Aldehydes, Ketones and Carboxylic Acids

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

Solution

i) Cyanohydrin: The addition compound formed when HCN is added to aldehyde or a ketone is a cyanohydrin.

\[ \text{CH}_3 - \text{C} - \text{CH}_3 + \text{HCN} \rightarrow \text{CH}_3 - \text{C} \equiv \text{CH}_3 \]

Propanone (Acetone) Acetone cyanohydrin

ii) Acetal: Dialkoxy derivative of an aldehyde is an acetal.

\[ \text{CH}_3 - \text{CH} = \text{O} + 2\text{CH}_3 - \text{OH} \xrightarrow{\text{HCl}} \text{CH}_3 - \text{CH} - \text{OCH}_3 + \text{H}_2\text{O} \]

Acetal

iii) Semicarbazone: The addition compound formed when semicarbazide is added to an aldehyde or a ketone is a semicarbazide.

\[ \text{CH}_3 - \text{CH} = \text{O} + \text{N}_2\text{N}.\text{NH} - \text{C} - \text{NH}_2 \xrightarrow{\text{H}^+} \text{CH}_3 - \text{CH} = \text{N}.\text{NH} - \text{C} - \text{NH}_2 \]

Ethanal Semicarbazide Acetaldehyde semicarbazone

(Acetaldehyde)
iv) Aldol: Product obtained on condensation of 2 molecules of aldehyde with at least one aldehyde having an $\alpha$-H atom in presence of an alkali is aldol or $\beta$-hydroxy aldehyde.

\[
2\text{CH}_3\text{—CH = O } \xrightarrow{\text{O\text{H}} \text{(aq)}} \text{CH}_3\text{—CH—CH}_2\text{—CH = O}
\]

Ethanal

Aldol 3-Hydroxybutanal

v) Hemiacetal: The addition compound formed on addition of an alcohol molecule to an aldehyde molecule is hemiacetal.

\[
\text{CH}_3\text{—CH = O } + \text{CH}_3\text{—OH} \xrightarrow{} \text{CH}_3\text{—CH—OCH}_3
\]

Ethanl

Methanol

Hemiacetal

vi) Oxime vii) Ketal viii) Imine

ix) 2,4-DNP-derivative x) Schiff’s base

Solution

vi) Oxime: Derivative of hydroxyl amine with aldehyde or ketone is called an oxime.

\[
\text{CH}_3\text{—CH = O } + \text{H}_2\text{NOH} \xrightarrow{\text{H}^+} \text{CH}_3\text{—CH = N.OH } + \text{H}_2\text{O}
\]

Ethanl

Hydroxylamine

Acetaldoxime

(Acetaldehyde)

vii) Ketal: A compound formed on addition of an alcohol molecule to a ketone is a ketal.
viii) Imine: Imine is the compound obtained on partial reduction of alkanenitrile.

\[ RC = N + 2[H] \xrightarrow{Sn/HCl} RCH = NH \]

Alkanenitrile Imine

ix) 2,4-DNP derivative: The addition product obtained when 2,4-DNP is added to an aldehyde or a ketone is its 2,4-DNP derivative.

\[ CH_3CH = O + H_2NNH \xrightarrow{2,4-DNP} CH_3CH = NNH \]

Ethanol 2,4-DNP 2,4-DNP derivative of ethanal

x) Schiff’s base: The product obtained when an aldehyde or a ketone reacts with an aliphatic or aromatic amine is Schiff’s base.

\[ RCH = O + H_2NR \xrightarrow{} RCH_2 = N.R + H_2O \]

Aldehyde Primary amine Schiff’s base

\[ CH_3CH = O + H_2NCH_3 \xrightarrow{} CH_3CH = NH \]

Ethanal Methylamine N-alkylethnoldime (Schiff’s base)

2) Name of 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} \quad \text{ii) CH}_3\text{CH}_2\text{COCH}((\text{C}_2\text{H}_5)\text{CH}_2\text{CH}_2\text{Cl} \\
\text{iii) CH}_3\text{CH}=\text{CHCHO} \quad \text{iv) CH}_3\text{COCH}_2\text{COCH}_3 \\
\text{v) CH}_3\text{CH}((\text{CH}_3)\text{CH}_2\text{C}((\text{CH}_3)\text{2COCH}_3 \quad \text{vi) (CH}_3)_3\text{CCH}_2\text{COCH}_3 \\
\text{vii) OHCC}_6\text{H}_4\text{CHO}-p \\
\textbf{Solution} \\
i) 4-\text{Methylpentan} \\
\text{ii) 6-\text{Chloro-4-ethylhexan}-3\text{-one} \\
\text{iii) But-2-enal} \\
\text{iv) Pentane-2,4-dione} \\
\text{v) 3,3,5-\text{Trimethylhexan-2-one} \\
\text{vi) 3,3-\text{Dimethylbutanoic acid} \\
\text{vii) Benzene-1,4-\text{dicarbaldehyde} \\

3) \text{Draw the structures of the following compounds.} \\
i) \text{3-Methylbutanal} \quad \text{ii) p-Nitropropiopehnone} \\
\text{iii) p-Methylbenzaldehyde} \quad \text{iv) 4-Methylpent-en-2-one} \\
\text{v) 4-Chloropentan-2-one} \quad \text{vi) 3-Bromo-4-phenylpentanoic acid} \\
\text{vii) p,p’-Dihydroxybenzophenone} \quad \text{viii) Hex-2-en-4-ynoic acid}
Solution

i) 3-Methylbutanal

\[ \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CH} = \text{O} \]

ii) p-Nitropropiophenone

\[ \text{O} \quad \text{C} - \text{CH}_2 - \text{CH}_3 \]

\[ \text{NO}_2 \]

iii) p-Methylbenzaldehyde

\[ \text{CH} = \text{O} \]

\[ \text{CH}_3 \]

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

\[ \text{CH}_3 - \text{C} - \text{CH} = \text{C} - \text{CH}_3 \]

v) 4-Chloropentan-2-one

\[ \text{Cl} \quad \text{O} \quad \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{C} - \text{CH}_3 \]

vi) 3-Bromo-4-phenylpentanoic acid

\[ \text{Br} \quad \text{O} \quad \text{CH}_2 - \text{CH} - \text{CH}_2 - \text{C} - \text{OH} \]

vii) p,p’-Dihydroxybenzophenone

\[ \text{OH} \quad \text{OH} \]

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

\[ \text{CH}_3 - \text{C} = \text{C} - \text{CH} = \text{CH} - \text{C} - \text{OH} \]
4) Write the IUPAC names of the following ketones and aldehydes. Wherever possible, give also common names.

i) CH₃CO(CH₂)₄CH₃

ii) CH₃CH₂CHBrCH₂CH(CH₃)CHO

iii) CH₃(CH₂)₅CHO

iv) Ph-CH=CH-CHO

v) PhCOPh

Solution

<table>
<thead>
<tr>
<th>IUPAC Name</th>
<th>Common Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>i) Heptan-2-one</td>
<td>Methyl-n-pentylketone</td>
</tr>
<tr>
<td>ii) 4-Bromo-2-methyl hexanal</td>
<td>-------n-heptylaldehyde</td>
</tr>
<tr>
<td>iii) Heptanal</td>
<td></td>
</tr>
<tr>
<td>iv) 3-Phenylpropenal</td>
<td>-------</td>
</tr>
<tr>
<td>v) Cyclopentanecarbaldehyde</td>
<td>Cinnamaldehyde</td>
</tr>
<tr>
<td>vi) Diphenylmethanone</td>
<td>Benzophenone</td>
</tr>
</tbody>
</table>

5) Draw structures of the following derivatives.

i) The 2,4-dinitrophenylhydrazone of benzaldehyde

ii) Cyclopropanone oxime

iii) Acetaldehydedimethylacetal

iv) The semicarbazone

v) The ethylene ketal of hexan-3-one

vi) The methyl hemiacetal of formaldehyde

Solution

i) The 2,4-dinitrophenylhydrazone of benzaldehyde
ii) Cyclopropanone oxime

iii) Acetaldehydedimethylacetal

iv) Semicarbazone of cyclobutanone

v) Ethylene ketal of hexan-3-one

vi) Methyl hemiacetal of formaldehyde

6) Predict the products formed when cyclohexanecarbaldehyde reacts with following reagents.

i) PhMgBr and then H$_3$O$^+$

ii) Tollen’s reagent

iii) Semicarbazide and weak acid

iv) Excess ethanol and acid
v) Zinc amalgam and dilute hydrochloric acid

Solution

(i) \[
\text{Cyclohexyl phenylmethanol}
\]

(ii) \[
\text{Cyclohexane carboxylate ion}
\]

(iii) \[
\text{Cyclohexane carbaldehyde semicarbazone}
\]

(iv) \[
\text{Acetal}
\]

(v) \[
\text{Methylcyclohexane}
\]

7) i) 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
Solution

- Aldehydes and ketones with at least one $\alpha$-H atom undergo aldol condensation.
- Aldehydes with no $\alpha$-H atom undergo cannizzaro reaction.
- Compounds other than aldehydes and ketones do not undergo canizzaro or aldol condensation.
- Compounds undergoing aldol condensation
  
  ii) 2-Methylpentanal
  
  \[
  \text{CH}_3 \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{CH} \quad \text{CH} = \text{O}
  \]
  
  Product formed:

  \[
  \text{CH}_3 \quad \text{OH} \quad \text{CH}_3 \quad \text{CH}_2 \quad \text{CH} \quad \text{C} \quad \text{CH} = \text{O}
  \]

  \[
  \text{CH}_2 \quad \text{CH}_2 \quad \text{CH}_3
  \]

  v) Cyclohexanone

  vi) 1-phenylpropanone

  vii) Phenylacetaldehyde

Product formed:

Product formed:
7-ii)

Compounds undergoing cannizzaro reaction

i) Methanal

\[ \text{HCHO} \rightarrow \text{CH}_3\text{OH and HCOONa} \]

iii) Benzaldehyde

\[ \text{CHO} \rightarrow \text{CH}_2\text{OH and COONa} \]

ix) 2,2-Dimethylbutanal

\[ \text{CH}_3\text{CHCHC} - \text{CH} = \text{O} \rightarrow \text{CH}_3\text{CHCHCH}_2\text{OH and CH}_3\text{CHC} - \text{COONa} \]

Compounds which do not undergo aldol or cannizzaro reaction

iv) Benzophenone

\[ \text{O} \rightarrow \text{CH}_3\text{CHCHCH}_2\text{OH} \]

viii) Butan-1-ol

\[ \text{CH}_3\text{CHCHCH}_2\text{OH} \]
8) How will you convert ethanal into the following compounds?

i) Butane-1,3-diol  
ii) But-2-enal  
iii) But-2-enoic acid

**Solution**

(i) \[ \text{CH}_3 - \text{CH} + \text{CH}_3 - \text{CH} \xrightarrow{\text{Aldol condensation}} \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CH} \]

\[ \text{Aldol} \]

\[ \text{Reduction} \quad \text{LiAlH}_4 \]

\[ \text{OH} \]

\[ \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CH}_2 - \text{OH} \]

Butan-1,3-diol

(ii) \[ \text{CH}_3 - \text{CH} + \text{CH}_3 - \text{CH} \xrightarrow{\text{Aldol condensation}} \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CH} \]

\[ \Delta, -\text{H}_2\text{O} \]

\[ \text{CH}_3 - \text{CH} = \text{CH} - \text{CH} = \text{O} \]

But-2-enal

(iii) \[ \text{CH}_3 - \text{CH} + \text{CH}_3 - \text{CH} \xrightarrow{\text{Aldol condensation}} \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CH} \]

\[ \Delta, -\text{H}_2\text{O} \]
But-2-enal

\[
\text{CH}_3 \quad \text{CH} = \text{CH} \quad \text{CH}=\text{O} \\
\text{But-2-enal}
\]

\[
\xrightarrow{\text{Oxidation}} \\
\text{KMO}_4/\text{OH} \\
\downarrow \\
\text{CH}_3 \quad \text{CH} = \text{CH} \quad \text{C} \quad \text{OH} \\
\text{But-2-enoic acid}
\]

9) Write structural formulas and names of four possible aldol condensation products from propanal and butanal. In each case, include which aldehyde acts as nucleophile and which as electrophile.

**Solution**

<table>
<thead>
<tr>
<th>Electrophile</th>
<th>Nucleophile</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>i) (\text{CH}_3 \quad \text{CH}_2 \quad \text{CH} = \text{O})</td>
<td>(\text{CH}_3 \quad \text{CH}_2 \quad \text{CH} = \text{O}) Propanal</td>
<td>(\text{OH}) (\text{CH}_3 \quad \text{CH}_2 \quad \text{CH} = \text{O}) Propanal (3)-hydroxy-2-methyl pentanal</td>
</tr>
<tr>
<td>ii) (\text{CH}_3 \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{CH} = \text{O}) Butanal</td>
<td>(\text{CH}_3 \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{CH} = \text{O}) Butanal</td>
<td>(\text{OH}) (\text{CH}_3 \quad \text{CH}_2 \quad \text{CH} = \text{O}) Butanal (2)-ethyl-3-hydroxy hexanal</td>
</tr>
<tr>
<td>iii) (\text{CH}_3 \quad \text{CH}_2 \quad \text{CH} = \text{O}) Propanal</td>
<td>(\text{CH}_3 \quad \text{CH}_2 \quad \text{CH} = \text{O}) Butanal</td>
<td>(\text{OH}) (\text{CH}_3 \quad \text{CH}_2 \quad \text{CH} = \text{O}) Butanal (2)-ethyl-3-hydroxy pentanal</td>
</tr>
</tbody>
</table>
10) An organic compound with the molecular formula $C_9H_{10}O$ forms 2,4-DNP derivative, reduces Tollens’s reagent and undergoes Cannizzaro reaction. On vigorous oxidation, it gives 1,2-benzenedicarboxylic acid. Identify the compound.

**Solution**

i) The compound undergoes 2,4-DNP test, so it must be an aldehyde or a ketone.

ii) It reduces Tollens’s reagent and undergoes Cannizzaro’s reaction, so it must be an aldehyde with no $\alpha$-hydrogen and not a ketone.

iii) The C: H ratio in the molecular formula suggest that the compound must be aromatic compound.

Thus, the compound may be benzaldehyde ($C_6H_5CH=O$) with a group $-C_2H_5$ on any of the C-atoms of the benzene ring.

Since, the compound on vigorous oxidation gives benzene-1,2-dicarboxylic acid, so an ethyl group($C_6H_5$) must be present on the second position of the benzene ring. Thus, the compound is 2-Ethylbenzaldehyde.

2-Ethyl benzaldehyde

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.
Solution

An organic compound (A) (molecular formula C₈H₁₆O₂) was hydrolysed with dilute sulphuric acid to give a carboxylic acid (B) and an alcohol (C). Since the compound on hydrolysis with dilute H₂SO₄ gives a carboxylic acid (B) and an alcohol (C) so the compound (A) must be an ester. Since alcohol (C) on oxidation gives carboxylic acid (B) and also on dehydration gives but-1-ene, it must be butan-1-ol. The acid must contain four C-atoms, as butanol has 4 carbon atoms.

Thus, the compound (A) may be butylbutanoate.

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_2 & \quad \text{CH}_2 & \quad \text{C} & \quad \text{O} & \quad \text{CH}_2 & \quad \text{CH}_2 & \quad \text{CH}_3 \\
\text{(A) Butyl butanoate} \\
\downarrow & \quad \text{dil. H}_2\text{SO}_4 & \quad \text{O} \\
\text{CH}_3 & \quad \text{CH}_2 & \quad \text{CH}_2 & \quad \text{C} & \quad \text{OH} & \quad + & \text{CH}_3 & \quad \text{CH}_2 & \quad \text{CH}_2 & \quad \text{CH}_2 \text{OH} \\
\text{Butanoic acid (B)} & & & & & & \text{Butan-1-ol (C)}
\end{align*}
\]

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) \( \text{CH}_3\text{CH}_2\text{CH(Br)COOH} , \text{CH}_3\text{CH(Br)CH}_2\text{COOH} , (\text{CH}_3)_2\text{CHCOOH} , \text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} \) (acid strength)

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

**Solution**

i) Di-tertbutyl ketone < Methyl –tert-butyl ketone < Acetone < Acetaldehyde

ii) \((\text{CH}_3)_2\text{CH-COOH} < \text{CH}_3\text{-CH}_2\text{-CH}_2\text{-COOH} < \text{CH}_3\text{-CH(Br) CH}_2\text{-COOH} < \text{CH}_3\text{-CH}_2\text{-CH(Br) COOH}\)

iii) 4-Methoxy benzoic acid < Benzoic acid < 4-Nitrobenzoic acid < 3,4-Dinitrobenzoic acid.

13) i) Give simple chemical tests to distinguish between the following pairs of compounds.

i) Propanal and Propanone

**Solution**

i) Propanal and propanone

Propanone gives iodoform test whereas propanal does not.

\[
\text{Propanone + I}_2 + 4\text{NaOH} \rightarrow \text{CH}_3\text{I} \downarrow + 3\text{NaI} + \text{CH}_3\text{COONa} + 3\text{H}_2\text{O}
\]

**Propanone** Iodoform

\[
\text{CH}_3 \text{CHO} \quad \text{I}_2 + \text{NaOH} \rightarrow \text{No reaction}
\]

**Propanal**

ii) Acetophenone and benzophenone

Acetophenone gives iodoform test whereas benzophenone does not.
iii) Phenol and benzoic acid

Phenol on treatment with ferric chloride forms violet colouration whereas benzoic acid does not give violet colouration with ferric chloride.
iv) Benzoic acid and ethyl benzoate

Benzoic acid on treatment with sodium hydrogen carbonate gives brisk effervescence of carbon dioxide gas. Whereas, ethyl benzoate on treatment with sodium hydrogen carbonate does not form brisk effervescence.

\[
\text{Benzoic acid} + \text{NaHCO}_3 \rightarrow \text{Brisk effervescence}
\]

\[
\text{Ethyl benzoate} + \text{NaHCO}_3 \rightarrow \text{No brisk effervescence}
\]

v) Pentan-2-one and Pentan-3-one

Pentan-2-one gives yellow crystals of iodoform with iodine and sodium hydroxide. whereas, pentan-3-one does not give iodoform.

\[
\text{Pentan-2-one} \xrightarrow{\text{I}_2/\text{NaOH}} \text{Yellow crystals of Iodoform (CH}_3\text{I)}\text{are obtained}
\]

\[
\text{Pentan-3-one} \xrightarrow{\text{I}_2/\text{NaOH}} \text{No reaction}
\]
Pentan-2-one

vi) Benzaldehyde and acetophenone

Acetophenone gives yellow crystals of iodoform with iodine and sodium hydroxide. Whereas, benzaldehyde does not give iodoform with iodine and sodium hydroxide.

\[
\text{CH} = O \xrightarrow{\text{I}_2/\text{NaOH}} \text{CH}_3 + \text{O} + 3\text{NaI} + 3\text{H}_2\text{O}
\]

No yellow crystals of Iodoform are formed

Benzaldehyde

\[
\text{C} = \text{CH}_3 + 3\text{I}_2 + 4\text{NaOH} \rightarrow \text{CH}_3 + \text{O} + 3\text{NaI} + 3\text{H}_2\text{O}
\]

vii) Ethanal and propanal

\[
\text{CH}_3 - \text{CH} = O \xrightarrow{\text{I}_2/\text{NaOH}} \text{CH}_3 \quad \text{Yellow crystals of iodoform (CH}_3\text{)}\text{ are obtained.}
\]

\[
\text{CH}_3-\text{CH}_2-\text{CH}=O \xrightarrow{\text{I}_2/\text{NaOH}} \text{No yellow crystals are obtained.}
\]

Propanal

14) How will you prepare the following compounds from benzene? You may use any inorganic reagent and any organic reagent not more than one carbon atom

i) Methyl benzoate ii) m- Nitrobenzoic acid iii) p-Nitrobenzoic acid

Solution

i) Methyl benzoate
ii) m-Nitrobenzoic acid

$$\text{Benzene} \xrightarrow{\text{CH}_3\text{Cl}/\text{AlCl}_3} \text{Toluene} \xrightarrow{\text{KMnO}_4/\text{O}_2} \text{Benzoic acid}$$

$$\text{CH}_3\text{OH} \xrightarrow{\text{H}_2\text{SO}_4} \text{COOCH}_3$$

Methyl benzoate

$$\text{Benzene} \xrightarrow{\text{CH}_3\text{Cl}/\text{AlCl}_3} \text{Toluene} \xrightarrow{\text{KMnO}_4/\text{O}_2} \text{Benzoic acid}$$

$$\text{COOH} \xrightarrow{\text{Conc (HNO}_3 + \text{H}_2\text{SO}_4)} \text{NO}_2$$
m- Nitrobenzoic acid

iii) Benzene $\xrightarrow{\text{CH}_3\text{Cl}/\text{AlCl}_3}$ Toluene $\xrightarrow{\text{Conc.} \left(\text{HNO}_3 + \frac{\text{H}_2\text{SO}_4}{\text{H}_2\text{O}}\right)}$ p- Nitrotoluene

$\xrightarrow{\text{KMnO}_4/\text{OH}}$ COOH

p-Nitrobenzoic acid

iv) Phenylacetic acid

Benzene $\xrightarrow{\text{CH}_3\text{Cl}/\text{AlCl}_3}$ Toluene $\xrightarrow{\text{Cl}_2/\text{Sunlight}}$ Benzylchloride
v) p-Nitrobenzaldehyde.

Benzene $\xrightarrow{\text{CH}_3\text{Cl/AlCl}_3}$ Toluene $\xrightarrow{\text{Conc (HNO}_3 + \text{H}_2\text{SO}_4)}$ p-Nitrotoluene
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

**Solution**

i) Propanone to Propene

\[
\begin{align*}
\text{Propanone} & \quad \xrightarrow{\text{LiAlH}_4, [\text{H}]} \quad \text{2-Propanol} \\
& \quad \xrightarrow{\text{Conc H}_2\text{SO}_4, \Delta} \quad \text{Propene}
\end{align*}
\]

ii) Benzoic acid to Benzaldehyde
Benzoic acid \rightarrow \text{Benzoylchloride} \rightarrow \text{Benzaldehyde}

iii) Ethanol to 3-Hydroxybutanal

\begin{align*}
\text{CH}_3 - \text{CH}_2 - \text{OH} & \xrightarrow{\text{CrO}_3, \text{Oxidation}} \text{CH}_3 - \text{CH} = \text{O} \\
& \xrightarrow{0\text{H}, \text{Aldol condensation}} \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CH} = \text{O} \\
\text{Ethanol} & \rightarrow \text{Ethanal} \rightarrow 3\text{-Hydroxybutanal}
\end{align*}

iv) Benzene to m-Nitroacetophenone

\begin{align*}
\text{Benzene} & \rightarrow \text{Acetophenone} \\
& \xrightarrow{\text{Conc} \{\text{HNO}_3 + \text{H}_2\text{SO}_4\}} \text{m-Nitroacetophenone}
\end{align*}
v) Benzaldehyde to Benzophenone

\[
\begin{align*}
\text{CH}_2\text{O} & \xrightarrow{\text{KMnO}_4} \text{CHO} \\
\text{O} & \xrightarrow{\text{Sodalime Decarboxylation}} \text{O} \\
\text{O} & \xrightarrow{\text{Benzoylation C}_6\text{H}_5\text{COCl}} \text{O}
\end{align*}
\]

Benzaldehyde       Benzoic acid       Benzene       Benzophenone

vi) Bromobenzene to 1-Phenylethanol

\[
\begin{align*}
\text{Br} & \xrightarrow{\text{Mg, } \Delta \text{ ether}} \text{MgBr} \\
\text{O} & \xrightarrow{\text{CH}_3\text{CH} = \text{O}} \text{CH} - \text{CH}_3 \\
\text{Br} & \xrightarrow{\text{Mg, } \Delta \text{ ether}} \text{MgBr} \\
\text{O} & \xrightarrow{\text{CH}_3\text{CH} = \text{O}} \text{CH} - \text{CH}_3
\end{align*}
\]

Bromobenzene       Phenyl magnesium       1-Phenylethanol
bromide

vii) Benzaldehyde to 3-Phenylpropan-1-ol

\[
\begin{align*}
\text{CH} = \text{O} \\
\text{O} + \text{CH}_3 - \text{C} - \text{H} \xrightarrow{\text{OH}^-} \text{C}_6\text{H}_5 - \text{C} - \text{CH}_2 - \text{C} - \text{H}
\end{align*}
\]

Benzaldehyde       Acetaldehyde

viii) Benzaldehyde to \(\alpha\)-Hydroxyphenylacetic acid

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

Solution

vi) Bromobenzene to 1-Phenylethanol
viii) Benzaldehyde to \(\alpha\)-Hydroxyphenylacetic acid

\[
\begin{align*}
\Delta &- H_2O \\
\text{C}_6\text{H}_5 &- \text{CH} = \text{CH} - \text{C} - \text{H} \\
\text{Reduction} &- \text{H}_2/\text{Ni} \\
\text{C}_6\text{H}_5 &- \text{CH}_2 - \text{CH}_2 - \text{C} - \text{H}
\end{align*}
\]

3-Phenyl propan -1-ol

ix) Benzoic acid to m-Nitrobenzyl alcohol

\[
\begin{align*}
\text{CH} = 0 & \quad \text{HO} - \text{CH} - \text{CN} & \quad \text{HO} - \text{CH} - \text{COOH} \\
\text{Benzoic acid} & \quad \text{Benzaldehyde} & \quad \alpha\text{-Hydroxy phenyl cyanohydrin} & \quad \alpha\text{-Hydroxy phenyl acetic acid} \\
& \quad \text{HCN} & \quad \text{2H}_2\text{O}/\text{H}^+ & \quad \text{Boil, } -\text{NH}_3 \\
& \quad \text{Benzaldehyde} & \quad \text{cyanohydrin} & \quad \text{acetic acid}
\end{align*}
\]
16) Describe the following:

i) Acetylation

ii) Cannizzaro reaction

iii) Cross aldol condensation

iv) Decarboxylation

**Solution**

i) Acetylation: Reaction of benzene or its derivatives with acetyl chloride in presence of anhydrous AlCl₃ to give acetylated product is called acetylation. It is also called Friedal craft’s acylation.

\[
\text{Benzene} + \text{CH}_3\text{C} = \text{Cl} \xrightarrow{\text{Anhydrous AlCl}_3} \text{Acetphenone} + \text{HCl}
\]

Benzene  Acetaldehyde  Acetphenone

ii) Cannizzaro Reaction: Disproportionation reaction of an aldehyde having no α-H atom into corresponding acid and alcohol in presence of a concentrated alkali is called cannizzaro reaction.

\[
2\text{CHO} + \text{KOH} \xrightarrow{\Delta} \text{COOK} + \text{CH}_2\text{OH}
\]
iii) Cross aldol condensation: Condensation of two different aldehydes having \( \alpha \)-H atom in presence of an alkali to give \( \beta \)-hydroxyaldehydes is called cross aldol condensation.

\[
\begin{align*}
\text{CH}_3\text{CH} + \text{CH}_3\text{CH}_2\text{CHO} & \rightarrow \text{CH}_3\text{CH} - \text{CHCH}_2\text{CHO} + \text{CH}_3\text{CH}_2\text{CHCH}_2\text{CHO} \\
\text{Ethanal} & \quad \text{Propanal} & 3\text{-Hydroxy} & \quad 3\text{-Hydroxy pentanal} \\
& & 2\text{-Methyl butanal} & 
\end{align*}
\]

iv) Decarboxylation : Loss of carbon dioxide from a sodium salt of an acid by heating with soda lime(mixture of NaOH and CaO) is called decarboxylation.

\[
\begin{align*}
\text{COONa} + \text{NaOH} & \xrightarrow{\text{CaO}} \text{C} + \text{Na}_2\text{CO}_3 \\
\text{Sodium benzoate} & \quad \text{Benzene}
\end{align*}
\]

17) i) Complete each synthesis by giving missing starting material, reagent or products.

(i) \[
\begin{align*}
\text{CH}_2 - \text{CH}_4 & \quad \text{KMnO}_4, \text{KOH, } \Delta \\
\text{ } & \quad \text{COOH}
\end{align*}
\]

(ii) \[
\begin{align*}
\text{COOH} & \xrightarrow{\text{SOCl}_2, \Delta} \\
\text{COOH}
\end{align*}
\]

(iii) \[
\begin{align*}
\text{C}_6\text{H}_5\text{CHO} & \xrightarrow{\text{H}_2\text{N},\text{NH}} \text{C} - \text{NH}_2 \\
\text{O}
\end{align*}
\]
Solution

(i) \( \text{CH}_2 - \text{CH}_3 \xrightarrow{\text{KMnO}_4, \text{KOH}, \Delta} \text{COOK} \)

(ii) \( \text{COOH} \xrightarrow{\text{SOCl}_2, \Delta} \text{COCl} \)

(iii) \( \text{C}_6\text{H}_5 - \text{CHO} \xrightarrow{\text{H}_2\text{N.NH} - \text{C} - \text{NH}_2} \text{C}_6\text{H}_5 - \text{CH} = \text{N.NH} - \text{C} - \text{NH}_2 \)

(iv) \( \text{CHO} \xrightarrow{\text{NaCN/HCl}} \text{CHO} \)

(v) \( \text{CHO} \xrightarrow{[\text{Ag(NH}_3\text{)}]^+} \)

17) **Solution**

(iv) \( \text{CHO} \xrightarrow{\text{C}_6\text{H}_5 - \text{Cl}/\text{Anhydrous AlCl}_3} \)

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17)

(vi) $\text{CHO} \xrightarrow{[\text{Ag(NH}_3\text{)}_2]^+} \text{COO}^-$

(vii) $\text{CHO} + \text{CH}_3 - \text{CH}_2 - \text{CHO} \xrightarrow{\text{dil. NaOH}} \text{CHO} + \text{CH}_3 - \text{CH}_2 - \text{CH} = \text{O}$

(viii) $\text{CH}_3 - \text{C} \xrightarrow{\text{i) NaBH}_4} \text{CH}_2 - \text{C} - \text{OC}_2\text{H}_5 \xrightarrow{\text{ii) H}^+} \text{CH}_3 - \text{CH} \xrightarrow{\text{OH}} \text{CH}_2 - \text{C} - \text{CH}_2 - \text{OH} + \text{C}_2\text{H}_5\text{OH}$

Solution

(vii) $\text{CHO} + \text{CH}_3 - \text{CH}_2 - \text{CHO} \xrightarrow{\text{dil. NaOH}} \text{CHO} + \text{CH}_3 - \text{CH}_2 - \text{CH} = \text{O}$

(viii) $\text{CH}_3 - \text{C} \xrightarrow{\text{i) NaBH}_4} \text{CH}_2 - \text{C} - \text{OC}_2\text{H}_5 \xrightarrow{\text{ii) H}^+} \text{CH}_3 - \text{CH} \xrightarrow{\text{OH}} \text{CH}_2 - \text{C} - \text{CH}_2 - \text{OH} + \text{C}_2\text{H}_5\text{OH}$
18) Give plausible explanation for each of the following:

i) Cyclohexane forms cyanohydrins in good yield but 2,2,6 trimethylcyclohexanone does not.

ii) There are two –NH\textsubscript{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 eater should be removed as soon as it is formed.

Solution

i) Formation of cyanohydrins by ketones is a nucleophilic addition reaction. Presence of three electron releasing alkyl groups in 2,2,6-trimethylcyclohexanone reduces the extent of attack of nucleophile due to very large steric hinderance.
ii) Formation of semicarbazone from semicarbazide is an acid catalysed nucleophilic addition reaction. Since, one of the \(-\text{NH}_2\) group of semicarbazide has involved its lone pair of electrons in the resonance, only one-\(\text{NH}_2\) group has its electron pair available for donation to the carbonyl carbon atom during reaction.

\[
\begin{align*}
\text{NH}_2 - \text{NH} & \xrightarrow{\text{O}} \text{NH}_2 - \text{NH} - \text{C} - \text{NH}_2 \\
\text{NH}_2 - \text{NH} & \xrightarrow{\text{O}^-} \text{NH}_2 - \text{NH} - \text{C} = \text{NH}_2
\end{align*}
\]

So, only one \(-\text{NH}_2\) groups is involved in the formation of semicarbazone.

iii) The formation of esters from carboxylic acids and alcohols is an acid catalysed reversible reaction. If the water or ester is not removed as soon as they are formed, it is possible that reaction may take backward shift (according to Lechtelier’s Principle) leading to hydrolysis of ester into carboxylic acids and alcohols.

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 Tollen’s reagent but forms an addition compound with sodium hydrosulphite and give positive iodoform test. On vigorous oxidation it gives ethanoic and propanoic acid. Write the possible structure of the compound.

**Solution**

Step I Calculation of molecular formula of the compound

% of C= 69.77
% of H= 11.69
So, % of O = 100-(69.77+11.03) = 18.60
So,
C:H:O= 69.77/12 : 11.63/1 : 18.6/16
= 5.81:11.63:1.16
Simplest ratio of atom C,H and O
= 5.81/1.16 : 11.63/1.16 : 18.6/16
Hence, Empirical formula of the compound is \( \text{C}_5\text{H}_{10}\text{O} \).

Empirical mass of the compound = 86

Given,

Molecular mass of the compound = 86

So,

Molecular formula of the compound is

\( \text{C}_5\text{H}_{10}\text{O} \times \frac{\text{Molecular formula mass}}{\text{Empirical formula mass}} \)

\( \text{C}_5\text{H}_{10}\text{O} \times \frac{86}{86} \)

= \( \text{C}_5\text{H}_{10}\text{O} \)

Molecular formula of the compound = \( \text{C}_5\text{H}_{10}\text{O} \)

Step II Structure of the compound
Since compound forms sodiumbisulphite compound, it must be an aldehyde or ketone. Since it does not reduce Tollens’s reagent, it must not be aldehyde and hence must be a ketone. Since compound is giving a positive iodoform test so, it must be a methyl ketone.

\[
\begin{array}{c}
\text{O} \\
(R \quad \text{C} \quad \text{CH}_3)
\end{array}
\]

Since, the compound on vigorous oxidation gives ethanoic acid and propanoic acid, the compound must be penta-2-one.

\[
\begin{array}{c}
\text{O} \\
\text{CH}_3 \quad \text{C} \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{CH}_3
\end{array}
\]

Hence,
Pentan-2-one  
\[
\text{CH}_3 - \text{C} - \text{CH}_2 - \text{CH}_2 - \text{CH}_3 \quad \text{NaHSO}_3 \quad \rightarrow \quad \text{CH}_3 - \text{C} - \text{CH}_2 - \text{CH}_2 - \text{CH}_3 \quad \text{SO}_3\text{Na}
\]
Sodium bisulphite compound of Pentan-2-one

\[
\text{CH}_3 - \text{C} - \text{CH}_2 - \text{CH}_2 - \text{CH}_3 + 3\text{I}_2 + 4\text{NaOH} \quad \rightarrow \quad \text{CH}_3 + 3\text{NaI} + \text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{COONa} + 3\text{H}_2\text{O}
\]
Pentan-2-one  Iodoform

\[
\text{CH}_3 - \text{C} - \text{CH}_2 - \text{CH}_2 - \text{CH}_3 \quad \text{Oxidation} \quad \rightarrow \quad \text{CH}_3 - \text{C} - \text{OH} + \text{CH}_3 - \text{CH}_2 - \text{C} - \text{OH}
\]
Pentan-2-one  Ethanoic acid  Propanoic acid

\[
\text{CH}_3 - \text{C} - \text{CH}_2 - \text{CH}_2 - \text{CH}_3 \quad \text{[Ag (NH}_3)_2]^+ \quad \text{Tollen's reagent} \quad \rightarrow \quad \text{No silver mirror formed}
\]
Pentan-2-one  (No reaction)

Therefore, the structure of the compound is

\[
\text{CH}_3 - \text{C} - \text{CH}_2 - \text{CH}_2 - \text{CH}_3
\]

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

**Solution**

The carboxylate ion and the phenoxide ion are resonance stabilized. But the phenoxide ion has larger number of resonating structures.

Resonance structures of carboxylate ion.
Resonance structures of phenoxide ion

In carboxylate ion, the negative charge is delocalized between two oxygen atoms while it is present on only one oxygen atom of phenoxide ion. The dispersal of charge leads to higher stability of carboxylate ion in comparison to phenoxide ion. This makes carboxylic acids more acidic than phenols.