of IUPAC names. The common names of most aldehydes are derived from the common names of the corresponding carboxylic acids [Section 12.6.1] by replacing the ending *–ic* of acid with aldehyde. At the same time, the names reflect the Latin or Greek term for the original source of the acid or aldehyde. The location of the substituent in the carbon chain is indicated by Greek letters α, β, γ, δ, etc. The α-carbon being the one directly linked to the aldehyde group, β-carbon the next, and so on. For example

Acetaldehyde



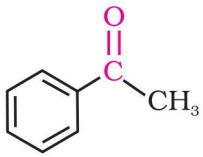
Benzaldehyde

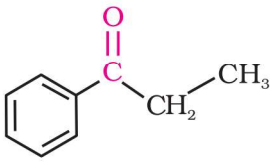


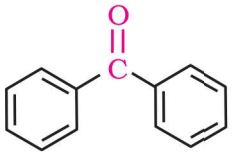
β-Bromobutyraldehyde

The common names of ketones are derived by naming two alkyl or aryl groups bonded to the carbonyl group. The locations of substituents are indicated by Greek letters, α α′, β β′ and so on beginning with the carbon atoms next to the carbonyl group, indicated as αα′. Some ketones have historical common names, the simplest dimethyl ketone is called acetone. Alkyl phenyl ketones are usually named by adding the acyl group as prefix to phenone. For example


Acetone

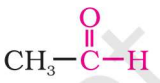

Acetophenone

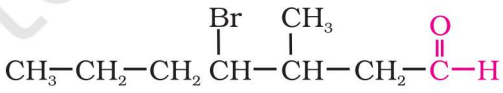

Propiophenone

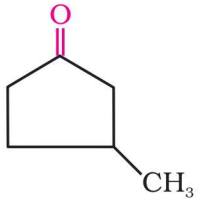

Benzophenone

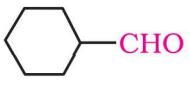
(b) IUPAC names

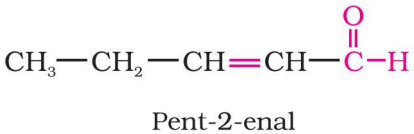
The IUPAC names of open chain aliphatic aldehydes and ketones are derived from the names of the corresponding alkanes by replacing the ending *–e* with *–al* and *–one* respectively. In case of aldehydes the longest carbon chain is numbered starting from the carbon of the aldehyde group while in case of ketones the numbering begins from the end nearer to the carbonyl group. The substituents are prefixed in alphabetical order along with numerals indicating their positions in the carbon chain. The same applies to cyclic ketones, where the carbonyl carbon is numbered one. When the aldehyde group is attached to a ring, the suffix carbaldehyde is added after the full name of the cycloalkane. The numbering of the ring carbon atoms start from the carbon atom attached to the aldehyde group. The name of the simplest aromatic aldehyde carrying the aldehyde group on a benzene ring is benzenecarbaldehyde. However, the common name benzaldehyde is also accepted by IUPAC. Other aromatic aldehydes are hence named as substituted benzaldehydes.

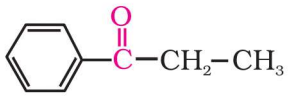

Ethanal


4-Bromo-3-methylheptanal

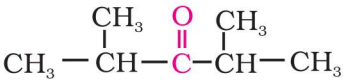

3-Methylcyclopentanone


Cyclohexanecarbaldehyde

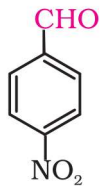

Pent-2-enal


1-Phenylpropan-1-one

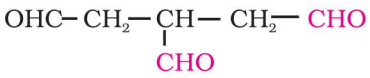
3-Oxopentanal



2,4-Dimethylpentan-3-one



4-Nitrobenzenecarbaldehyde
or
4-Nitrobenzaldehyde

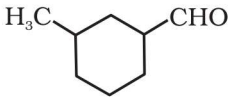
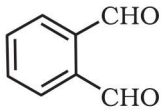
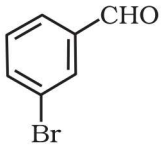
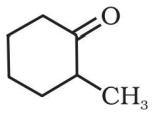


Propane–1,2,3-tricarbaldehyde

[Note: To give identical treatment to all aldehydic groups, the compound is named as shown above.]

The common and IUPAC names of some aldehydes and ketones are given in Table 12.1.

Table 12.1: Common and IUPAC Names of Some Aldehydes and Ketones

Structure	Common name	IUPAC name
Aldehydes		
HCHO	Formaldehyde	Methanal
CH_3CHO	Acetaldehyde	Ethanal
$(CH_3)_2CHCHO$	Isobutyraldehyde	2-Methylpropanal
	γ-Methylcyclohexanecarbaldehyde	3-Methylcyclohexanecarbaldehyde
$CH_3CH(OCH_3)CHO$	α-Methoxypropionaldehyde	2-Methoxypropanal
$CH_3CH_2CH_2CH_2CHO$	Valeraldehyde	Pentanal
$CH_2=CHCHO$	Acrolein	Prop-2-enal
	Phthaldehyde	Benzene-1,2-dicarbaldehyde
	*m*-Bromobenzaldehyde	3-Bromobenzenecarbaldehyde or 3-Bromobenzaldehyde
Ketones		
$CH_3COCH_2CH_2CH_3$	Methyl *n*-propyl ketone	Pentan-2-one
$(CH_3)_2CHCOCH(CH_3)_2$	Diisopropyl ketone	2,4-Dimethylpentan-3-one
	α-Methylcyclohexanone	2-Methylcyclohexanone
$(CH_3)_2C=CHCOCH_3$	Mesityl oxide	4-Methylpent-3-en-2-one

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

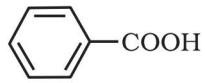
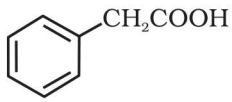
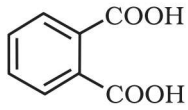
12.6.1 Nomenclature

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 is numbered and the number of carboxyl groups are 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.

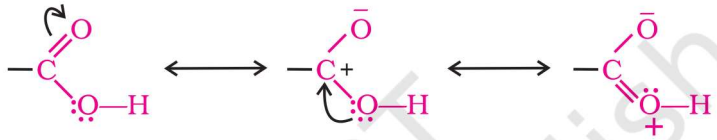
Table 12.3 Names and Structures of Some Carboxylic Acids

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	–	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

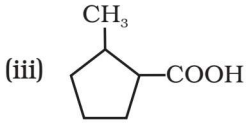
In carboxylic acids, the bonds to the carboxyl carbon lie in one plane and are separated by about 120°. The carboxylic carbon is less electrophilic than carbonyl carbon because of the possible resonance structure shown below:

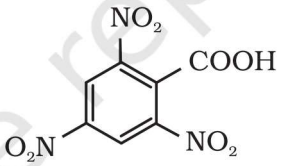


Intext Question

12.6 Give the IUPAC names of the following compounds:

(i) $PhCH_2CH_2COOH$ (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).

$$RCH_2OH \xrightarrow[2.\ H_3O^+]{1.\ \text{alkaline } KMnO_4} RCOOH$$

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