12 Aldehydes, Ketones and Carboxylic Acids

LESSON AT A GLANCE

- **Carbonyl group:** A compound containing the carbonyl group (>C=O) aldehydes, ketons, carboxylic acids, amids are collectively called carbonyl compounds.
- **Carboxylic acid:** Organic compounds containing the group –CO.OH (the carbonyl group, *i.e.* the group attached to a hydroxyl group). In systematic chemical nomenclature carboxylic acid names ends in the suffix –oic, *e.g.* ethanoic acid CH_3COOH. They are generally weak acids.
- **Aldol condensation:** Aldehydes and ketones having at least one α–hydrogen undergo aldol condensation in the presence of a base to give α-hydroxyaldehydes (aldol) and α– hydroxy–ketones (ketol) respectively.
- **Cannizaro reaction:** A reaction of aldehydes to give carboxylic acids and alcohols. It occurs in the presence of strong bases with aldehydes that do not have alpha hydrogen atoms.
- **Clemmensen reduction:** The carbonyl group of aldehydes and ketones can be reduced to hydrocarbon group by clemmensen reduction or wolf–Kishner reduction.
- **Oxidation of aldehydes:** By mild oxidising agents. Tollen's reagent and Fehling's reagent. These oxidation reactions are used to distingnish aldehydes from ketons.
- **Carbonyl group:** Organic compounds containing carbon–oxygen double bond (>C=O) called carbonyl group.
- **Carbonyl Compounds:** Aldehydes and ketones are collectively called carbonyl compounds.
- **Aldehydes:** The carbonyl carbon is bonded to one hydrogen and one alkyl group.

- **Ketones:** In ketones the carbonyl carbon is always bonded to two alkyl groups. These alkyl groups may be same or different.
- The carbonyl carbon is sp^2 hybridized, the three atoms attached to it lie in the same plane. The bond angles between the attached atoms are approximately 120°.
- **IUPAC System:** IUPAC names for aldehydes are obtained by replacing the ending *–e* of the corresponding alkane with *–al*. Since the aldehyde functional group is always at the end of the chain, there is no need to specify its position. However, when other substituents are present, the carbonyl carbon is assigned number 1.
- **Wolf–Kisher Reduction:** This involves the use of a basic solution of hydrazine as the reducing agent.
- **Oxidation Reaction:** Aldehydes can be oxidised with sodium (or potassium) dichromate in acidic medium to form carboxylic acids containing the same number of carbon atoms.
- **Tollen's Reagent:** Tollen's reagent is an ammonical solution of silver oxide. It is obtained by adding ammonia to a precipitate of silver oxide present in a solution of silver nitrate and sodium hydroxide. When Tollen's reagent is used to oxidise an aldehyde, the silver ion is reduced to metallic form and if the reaction is carried out in a clean test tube, deposits as a mirror. The silver mirror formed indicates the presence of an aldehyde group in a molecule.
- **Fehling's Solution:** Fehling's solution is an alkaline solution of cupric ion complexed with sodium potassium tartrate ions.
- **Benedict's Solution:** It is an alkaline solution of cupric ion complexed with citrate ions. It reacts in the same way as Fehling's solution.
- **Oxidation of Ketones:** Ketones can be oxidised by strong oxidising agents such as alkaline $KMnO_4$ or hot conc. HNO_3 to form two carboxylic acid with former carbon atoms than the original ketone. This is because the ketone is broken into two fragements by attack on either side of the carbonyls group.
- **Carboxylic acid:** Organic compounds which contain the carbonyl group (—COOH) are called the carboxylic acid.

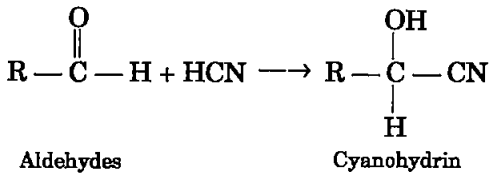
- **Esterification:** Carboxylic acids react with alcohols in the presence of a strong acid catalyst like H_2SO_4 or HCl to form esters. The reaction is reversible and is called esterification.

TEXTBOOK QUESTIONS SOLVED

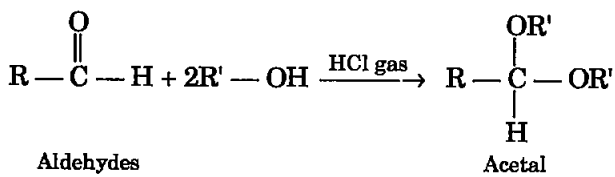
12.1 *What is meant by the following terms? Give an example of the reaction in each case.*

(*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*

Ans. (*i*) **Cyanohydrin.** Aldehydes or ketones react with hydrogen cyanide to form the addition products called cyanohydrins.

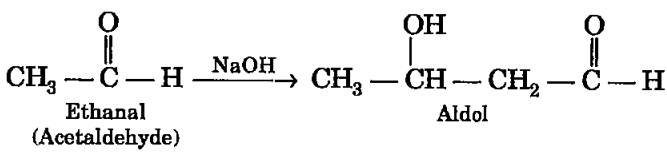


(*ii*) **Acetal.** Acetals are the diethers which are formed by the addition of two molecules of alcohols to aldehydes in the presence of dry hydrogen chloride.

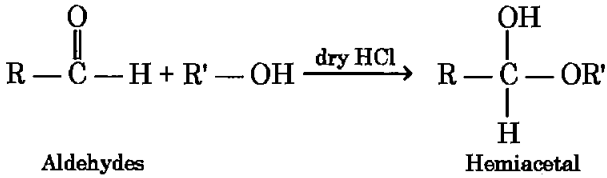


(*iii*) **Semicarbazone.** Aldehydes or ketones react with semicarbazide to form semicarbazones

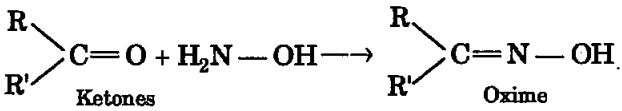
(*iv*) **Aldol.** Ethanal on treatment with dil. alkali forms a dimer, known as aldol (3-hydroxybutanal).



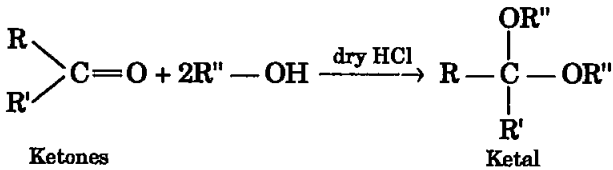
(*v*) **Hemiacetal.** Aldehydes react with one molecule of alcohol in the presence of dry hydrogen chloride to form alkoxy alcohol, also known as hemiacetal.



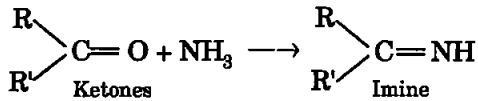
(*vi*) **Oxime.** Aldehydes or ketones condense with hydroxylamine to form the derivatives, known as oximes.



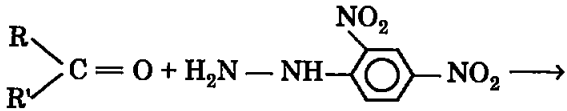
(*vii*) **Ketal.** Ketones react with two molecules of alcohols in the presence of dry hydrogen chloride to form diethers which are called ketals.



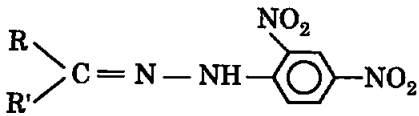
(*viii*) **Imine.** Products formed by the condensation of aldehydes or ketones with ammonia gas are known as imines.



(*ix*) **2, 4-DNP derivative.** Aldehydes or ketones react with 2,4-dinitro-phenylhydrazine to form yellow, orange or red coloured derivatives named as 2, 4-dinitrophenyl hydrazones. These are also called as 2, 4-DNP derivatives.

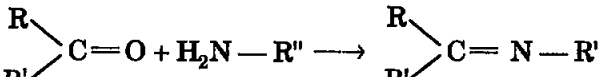


Ketones



2, 4-DNP derivatives

(*x*) **Schiff's base.** Aldehydes or ketones react with primary amines to form condensation products which are known as Schiff's bases.



Ketones Schiff's bases

12.2 *Name the following compounds according to IUPAC system of nomenclature:*

(*i*) $CH_3CH(CH_3)CH_2CH_2CHO$

(*ii*) $CH_3CH_2COCH(C_2H_5)CH_2CH_2Cl$

(*iii*) $CH_3CH = CHCHO$

(*iv*) $CH_3COCH_2COCH_3$

(*v*) $CH_3CH(CH_3)CH_2C(CH_3)_2COCH_3$

(*vi*) $(CH_3)_3CCH_2COOH$

(*vii*) $OHCC_6H_4CHO\text{-}p$

Ans. (*i*) 4-Methylpentanal

(*ii*) 6-Chloro-4-ethylhexan-3-one

(*iii*) But-2-enal

(*iv*) Pentane-2, 4-dione

(*v*) 3, 3, 5-Trimetylhexan-2-one

(*vi*) 3, 3-Dimethylbutanoic acid

(*vii*) Benzene-1, 4-dicarbaldehyde

12.3 *Draw the structures of the following compounds:*

(*i*) *3-Methylbutanal*

(*ii*) *p-Nitropropiophenone*

(*iii*) *p-Methylbenzaldehyde*

(*iv*) *4-Methylpent-3-en-2-one*

(*v*) *4-Chloropentan-2-one*

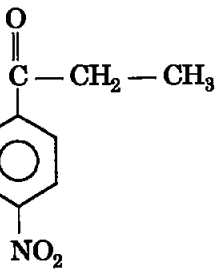
(*vi*) *3-Bromo-4-phenylpentanoic acid*

(*vii*) *p,p Dihydroxybenzophenone*

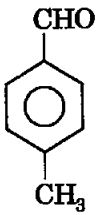
(*viii*) *Hex-2-en-4-ynoic acid*

Ans. (*i*) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CHO$

(*ii*)



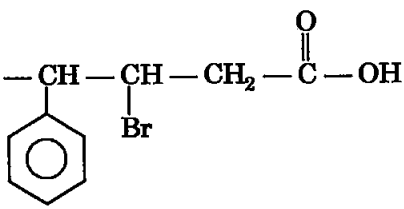
(*iii*)



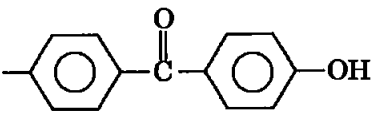
(*iv*) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3$

(*v*) $CH_3-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3$

(*vi*)



(*vii*)



(*viii*) $CH_3-C\equiv C-CH=CH-\overset{\overset{O}{\|}}{C}-OH$

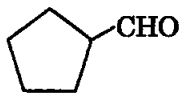
12.4 *Write the IUPAC names of the following ketones and aldehydes. Wherever possible, give also common names.*

(*i*) $CH_3CO(CH_2)_4CH_3$

(*ii*) $CH_3CH_2CHBrCH_2CH(CH_3)CHO$

(*iii*) $CH_3(CH_2)_5CHO$

(*iv*) $Ph—CH = CH—CHO$

(*v*) 

(*vi*) $PhCOPh$

Ans. Common names of the compounds are given in the brackets:

(*i*) Heptan-2-one (Methyl pentyl ketone)

(*ii*) 4-Bromo-2-methylhexanal

(*iii*) Heptanal

(*iv*) 3-Phenylpropenal (Cinnamaldehyde)

(*v*) Cyclopentane carbaldehyde

(*vi*) Diphenylmethanone (Benzophenone)

12.5 *Draw structures of the following derivatives:*

(*i*) *The 2,4-dinitrophenylhydrazone of benzaldehyde*

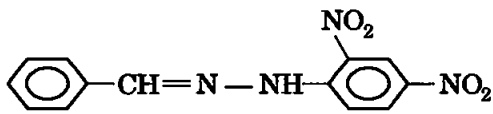
(*ii*) *Cyclopropanone oxime*

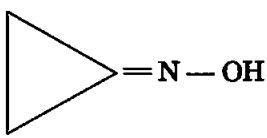
(*iii*) *Acetaldehydedimethylacetal*

(*iv*) *The semicarbazone of cyclobutanone*

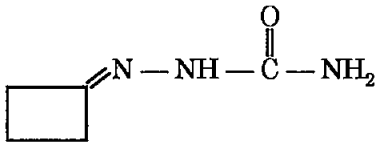
(*v*) *The ethylene ketal of hexan-3-one*

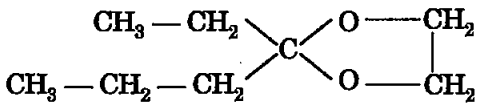
(*vi*) *The methyl hemiacetal of formaldehyde*

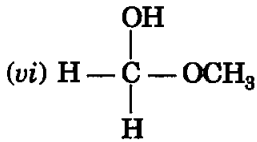
Ans. (*i*) 

(*ii*) 

(*iii*) $CH_3-\underset{\underset{H}{|}}{\overset{\overset{OCH_3}{|}}{C}}-OCH_3$

(iv) 

(v) 

(vi) 

12.6 *Predict the products formed when cyclohexanecarbaldehyde reacts with following reagents:*

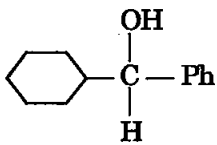
(i) PhMgBr and then H_3O^+

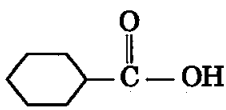
(ii) Tollens' reagent

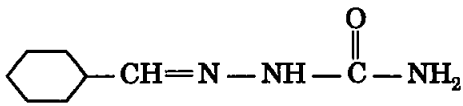
(iii) Semicarbazide and weak acid

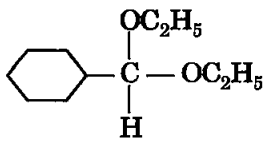
(iv) Excess ethanol and acid

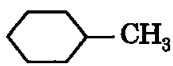
(v) Zinc amalgam and dilute hydrochloric acid

Ans. (i) 

(ii) 

(iii) 

(iv) 

(v) 

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

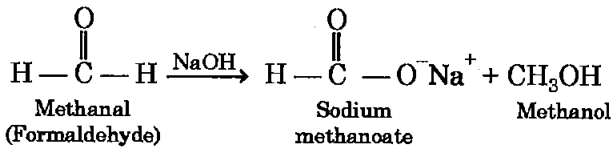
(vi) 1-Phenylpropanone

(vii) Phenylacetaldehyde

(viii) Butan-1-ol

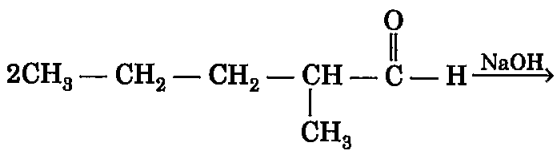
(ix) 2,2-Dimethylbutanal

Ans. (i) Methanal will undergo Cannizzaro reaction.

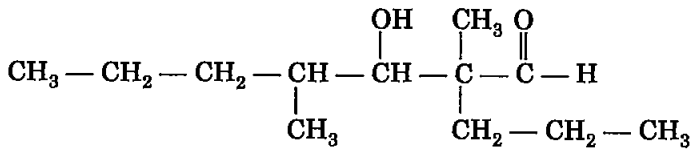


Methanal (Formaldehyde) | Sodium methanoate | Methanol

(ii) 2-Methylpentanal will undergo aldol condensation.

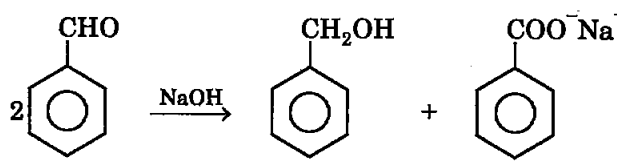


2-Methylpentanal



2,4-Dimethyl-3-hydroxy-2-propylheptanal

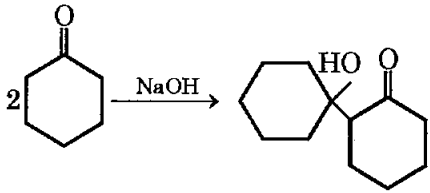
(iii) Benzaldehyde will undergo Cannizzaro reaction.



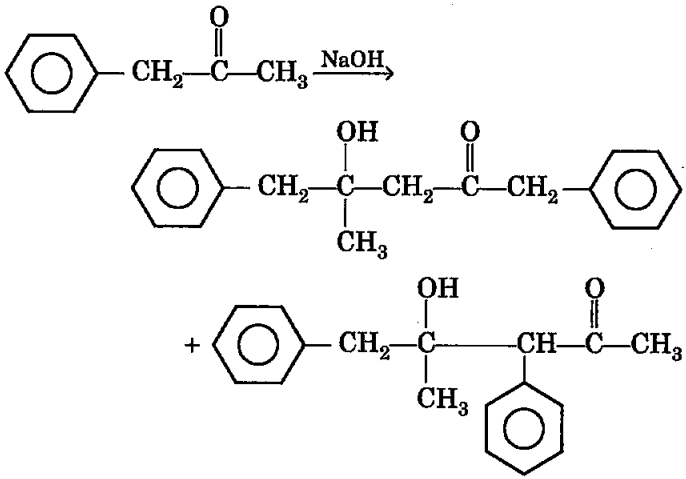
Benzaldehyde | Benzyl alcohol | Sodium benzoate

(*iv*) Benzophenone will not undergo any of these two reactions.

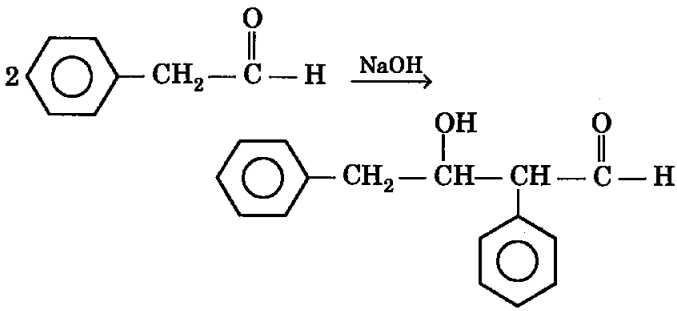
(*v*) Cyclohexanone will undergo aldol condensation.



(*vi*) 1-Phenylpropanone will undergo aldol condensation.

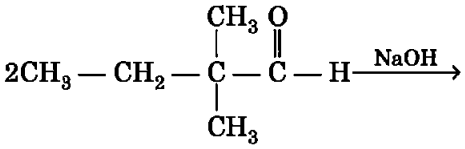


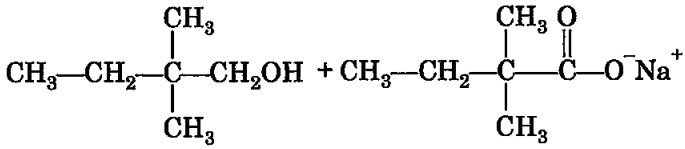
(*vii*) Phenylacetaldehyde will undergo aldol condensation.



(*viii*) Butan-1-ol will not undergo any of these two reactions.

(*ix*) 2, 2-Dimethybutanal will undergo Cannizzaro reaction.





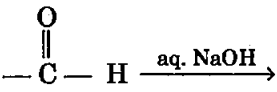
12.8 *How will you convert ethanal into the following compounds?*

(i) Butane-1, 3-diol

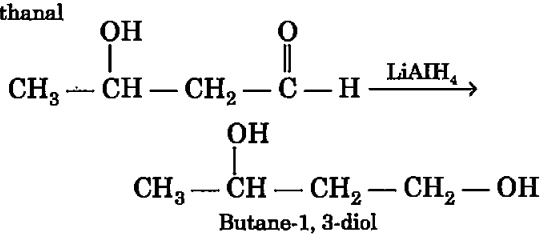
(ii) But-2-enal

(iii) But-2-enoic acid

Ans. *(i)*

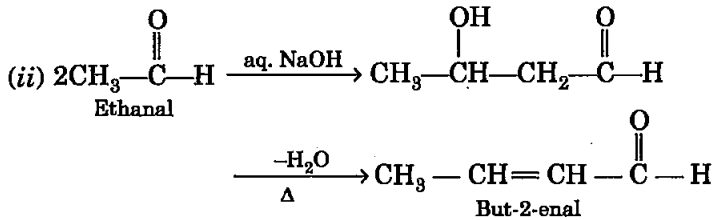


Ethanal



Butane-1, 3-diol

(ii)



Ethanal

But-2-enal

(*iii*) $2CH_3-\overset{O}{\overset{\|}{C}}-H \xrightarrow{\text{aq. NaOH}} CH_3-\overset{OH}{\underset{|}{C}}H-CH_2-\overset{O}{\overset{\|}{C}}-H$

$\xrightarrow[-H_2O]{\Delta} CH_3-CH=CH-\overset{O}{\overset{\|}{C}}-H \xrightarrow{\text{Tollen's reagent}}$

$CH_3-CH=CH-\overset{O}{\overset{\|}{C}}-OH$

But-2-enoic acid

12.9 *Write structural formulae 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.*

Ans. The four possible products are written below:

(*i*) $CH_3-CH_2-\underset{OH}{\underset{|}{C}}H-\underset{CH_3}{\underset{|}{C}}H-\overset{O}{\overset{\|}{C}}-H$

(Condensation product from two propanal molecules)

(*ii*) $CH_3-CH_2-CH_2-\underset{OH}{\underset{|}{C}}H-\underset{CH_2-CH_3}{\underset{|}{C}}H-\overset{O}{\overset{\|}{C}}-H$

(Condensation product from two butanal molecules)

(*iii*) $CH_3-CH_2-\underset{OH}{\underset{|}{C}}H-\underset{CH_2-CH_3}{\underset{|}{C}}H-\overset{O}{\overset{\|}{C}}-H$

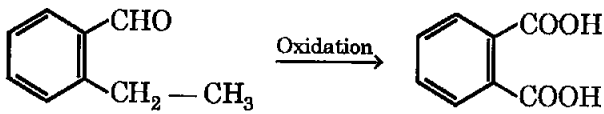
(Propanal as electrophile and butanal as nucleophile)

(*iv*) $CH_3 - CH_2 - CH_2 - \underset{\displaystyle CH_3}{\overset{\displaystyle OH}{\underset{|}{\overset{|}{CH}}}} - \underset{}{\overset{\displaystyle O}{\overset{\|}{C}}} - H$

(Butanal as electrophile and propanal as nucleophile)

12.10 *An organic compound with the molecular formula $C_9H_{10}O$ forms 2,4-DNP derivative, reduces Tollens' reagent and undergoes Cannizzaro reaction. On vigorous oxidation, it gives 1,2-benzenedicarboxylic acid. Identify the compound.*

Ans. The compound forms 2,4-DNP derivative. It shows that it is a carbonyl compound. Further it reduces Tollens' reagent which shows that it contains aldehydic group. It undergoes Cannizzaro reaction indicating that aldehyde group is without any α-hydrogen. On vigorous oxidation, it gives 1,2-benzenedicarboxylic acid which shows that *there are two carbon residues on benzene ring. Since the molecular formula is $C_9H_{10}O$, it fits into the structure, 2-ethylbenzaldehyde.*



2-Ethylbenzaldehyde 1,2-Benzenedicarboxylic acid

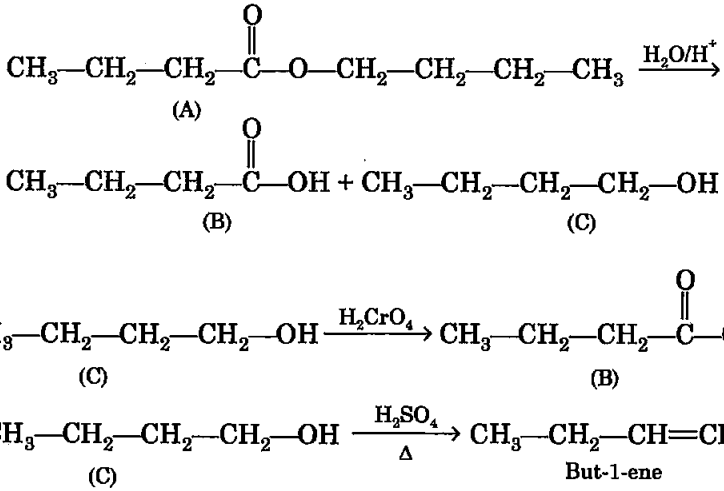
12.11 *An organic compound (A) [molecular formula $C_8H_{16}O_2$] was hydrolysed with dilute sulphuric acid to give a carboxylic acid (B) and an alcohol (C). Oxidation of (C) with chromic acid produced (B). (C) on dehydration gives but-1-ene. Write equations for the reactions involved.*

Ans. Compound '*A*' ($C_8H_{16}O_2$) on hydrolysis gives an acid '*B*' and an alcohol '*C*'. It shows that '*A*' is an ester. Since the oxidation of alcohol '*C*' also gives the acid 'B' indicates that '*B*' and '*C*' both contain same number of carbon atoms, *i.e.*, four carbon atoms each and same arrangement of atoms. Formation of but-1-ene on dehydration of '*C*' indicates it to be butan-1-ol, so the possible structure for '*A*' could be

$$CH_3 - CH_2 - CH_2 - \overset{\displaystyle O}{\overset{\|}{C}} - O - CH_2 - CH_2 - CH_2 - CH_3$$

Butyl butanoate

The various reactions involved are written as follows:



12.12 *Arrange the following compounds in increasing order of their properties as indicated:*

(*i*) *Acetaldehyde, Acetone, Di-tert-butyl ketone, Methyl tert-butyl ketone [reactivity towards HCN]*

(*ii*) *$CH_3CH_2CH(Br)COOH$, $CH_3CH(Br)CH_2COOH$, $(CH_3)_2CHCOOH$, $CH_3CH_2CH_2COOH$ (acid strength)*

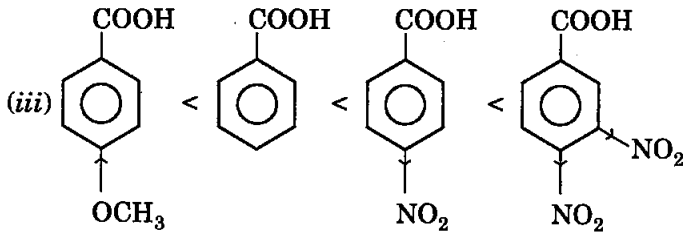
(*iii*) *Benzoic acid, 4-Nitrobenzoic acid, 3, 4-Dinitrobenzoic acid, 4-Methoxybenzoic acid (acid strength)*

Ans. (*i*) Di-*tert*-butyl ketone < Methyl-*tert*-butyl ketone < Acetone < Acetaldehyde (Increasing order of reactivity with HCN due to decreasing steric hindrance).

(*ii*) $(CH_3)_2CH - COOH > CH_3 - CH_2 - CH_2 - COOH <$

$CH_3 - \underset{\underset{Br}{|}}{CH} - CH_2 - COOH < CH_3 - CH_2 - \underset{\underset{Br}{|}}{CH} - COOH$

(*iii*)



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

Ans. (i) Propanal and propanone can be distinguished by their reactions with Tollens' reagent. Propanal will form the silver mirror.

(ii) Acetophenone and benzophenone can be distinguished by iodoform test. Acetophenone will give the yellow precipitate of iodoform.

(iii) Phenol and benzoic acid can be distinguished by their reactions with sodium bicarbonate solution. Benzoic acid will give effervescence.

(iv) Benzoic acid and ethyl benzoate can also be distinguished by their reactions with sodium bicarbonate solution. Benzoic acid will give effervescence.

(v) Pentan-2-one and pentan-3-one can be distinguished by iodoform test. Pentan-2-one being a methyl ketone, forms yellow precipitate of iodoform, on treatment with iodine and sodium hydroxide.

(vi) Benzaldehyde and acetophenone can be distinguished by Tollens' test. Benzaldehyde will form silver mirror, on treatment with Tollens' reagent.

(vii) Ethanal and propanal can be distinguished by iodoform test. Yellow precipitate of iodoform will be formed from ethanal on heating with iodine and sodium hydroxide solution.

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

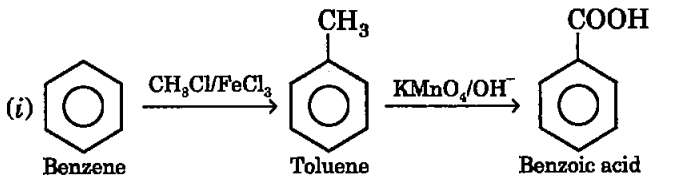
(ii) m-Nitrobenzoic acid

(iii) p-Nitrobenzoic acid

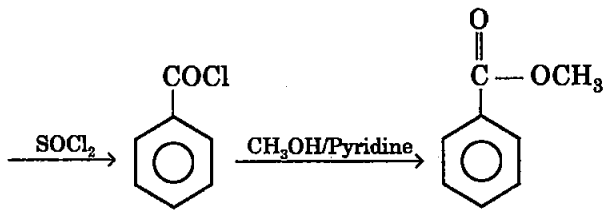
(iv) Phenylacetic acid

(v) p-Nitrobenzaldehyde.

Ans. (*i*)

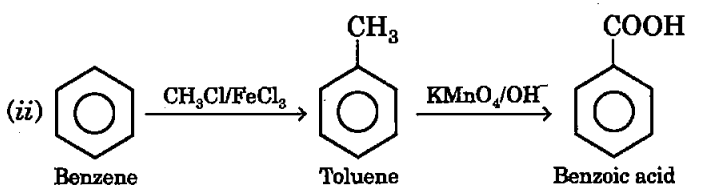


Benzene → Toluene → Benzoic acid

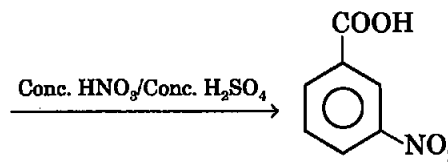


Benzoyl chloride → Methyl benzoate

(*ii*)

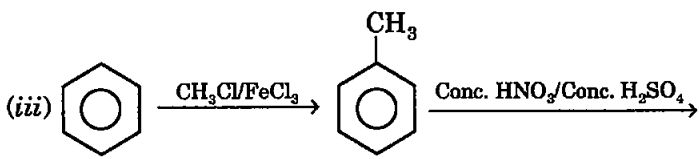


Benzene → Toluene → Benzoic acid

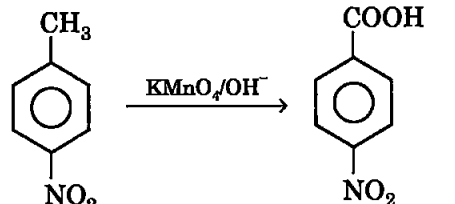


m-Nitrobenzoic acid

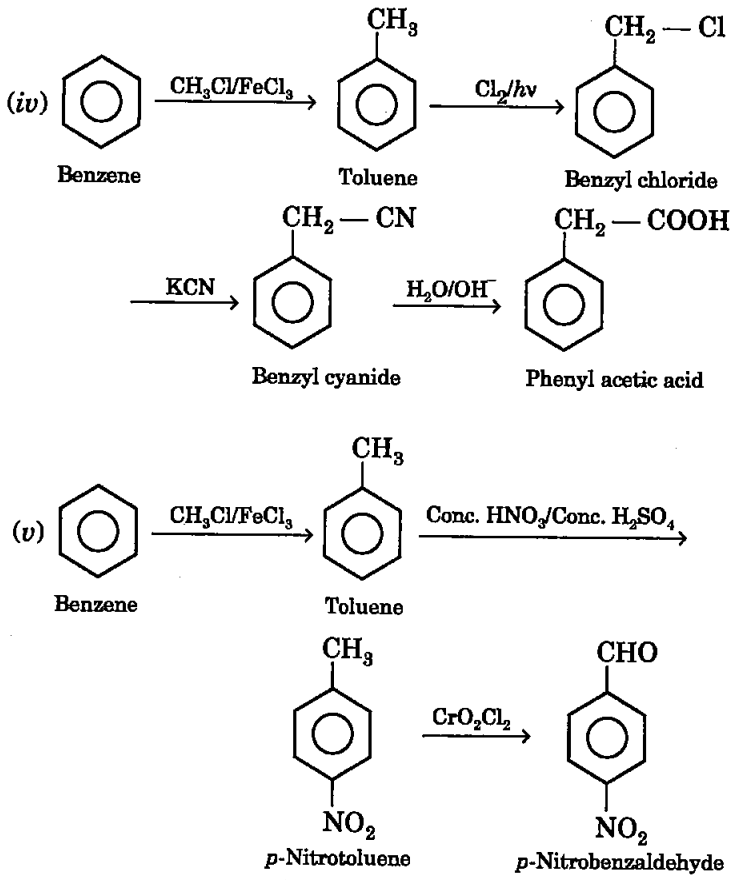
(*iii*)



Benzene → Toluene



p-Nitrotoluene → *p*-Nitrobenzoic acid



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 α-Hydroxyphenylacetic acid*

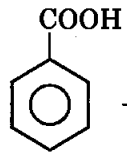
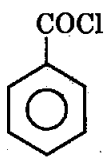
(*ix*) *Benzoic acid to m-Nitrobenzyl alcohol*

Ans. (*i*) $CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{LiAlH_4} CH_3-\overset{\overset{OH}{|}}{CH}-CH_3$

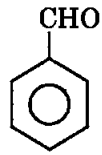
Propanone (Acetone) → Propan-2-ol

$\xrightarrow[443\ K]{Conc.\ H_2SO_4} CH_3-CH=CH_2$

Propene

(*ii*)  $\xrightarrow{SOCl_2}$ 

Benzoic acid → Benzoyl chloride

$\xrightarrow{H_2/Pd\text{-}C,\ BaSO_4}$ 

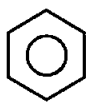
Benzaldehyde

(*iii*) $CH_3-CH_2-OH \xrightarrow{PCC} CH_3-\overset{\overset{O}{\|}}{C}-H$

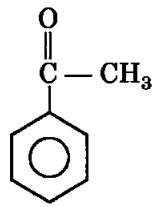
Ethanol → Ethanal (Acetaldehyde)

$\xrightarrow{dil.\ NaOH} CH_3-\overset{\overset{OH}{|}}{CH}-CH_2-\overset{\overset{O}{\|}}{C}-H$

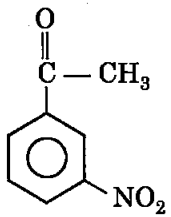
3-Hydroxybutanal

(*iv*) 

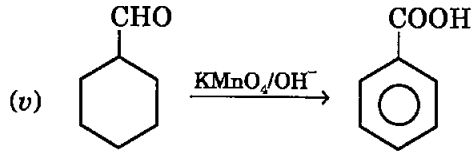
Benzene

$\xrightarrow{CH_3-\overset{\overset{O}{\|}}{C}-Cl/AlCl_3}$ 

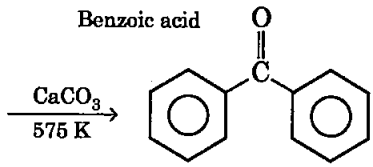
Acetophenone

$\xrightarrow[Conc.\ H_2SO_4]{Conc.\ HNO_3}$ 

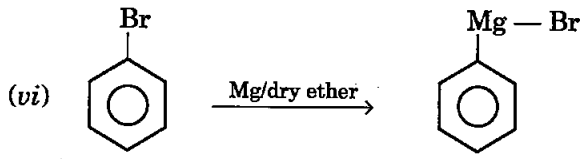
m-Nitroacetophenone



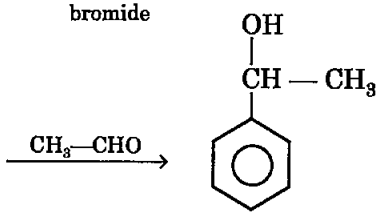
Benzaldehyde Benzoic acid



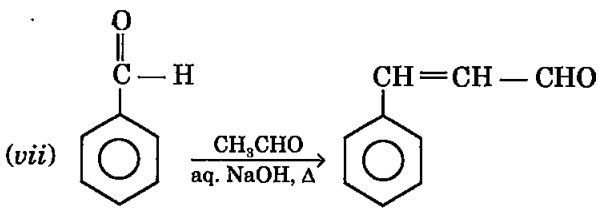
Benzophenone



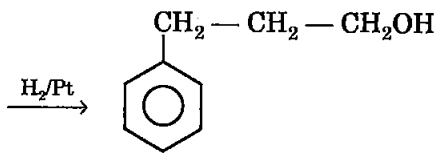
Bromobenzene Phenyl magnesium bromide



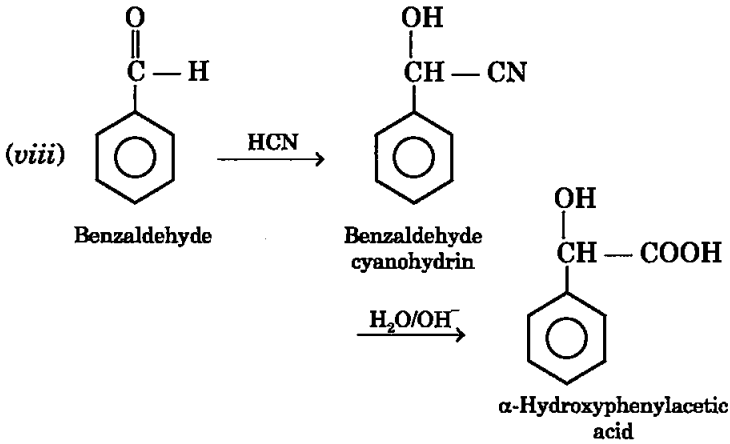
1-Phenylethanol

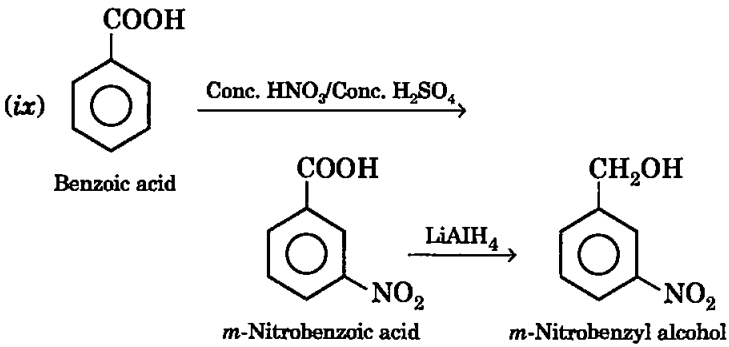


Benzaldehyde Cinnamaldehyde



3-Phenylpropan-1-ol





12.16 *Describe the following:*

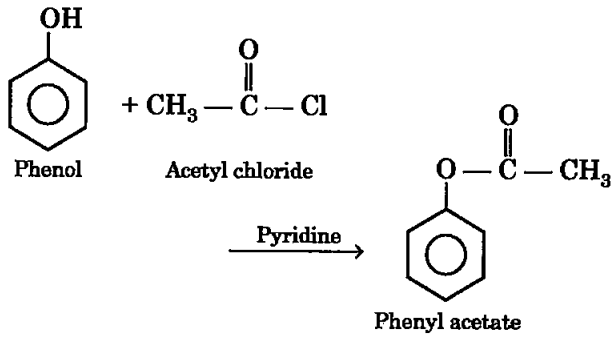
(i) Acetylation

(ii) Cannizzaro reaction

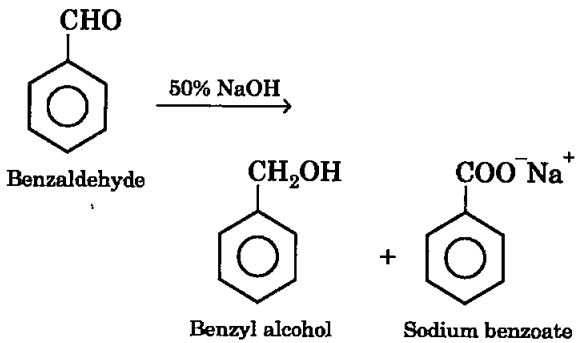
(iii) Cross aldol condensation

(iv) Decarboxylation

Ans. *(i)* **Acetylation.** Introduction of acetyl group $\left(-\overset{\overset{O}{\|}}{C}-CH_3\right)$ on alcohols, phenols or amines is called their acetylation. The reaction can be carried out by the treatment with acetyl chloride or acetic anhydride in the presence of a base like pyridine. Such as phenol on reaction with acetyl chloride gives phenyl acetate.

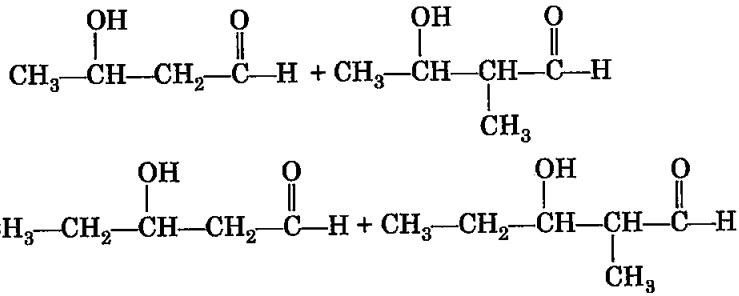


(*ii*) **Cannizzaro reaction.** Aldehydes which do not contain an a-hydrogen, undergo this reaction on heating with concentrated alkali solution. They undergo a self oxidation reduction reaction and give a mixture of alcohol and the salt of carboxylic acid. Such as benzaldehyde gives benzyl alcohol and sodium benzoate, when heated with 50% solution of sodium hydroxide.



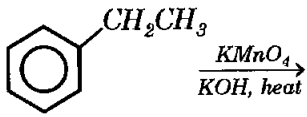
(*iii*) **Cross aldol condensation.** When two different aldehydes or ketones having a-hydrogen atoms are mixed and treated with aqueous sodium hydroxide, they undergo aldol condensation with each other. This reaction gives a mixture of four products and is known as cross aldol condensation. Such as a mixture of ethanal and propanal yields the following four products.

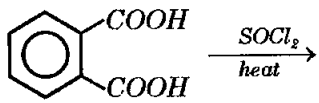
$$CH_3-CHO + CH_3-CH_2-CHO \longrightarrow$$



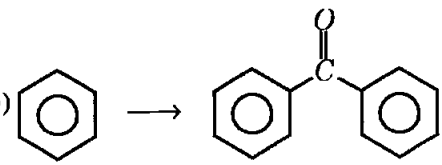
(*iv*) **Decarboxylation.** Sodium or potassium salt of carboxylic acids on heating with soda lime (NaOH and CaO), loses a molecule of carbon dioxide and alkanes are obtained as products.

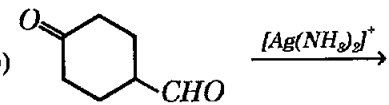
12.17 *Complete each synthesis by giving missing starting material, reagents or products*

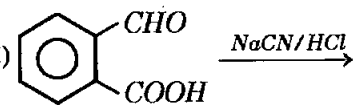
(*i*) 

(*ii*) 

(*iii*) $C_6H_5CHO \xrightarrow{H_2NCONHNH_2}$

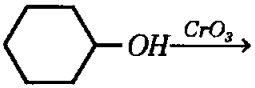
(*iv*) 

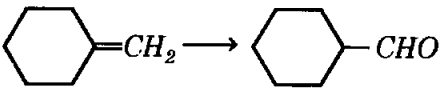
(*v*) 

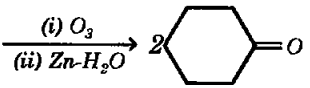
(*vi*) 

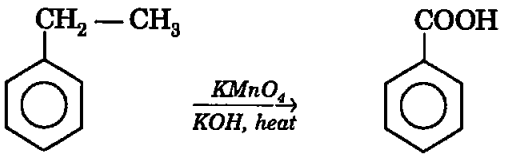
(*vii*) $C_6H_5CHO + CH_3CH_2CHO \xrightarrow{dil.\ NaOH}$

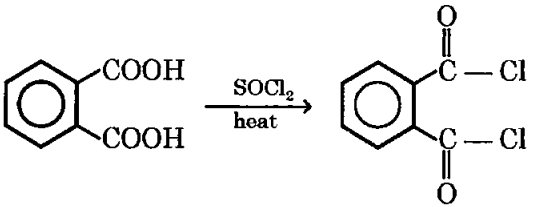
(viii) $CH_3COCH_2COOC_2H_5 \xrightarrow[(ii)\ H^+]{(i)\ NaBH_4}$

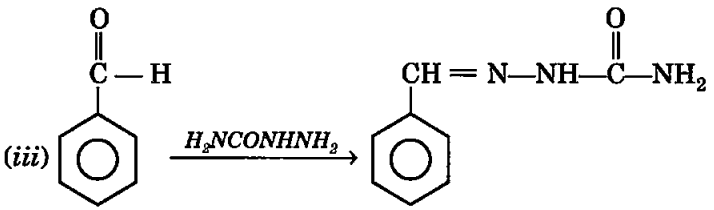
(ix) 

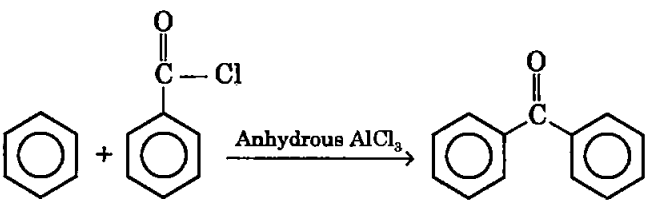
(x) 

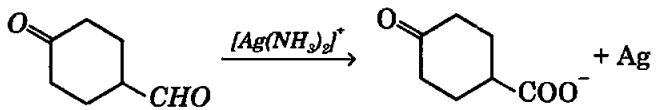
(xi) 

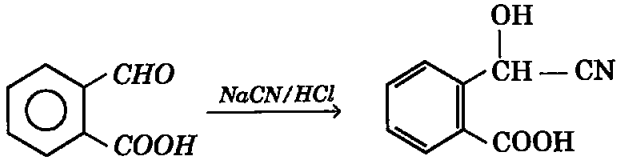
Ans. (i) 

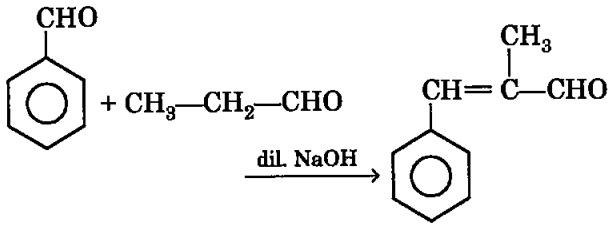
(ii) 

(iii) 

(iv) 

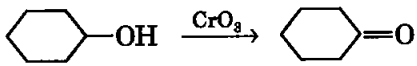
(v) 

(vi) 

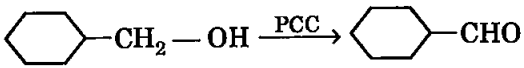
(vii) 

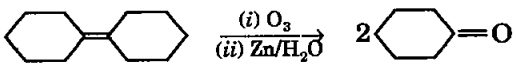
(viii) $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-O-C_2H_5 \xrightarrow[(ii)\ H^+]{(i)\ NaBH_4}$

$CH_3-\underset{OH}{\underset{|}{CH}}-CH_2-\overset{O}{\overset{\|}{C}}-O-C_2H_5$

(ix) 

(x) 



(xi) 

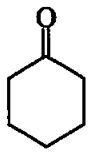
12.18 *Give plausible explanation for each of the following:*

(i) *Cyclohexanone forms cyanohydrin in good yield but 2,2,6-trimethylcyclo-hexanone does not.*

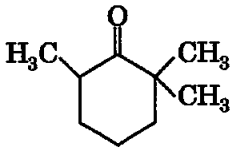
(ii) *There are two —NH_2 groups in semicarbazide. However, only one is involved in the formation of semicarbazones.*

(iii) *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.*

Ans. (*i*) Formation of cyanohydrin involves the nucleophilic attack of cyanide ions (CN^-) at the carbonyl carbon. In cyclohexanone, reaction proceeds but in 2,2,6-trimethylcyclohexanone, the methyl groups cause steric hindrance and yields are poor.



Cyclohexanone

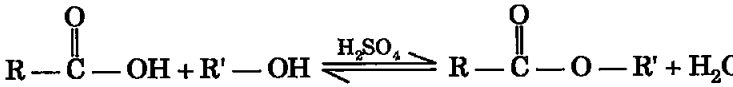


2,2,6-Trimethylcyclohexanone

(*ii*) In semicarbazide, one $—NH_2$ group is attached to carbonyl group which is an electron withdrawing group. So this nitrogen is not able to act as an effective nucleophile.

So it is the other $—NH_2$ group which acts as nucleophile and is involved in condensation with aldehydes and ketones to give semicarbazone derivatives.

(*iii*) During the preparation of ester from alcohol and carboxylic acid in presence of acid, the water or ester should be removed as fast as it is formed because it is a reversible reaction. if they are not separated, then the reverse reaction also starts and an equilibrium is established, so the overall yield of the ester will be low.



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.*

Ans. Calculation of the empirical formula of the compound

Element	*Percentage*	*Atomic mass*	*Relative number of atoms*	*Simple molar ratio*	*Simple ratio*
C	69.77	12	$\frac{69.77}{12} = 5.814$	5	5
H	11.63	1	$\frac{11.63}{1} = 11.63$	10	10
O	18.6	16	$\frac{18.6}{16} = 1.163$	1	1

So, the empirical formula is $C_5H_{10}O$

Empirical formula mass = $(5 \times 12) + (10 \times 1) + (1 \times 16) = 86$

Given that molecular mass of the compound = 86

Hence, the molecular formula of the compound is $C_5H_{10}O$.

The given compound does not reduce Tollens' reagent, so it is not an aldehyde but the formation of addition compound with sodium hydrogen- sulphite indicates it to be a carbonyl compound. Since this compound gives positive iodoform test, so it should contain $-\overset{\overset{O}{\|}}{C}-CH_3$ group. On the basis of this information, two possible structures are written as under:

$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-CH_3 \quad \text{and} \quad CH_3-\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{CH}-CH_3$$

I II

On oxidation, this compound gives ethanoic and propanoic acids which confirm its structure to be I.

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

Ans. In carboxylation –ve charge is delocalised over two oxygen atoms whereas in phenoxide ion –ve charge is delocalised over one oxygen. Therefore carboxylate ion is more stable than phenoxide ion that is why carboxylic acids are more acidic than phenols.

❑❑❑