Notes

313en27

27

ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

In the last lesson, you studied about organic compounds containing functional groups having carbon-oxygen single bond. There are other classes of organic compounds in which the functional group contains the carbon- oxygen double bond. The examples of these classes of compounds being carbonyl compounds such as *aldehydes* and *ketones* as well as *carboxylic acids* and their *derivatives*. These organic compounds are very important both in the industry and in the synthesis of other organic compounds. Therefore, their study forms an important part of the organic chemistry. Let us study the chemistry of these classes of compounds in detail.

OBJECTIVES

After reading this lesson, you should be able to

- give IUPAC names of aldehydes and ketones;
- describe the general methods of preparation of aldehydes and ketones;
- discuss the trends in physical properties of the aldehydes and ketones in the light of the polar nature of the carbonyl group;
- explain important reactions exhibited by aldehydes and ketones;
- distinguish between aldehydes and ketones on the basis of certain reactions and tests based on them;
- give IUPAC names of carboxylic acids;
- explain general methods of preparation of carboxylic acids;
- discuss the physical properties and their trends for simple monocarboxylic acids;
- describe important reactions exhibited by carboxylic acids;

- explain the preparation and some interconversion reactions of carboxylic acid derivatives, and

- highlight the importance of aldehydes, ketones and carboxylic acids.

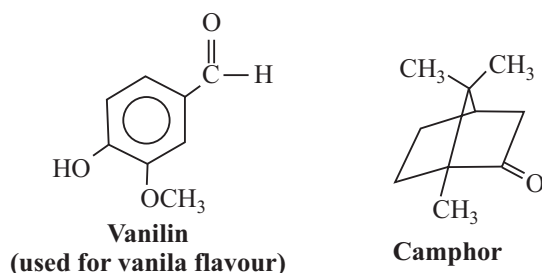## 27.1 ALDEHYDES AND KETONES

You have some familiarity with these classes of compounds from previous lessons. These compounds are also referred to as *carbonyl compounds* and have

$$-\overset{\overset{\displaystyle O}{\|}}{C}-$$ functionality present in them. These compounds exist widely in nature and are responsible for the flavour and aroma of many foods. They are also important industrially both as reagents in synthesis and as solvents.

Aldehydes have at least one hydrogen atom bonded to the carbonyl group, the other group may be either a hydrogen or an alkyl (or aryl) group. In *ketones*, the carbonyl group is bonded to two alkyl or aryl groups. The two groups bonded to a ketone may be similar or different resulting in a symmetrical or an unsymmatrical ketone, respectively.

Notes

| Carbonyl group | an aldehyde | a ketone |
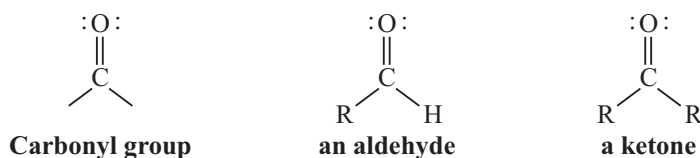
You must be familiar with vanilin and camphor. Their structures are given below. You can see that they contain an aldehyde and a keto functional group, respectively.

Vanilin
(used for vanila flavour)

Camphor

27.1.1 Nomenclature of Aldehydes and Ketones

In the IUPAC system of nomenclature, aliphatic *aldehydes* are named as *alkanals*. The final *-e* in the name of the corresponding alkane is substituted by *-al*.
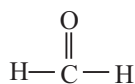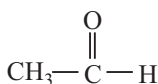
Notes

Some common examples of aldehydes and their names are given below :
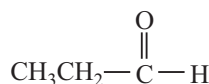
| **Methanal** | **Ethanal** | **Propanal** | **Benzenecarbaldehyde** |
| (Formaldehyde) | (Acetaldehyde) | (Propionaldehyde) | (Benzaldehyde) |
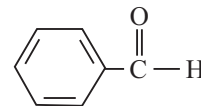
Note that when the -CHO group is attached to a ring, then the compound is called a *carbaldehyde*.

Remember that the carbonyl carbon of the aldehydes is present at the end of the chain and is assigned 1 position. Therefore, it is not necessary to specify its position in the name of the aldehyde. The examples given below illustrate this point.
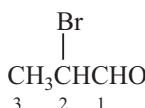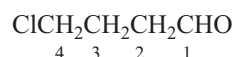
2-Bromopropanal   **4-Chlorobutanal**

Ketones are named as **alkanones** in the IUPAC namenclature. Their names are obtained by replacing final -*e* in the name of alkane by -*one*. The carbon chain is numbered in such a way that the carbonyl group gets the lowest number. Some examples of ketones are mentioned below :

Propanone
(Acetone)

Butan-2-one
(Ethyl methyl ketone)

Cyclohexanone

Pentan-3-one
(Diethyl ketone)

Pent-4-en-2-one

1-Phenylethanone
(Acetophenone)

(Benzophenone)
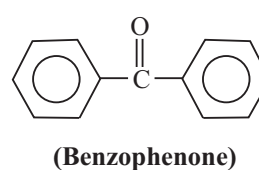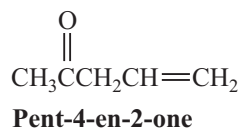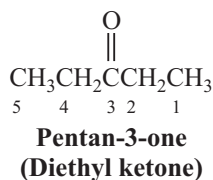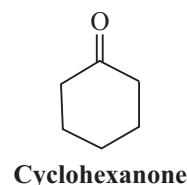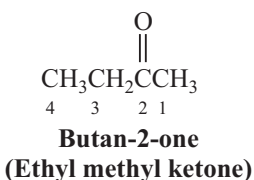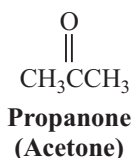
27.1.2 Preparation of Aldehydes and Ketones

You have already studied most of the methods used in the synthesis of aldehydes and ketones in the previous lesson. Let us now refresh them.

1. Oxidation of Primary and Secondary Alcohols

From the last lesson, you know that primary alcohols can be oxidised to aldehydes and secondary alcohols can be oxidised to ketones.

2. Ozonolysis of Alkenes

This reaction has been discussed in lesson 26. The products obtained are aldehydes or ketones depending upon the structure of the starting alkene.

3. Hydration of Alkynes

Hydration of alkynes can give an aldehyde or a ketone. Markovnikov's hydration yields ketones whereas anti-Markovnikov's hydration gives aldehydes.
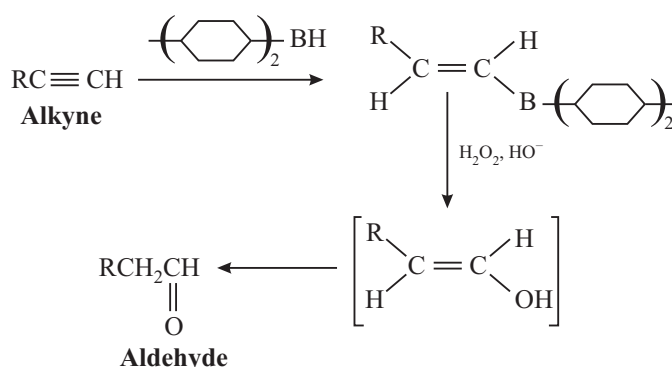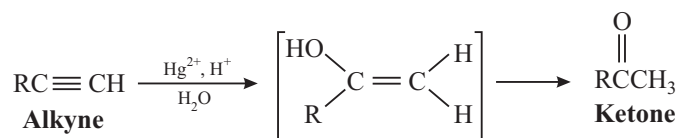
You can go through the details of these reactions as discussed in lesson 26.

4. Friedal-Crafts Acylation

Aromatic ketones can be prepared by Friedel-Crafts acylation (alkanoylation) reaction. One example of this reaction is given below:
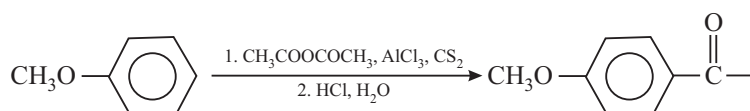
Similar acylation reaction using ethanoyl chloride was also discussed in lesson 26 under the **electrophilic substitution** reactions of aromatic hydrocarbons.

27.1.3 Structure and Physical Properties

In both aldehydes and ketones, the carbonyl carbon and oxygen atoms are sp^2 hybridised. Therefore, the groups attached to the carbon atom and oxygen are present in a plane. This is shown in Fig. 27.1.
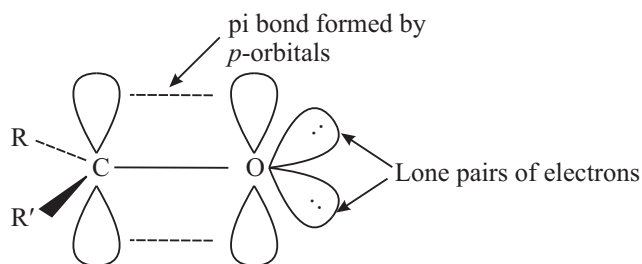
Fig. 27.1 : *The structure of the carbonyl functional group*

You can see in the figure that a π-bond is formed by the overlap of p-orbitals of carbon and oxygen atoms. The p-orbitals are present in a plane perpendicular to the plane of the molecule. Note the presence of two lone pairs of electrons on oxygen atom.

You also know that oxygen is more electronegative than carbon. Hence, it attracts the electrons of the carbon-oxygen double bond ($\diagup\!\!\!\!\diagdown C{=}O$ bond) resulting in its appriciable polarisation.

$$\left[\diagup\!\!\!\!\diagdown C{=}\ddot{O} \longleftrightarrow \diagup\!\!\!\!\diagdown \overset{+}{C}{-}\ddot{O}^{-} \right] \text{ or } \overset{\delta+}{\diagup\!\!\!\!\diagdown C}{=}\overset{\delta-}{\ddot{O}}$$
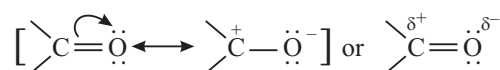
The oxygen atom, thus, acquires a partial negative charge (δ^-) whereas the carbon atom gets a partial positive charge (δ^+). This polar nature of the carbonyl group makes the oxygen atom ***nucleophilic*** and **basic** while the carbon atom becomes ***electrophilic***. The physical properties and chemical reactions of aldehydes and ketones are a direct consequence of this polarisation.

The dipole-dipole attraction between the molecules of aldehydes and ketones results in their higher boiling points as compared to the hydrocarbons of similar molecular weight. The physical properties of some aldehydes and ketones are given in Table 27.1.

Table 27.1 Physical properties of some representative aldehydes and ketones

Compound	m.p. (K)	b.p. (K)	Water Solubility (%)
Methanal	181	252	55
Ethanal	150	294	∞
Propanal	192	322	20

Aldehydes, Ketones and Carboxylic Acids

Butanal	166	348	7.1
Benzaldehyde	217	452	0.3
Propan-2-one	178	329	∞
Butan-2-one	187	353	25.6
Pentan-2-one	195	375	5.5
Pentan-3-one	232	374	4.8
Acetophenone	294	475	15
Benzophenone	321	578	–

You can see from Table 27.1 that these compounds have appriciable water solubility. This is because of the hydrogen bonding possible between the oxygen atom of the aldehyde (or the ketone) with hydrogen atom of water molecule, as shown in Fig 27.2.
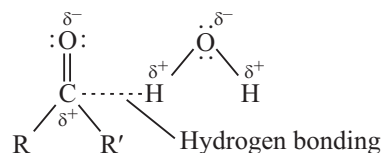
Fig. 27.2 : *Hydrogen bonding between carbonyl compound and water molecule*

27.1.4 Reactions of Aldehydes and Ketones

If you examine the structure of a molecule of the carbonyl compound, you will find that there are three centres of reactivity in it as shown below :
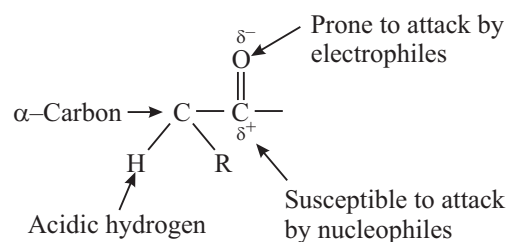
Since the oxygen atom is *nucleophilic* in nature, it is attacked by the *electrophiles*, whereas the carbonyl carbon is *electrophilic* in nature and hence is attacked by *nucleophiles*. The third site of reactivity is hydrogen atom present at the α- carbon atom. It is *acidic* in nature and gives typical reactions which you will study in this section.

It is also important to know here that aldehydes are more reactive than ketones. This is because of the following two reasons :

(i) Aldehydes have only one alkyl group whereas ketones have two. Since the alkyl groups are electron donating in nature, the carbonyl carbon in ketones which is bonded to two alkyl groups, is less positive (electrophilic) as compared to the aldehydic carbonyl carbon. Hence, it is less susceptible to attack by nucleophiles.

(ii) The two alkyl groups in ketones also make the carbonyl carbon more crowded as compared to carbonyl carbon in aldehydes. This factor also makes the aldehydic carbonyl carbon more accessible for attack by the nucleophiles as compared to carbonyl carbon of the ketone.

With this background in mind, let us now study the reactions of aldehydes and ketones.

A. Nucleophilic Addition Reactions

The general reaction of addition of nucleophiles on the carbonyl group can be represented as follows :
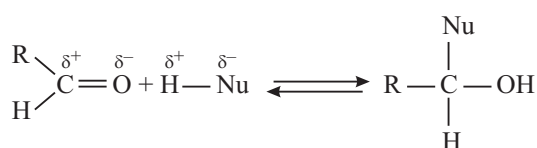
Mechanism of Nucleophilic Addition

Under basic conditions, the nucleophile attacks at the carbonyl group yields a tetrahedral intermediate. Subsequent to this, the protonation from a solvent (H_2O or alcohol) takes place. This is shown below:
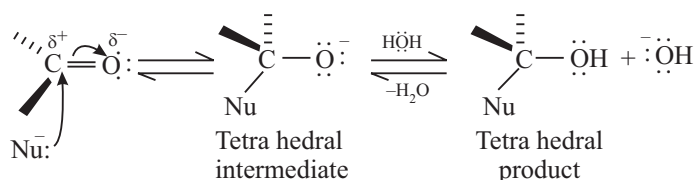
However, in acidic additions, in the first step the protonation of the carbonyl oxygen takes place.
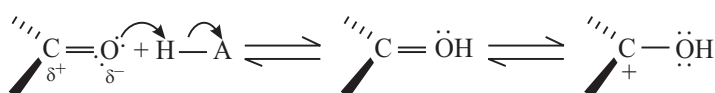
The nucleophile then attacks in the second step to carbonyl carbon and the addition process is completed.
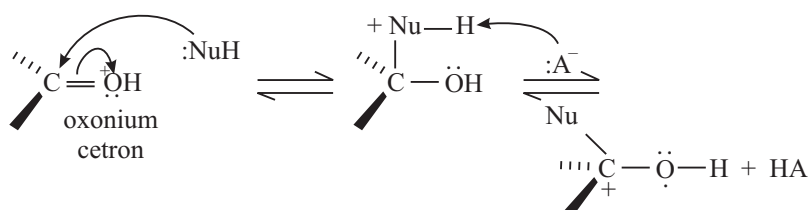
Some specific reactions of this category are discussed below :

1. Formation of Cyanohydrins

Carbonyl compounds react with hydrogen cyanide to yield *cyanohydrins*.

$$H_3C—\overset{\overset{O}{\|}}{C}—CH_3 + H—CN \rightleftharpoons CH_3—\overset{\overset{CN}{|}}{\underset{\underset{CH_3}{|}}{C}}—OH$$

Propanone
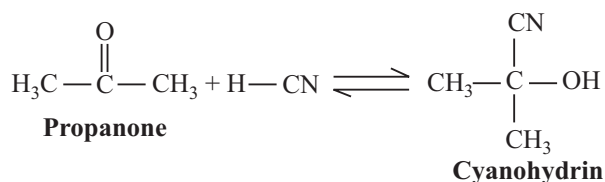
Cyanohydrin

Note that one more carbon atom is present in the cyanohydrin as compared to the starting carbonyl compound.

Cyanohydrins are useful in the synthesis of carboxylic acids about you will study in the next section.

2. Formation of Hemiacetals

Aldehydes and ketones react with alcohols to give *hemiacetals*. *Hemi* in Greek means *half*. Hemiacetals have an –OH and an –OR group attached to the same carbon atom in their molecules.

When an excess of the alcohol is used, a second molecule of the alcohol reacts to give an *acetal.*

$$\overset{\overset{O}{\|}}{CH_3CH} + CH_3OH \underset{}{\overset{HCl\,(g)}{\rightleftharpoons}} CH_3\overset{\overset{OH}{|}}{\underset{\underset{OCH_3}{|}}{CH}} \overset{CH_3OH}{\rightleftharpoons} CH_3—\overset{\overset{OCH_3}{|}}{\underset{\underset{OCH_3}{|}}{C}}—OH$$

Ethanal Methanol

a Hemiacetal

an Acetal

$$\overset{\overset{O}{\|}}{CH_3CH} + CH_3OH \underset{}{\overset{HCl\,(g)}{\rightleftharpoons}} CH_3\overset{\overset{OH}{|}}{\underset{\underset{OCH_3}{|}}{CH}}\ CH_3 \overset{CH_3OH}{\rightleftharpoons} CH_3—\overset{\overset{OCH_3}{|}}{\underset{\underset{OCH_3}{|}}{C}}—OH$$

Propanone Methanol

a Hemiacetal
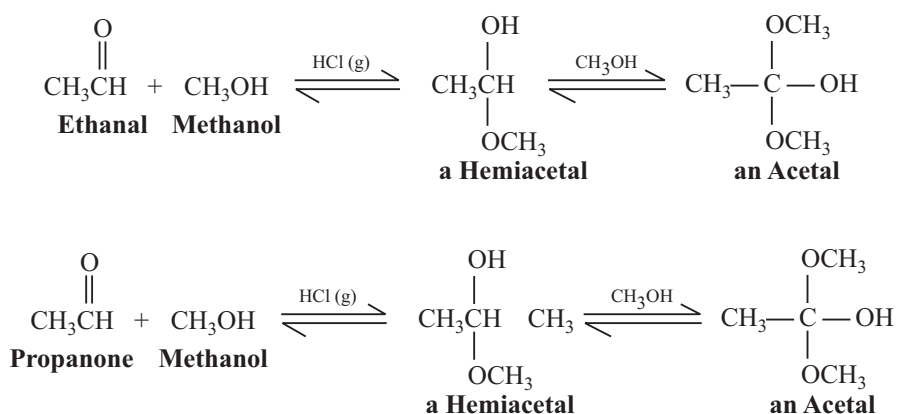
an Acetal

Note that an acetal has two —OR groups attached to the same carbon atom.

Acetals are stable in basic solutions and are 'therefore' used as protecting groups for aldehydes and ketones. Acetals can be converted back to the carbonyl compounds by treating them with dilute acids because of the reversible nature of the above reaction.

3. Formation of Alcohols

Grignard reagents (RMgX) react with aldehydes and ketones to give alcohols as shown below :

Notes

$$CH_3CH_2MgBr + H-\overset{\overset{O}{\|}}{C}-H \longrightarrow H-\overset{\overset{H}{|}}{\underset{|}{C}}-OH$$
$$\underset{\substack{\textbf{Ethyl} \\ \textbf{magnesium bromide}}}{} \quad \underset{\textbf{Methanal}}{} \qquad\qquad \underset{\substack{CH_2CH_3 \\ \textbf{a Primary alcohol}}}{}$$

$$CH_3CH_2MgBr + CH_3\overset{\overset{O}{\|}}{C}-H \longrightarrow CH_3-\overset{\overset{H}{|}}{\underset{|}{C}}-OH$$
$$\underset{\substack{\textbf{Ethyl magnesium} \\ \textbf{bromide}}}{} \quad \underset{\textbf{Ethanal}}{} \qquad\qquad \underset{\substack{CH_2CH_3 \\ \textbf{a Secondary alcohol}}}{}$$

$$CH_3CH_2MgBr + CH_3\overset{\overset{O}{\|}}{C}-CH_3 \longrightarrow CH_3-\overset{\overset{CH_3}{|}}{\underset{|}{C}}-OH$$
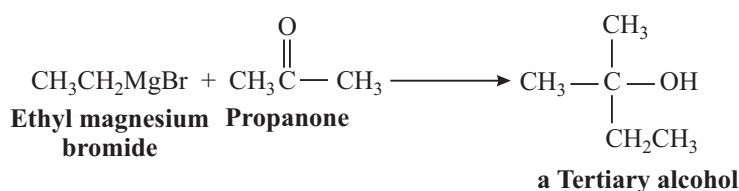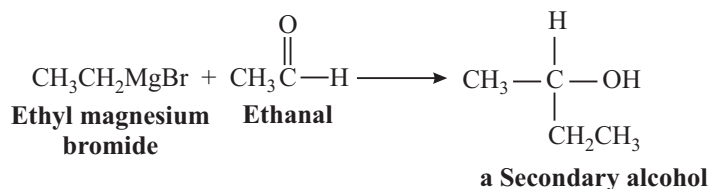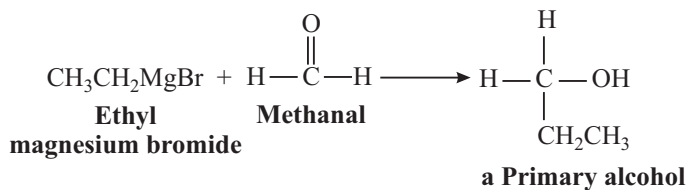$$\underset{\substack{\textbf{Ethyl magnesium} \\ \textbf{bromide}}}{} \quad \underset{\textbf{Propanone}}{} \qquad\qquad \underset{\substack{CH_2CH_3 \\ \textbf{a Tertiary alcohol}}}{}$$

You have already studied these reactions under the preparation of alcohols in lesson 28.

B. Addition-Elimination or Condensation Reactions

1. Reaction with Ammonia and its Derivatives

Aldehydes and ketones react with ammonia and primary amines to give **imines** which are compounds having carbon-nitrogen double bond.

$$R-\underset{\cdot\cdot}{N}H_2 + \underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}=C\diagdown \underset{\substack{\longleftrightarrow \\ H_3O^+}}{\rightleftharpoons} R-N=C\diagdown \;\; or \;\; \diagup C=N-R$$
$$\underset{\substack{\textbf{Primary} \\ \textbf{amine}}}{} \qquad\qquad\qquad\qquad\qquad \underset{\substack{\textbf{Imine} \\ \textbf{(a Schiff base)}}}{}$$
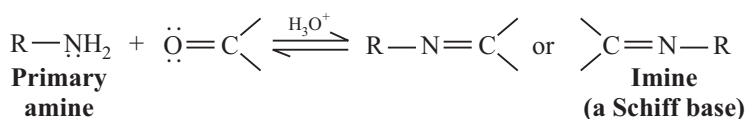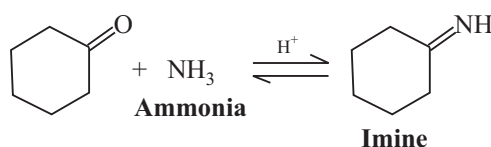
It appears that during the above reaction a molecule of water is lost from the primary amine and the carbonyl compound. The reactions with other derivatives of ammonia are given below:

$$\bigcirc-CH=H_2NOH \longrightarrow \bigcirc-CH=N-OH + H_2O$$
$$\qquad\quad \underset{\textbf{Hydroxylamine}}{} \qquad\qquad\qquad \underset{\textbf{an Oxime}}{}$$

$$\bigcirc-\overset{\overset{CH_3}{|}}{C}=O + H_2NNH_2 \longrightarrow \bigcirc-\overset{\overset{CH_3}{|}}{C}=NNH_2$$
$$\qquad\qquad \underset{\textbf{Hydrazine}}{} \qquad\qquad\qquad\qquad \underset{\textbf{a Hydrazone}}{}$$

Notes
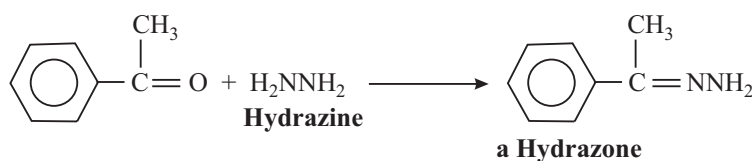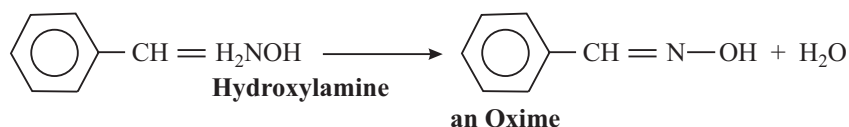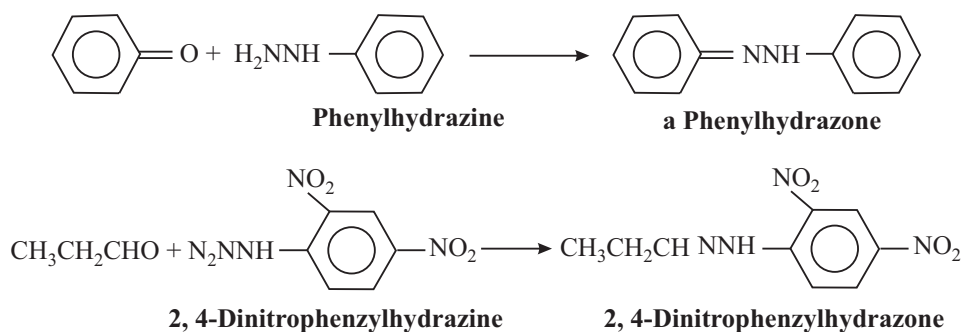
The compounds formed above are relatively insoluble solids and have characteristic melting points. These compounds can be prepared for the unknown aldehyde or ketone and their melting points can be determined. These melting points are matched with the derivatives of already known aldehydes and ketones listed in standard tables and the carbonyl compound is thus identified.

C. De-oxygenation Reactions

De-oxygenation reactions are reactions involving removal of oxygen. Aldehydes and ketones can be reduced to the corresponding alkanes by the following two reactions:

1. Wolff-Kishner Reduction

When an aldehyde or a ketone is heated in a basic solution of hydrazine in a high-boiling alcohol, then the carbonyl group gets converted to a methylene ($>CH_2$) group.

Ethylbenzene

2. Clemmensen Reduction

It is carried out in acidic medium using amalgamated zinc and hydrochloric acid.

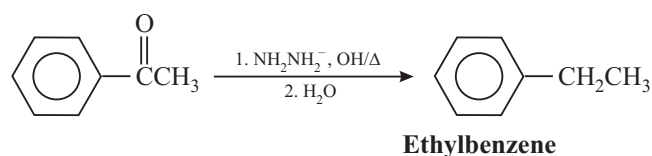$$CH_3(CH_2)_5CHO \xrightarrow[\text{HCl, H}_2\text{O}]{\text{Zn(Hg)}} CH_3(CH_2)_5 - CH_3$$

Heptanal **Heptane**
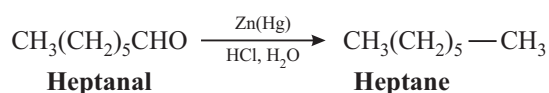
D. Oxidation of Aldehydes

Unlike ketones, aldehydes can be easily oxidised to carboxylic acids using a variety of oxidising agents. These reagents can be chromic acid, chromium trioxide, permanaganate or silver oxide. You have already read about oxidation with some of these reagents. *Silver ions selectively oxidise —CHO group*. This forms the basis of *Tollen's test*. It involves the addition of a mixture of aqueous silver nitrate and aqueous ammonia which is known as *Tollen's reagent* to the

carbonyl compound. Tollen's reagent contains $[Ag(NH_3)_2]^+$ complex ion. If an aldehyde is present, it gets oxidised to the carboxylic acid whereas the Ag^+ ions are reduced to form silver metal which gets deposited on the walls of the test tube and this gives a mirror like shining appearance.

$$R-\overset{\overset{O}{\|}}{C}-H \xrightarrow[H_2O]{[Ag(NH_3)_2]^+} R-\overset{\overset{O}{\|}}{C}-O^- + Ag\downarrow$$

Aldehyde   **mirror**

Aldehydes are also oxidised by *Fehling solution*, which contain Cu^{2+} (cupric) ions complexed with tartarate ions as the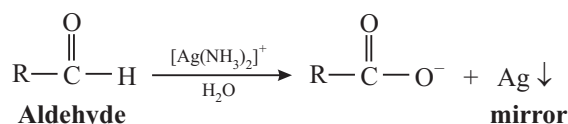 oxidant. These Cu^{2+} ions are reduced by the aldehydes in alkaline medium to give a brick red precipitate of cuprous oxide.

$$R-\overset{\overset{O}{\|}}{C}-H + Cu^{2+} \xrightarrow[H_2O]{NaOH} Cu_2O\downarrow + RCOOH$$

Aldehyde   **blue**   **brick red ppt.**
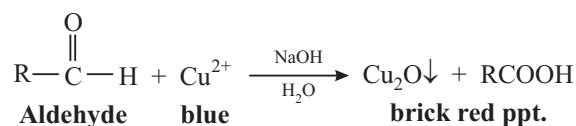
E. Reactions at α-carbon

The $\alpha-$ hydrogen in aldehydes and ketones is quite acidic and can be easily abstrated by a strong base.

keto form **α-Hydrogen**   **enolate ion**
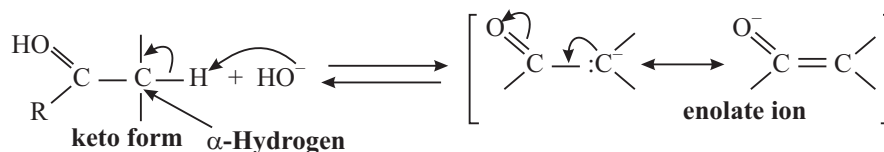
The resulting anion can stabilise by resonance as shown above. It is called an *enolate ion*. On protonation, it gives an *enol*.

enolate   **enol**
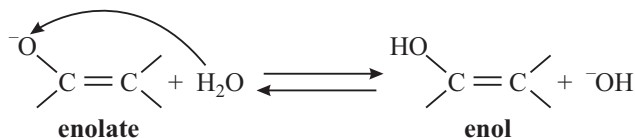
Thus, keto form and enol form are in equilibrium. This is also known as ***keto-enol tautomerism.***

Other reactions feasible due to the presence of α- hydrogen are as follows:

1. Halogenation

Ketones having an α- hydrogen atom react readily with halogens and α- haloketones are obtained as the product. The reaction is promoted both by acids and bases.

$$-\overset{\underset{|}{H}}{\underset{|}{C}}-\overset{\overset{O}{\|}}{C}- \ + \ X_2 \ \xrightarrow[\text{or } ^-OH]{H^+} \ -\overset{\underset{|}{X}}{\underset{|}{C}}-\overset{\overset{O}{\|}}{C}-$$

α-halo product

$(X_2 = Cl_2, Br_2 \text{ or } I_2)$

$$H-CH_2\overset{\overset{O}{\|}}{C}CH_3 \ \xrightarrow[\text{H}_2\text{O, 343 K}]{Br_2, CH_3COOH} \ BrCH_2\overset{\overset{O}{\|}}{C}CH_3 \ + \ HBr$$

Propanone   **Bromopropanone**

In presence of the base, multiple halogenation occurs to give the trihalo product.

$$\bigcirc-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{\underset{|}{\underset{H}{C}}}-H \ + \ \xrightarrow{3X_2 + NaOH} \ \bigcirc-\overset{\overset{O}{\|}}{C}-\overset{\overset{X}{|}}{\underset{|}{\underset{X}{C}}}-X \ + \ 3NaX + 3H_2O$$

trihaloketone

The trihalo group is a good leaving group and the trihalo ketone reacts with OH^- which finally gives a carboxylate ion and a *haloform*.
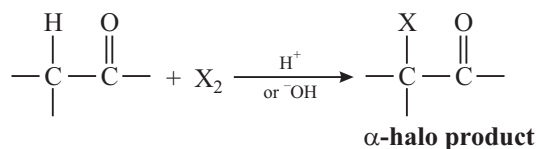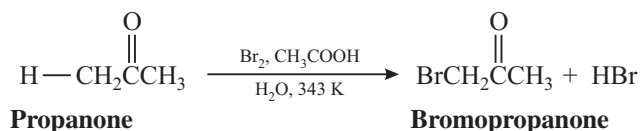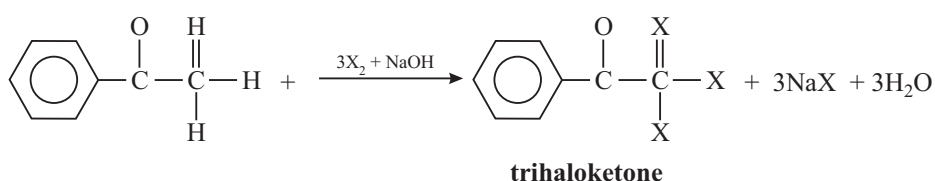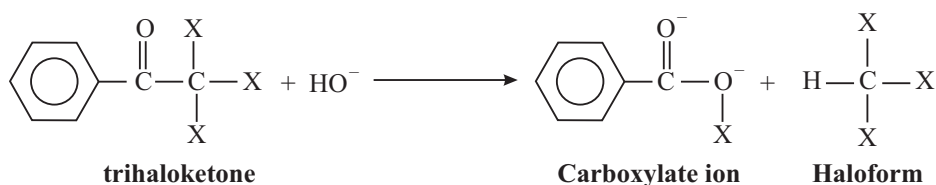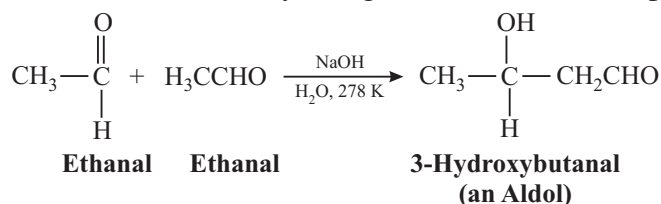
$$\bigcirc-\overset{\overset{O}{\|}}{C}-\overset{\overset{X}{|}}{\underset{|}{\underset{X}{C}}}-X \ + \ HO^- \ \longrightarrow \ \bigcirc-\overset{\overset{O^-}{\|}}{C}-O^- \ + \ H-\overset{\overset{X}{|}}{\underset{|}{\underset{X}{C}}}-X$$

trihaloketone   **Carboxylate ion**   **Haloform**

This reaction is called the **haloform reaction** after the name of the product.

If iodine is used as the halogen, then we get *iodoform* (CHI_3) as the product. The iodoform is a bright yellow solid having a characterstic melting point. This reaction, thus, forms the basis of the *iodoform test*. Thus, methyl ketones give a positive iodoform test. You had studied the iodoform formation in lesson 27 also.

2. Aldol Condensation

Aldehydes having α – hydrogen atom on reaction with dil. NaOH give *aldols*. The reaction is illustrated below by using ethanal as the example.

$$CH_3-\overset{\overset{O}{\|}}{\underset{|}{\underset{H}{C}}} \ + \ H_3CCHO \ \xrightarrow[\text{H}_2\text{O, 278 K}]{NaOH} \ CH_3-\overset{\overset{OH}{|}}{\underset{|}{\underset{H}{C}}}-CH_2CHO$$

Ethanal   **Ethanal**   **3-Hydroxybutanal**
(**an Aldol**)

Note that the product contains both the *aldehyde* and the *alcohol* functional groups and therefore, it is called an *aldol*. The aldol addition product on heating undergoes dehydration to give an α, β– unsaturated aldehyde which is a condensation product.
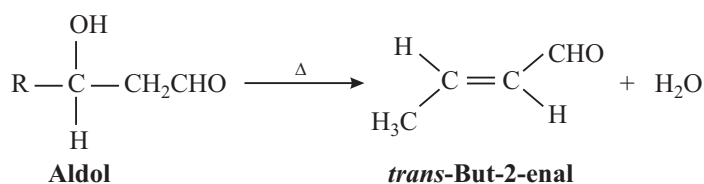
Notes

Aldol   *trans*-But-2-enal

This complete sequence of reactions is called *aldol condensation*.

Aldol condensation is also possible with ketones. Can you now think of a little more complex situation? What will be the products of aldol condensation when two diffrent aldehydes having α – hydrogen atoms are used as reactants. In this case, the reaction is called a *crossed-aldol condensation*. This is left as an exercise for you. There is a hint of course. Suppose, the two aldehyde molecules are represented by A and B; then condensation can occur between two molecules of the same aldehyde or diffrent aldehydes. Thus, the products obtained would be the following types:

A-A,   B-B,   A-B   and   B-A.

With this background in mind, you can now proceed to write the aldol addition products of ethanal and propanal.

3. Cannizzaro Reaction

Aromatic or aliphatic aldehydes which do not have α-hydrogen, an reaction with conc. KOH/NaOH give one molecule of and alcohol and sodium salt of the carboxylic acids. This reaction is known as **Carnizzaro reaction.**

In this reaction, one molecule of the aldehyde is oxidised to carboxylic acid salt (sod. or pot. salt) and another molecule of the aldehyde is reduced to alcohol molecule. For example,
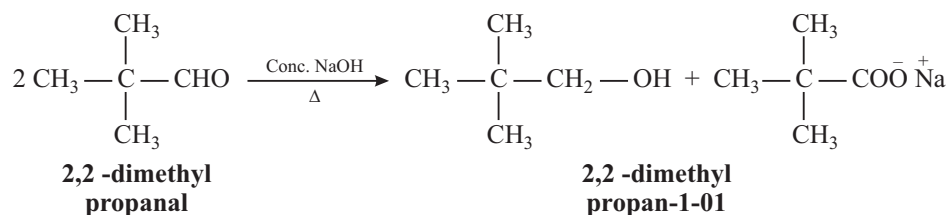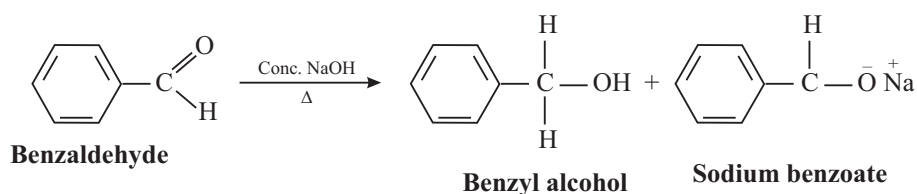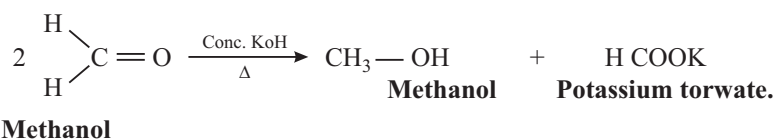
This reaction takes place by nucleophilic addition of —OH to an aldehyde to give tetrahedral intermediate. This intermediate expels a hydride ion as the leaving group.

tetra hedral intermediate
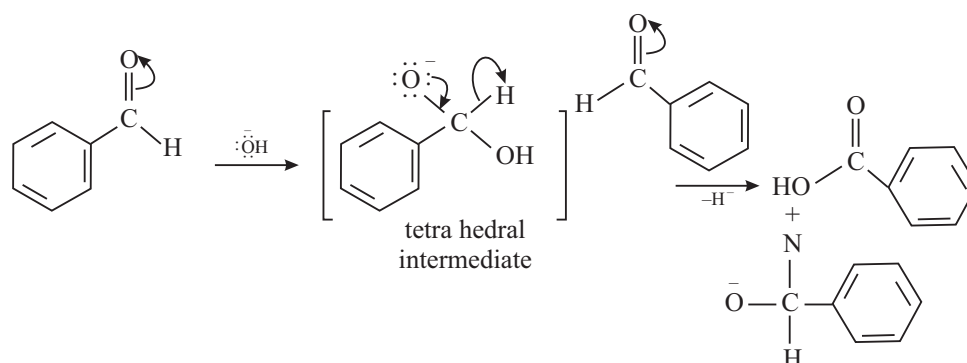
This hydride ion is accepted by second molecule of aldehyde

Carboxylic acid
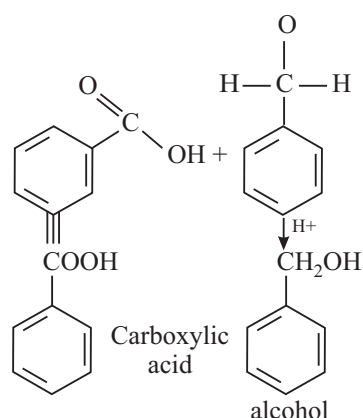
alcohol

Thus, we can say, that *disproportonation* has occurred and simultaneous *oxidation* and *reduction* has taken place to give one molecule of a carboxylic acid and are molecule of an alcohol from the two molecules of the starting aldehyde. This reaction is limited to those aldehydes only which have no hydrogen on carbon next to the CHO group.

INTEXT QUESTIONS 27.1

1. Classify the following as aldehydes or ketones and give their IUPAC names:
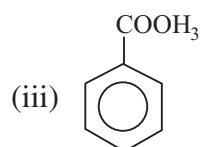
    (i) CH_3CHO (ii) $CH_3COCH_2CH_3$

    (iii)   (iv) $OHCCH_2CH_3$

2. How will you prepare propanone from propyne ?
3. Why are aldehydes more reactive than ketones towards nucleophilic addition reactions?
4. Write the general structure for the following :
   (i) a cyanohydrin   (ii) an acetal   (iii) a hemiacetal
5. How can you convert the carbonyl $\left(\!\!\begin{array}{c}\\ \end{array}\!\!C\!=\!O\right)$ group to $\left(\!\!\begin{array}{c}\\ \end{array}\!\!CH_2\right)$ group ?
6. What is an aldol?
7. Write the equation for cannizzaro reaction using a suitable example.

27.2 CARBOXYLIC ACIDS

You already know that carboxylic acids contain a **carboxyl (—COOH)** funtional group. They are most widely distributed in nature and are also industrially important chemicals. *Acetic acid* in the form of vinegar is produced in large quantities. It is also a very important building block in complex biological molecules. You must have also heard about *fatty acids* which are long chain aliphatic acids derived from the hydrolysis of fats and oils. Stearic acid is a fatty acid containing a long chain of eighteen carbon atoms.

27.2.1 Nomenclature

Several carboxylic acids have been known since long and their common names are based on their sources. However, in the IUPAC nomenclature, carboxylic acids are named by choosing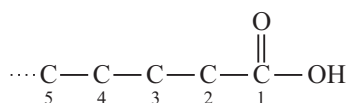 the longest carbon chain containing the –COOH group. The final -*e* in the name of the alkane is replaced by *-oic acid.* While numbering the carbon chain, the –COOH carbon is always given number 1 as shown below :

$$\cdots\overset{}{\underset{5}{C}}-\overset{}{\underset{4}{C}}-\overset{}{\underset{3}{C}}-\overset{}{\underset{2}{C}}-\overset{\overset{O}{\|}}{\underset{1}{C}}-OH$$

The other groups and substituents are numbered and named according to the usual rules of nomenclature which you have already studied.

Some common carboxylic acids and their names are given below :

$$H-\overset{\overset{O}{\|}}{C}-OH$$
Methanoic acid
(Formic acid)

$$CH_3-\overset{\overset{O}{\|}}{C}-OH$$
Ethanoic acid
(Acetic acid)

$$\underset{\text{Phenylmethanoic acid}}{C_6H_5}-\overset{\overset{O}{\|}}{C}-OH$$
Phenylmethanoic acid
(Benzoic acid)
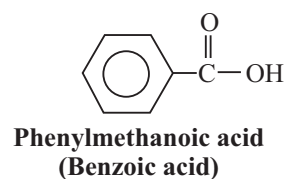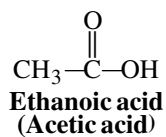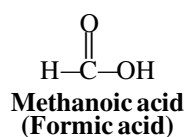
Carboxylic acids containing two carboxyl groups are called **dicarboxylic acids.**

They are named by adding **dioic acid** as a suffix to the name of the corresponding hydrocarbon. Both the carboxyl carbon atoms are numbered as a part of the main chain. Note that in this case, final-e of the alkane is **not** dropped.

**Ethanedioic acid
(Oxalic acid)**

**Propanedioic acid
(Malonic acid)**

**Butane-1,4-dioic acid
(Succinic acid)**

**o-Phthalic acid
(Phthalic acid)**

**m-Phthalic acid
(Isophthalic acid)**

**o-Phthalic acid
(Terephtyhalic acid)**
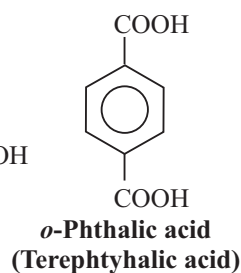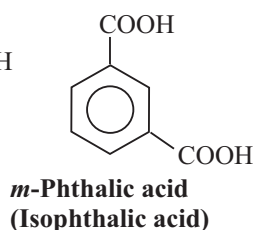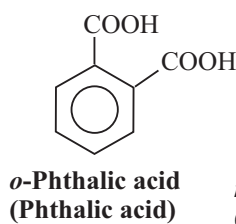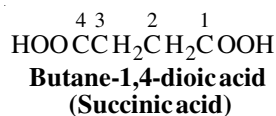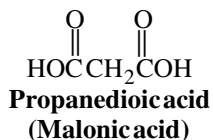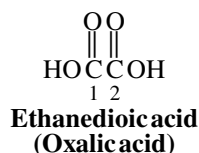
27.2.2 Preparation of Carboxylic Acids

The following methods are generally used for the synthesis of carboxylic acids. You have already studied some of these methods in the earlier lessons.

1. Oxidation of Alkenes

Alkenes on oxidation with hot alkaline $KMnO_4$ yield carboxylic acids.

$$RCH{=}CHR' \xrightarrow[2 \cdot H_3O^+]{1 \cdot KMnO_4, \, ^-OH} RCOOH + R'COOH$$
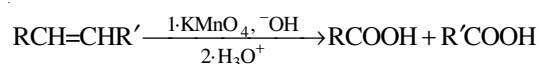
2. Oxidation of Alcohols and Aldehydes

You have read in the last lesson and the previous section of this lesson that alcohols and aldehydes can be oxidized to carboxylic acids using a variety of oxidising agent. You can refer back to the details of these reactions.

3. Oxidation of Alkylbenzenes

Primary and secondary alkyl groups attached to the benzene ring can be oxidised, using alkaline $KMnO_4$, to the carboxyl group.

Methylbenzene

Benzoic acid
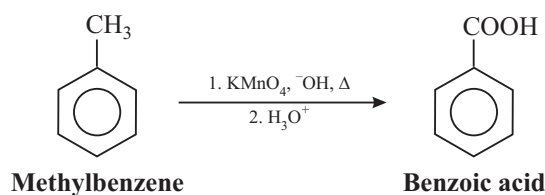
Acidified sodium dichromate can also be used for this oxidation.

Notes

$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{CH}\text{-}\underset{\underset{\displaystyle Cl}{}}{\bigcirc} \xrightarrow[\Delta]{Na_2Cr_2O_7,\ H_2SO_4} \underset{\underset{\displaystyle Cl}{}}{\overset{\overset{\displaystyle COOH}{}}{\bigcirc}}$$

p-**Chlorobenzoic acid**
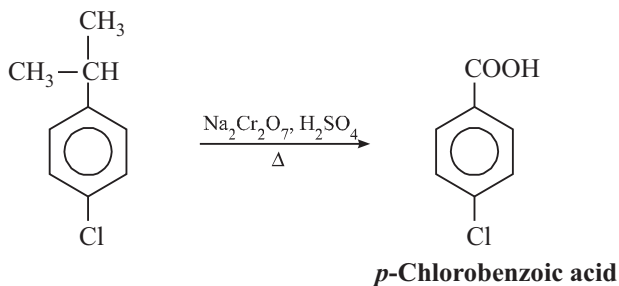
4. Carbonation of Grignard Reagents

Grignard reagents (RMgX) react with carbon dioxide to give magnesium carboxylates which on acidification yield carboxylic acids.

$$RMgX + CO_2 \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}O^-Mg^+X \xrightarrow{\ ^+H\ } RCOOH$$

$$\underset{\substack{\textbf{Chloroethane} \\ \textbf{(an alkyl halide)}}}{CH_3CH_2Cl} \xrightarrow[Et_2O]{Mg} \underset{\textbf{Grignard reagent}}{CH_3CH_2MgCl} \xrightarrow[2\cdot H_3O^+]{1\cdot CO_2} \underset{\textbf{Propanoic acid}}{CH_3CH_2COOH}$$

$$\underset{\textbf{Phenyl magnesium bromide}}{\overset{\overset{\displaystyle MgBr}{}}{\bigcirc}} \xrightarrow[2.\ H_2O^+]{1.\ CO_2} \underset{\textbf{Benzoic acid}}{\overset{\overset{\displaystyle COOH}{}}{\bigcirc}}$$
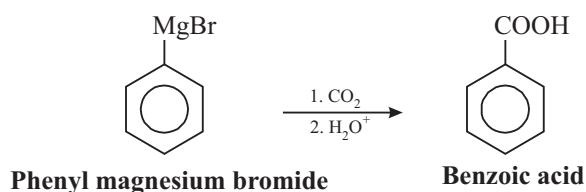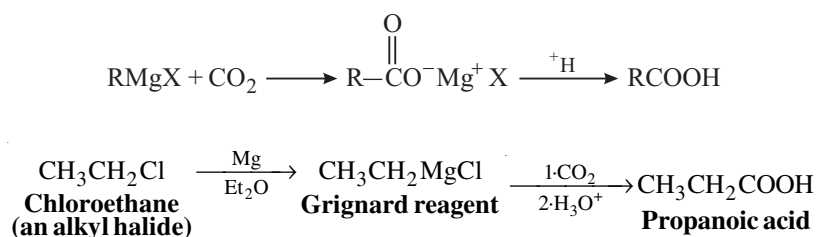
Note that there is an increase of one carbon atom in the carboxylic acid as compared to the starting alkyl halide.

5. Hydrolysis of Nitriles and Cyanohydrins

Alkyl halides can be converted to *nitriles* which on hydrolysis yield carboxylic acids having *one more carbon atom than the starting alkyl halide.*

$$\underset{\textbf{Alkyl halide}}{R-CH_2X + CN^-} \longrightarrow \underset{\substack{\textbf{Nitrile} \\ + \\ X^-}}{RCH_2CN}$$

$$\begin{array}{l} \xrightarrow{H_3O^+,\Delta} \underset{\substack{\textbf{Ethene} \\ \textbf{(Alkene)}}}{CH_2{=}CH_2} \\ \xrightarrow{^-OH,\ \Delta} \underset{+\ NH_3}{RCH_2COO^-} \xrightarrow{H_3O^+} RH_2COOH \end{array}$$

$$\underset{\textbf{1, 2-Dibromoethane}}{Br-CH_2CH_2-Br} \xrightarrow{NaCN} \underset{\textbf{Butane dinitrile}}{NC-CH_2CH_2-CN} \xrightarrow{H_3O^+} \underset{\textbf{Butanedioic acid}}{HOOCCH_2CH_2COOH}$$
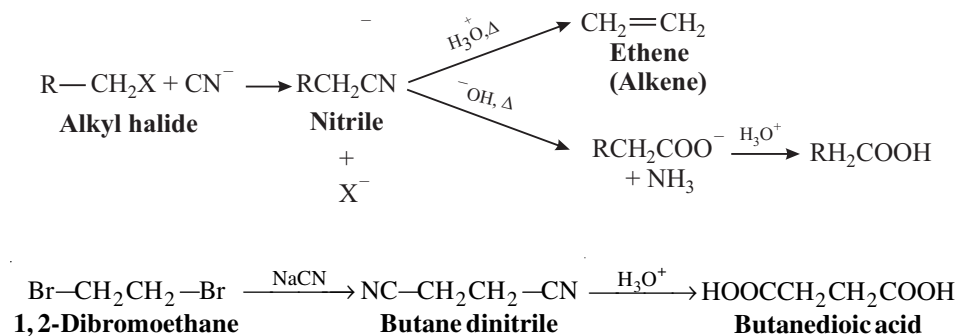
Cyanohydrins obtained from aldehydes also yield 2-hydroxycarboxylic acids on hydrolysis.

$$CH_3CH_2 - \underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}} - CN \xrightarrow{H_3O^+} CH_3CH_2 - \underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}} - COOH$$

2-Hydroxybutanenitrile   **2-Hydroxybutanoic acid**
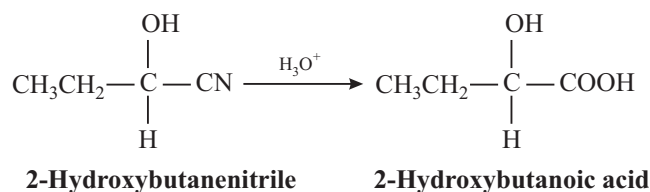
27.2.3 Structure and Physical Properties

Similar to the aldehydes and ketones, the carboxyl carbon atom is sp^2 hybridised. Thus, the three atoms attached to this carbon which lie in the same plane with an approximate bond angle of 120º between them, see Fig. 27.3.
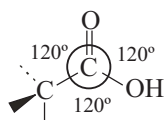
Fig. 27.3 : *Structure of the carboxyl group*

Carboxylic acids form hydrogen bonds because of the presence of polar carbonyl and hydroxyl groups. Most carboxylic acids exist in dimeric form in which two carboxylic acid molecules are held together by two hydrogen bonds. This is shown below :

Dimer of a carboxylic acid
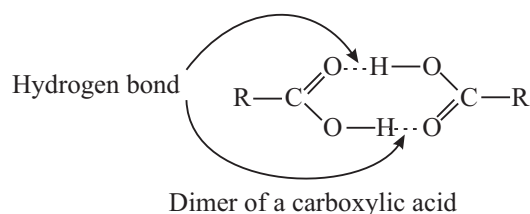
Intermolecular hydrogen bonding is in fact responsible for high melting and boiling points of carboxylic acids. The melting and boiling points of some carboxylic acids are listed in Table 27.2. You can also see in the table that the lower members have appreciable solubility in water. This is also due to the presence of hydrogen bonding between the carboxylic acid molecule and solvent water molecules.

Table 27.2 : Some Physical Properties of Carboxylic Acids

Carboxylic Acid	m. p. (K)	b. p. (K)	Water solubility gmL^{-1} of H$_2$O at 298K	pK_a
HCOOH	281	373·5	∞	3·75
CH$_3$COOH	289.6	391	∞	4·76

CH_3CH_2COOH	252	414	∞	4·87
$CH_3CH_2CH_2COOH$	267	437	∞	4·82
$CH_3CH_2CH_2CH_2COOH$	239	460	4·97	4·81
$ClCH_2COOH$	336	462	very soluble	2·86
$Cl_2CHCOOH$	283.8	465	very soluble	1·48
Cl_3CCOOH	329.3	471	very soluble	0·70
C_6H_5COOH	295	523	0·34	4·19
$p\text{-}CH_3C_6H_4COOH$	450	548	0·03	4·36
$p\text{-}ClC_6H_4COOH$	515		0.009	3.98
$p-NO_2C_6H_4COOH$	515		0.03	3.41

Do not worry about the pK_a values listed in the last column of the table. We will refer to them when we discuss the acidic nature of carboxylic acids in the following section.

27.2.4 Acidity of Carboxylic Acids

Carboxylic acids are acidic in nature. They dissociate in water according to following equilibrium to give a proton and the carboxylate ion.

$$R-\overset{\overset{O}{\|}}{C}-O-H + H_2O \rightleftharpoons R-\overset{\overset{O}{\|}}{C}-O^- + H_2O^+$$

Carboxylic acid　　　　　**Carboxylate ion**
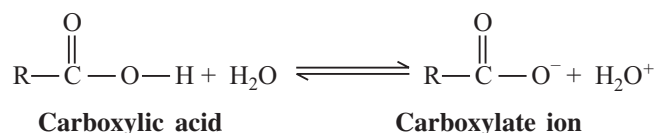
The pK_a values of some carboxylic acids are given in the last column of Table 27.2. Remember that the *lower pK_a indicates greater acidity*. If you compare these pK_a value with those of alcohols, you will note that the carboxylic acids are much more acidic than alcohols. This can be explained on the basis of the anion formed as a result of ionisation. The carboxylate ion obtained by the dissociation of carboxylic acids can be represented as a resonance hybrid of the following two structures:

$$R-C\overset{O}{\underset{:O^-}{\diagdown}} \longleftrightarrow R-C\overset{:\ddot{O}:^-}{\underset{O}{\diagup}}$$
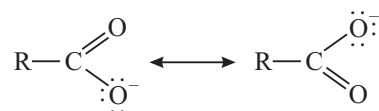
Resonance structures of Carboxylate Ion

These structures show that the negative charge is delocalised over two oxygen atoms. Thus, the carboxylate ion gets stabilised. The greater stability of carboxylate ion facilitates the release of proton from the –COOH group.

Notes

If you compare this situation with the alkoxide ion (RO^-) obtained by the dissociation of an alcohol molecule, you will see that no such resonance stabilisation is possible in the alkoxide ion.

Let us now analyse the acid strength of different acids and correlate them with their structure. If we examine the first five acids listed in table 27.2, we find that their pK_a values keep on increasing which means that as we go down, their acid strength decreases. Since the alkyl groups are electron releasing in nature, they make the release of H^+ difficul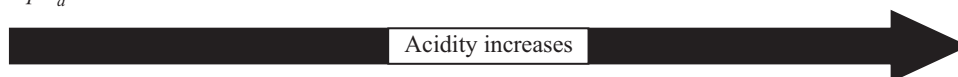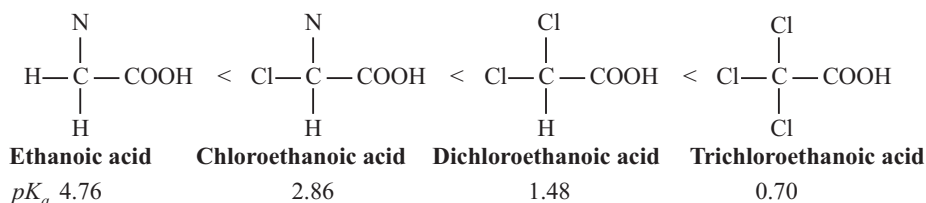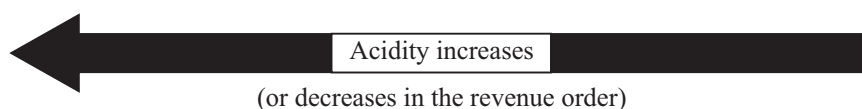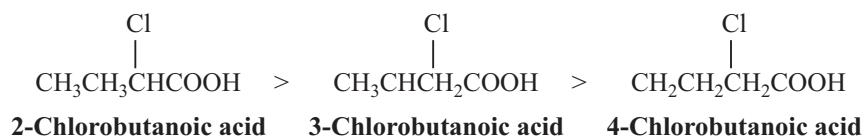t and hence decrease the acidity. Thus, ethanoic acid is less acidic than methanoic acid. Therefore, we can say that the **electron-donating substitutents decrease the acidity of carboxylic acids.**

Let us next see what will be the effect of electron withdrawing substituents such as halogens and nitro-group on the acidity. The comparison of pK_a values of ethanoic acid (4·76) and chloroethanoic acid (2·86) suggests that chloroethanoic acid is a stronger acid than ethanoic acid. The chloro substituent has $-_I$ effect and pulls the electrons towards itself which facilitates the release of H^+ ions.

You can also see below that as the number of halogen groups increases in the carboxylic acid, its acidity increases. This is because they make the release of H^+ ion more and more easy.

$$
\underset{\substack{\textbf{Ethanoic acid}\\ pK_a\ 4.76}}{H\!-\!\overset{\displaystyle N}{\underset{\displaystyle H}{C}}\!-\!COOH} \ < \ \underset{\substack{\textbf{Chloroethanoic acid}\\ 2.86}}{Cl\!-\!\overset{\displaystyle N}{\underset{\displaystyle H}{C}}\!-\!COOH} \ < \ \underset{\substack{\textbf{Dichloroethanoic acid}\\ 1.48}}{Cl\!-\!\overset{\displaystyle Cl}{\underset{\displaystyle H}{C}}\!-\!COOH} \ < \ \underset{\substack{\textbf{Trichloroethanoic acid}\\ 0.70}}{Cl\!-\!\overset{\displaystyle Cl}{\underset{\displaystyle Cl}{C}}\!-\!COOH}
$$

Acidity increases →

Since the inductive effect decreases with increase in the distance of the group in the carbon chain, 2-chlorobutanoic acid (pK_a 2·86) is more acidic than 3-chlorobutanoic acid (pK_a 4.05) which is in turn more acidic than 4-chlorobutanoic acid (pK_a 4.50).

$$
\underset{\textbf{2-Chlorobutanoic acid}}{CH_3CH_3\overset{\displaystyle Cl}{C}HCOOH} \ > \ \underset{\textbf{3-Chlorobutanoic acid}}{CH_3\overset{\displaystyle Cl}{C}HCH_2COOH} \ > \ \underset{\textbf{4-Chlorobutanoic acid}}{\overset{\displaystyle Cl}{C}H_2CH_2CH_2COOH}
$$

← Acidity increases
(or decreases in the revenue order)

27.2.5 Reactions of Carboxylic Acids

Let us now study the reactions given by carboxylic acids.

1. Formation of Salts

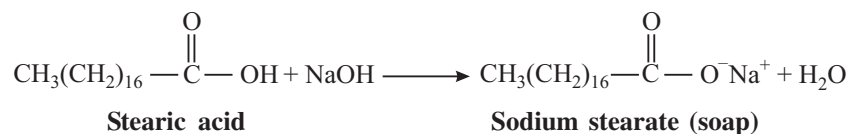Carboxylic acids are completely deprotonated by strong bases such as metal hydroxides to give salts.

$$CH_3\overset{\overset{\displaystyle O}{\|}}{C}—O—H + NaOH \longrightarrow CH_3\overset{\overset{\displaystyle O}{\|}}{C}—O^-Na^+ + H_2O$$

Ethanoic acid   **Sodium ethanoate**
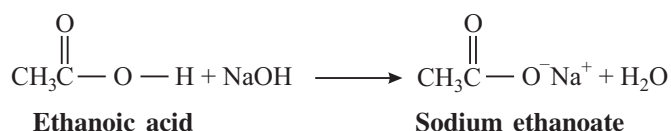
It will be interesting to know that *soaps* are sodium salts of long chain carboxylic acids which are called **fatty acids**.

$$CH_3(CH_2)_{16}—\overset{\overset{\displaystyle O}{\|}}{C}—OH + NaOH \longrightarrow CH_3(CH_2)_{16}—\overset{\overset{\displaystyle O}{\|}}{C}—O^-Na^+ + H_2O$$

Stearic acid   **Sodium stearate (soap)**

Caboxylic acids are also deprotonated by the weak bases such as sodium bicarbonate. In this reaction, they form sodium salt of the acid, carbon dioxide and water.

$$R—\overset{\overset{\displaystyle O}{\|}}{C}—O—H + NaHCO_3 \longrightarrow R—\overset{\overset{\displaystyle O}{\|}}{C}—O^-Na^+ + H_2O + CO_2\uparrow$$
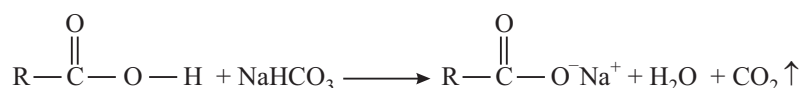
This reaction is also used as a test for carboxylic acids in the laboratory. The liberation of CO_2 in the form of bubbles on treatment with $NaHCO_3$ indicates a carboxyl functional group in the compound.

This test is not given by phenols since they are weaker acids than the carboxylic acids. Hence, the two categories of compounds can be distinguished on the basis of the above test.

2. Reduction of Carboxylic Acids

Carboxylic acids are reduced to primary alcohols by lithium aluminium hydride $(LiAlH_4)$.

Phenylethanoic acid   **2-Phenylethanol**
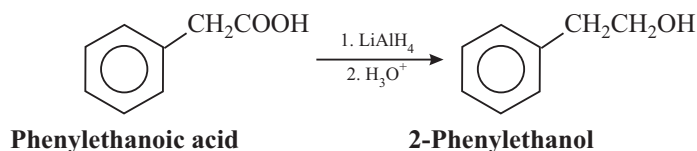
3. Hell-Volhard-Zelinski Reaction

Similar to aldehydes and ketones, carboxylic acids undergo halogenation at α-carbon atom using $Br_2(or Cl_2)$ in the presence of phosphorus or phosphorus trihalide.

$$CH_3CH_2CH_2COOH \xrightarrow[\text{2. HO}_2]{\text{1. Br}_2\text{P}} \underset{\text{2 - Bromobutanoic acid}}{CH_3CH_2\overset{\overset{\displaystyle Br}{\displaystyle |}}{C}HCOOH}$$

Butanoic acid

α-Haloacids so obtained are useful intermediates in the synthesis of other organic compounds.

4. Synthesis of Acid Derivatives

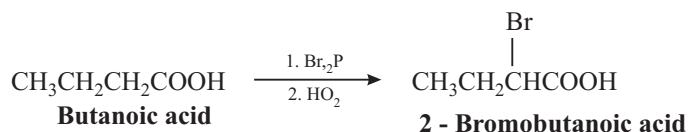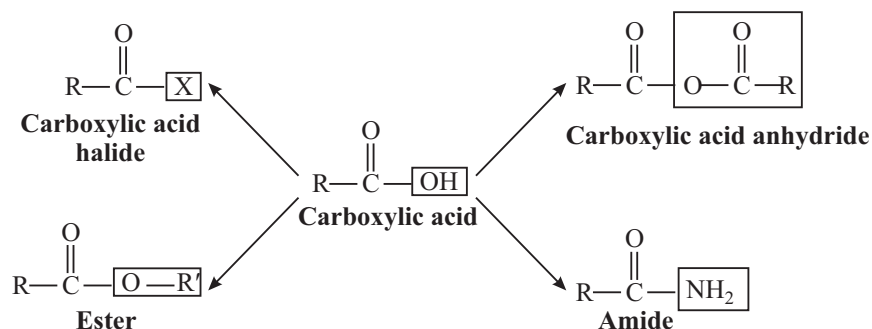This is one of the very important reactions of carboxylic acids. The nucleophilic addition to the carboxyl carbon of the carboxylic acids is followed by elimination of the leaving group leading to a **substitution product.** If you remember the reactions of aldehydes and ketones, the addition of nucleophile is followed by addition of the proton to give an **addition product.**

In case of carboxylic acids, since the substitution takes place at the acyl carbon atom as shown below. It is also known as **nucleophilic acyl substitution.**

$$R-\overset{\overset{\displaystyle O}{\displaystyle \|}}{C}-X + :Nu^- \;\rightleftharpoons\; R-\overset{\overset{\displaystyle O}{\displaystyle \|}}{C}-Nu + X^-$$

Here, X = OH in case of the carboxylic acids and Nu^- can be a halide ion,

$^-O-\overset{\overset{\displaystyle O}{\displaystyle \|}}{C}-R,$ $^-O-R'$ or $^-NH_2$ group leading, respectively to **carboxyl acid halides, anhydrides, esters** or **amides** as the substitution products which are known as **derivatives of carboxylic acids** because they are derived from carboxylic acids.

$$R-\overset{\overset{\displaystyle O}{\displaystyle \|}}{C}-\boxed{X}$$
Carboxylic acid halide

$$R-\overset{\overset{\displaystyle O}{\displaystyle \|}}{C}-\boxed{O-R'}$$
Ester

$$R-\overset{\overset{\displaystyle O}{\displaystyle \|}}{C}-\boxed{OH}$$
Carboxylic acid

$$R-\overset{\overset{\displaystyle O}{\displaystyle \|}}{C}-O-\overset{\overset{\displaystyle O}{\displaystyle \|}}{C}-R$$
Carboxylic acid anhydride

$$R-\overset{\overset{\displaystyle O}{\displaystyle \|}}{C}-\boxed{NH_2}$$
Amide

(i) Formation of Acid Chlorides

Carboxylic acids react with $SOCl_2, PCl_3$ or PCl_5 to give carboxylic acid chlorides also known as **acyl chlorides,** as shown below :
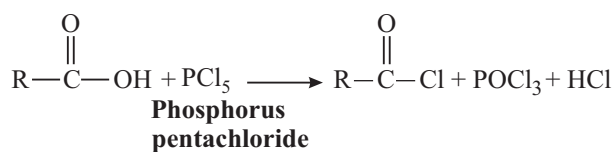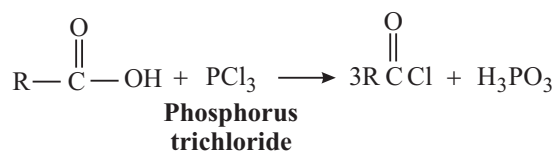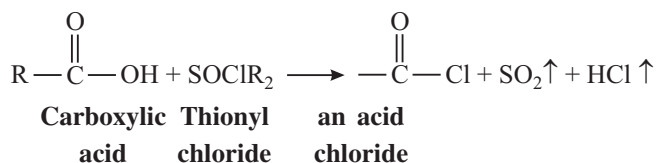
$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH + SOClR_2 \longrightarrow -\overset{\overset{\displaystyle O}{\|}}{C}-Cl + SO_2\uparrow + HCl\uparrow$$

Carboxylic   **Thionyl**   **an acid**
acid   **chloride**   **chloride**

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH + PCl_3 \longrightarrow 3R\,\overset{\overset{\displaystyle O}{\|}}{C}\,Cl + H_3PO_3$$

Phosphorus
trichloride

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH + PCl_5 \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl + POCl_3 + HCl$$

Phosphorus
pentachloride

(ii) Formation of Acid Anhydrides

$$2\,RCOOH \xrightarrow[-H_2O]{P_2O_5} R\,\overset{\overset{\displaystyle O}{\|}}{C}-O-\overset{\overset{\displaystyle O}{\|}}{C}-R$$

aCarboxylicacid   **an Acid Anhydride**

$$2\,CH_3COOH \xrightarrow[-H_2O]{P_2O_5} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

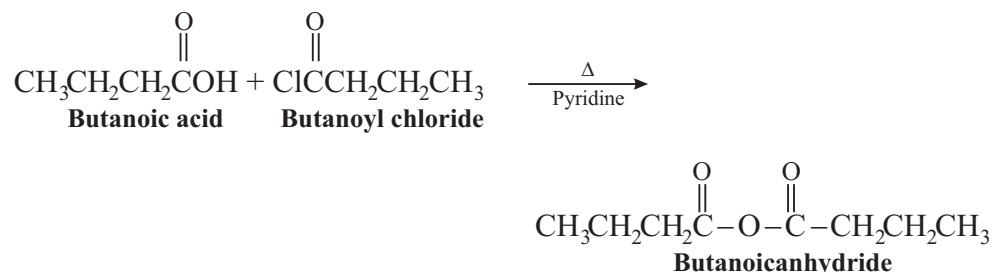**Ethanoicanhydride**
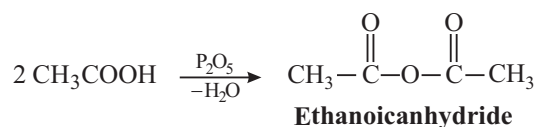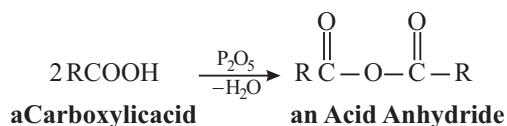
Since the carboxylic acid anhydrides are formally derived from carboxylic acids by loss of water, their names are derived from the corresponding acids by using the word *anhydride* in place of the acid. As the anhydride formed in the above reaction is derived from ethanoic acid, it is called ethanoic anhydride.

This method is used for the *preparation of symmetrical anhydrides.*

Carboxylic acid also react with acyl chlorides in the presence of pyridine to give carboxylic acid anhydrides.

$$CH_3CH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}OH + ClC\overset{\overset{\displaystyle O}{\|}}{C}CH_2CH_2CH_3 \xrightarrow[Pyridine]{\Delta}$$

Butanoic acid   **Butanoyl chloride**

$$CH_3CH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}-O-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2CH_2CH_3$$
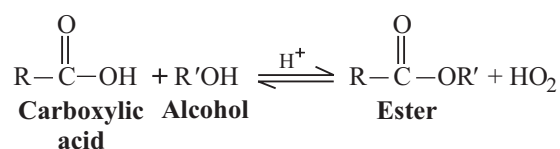
Butanoicanhydride

We can prepare unsymmetrical anhydrides by this method.

Cylic anhydrides are obtained by the dehydration of dicarboxylic acids at higher temperature.

**Butanedioic acid
(Succinic acid)**

573 K
−H₂O

**Butanedioic anhydride
(Succinic anhydride)**

Notes
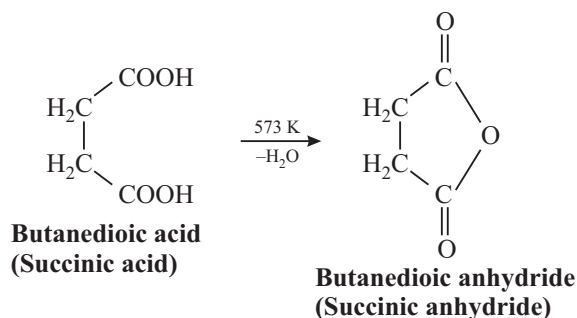
(iii) Formation of Esters

Carboxylic acids react with alcohols to form esters.

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH + R'OH \underset{}{\overset{H^+}{\rightleftharpoons}} R-\overset{\overset{\displaystyle O}{\|}}{C}-OR' + HO_2$$
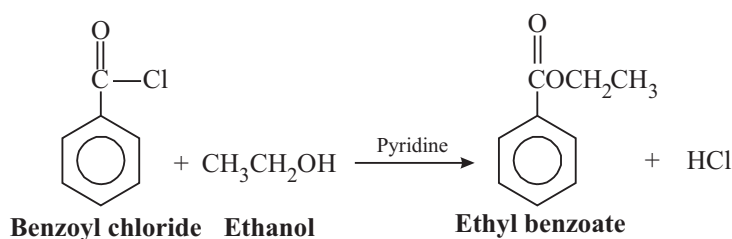
Carboxylic **Alcohol**   **Ester**
acid

Note that the acid catalysed esterification is an equilibrium reaction. The equilibrium can be shifted to the right side towards products it we are able to remove water or the ester from the reaction mixture. Also if we use excess of one reagent, then the equilibrium shifts towards the right side to give the ester. Normally, we take excess of alcohol and use it as a solvent to carry out esterification.

$$CH_3\overset{\overset{\displaystyle O}{\|}}{C}-OH + CH_3OH \underset{-H_2O}{\overset{H_2SO_4, \Delta}{\rightleftharpoons}} CH_3\overset{\overset{\displaystyle O}{\|}}{C}OCH_3$$

Ethanoic acid Methanol   **Methyl ethanoate**
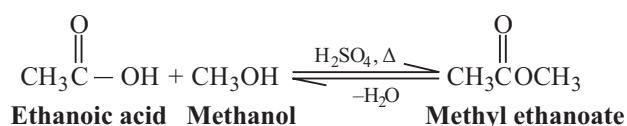
Esters are named as a**lkyl alkanoates.** The alkyl part comes from the alcohol while the alkanoate portion is derived from the carboxylic acid. Therefore, the above ester is called **methyl ethanoate** because it is obtained from *methyl alcohol* and *ethanoic* **acid.**

Esters can also be prepared by the reaction of **acid chlorides** or **acids anhydrides** with alcohols. Thus, we can see that these acid derivatives can be converted to one-another.
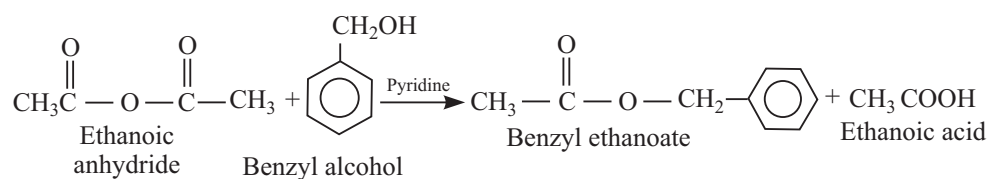

Benzoyl chloride   Ethanol   **Ethyl benzoate**

$+ \; CH_3CH_2OH \xrightarrow{\text{Pyridine}}$ $+ \;\; HCl$

$$CH_3C \overset{O}{\overset{\|}{}} - O - \overset{O}{\overset{\|}{C}} - CH_3 + \overset{CH_2OH}{\bigcirc} \xrightarrow{Pyridine} CH_3 - \overset{O}{\overset{\|}{C}} - O - CH_2 - \bigcirc + CH_3COOH$$

Ethanoic anhydride   Benzyl alcohol   Benzyl ethanoate   Ethanoic acid

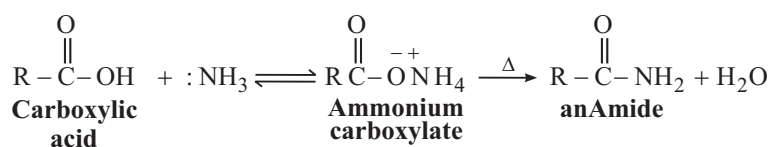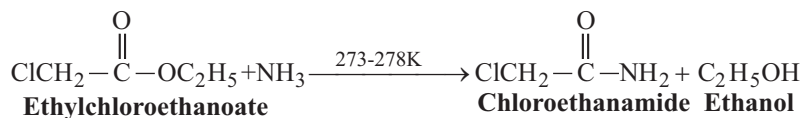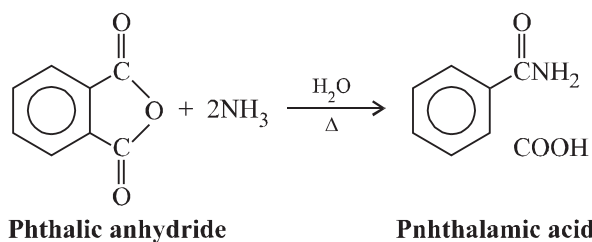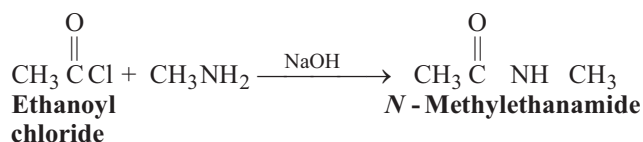### (iv) Formation of Amides

Carboxylic acids react with ammonia or amines to give amides. The reaction involves the formation of an ammonium carboxylate salt as an intermediate which on heating gives amide.

$$R - \overset{O}{\overset{\|}{C}} - OH \; + \; :NH_3 \rightleftharpoons R\overset{O}{\overset{\|}{C}} - O \overset{-}{}N \overset{+}{H_4} \xrightarrow{\Delta} R - \overset{O}{\overset{\|}{C}} - NH_2 + H_2O$$

Carboxylic acid   **Ammonium carboxylate**   **anAmide**

$$R - \overset{O}{\overset{\|}{C}} - OH \; + \; R'NH_2 \longrightarrow R - \overset{O}{\overset{\|}{C}} - NHR' + HO_2$$

Carboxylic acid   **Primary amine**   **Amide (Substituted)**
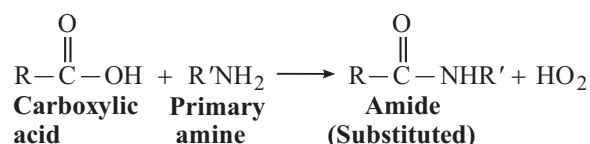
Amides can also be obtained by the reaction of ammonia or amines with **carboxylic acid halides, anhydrides** and **esters.**

$$CH_3 \overset{O}{\overset{\|}{C}}Cl + CH_3NH_2 \xrightarrow{NaOH} CH_3 \overset{O}{\overset{\|}{C}} NH \; CH_3$$

Ethanoyl chloride   **N - Methylethanamide**

Phthalic anhydride $+ 2NH_3 \xrightarrow[\Delta]{H_2O}$ Pnhthalamic acid

Phthalic anhydride   **Pnhthalamic acid**

$$ClCH_2 - \overset{O}{\overset{\|}{C}} - OC_2H_5 + NH_3 \xrightarrow{273-278K} ClCH_2 - \overset{O}{\overset{\|}{C}} - NH_2 + C_2H_5OH$$

**Ethylchloroethanoate**   **Chloroethanamide Ethanol**

Thus, we can make one carboxylic acid derivative from another. Generally, the **less reactive acid (acyl) derivatives can be prepared from the more reactive ones.**

The order of reactivity of various carboxylic acid derivatives is as follows :

Acid chloride > Acid anhydride > Ester > Amide

Thus, acid chlorides are the most reactive ones whereas the amides are the least reactive.

Since the least reactive derivative can be prepared from the more reactive ones, we can summarise which derivative can be prepared from which other one in the following way:
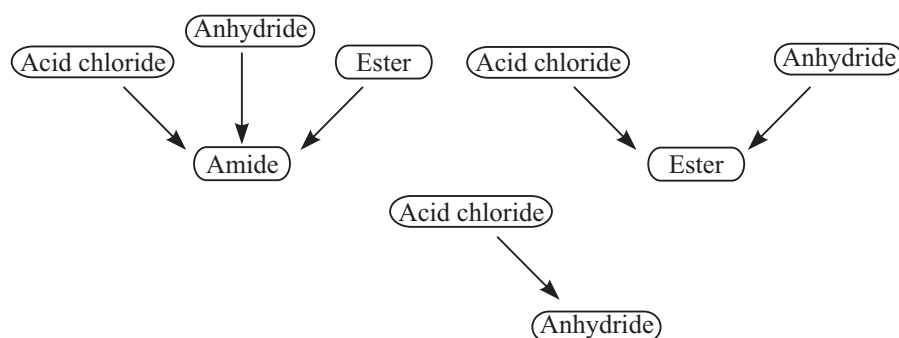
Of course, *these derivatives can be synthesised from the carboxylic acids as well.*
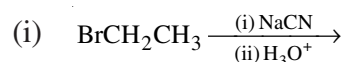
INTEXT QUESTIONS 27.2

1. Match the following compounds given in column I and their classes given in column II:

   Column I   **Column II**

   (i) CH_3COOH (a) Carboxylic acid halide

   (ii) CH_3CONH_2 (b) Carboxylic acid

   (iii) CH_3COOCH_3 (c) Carboxylic acid anhydride

   (iv) CH_3COCl (d) Carboxylic acid amide

   (v) $CH_3COOCOCH_2Cl$ (e) Ester

2. Arrange the following acids in the increasing order of their solubility in water:

   CH_3COOH, $CH_3(CH_2)_3COOH$ $p\text{-}ClC_6H_4COOH$

3. Which one of the following will be most acidic and why ?

   Butanoic acid, 2-Chlorobutanoic acid, 3-Chlorobutanoic acid, 4-Chlorobutanoic acid
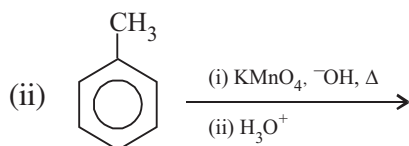
4. Give the products of the following reactions :

   (i) $BrCH_2CH_3 \xrightarrow[\text{(ii) H}_3\text{O}^+]{\text{(i) NaCN}}$

(ii) [benzene ring with CH$_3$ substituent] $\xrightarrow[\text{(ii) } H_3O^+]{\text{(i) KMnO}_4, \,^-\text{OH}, \Delta}$

(iii) $CH_3COOH + PCl_3 \longrightarrow$

5. Why are carboxylic acids more acidic than alcohols ?

WHAT YOU HAVE LEANT

In this lesson, you have learnt that

- Aldehydes and ketones constitute the carbonyl compounds. Aldehydes are known as **alkanals** whereas ketones are called **alkanones.**

- Aldehydes and ketones can be prepared by oxidation of alcohols, ozonolysis of alkenes, hydration of alkynes and Friedel–Craft's acylation.

- Carbonyl group is polar in nature and carbonyl-carbon is susceptible to nucleophilic attack. Thus, aldehydes and ketones undergo nucleophilic addition reactions with many reagents. They also exhibit condensation reactions.

- Since the α-hydrogen is acidic in nature, aldehydes and ketones show specefic reactions at α-carbon atom such as halogenation and aldol condensation.

- Carboxylic acids are an important class of compounds.

- The methods of preparation of carboxylic acids being oxidation of alkenes, aldehydes and ketones and alkylbenzene, hydrolysis of nitriles and carbonation of Grignard reagents.

- The molecules of carboxylic acids show hydrogen bonding and can exist as dimers.

- Carboxylic acids are acidic in nature. Their acidity is affected by various factors including the nature of substituents attached to the carbon chain bearing the carboxylic group.

- Carboxylic acids form salts with strong bases such as metal hydroxides. They undergo halogenation at α-carbon atom and can be reduced to primary alcohols using $LiAIH_4$.

- Carboxylic acids gives rise to a number of carboxylic acid derivatives such as carboxylic acid halides, anhydrides, esters and amides by nucleophilic acyl substitution reactions. They can be prepared from one another as shown below :

Carboxylic Acid → Acid chloride → Anhydride → Ester → Amide
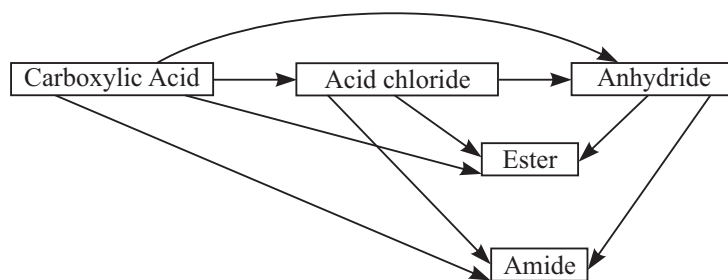
TERMINAL EXERCISE

1. Write the structural formulae and IUPAC names of the compounds containing a carbonyl functional group and having the molecular formula C_3H_6O.

2. How can you prepare primary, secondary or tertiary alcohols using aldehydes or ketones?

3. Write the mechanism of addition of HCN to propanone.

4. What is Tollen's Test?

5. Explain keto-enol tautomerism.

6. What is haloform reaction?

7. How will you test a carboxylic acid in the laboratory?

8. Which reagent can reduce a carboxylic acid to a primary alcohol?

9. What are carboxylic acid anhydrides ? Give their method of preparation from carboxylic acids.

10. Which carboxylic acid derivative is most reactive?

    (a) Acid amide (b) Ester (c) Acid halide (d) Acid anhydride

ANSWERS TO INTEXT QUESTIONS

27.1

1. (i) aldehyde, Ethanal

   (ii) ketone, Butan-2-one

   (iii) ketone, 1-Phenylethanone

   (iv) aldehyde, Propanal

2. Using hydration with Hg^{2+}, H^+.

3. Because they have one alkyl group whereas a ketone has two alkyl group. Hence, the carbonyl carbon in aldehydes is more positive.

   Also, the two alkyl groups lead to more crowding in ketones.

4. (i) $R-\overset{\displaystyle OH}{\underset{\displaystyle R'}{C}}-CN$ (ii) $R-\overset{\displaystyle OR''}{\underset{\displaystyle OR'}{C}}-R'''$ (iii) $R-\overset{\displaystyle R'}{\underset{\displaystyle OH}{C}}-R''$
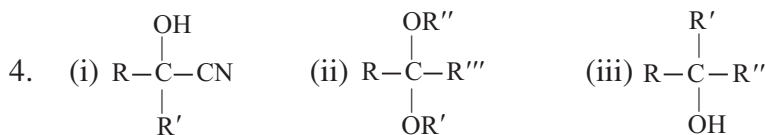
5. By Wolff- Kishner reduction or Clemmensen reduction.

6. The product formed by the condensation of two aldehyde molecules having α-hydrogen atom. Aldol contains both an aldehyde and an alcohol functional group.

7.

27.2
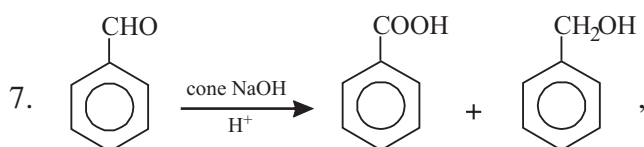
1. (i). (b)   (ii). (d)   (iii). (e)   (iv). (a)   (v) e

2. $p - ClC_6H_4COOH < CH_3(CH_2)_3COOH < CH_3COOH$

3. 2-Chlorobutanoic acid, because of maximum $-I$ effect of $-Cl$ at 2 – position.

4. (i) $HOOCCH_2CH_3$,   (ii)

   (iii) $3CH_3COCl + H_3PO_3$
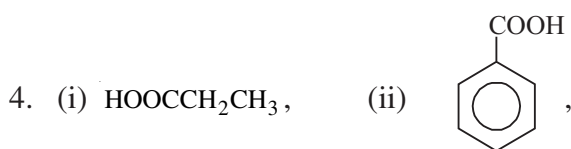
5. Because of resonance stabilization of carboxylate anion. The alkoxide ion cannot stabilize by resonance.