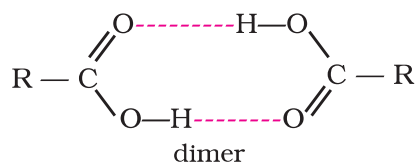
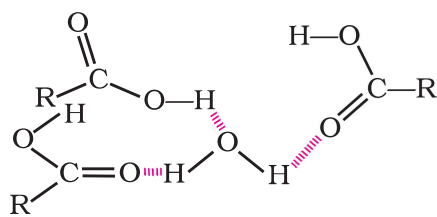


## 12.8 Physical Properties



In vapour state or in aprotic solvent



Hydrogen bonding of RCOOH with H<sub>2</sub>O

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

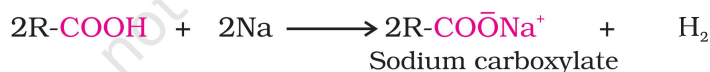
The reaction of carboxylic acids are classified as follows:

### 12.9.1 Reactions Involving Cleavage of O-H Bond

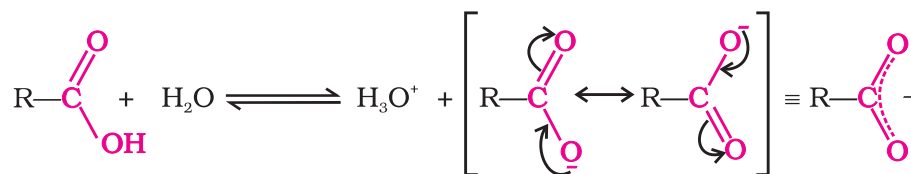
#### Acidity

Reactions with metals and alkalis

The carboxylic acids like alcohols evolve hydrogen with electropositive metals and form salts with alkalis 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.



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



For the above reaction:

$$K_{eq} = \frac{[\text{H}_3\text{O}^+][\text{RCOO}^-]}{[\text{H}_2\text{O}][\text{RCOOH}]} \quad K_a = K_{eq} [\text{H}_2\text{O}] = \frac{[\text{H}_3\text{O}^+][\text{RCOO}^-]}{[\text{RCOOH}]}$$

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

For convenience, the strength of an acid is generally indicated by its  $\text{p}K_a$  value rather than its  $K_a$  value.

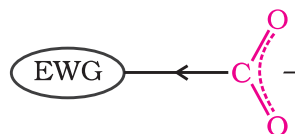
$$\text{p}K_a = -\log K_a$$

The  $\text{p}K_a$  of hydrochloric acid is  $-7.0$ , where as  $\text{p}K_a$  of trifluoroacetic acid (the strongest carboxylic acid), benzoic acid and acetic acid are  $0.23$ ,  $4.19$  and  $4.76$ , respectively.

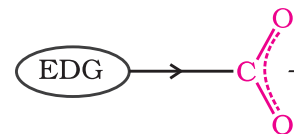
Smaller the  $\text{p}K_a$ , the stronger the acid (the better it is as a proton donor). Strong acids have  $\text{p}K_a$  values  $< 1$ , the acids with  $\text{p}K_a$  values between  $1$  and  $5$  are considered to be moderately strong acids, weak acids have  $\text{p}K_a$  values between  $5$  and  $15$ , and extremely weak acids have  $\text{p}K_a$  values  $> 15$ .

Carboxylic acids are weaker than mineral acids, but they are stronger acids than alcohols and many simple phenols ( $\text{p}K_a$  is  $\sim 16$  for ethanol and  $10$  for phenol). In fact, carboxylic acids are amongst the most acidic organic compounds you have studied so far. You already know why phenols are more acidic than alcohols. The higher acidity of carboxylic acids as compared to phenols can be understood similarly. The conjugate base of carboxylic acid, a carboxylate ion, is stabilised by two equivalent resonance structures in which the negative charge is at the more electronegative oxygen atom. The conjugate base of phenol, a phenoxide ion, has non-equivalent resonance structures in which the negative charge is at the less electronegative carbon atom. Therefore, resonance in phenoxide ion is not as important as it is in carboxylate ion. Further, the negative charge is delocalised over two electronegative oxygen atoms in carboxylate ion whereas it is less effectively delocalised over one oxygen atom and less electronegative carbon atoms in phenoxide ion (Unit 11, Class XII). Thus, the carboxylate ion is more stabilised than phenoxide ion, so carboxylic acids are more acidic than phenols.

*Effect of substituents on the acidity of carboxylic acids:* Substituents may affect the stability of the conjugate base and thus, also affect the acidity of the carboxylic acids. Electron withdrawing groups increase the acidity of carboxylic acids by stabilising the conjugate base through delocalisation of the negative charge by inductive and/or resonance effects. Conversely, electron donating groups decrease the acidity by destabilising the conjugate base.



Electron withdrawing group (EWG) stabilises the carboxylate anion and strengthens the acid

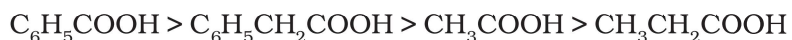


Electron donating group (EDG) destabilises the carboxylate anion and weakens the acid

The effect of the following groups in increasing acidity order is



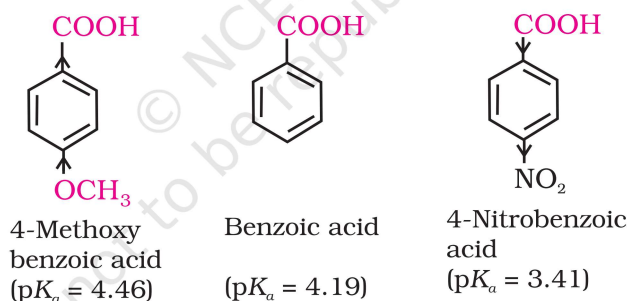
Thus, the following acids are arranged in order of increasing acidity (based on  $pK_a$  values):



Direct attachment of groups such as phenyl or vinyl to the carboxylic acid, increases the acidity of corresponding carboxylic acid, contrary to the decrease expected due to resonance effect shown below:



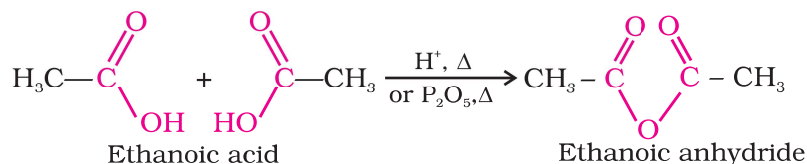
This is because of greater electronegativity of  $sp^2$  hybridised carbon to which carboxyl carbon is attached. The presence of electron withdrawing group on the phenyl of aromatic carboxylic acid increases their acidity while electron donating groups decrease their acidity.



### 12.9.2 Reactions Involving Cleavage of C-OH Bond

#### 1. Formation of anhydride

Carboxylic acids on heating with mineral acids such as  $\text{H}_2\text{SO}_4$  or with  $\text{P}_2\text{O}_5$  give corresponding anhydride.

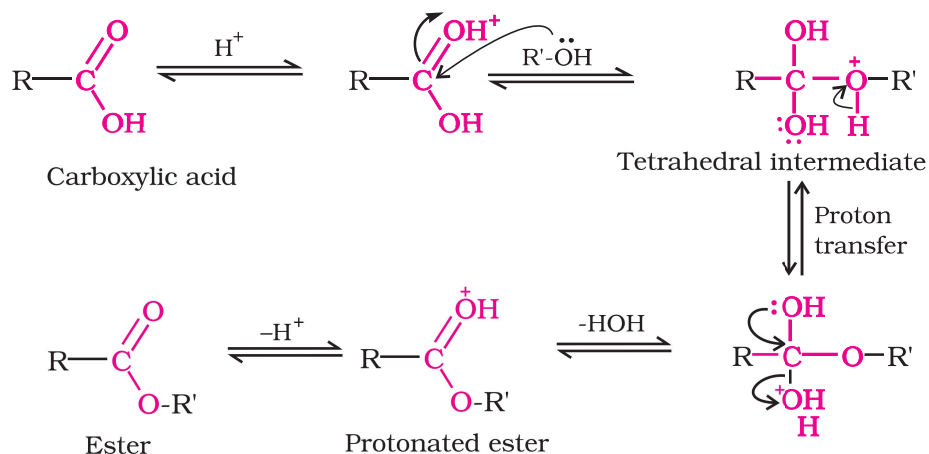


#### 2. Esterification

Carboxylic acids are esterified with alcohols or phenols in the presence of a mineral acid such as concentrated  $\text{H}_2\text{SO}_4$  or  $\text{HCl}$  gas as a catalyst.

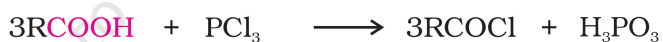


**Mechanism of esterification of carboxylic acids:** The esterification of carboxylic acids with alcohols is a kind of nucleophilic acyl substitution. Protonation of the carbonyl oxygen activates the carbonyl group towards nucleophilic addition of the alcohol. Proton transfer in the tetrahedral intermediate converts the hydroxyl group into  $^{-}\text{OH}_2$  group, which, being a better leaving group, is eliminated as neutral water molecule. The protonated ester so formed finally loses a proton to give the ester.



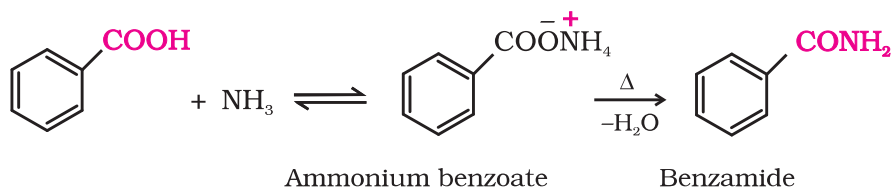
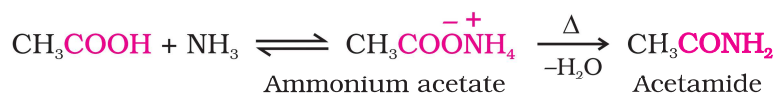
### 3. Reactions with $\text{PCl}_5$ , $\text{PCl}_3$ and $\text{SOCl}_2$

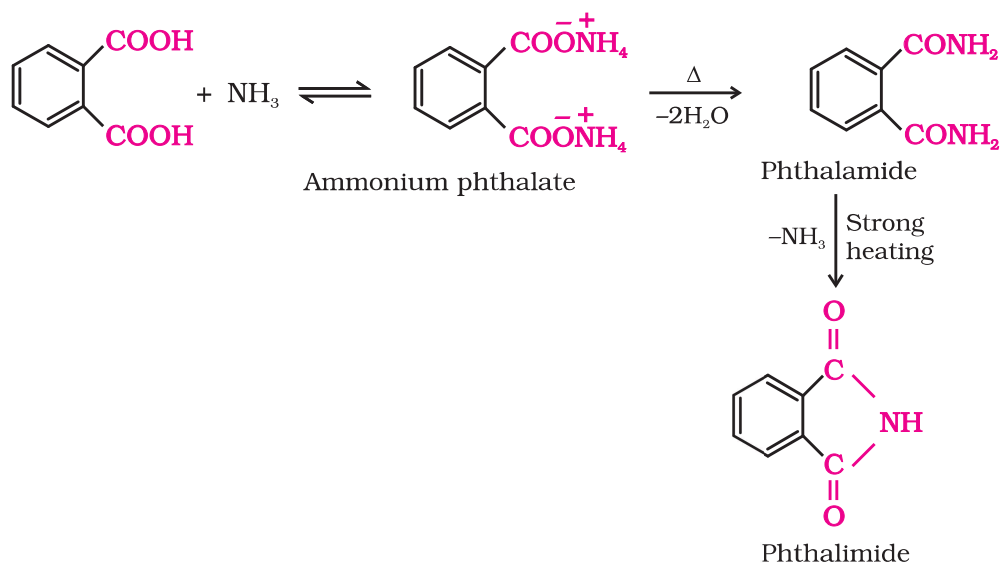
The hydroxyl group of carboxylic acids, behaves like that of alcohols and is easily replaced by chlorine atom on treating with  $\text{PCl}_5$ ,  $\text{PCl}_3$  or  $\text{SOCl}_2$ . Thionyl chloride ( $\text{SOCl}_2$ ) is preferred because the other two products are gaseous and escape the reaction mixture making the purification of the products easier.



### 4. Reaction with ammonia

Carboxylic acids react with ammonia to give ammonium salt which on further heating at high temperature give amides. For example:





### 12.9.3 Reactions Involving -COOH Group

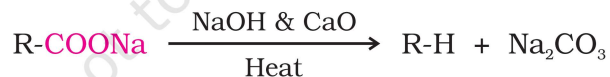
#### 1. Reduction

Carboxylic acids are reduced to primary alcohols by lithium aluminium hydride or better with diborane. Diborane does not easily reduce functional groups such as ester, nitro, halo, etc. Sodium borohydride does not reduce the carboxyl group.



#### 2. Decarboxylation

Carboxylic acids lose carbon dioxide to form hydrocarbons when their sodium salts are heated with sodalime (NaOH and CaO in the ratio of 3 : 1). The reaction is known as decarboxylation.

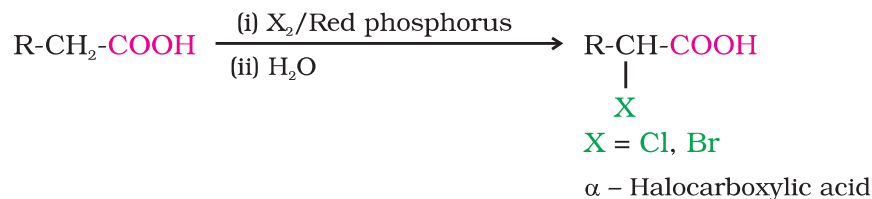


Alkali metal salts of carboxylic acids also undergo decarboxylation on electrolysis of their aqueous solutions and form hydrocarbons having twice the number of carbon atoms present in the alkyl group of the acid. The reaction is known as **Kolbe electrolysis** (Unit 13, Class XI).

### 12.9.4 Substitution Reactions in the Hydrocarbon Part

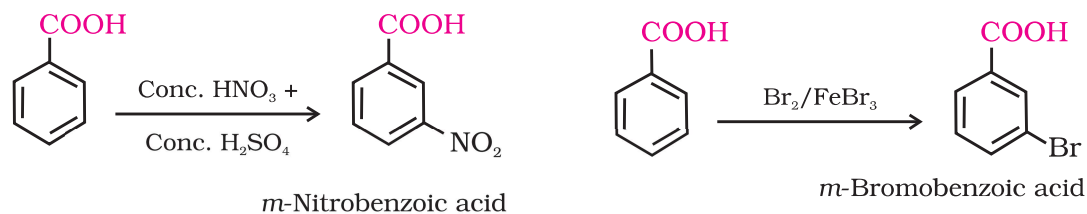
#### 1. Halogenation

Carboxylic acids having an  $\alpha$ -hydrogen are halogenated at the  $\alpha$ -position on treatment with chlorine or bromine in the presence of small amount of red phosphorus to give  $\alpha$ -halocarboxylic acids. The reaction is known as **Hell-Volhard-Zelinsky reaction**.



## 2. Ring substitution

Aromatic carboxylic acids undergo electrophilic substitution reactions in which the carboxyl group acts as a deactivating and meta-directing group. They however, do not undergo **Friedel-Crafts reaction** (because the carboxyl group is deactivating and the catalyst aluminium chloride (Lewis acid) gets bonded to the carboxyl group).



### Intext Question

12.8 Which acid of each pair shown here would you expect to be stronger?

(i) CH<sub>3</sub>CO<sub>2</sub>H or CH<sub>2</sub>FCO<sub>2</sub>H      (ii) CH<sub>2</sub>FCO<sub>2</sub>H or CH<sub>2</sub>ClCO<sub>2</sub>H

(iii) CH<sub>2</sub>FCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H or CH<sub>3</sub>CHFCH<sub>2</sub>CO<sub>2</sub>H

(iv) or

## 12.10 Uses of Carboxylic Acids

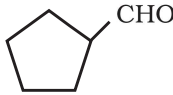
Methanoic acid is used in rubber, textile, dyeing, leather and electroplating industries. Ethanoic acid is used as solvent and as vinegar in food industry. Hexanedioic acid is used in the manufacture of nylon-6, 6. Esters of benzoic acid are used in perfumery. Sodium benzoate is used as a food preservative. Higher fatty acids are used for the manufacture of soaps and detergents.

### Summary

**Aldehydes, ketones and carboxylic acids** are some of the important classes of organic compounds containing carbonyl group. These are highly polar molecules. Therefore, they boil at higher temperatures than the hydrocarbons and weakly polar compounds such as ethers of comparable molecular masses. The lower members are more soluble in water because they form hydrogen bonds with water. The higher members, because of large size of hydrophobic chain of carbon atoms, are insoluble in water but soluble in common organic solvents. Aldehydes are prepared by dehydrogenation or controlled oxidation of primary alcohols and controlled or selective reduction of acyl halides. Aromatic aldehydes may also be prepared by oxidation of (i) methylbenzene with chromyl chloride or CrO<sub>3</sub> in the presence of acetic anhydride, (ii) formylation of arenes with carbon monoxide and hydrochloric acid in the presence of anhydrous aluminium chloride, and (iii) cuprous chloride or by hydrolysis of benzal chloride. Ketones are prepared by oxidation of secondary alcohols and hydration of alkynes. Ketones are also prepared by reaction of acyl chloride with dialkylcadmium. A good method for the preparation of aromatic ketones is the **Friedel-Crafts acylation** of aromatic hydrocarbons with acyl chlorides or anhydrides. Both aldehydes and ketones can be prepared by ozonolysis of alkenes. Aldehydes and ketones undergo nucleophilic addition reactions onto the carbonyl group with a number of nucleophiles such as, HCN, NaHSO<sub>3</sub>, alcohols (or diols),

ammonia derivatives, and **Grignard reagents**. The  $\alpha$ -hydrogens in aldehydes and ketones are acidic. Therefore, aldehydes and ketones having at least one  $\alpha$ -hydrogen, undergo **Aldol condensation** in the presence of a base to give  $\alpha$ -hydroxyaldehydes (aldol) and  $\alpha$ -hydroxyketones (ketol), respectively. Aldehydes having no  $\alpha$ -hydrogen undergo **Cannizzaro reaction** in the presence of concentrated alkali. Aldehydes and ketones are reduced to alcohols with  $\text{NaBH}_4$ ,  $\text{LiAlH}_4$ , or by catalytic hydrogenation. The carbonyl group of aldehydes and ketones can be reduced to a methylene group by **Clemmensen reduction** or **Wolff-Kishner reduction**. Aldehydes are easily oxidised to carboxylic acids by mild oxidising reagents such as **Tollens' reagent** and **Fehling's reagent**. These oxidation reactions are used to distinguish aldehydes from ketones. Carboxylic acids are prepared by the oxidation of primary alcohols, aldehydes and alkenes by hydrolysis of nitriles, and by treatment of Grignard reagents with carbon dioxide. Aromatic carboxylic acids are also prepared by side-chain oxidation of alkylbenzenes. Carboxylic acids are considerably more acidic than alcohols and most of simple phenols. Carboxylic acids are reduced to primary alcohols with  $\text{LiAlH}_4$ , or better with diborane in ether solution and also undergo  $\alpha$ -halogenation with  $\text{Cl}_2$  and  $\text{Br}_2$  in the presence of red phosphorus (**Hell-Volhard Zelinsky reaction**). Methanal, ethanal, propanone, benzaldehyde, formic acid, acetic acid and benzoic acid are highly useful compounds in industry.

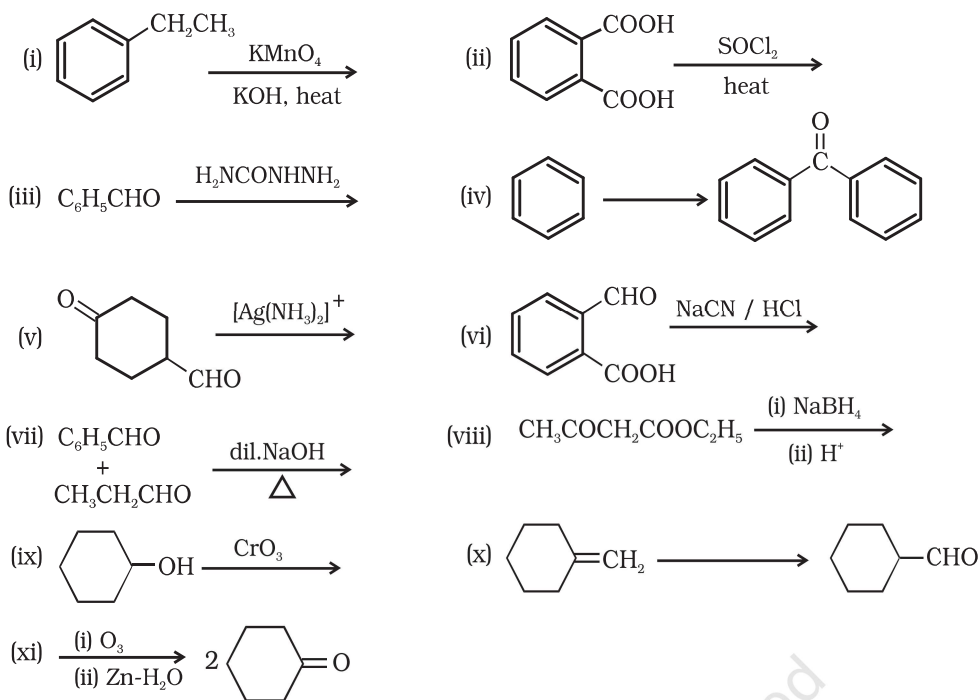
## Exercises

- 12.1** What is meant by the following terms? Give an example of the reaction in each case.
- |                   |                |                         |
|-------------------|----------------|-------------------------|
| (i) Cyanohydrin   | (ii) Acetal    | (iii) Semicarbazone     |
| (iv) Aldol        | (v) Hemiacetal | (vi) Oxime              |
| (vii) Ketal       | (viii) Imine   | (ix) 2,4-DNP-derivative |
| (x) Schiff's base |                |                         |
- 12.2** Name the following compounds according to IUPAC system of nomenclature:
- |                                                                                        |                                                                                               |
|----------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------|
| (i) $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CHO}$                | (ii) $\text{CH}_3\text{CH}_2\text{COCH}(\text{C}_2\text{H}_5)\text{CH}_2\text{CH}_2\text{Cl}$ |
| (iii) $\text{CH}_3\text{CH}=\text{CHCHO}$                                              | (iv) $\text{CH}_3\text{COCH}_2\text{COCH}_3$                                                  |
| (v) $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{C}(\text{CH}_3)_2\text{COCH}_3$ | (vi) $(\text{CH}_3)_3\text{CCH}_2\text{COOH}$                                                 |
| (vii) $\text{OHCC}_6\text{H}_4\text{CHO-p}$                                            |                                                                                               |
- 12.3** Draw the structures of the following compounds.
- |                                          |                                     |
|------------------------------------------|-------------------------------------|
| (i) 3-Methylbutanal                      | (ii) <i>p</i> -Nitropropiofenone    |
| (iii) <i>p</i> -Methylbenzaldehyde       | (iv) 4-Methylpent-3-en-2-one        |
| (v) 4-Chloropentan-2-one                 | (vi) 3-Bromo-4-phenylpentanoic acid |
| (vii) <i>p,p'</i> -Dihydroxybenzophenone | (viii) Hex-2-en-4-ynoic acid        |
- 12.4** Write the IUPAC names of the following ketones and aldehydes. Wherever possible, give also common names.
- |                                                      |                                                                              |
|------------------------------------------------------|------------------------------------------------------------------------------|
| (i) $\text{CH}_3\text{CO}(\text{CH}_2)_4\text{CH}_3$ | (ii) $\text{CH}_3\text{CH}_2\text{CHBrCH}_2\text{CH}(\text{CH}_3)\text{CHO}$ |
| (iii) $\text{CH}_3(\text{CH}_2)_5\text{CHO}$         | (iv) $\text{Ph-CH=CH-CHO}$                                                   |
- (v) 
- (vi)  $\text{PhCOPh}$
- 12.5** Draw structures of the following derivatives.
- The 2,4-dinitrophenylhydrazone of benzaldehyde
  - Cyclopropanone oxime
  - Acetaldehydedimethylacetal
  - The semicarbazone of cyclobutanone
  - The ethylene ketal of hexan-3-one
  - The methyl hemiacetal of formaldehyde

- 12.6** Predict the products formed when cyclohexanecarbaldehyde reacts with following reagents.
- (i)  $\text{PhMgBr}$  and then  $\text{H}_3\text{O}^+$  (ii) Tollens' reagent  
 (iii) Semicarbazide and weak acid (iv) Excess ethanol and acid  
 (v) Zinc amalgam and dilute hydrochloric acid
- 12.7** Which of the following compounds would undergo aldol condensation, which the Cannizzaro reaction and which neither? Write the structures of the expected products of aldol condensation and Cannizzaro reaction.
- (i) Methanal (ii) 2-Methylpentanal (iii) Benzaldehyde  
 (iv) Benzophenone (v) Cyclohexanone (vi) 1-Phenylpropanone  
 (vii) Phenylacetaldehyde (viii) Butan-1-ol (ix) 2,2-Dimethylbutanal
- 12.8** How will you convert ethanal into the following compounds?  
 (i) Butane-1,3-diol (ii) But-2-enal (iii) But-2-enoic acid
- 12.9** Write structural formulas and names of four possible aldol condensation products from propanal and butanal. In each case, indicate which aldehyde acts as nucleophile and which as electrophile.
- 12.10** An organic compound with the molecular formula  $\text{C}_9\text{H}_{10}\text{O}$  forms 2,4-DNP derivative, reduces Tollens' reagent and undergoes Cannizzaro reaction. On vigorous oxidation, it gives 1,2-benzenedicarboxylic acid. Identify the compound.
- 12.11** An organic compound (A) (molecular formula  $\text{C}_8\text{H}_{16}\text{O}_2$ ) was hydrolysed with dilute sulphuric acid to give a carboxylic acid (B) and an alcohol (C). Oxidation of (C) with chromic acid produced (B). (C) on dehydration gives but-1-ene. Write equations for the reactions involved.
- 12.12** Arrange the following compounds in increasing order of their property as indicated:
- (i) Acetaldehyde, Acetone, Di-*tert*-butyl ketone, Methyl *tert*-butyl ketone (reactivity towards HCN)  
 (ii)  $\text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{COOH}$ ,  $\text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{COOH}$ ,  $(\text{CH}_3)_2\text{CHCOOH}$ ,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$  (acid strength)  
 (iii) Benzoic acid, 4-Nitrobenzoic acid, 3,4-Dinitrobenzoic acid, 4-Methoxybenzoic acid (acid strength)
- 12.13** Give simple chemical tests to distinguish between the following pairs of compounds.
- (i) Propanal and Propanone (ii) Acetophenone and Benzophenone  
 (iii) Phenol and Benzoic acid (iv) Benzoic acid and Ethyl benzoate  
 (v) Pentan-2-one and Pentan-3-one (vi) Benzaldehyde and Acetophenone  
 (vii) Ethanal and Propanal
- 12.14** How will you prepare the following compounds from benzene? You may use any inorganic reagent and any organic reagent having not more than one carbon atom
- (i) Methyl benzoate (ii) *m*-Nitrobenzoic acid  
 (iii) *p*-Nitrobenzoic acid (iv) Phenylacetic acid  
 (v) *p*-Nitrobenzaldehyde.
- 12.15** How will you bring about the following conversions in not more than two steps?
- (i) Propanone to Propene (ii) Benzoic acid to Benzaldehyde  
 (iii) Ethanol to 3-Hydroxybutanal (iv) Benzene to *m*-Nitroacetophenone  
 (v) Benzaldehyde to Benzophenone (vi) Bromobenzene to 1-Phenylethanol  
 (vii) Benzaldehyde to 3-Phenylpropan-1-ol  
 (viii) Benzaldehyde to  $\alpha$ -Hydroxyphenylacetic acid  
 (ix) Benzoic acid to *m*- Nitrobenzyl alcohol
- 12.16** Describe the following:
- (i) Acetylation (ii) Cannizzaro reaction  
 (iii) Cross aldol condensation (iv) Decarboxylation



12.17 Complete each synthesis by giving missing starting material, reagent or products



12.18 Give plausible explanation for each of the following:

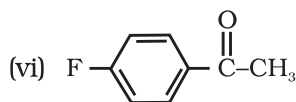
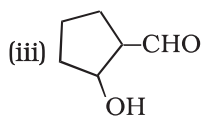
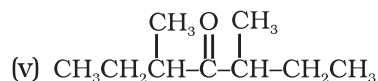
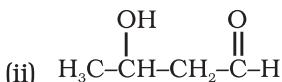
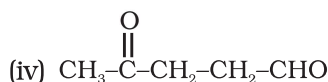
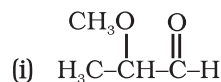
- Cyclohexanone forms cyanohydrin in good yield but 2,2,6-trimethylcyclohexanone does not.
- There are two  $\text{-NH}_2$  groups in semicarbazide. However, only one is involved in the formation of semicarbazones.
- During the preparation of esters from a carboxylic acid and an alcohol in the presence of an acid catalyst, the water or the ester should be removed as soon as it is formed.

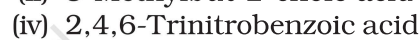
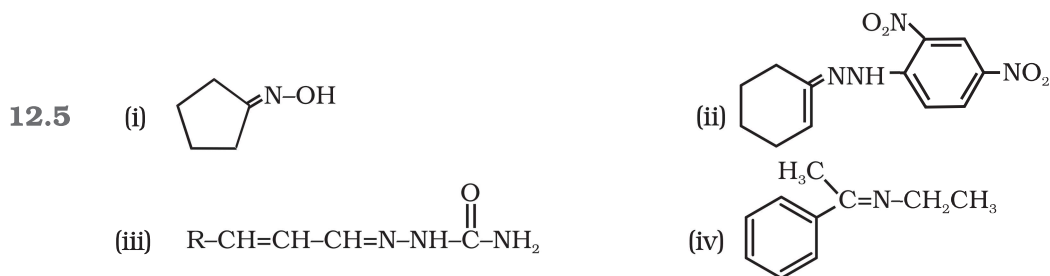
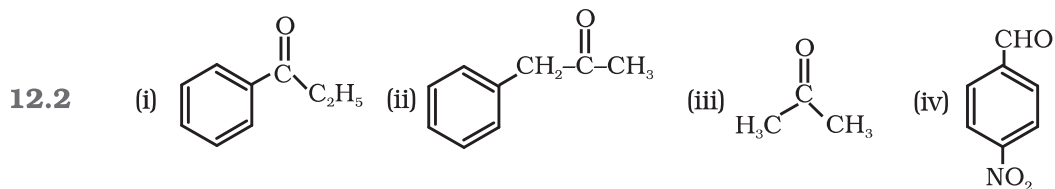
12.19 An organic compound contains 69.77% carbon, 11.63% hydrogen and rest oxygen. The molecular mass of the compound is 86. It does not reduce Tollens' reagent but forms an addition compound with sodium hydrogensulphite and give positive iodoform test. On vigorous oxidation it gives ethanoic and propanoic acid. Write the possible structure of the compound.

12.20 Although phenoxide ion has more number of resonating structures than carboxylate ion, carboxylic acid is a stronger acid than phenol. Why?

### Answers to Some Intext Questions

12.1





12.7

