ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

The π Electron cloud of >C=O is unsymmetrical . On the other hand, due to same electonegativity of the two carbon atoms, the π-electron of the >C=C< bond is symmetrical.

Nature of carbonyl group:- The Pi electron cloud of >C=O is unsymmetrical therefore, partial positive charge develop over carbon of carbonyl group while negative charge develop over oxygen of carbonyl group and dipole moment is approximate 2.6D.

<table>
<thead>
<tr>
<th>FORMULA</th>
<th>NAME OF THE CORRESPONDING ACID</th>
<th>COMMON NAME</th>
<th>IUPAC NAME</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCHO</td>
<td>HCOOH(formic acid)</td>
<td>Formaldehyde</td>
<td>Methanal</td>
</tr>
<tr>
<td>CH₃CHO</td>
<td>CH₃COOH(Acetic acid)</td>
<td>Acetaldehyde</td>
<td>Ethanal</td>
</tr>
<tr>
<td>CH₃CH₂CHO</td>
<td>CH₃CH₂COOH(Propanoic acid)</td>
<td>Propionaldehyde</td>
<td>Propanal</td>
</tr>
<tr>
<td>CH₃CH₂CH₂CHO</td>
<td>CH₃CH₂CH₂COOH(Butyric acid)</td>
<td>Butyraldehyde</td>
<td>Butanal</td>
</tr>
<tr>
<td>CH₃CH(CH₃)CHO</td>
<td>CH₃CH(CH₃)COOH(Isobutyric acid)</td>
<td>Isobutyraldehyde</td>
<td>2-Methylpropanal</td>
</tr>
<tr>
<td>CH₃CH₂CH(CH₃)CHO</td>
<td>CH₃CH₂CH(CH₃)COOH(α-Methylbutyric acid)</td>
<td>α-Methylbutyraldehyde</td>
<td>2-Methylbutanal</td>
</tr>
<tr>
<td>CH₃(CH₃)CH₂CHO</td>
<td>CH₃CH(CH₃)CH₂COOH(β-Methylbutyric acid)</td>
<td>B-Methylbutyraldehyde</td>
<td>2-Phenylethanal</td>
</tr>
</tbody>
</table>
Addition to C=O bonds

The structure of the carbonyl group in aldehydes and ketones is, not entirely adequately represented by >C=O, nor by the alternative >C⁺-O⁻. The real structure or resonance hybrid lies somewhere between the following structure:

\[ >\text{C}=\text{O} \rightleftharpoons >\text{C}⁺\text{=O}⁻ \]

For Mechanism

\[ >\text{C}=\text{O} + \text{H}⁺ \xrightarrow{\text{slow reaction}} >\text{C}⁺ - \text{OH} \xrightarrow{\text{slow}} >\text{C} - \text{A}⁺ \xrightarrow{\text{OH}} >\text{C} - \text{A}⁺\text{OH} \]

Second Mechanism

\[ >\text{C} = \text{O} + :\text{A}⁻ \xrightarrow{\text{SLOW REACTION}} >\text{C} - \text{O}⁻ - \text{A} \xrightarrow{\text{H}⁺ \text{ Fast}} >\text{C} - \text{A}⁻\text{OH} \xrightarrow{\text{A}⁺} >\text{C} - \text{A}⁻\text{OH} \]
As we know that anion is more stable than the cation, thus the addition to carbonyl groups should take place via mechanism second which has been further proved in the addition of HCN to carbonyl group.

Reactivity of aldehyde and Ketones is as HCHO>RCHO>RCOR>RCOOR>RCONH₂.

**POINTS TO REMEMBER**

:- Aldehydes, Ketones and Carboxylic acids are important classes of organic compounds containing carbonyl groups.
:- They are highly polar molecules.
:- They boil at higher temperatures than the corresponding hydrocarbons and weakly polar compounds such as ethers.
:- Lower members are soluble in water because they can form H-bond with water.
:- Higher members are insoluble in water due to large size of their hydrophobic group.
:- Aldehydes are prepared by-

a. Dehydrogenation of primary alcohols
b. Controlled oxidation of primary alcohols.
c. Controlled and selective reduction of acyl halides

Aromatic aldehydes can be prepared by-

a. Oxidation of toluene with chromyl chloride or CrO₃ in the presence of acetic anhydride
b. Formylation of arenes with carbon monoxide and Hydrochloric acid in the presence of anhydrous aluminiumchloride / Cuprous chloride
c. Hydrolysis of benzal chloride
Ketones are prepared by-

a. oxidation of secondary alcohols  
b. Hydration of alkenes  
c. Reaction acyl chlorides with dialkylcadmium  
d. By friedel crafts reaction  

Carboxylic acids are prepared by –

a. oxidation of primary alcohols, aldehydes and alkenes  
b. hydrolysis of nitriles  
c. Treatment of grignard reagent with carbondioxide.

**NAME REACTIONS**

**ROSENMUND REDUCTION:**

The catalytic hydrogenation of acid chlorides allows the formation of aldehydes.

**Mechanism of the Rosenmund Reduction**

*Side products:*
1. **ROSENMUND REDUCTION:**
Acyl chlorides when hydrogenated over catalyst, palladium on barium sulphate yield aldehydes

\[
\text{C-Cl} + (\text{H}) \xrightarrow{\text{Pd-BaSO}} \text{-CHO} \\
\text{Benzoyl chloride} \quad \text{Benzaldehyde 2}
\]

2. **STEPHEN REACTION**
Nitriles are reduced to corresponding imines with stannous chloride in the presence of Hydrochloric acid, which on hydrolysis give corresponding aldehyde.

\[
\text{RCN} + \text{SnCl}_2 + \text{HCl} \xrightarrow{\text{H}_2\text{O}} \text{RCH}==\text{NH} \xrightarrow{\text{RCHO}}
\]

3. **ETARD REACTION**
On treating toluene with chromyl chloride\( \text{CrO}_2\text{Cl}_2 \), the methyl group is oxidized to a chromium complex, which on hydrolysis gives corresponding benzaldehyde.

\[
\text{CH}_3 \quad \xrightarrow{\text{CrO}_2\text{Cl}_2} \quad \text{CHO}
\]

This reaction is called **Etard reaction.**
CLEMMENSEN REDUCTION
The carbonyl group of aldehydes and ketone is reduced to –CH₂ group on treatment with zinc amalgam and conc. Hydrochloric acid.

$$\text{C}=\text{O} \rightarrow_{\text{Zn-Hg}}^\text{HCl} \text{CH}_2 + \text{H}_2\text{O}$$

Alkanes

WOLFF- KISHNER REDUCTION
On treatment with hydrazine followed by heating with sodium or potassium hydroxide in high boiling solvent like ethylene glycol

$$\text{NH}_2\text{NH}_2 \rightarrow_{\text{KOH/ethylene glycol}}^\text{Heat} \text{CH}_2 + \text{N}_2$$

ALDOL CONDENSATION
Aldehydes and ketones having at least one α-hydrogen condense in the presence of dilute alkali as catalyst to form β-hydroxy aldehyde (aldol) or β-hydroxy ketones (ketol).

$$\text{CH}_3\text{CHO} + \text{NaOH} \rightarrow \text{CH}_3\text{CH}=(\text{CH})\text{CHO}$$

ethanal

OH (Aldol)

CROSS- ALDOL CONDENSATION
When aldol condensation is carried out between two different aldehydes and / or ketones, a mixture of self and cross-aldol products are obtained.

$$\text{CH}_3\text{CHO} + 2 \text{NaOH} \rightarrow \text{CH}_3\text{CH}=(\text{CH})\text{CHO} + \text{CH}_3\text{CH}_2\text{CH}=(\text{CH})\text{CHO}$$

But-2-enal

2-Methylpent-2-en-1-one
CANNIZARO REACTION

Aldehydes which do not have an $\alpha$-hydrogen atom, undergo self oxidation and reduction (disproportionation) reaction on treatment with concentrated alkali, to yield carboxylic acid salt and an alcohol respectively.

\[
\text{H-CHO} + \text{H-CHO} + \text{Conc. KOH} \rightarrow \text{CH}_3\text{OH} + \text{HCOOK}
\]

Formaldehyde

\[
\text{C}_6\text{H}_5\text{CH}_2\text{ONa} + \text{NaOH (con.)} \rightarrow \text{CH}_3\text{OH} + \text{C}_6\text{H}_5\text{COONa}
\]

Benzaldehyde

CARBOXYLIC ACID

1. HELLM-VOLHARD-ZELINSKY REACTION (HVZ)

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.

\[
\text{RCH}_2\text{-COOH} \overset{\text{i X}_2/ \text{Red phosphorus}}{\rightarrow} \text{R-CH-COOH} \overset{\text{ii H}_2\text{O}}{\rightarrow} \text{R-CH-COOH} \overset{\text{X}}{\rightarrow} \text{R-CH-COOH}
\]

\[X = \text{Cl, Br}\]

$\alpha$-halocarboxylic acids

2. ESTERIFICATION

Carboxylic acids react with alcohols or phenols in the presence of a mineral acid such as conc. $\text{H}_2\text{SO}_4$ as catalyst to form esters.
3. **DECARBOXYLATION:**

4. Carboxylic acids lose carbon dioxide to form hydrocarbons when their sodium salts are heated with sodalime NaOH and CaO in the ratio 3:1.

5. \[ \text{NaOH and CaO / } \Delta \]

\[ \text{RCOONa} \rightarrow \text{R-H} + \text{Na}_2\text{CO}_3 \]

**MECHANISMS**

1. \[ \text{CH}_3\text{CH}_2\text{OH} \xrightarrow{\text{Con H}_2\text{SO}_4} \text{CH}_2 = \text{CH}_2 + \text{H}_2\text{O} \]

\[ 443 \text{ K} \]

**Mechanism:**

(i) \[ \text{H}_2\text{SO}_4 \xrightarrow{} \text{H}^+ + \text{HSO}_4^- \]

(ii) \[ \text{CH}_3\text{CH}_2 - \text{O} - \text{H} + \text{H}^+ \xrightarrow{} \text{CH}_3 - \text{CH}_2 - \text{O}^+ - \text{H} \]

\[ / \]

\[ / \text{H} \]

(iii) \[ \text{CH}_3\text{CH}_2 - \text{O}^+ - \text{H} + \text{H}^+ \xrightarrow{} \text{CH}_3 - \text{CH}_2 + \text{H}_2\text{O} \]

\[ / \text{H} \]

(iv) \[ \text{CH}_3\text{CH}_2^+ \xrightarrow{} \text{CH}_2 = \text{CH}_2 + \text{H}^+ \]

(v) \[ \text{H}^+ + \text{HSO}_4^- \xrightarrow{} \text{H}_2\text{SO}_4 \]

2. \[ \text{2CH}_3\text{CH}_2\text{OH} \xrightarrow{\text{Con H}_2\text{SO}_4} \text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3 + \text{H}_2\text{O} \]

\[ 413 \text{ K} \]
Mechanism:

i) \( \text{H}_2\text{SO}_4 \rightarrow \text{H}^+ + \text{HSO}_4^- \)

+ 

ii) \( \text{CH}_3\text{CH}_2\text{OH} + \text{H}^+ \rightarrow \text{CH}_3 - \text{CH}_2 - \text{O} - \text{H} \)


\( \text{H} \)

(iii) \( \text{CH}_3\text{CH}_2 - \text{O}^+ - \text{H} \rightarrow \text{CH}_3 \text{CH}_2^+ + \text{H}_2\text{O} \)


\( \text{H} \)

(iv) \( \text{CH}_3\text{CH}_2 - \text{O} - \text{H} + \text{CH}_3\text{CH}_2^+ \rightarrow \text{CH}_3 - \text{CH}_2 - \text{O}^+ - \text{H} \)


\( \text{CH}_2\text{CH}_3 \)

(v) \( \text{CH}_3\text{CH}_2 - \text{O}^+ - \text{H} \rightarrow \text{CH}_3\text{CH}_2 - \text{O} - \text{CH}_2\text{CH}_3 + \text{H}^+ \)


\( \text{CH}_2\text{CH}_3 \)

(vi) \( \text{HSO}_4^- + \text{H}^+ \rightarrow \text{H}_2\text{SO}_4 \)
NOMENCLATURE

a. \( \text{CH}_3\text{CH} \text{CH}_3 \text{CH}_2\text{CH}_2\text{CHO} \)
   4-Methylpentanal

b. \( \text{CH}_3\text{CH}_2\text{COCH} \text{C}_2\text{H}_5 \text{CH}_2\text{CH}_2\text{Cl} \)
   6-chloro-4-ethylhexan-3-one

c. \( \text{CH}_3\text{CH}=\text{CHCHO} \)
   But-2- enal

d. \( \text{CH}_3\text{COCH}_2\text{COCH}_3 \)
   Pentane. 2,4-dione .

e. \( \text{OHCC}_6\text{H}_4\text{CHO}-\text{p} \)
   Benzene-1,4-di carbaldehyde

f. \( \text{CH}_3\text{CH}_2\text{CHC}_6\text{H}_5\text{CHO} \)
   2-Phenylbutanal

2. Draw the structures of the following compounds;

   (i) p-Methylbenzaldehyde
   Ans. OHC - - CH_3

   (ii) 4-Methylpent-3-en-2-one
   Ans. \( \text{CH}_3\text{-C-CH=C-CH}_3 \)
        \( \text{O} \text{CH}_3 \)

   (iii) 3-Bromo-4-phenylpentanoic acid
   Ans. \( \text{CH}_3\text{-CH -CH-CH}_2\text{-COOH} \)
        \( \text{C}_6\text{H}_5 \text{Br} \)

   iv) Hex-2-en-4-ynoic acid
   Ans. \( \text{CH}_3\text{-C C-CH=CH-COOH} \)
Q1:- Distinguish between the following:

(a) Phenol and alcohol
(b) Benzaldehyde and Propanal
(c) Acetic acid and formic acid
(d) Benzophenone and acetophenone
(e) Ethanal and propanal
(f) Propanol and ethanol
(g) Pentanone-2 and pentanone-3
(h) 2 Alcohol and 3 alcohol
(i) 1,2,3 amine
(j) Benzoic acid and benzene
(k) Phenol and benzoic acid
(l) Aniline and ethyl amine
(m) Aniline and nitrobenzene
(n) Benzaldehyde and acetophenone
(o) Methanol and benzaldehyde
(p) Chloro benzene and benzyl chloride
<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>ANSWERS</strong></td>
<td></td>
</tr>
<tr>
<td>(a) Phenol</td>
<td>Alcohol</td>
</tr>
<tr>
<td>It gives FeCl₃ test</td>
<td>It doesn't give this test</td>
</tr>
<tr>
<td>* (voielet colour)</td>
<td></td>
</tr>
<tr>
<td>(b) Benzaldehyde</td>
<td>Propanal</td>
</tr>
<tr>
<td>It gives tollen's</td>
<td>It also give tollen's reagent test</td>
</tr>
<tr>
<td>It doesn't give fehling solution test</td>
<td>It gives fehling solution test</td>
</tr>
<tr>
<td>(c) Acetic acid</td>
<td>Formic acid</td>
</tr>
<tr>
<td>It doesn't give tollen's reagent</td>
<td>It gives tollen's test</td>
</tr>
<tr>
<td>It doesn't give fehling's test</td>
<td>It gives fehling test</td>
</tr>
<tr>
<td>(d) Benzophenone</td>
<td>Acetophenone</td>
</tr>
<tr>
<td>It doesn't give iodoform test</td>
<td>It gives iodoform test</td>
</tr>
<tr>
<td>(e) Ethanal</td>
<td>Propanal</td>
</tr>
<tr>
<td>It gives iodoform test</td>
<td>It doesn't give iodoform test</td>
</tr>
<tr>
<td>(f) Propanol</td>
<td>Ethanol</td>
</tr>
<tr>
<td>It doesn't give iodoform test</td>
<td>It gives iodoform test</td>
</tr>
<tr>
<td>(g) Pentanone-2</td>
<td>Pentanone-3</td>
</tr>
<tr>
<td>It gives iodoform test</td>
<td>It doesn't give iodoform test</td>
</tr>
<tr>
<td>(h) 2 alcohol</td>
<td>3 alcohol</td>
</tr>
<tr>
<td><img src="image1" alt="Chemical structure" /></td>
<td><img src="image2" alt="Chemical structure" /></td>
</tr>
<tr>
<td>HCl + ZnCl₂</td>
<td>HCl + ZnCl₂</td>
</tr>
<tr>
<td>It takes 5 minutes</td>
<td>turbidity is formed within no seconds</td>
</tr>
</tbody>
</table>
(i) 1 amine
\[ \text{C}_2\text{H}_5\text{NH}_2 + \text{C}_6\text{H}_5\text{SO}_2\text{Cl} \rightarrow \text{C}_6\text{H}_5\text{NH-SO}_2\text{-C}_6\text{H}_5 \]
(benzene sulphonyl chloride) soluble in alkali

2 amine
\[ \text{C}_2\text{H}_5\text{-NH} + \text{C}_6\text{H}_5\text{SO}_2\text{Cl} \rightarrow \text{C}_2\text{H}_5\text{-N-SO}_2\text{C}_6\text{H}_5 \]
\[ \text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_5 \]
Insoluble in KOH

3 amine
\[ \text{C}_2\text{H}_5\text{-N-C}_2\text{H}_5 + \text{C}_6\text{H}_5\text{SO}_2\text{Cl} \rightarrow X \] (No reaction)
\[ \text{C}_2\text{H}_5 \]

(J) Benzoic acid
add NaHCO₃
Effervescence obtained (CO₂)

(k) Phenol
It gives violet colour with FeCl₃ test
It doesn't give violet colour with FeCl₃
It doesn't give effervescence of CO₂
Effervescence of CO₂ evolve when NaHCO₃ is added

(l) Aniline
It gives azo-dye test (orange dye)

(m) Aniline
It gives azo-dye test

(n) Benzaldehyde
It gives tollen's test
It doesn't give iodoform test

(o) Methanal
It gives fehling solution test

(p) Chloro benzene

Benzene
no effervescence
goed obtained

Benzoic acid
It doesn't give violet colour with FeCl₃

Ethyl amine
It doesn't give azo-dye

Nitrobenzene
It doesn't

Acetophenone
It doesn't

Benzaldehyde
It gives iodoform test

Benzyl chloride
CONCEPTUAL QUESTIONS

Q1) Although phenoxide ion has more no. of resonating structures than carboxylate ion, even though carboxylic acid is a stronger acid why?

Ans:- The phenoxide ion has non equivalent resonance structures in which –ve charge is at less electronegative C atom and +ve charge as at more electronegative O-atom.

In carboxylate ion –ve charge is delocalized on two electronegative O-atoms hence resonance is more effective and a stronger acid.

Q.2 Why Corboxylic acid have higher boiling point than alcohols as alcohol forms strongest intermolecular hydrogen bonding?

Ans. As Corboxylic acid forms a dimer due to which their surface area increases and forms strong intermolecular H-bonding

It having more boiling point than alcohols.

Q.3 There are two-NH2 group in semicarbazide. However only one is involved in formation of semicarbazones. Why?

Ans. Due to resonance one NH2 group undergoes or involved in resonance and hence can’t participate in the formation of semicarbazone.

Long pair of NH2 group is not involved in resonance and is available for nucleophillic attack.
Q.4 Why does solubility decreases with increasing molecular mass in carboxylic acid?

Ans. Because of increase in alkyl chain length which is hydrophobic in nature.

Hence solubility decreases.

Q.5 Why are aldehydes are more reactive than ketones when undergo nucleophillic addition reaction?

Ans. (a) + I effect:- The alkyl group in Ketones due to their e-releasing character decrease the +ve charge on C-Atom and thus reduce its reactivity.

(b) Steric hinderance:- Due to steric hinderance in ketones they are less reactive.

\[
\begin{align*}
\text{H} & \quad \text{R} \\
\text{C} = \text{O} & \quad \text{C} = \text{O} \\
\text{R} & \quad \text{R}
\end{align*}
\]

Q.6 Why PCC cannot oxidise methanol to methanoic acid and while KMNO\textsubscript{4} can?

Ans. This is because PCC is a mild oxidising agent and can oxide methanol to methanal only.

While KMNO\textsubscript{4} being strong oxidising agent oxidises it to methanoic acid.

Q.7 During preparation of esters from a carboxylic acid and an alcohol in the presence of acid catalyst water or ester formed should be removed as soon as it is formed.

Ans. The formation of esters from a carboxylic acid and an alcohol in the presence of acid catalyst in a reversible reaction.

\[
\text{R} - \text{COOH} + \text{R}^{\prime}\text{OH} \xrightleftharpoons{\text{H}_2\text{SO}_4} \text{R} - \text{COOR}^{\prime} + \text{H}_2\text{O}
\]

To shift the equilibrium in forward direction, the water or ester formed should be removed as fast as it is formed.
Q.8  Why HCOOH does not give HVZ reaction while CH₃COOH does?

Ans. CH₃COOH contains α-hydrogens and hence give HVZ reaction but HCOOH does not contain α-hydrogen and hence does not give HVZ reaction.

Q.9  Suggest a reason for the large difference in the boiling point of butanol and butanal although they have same solubility in water.

Ans. Because Butanol has strong intermolecular H-bonding while butanal has weak dipole-dipole interaction.

However both of them form H-bonds with water and hence are soluble.

Q.10  Would you expect benzaldehyde to be more reactive or less reactive in nucleophillic addition reaction than propanol. Explain.

Ans. C-atom of Carbonyl group of benzaldehyde is less electrophilic than C-atom of Carbonyl group in propanol.

Polarity of Carbonyl group is in bonzaldehyde reduced due to resonance making it less reactive in nucleophillic addition reactions.

\[
\begin{align*}
O = C – H & \quad \quad -O – C^+ – H \\
\text{O } & \quad \quad \text{O } \\
\end{align*}
\]

Q.11  Why does methanal not give aldol condensation while ethanol gives?

Ans. This is because only those compounds which have α-hydrogen atoms can undergo aldol reaction ethanol posses α-hydrogen and undergoes aldol condensation Methanal has no alpha hydrogen atoms hence does not undergo aldol condensation.

Q.12  Why does methanal undergo cannizaro’s reaction?

Ans. because it does not possesses α-hydrogen atom.
Q.13 Which acid is stronger and why?

F₃C-C₆H₄COOH and CH₃C₆H₄COOH

Ans. CF₃⁻ has strong (-I) effect
Whereas, CH₃⁻ has strong (+I) effect
Due to greater stability of F₃CC₆H₄COO⁻ ion over CH₃-C₆H₄COO⁻ ion
CF₃C₆H₄COOH is much stronger acid than CH₃-C₆H₄COOH.

Q.14 Explain why O-hydroxy benzaldehyde is a liquid at room temperature while p- hydroxy benzaldehyde is a high melting solid.

Ans. Due to intramolecular H-bonding in O-hydroxy benzaldehyde exists as discrete molecule whereas due to intermolecular H-bonding p-hydroxy benzaldehyde exist as associated molecules.

To break this intermolecular H-bonds a large amount of energy is needed. Consequently P-isomer has a much higher m.p. and b.p. than that of O-isomer. As a result O-hydroxy benzaldehyde is liquid.

Q.15 Why is the boiling point of an acid anhydride higher than the acid from which it is derived?

Ans. Acid anhydrides are bigger in size than corresponding acids have more surface area more van der Waals. Force of attraction hence have higher boiling point.

Q.16 Why do Carboxylic acids not give the characteristic reactions of a carbonyl group?

Ans. Due to resonance, It doesn’t give the characteristics reactions of carbonyl group. It does not have free \(\backslash C=O\) group
Q.17  Cyclohexanone forms cyanohydrin in good yield but 2,2,6 trimethyle cyclo-hexanone does not. Why?

Ans. In 2,2,6 trimethyl cyclohexaunone there is stearic hinderance of 3 methyl groups, It does not form cynohydrin in good yield.

Q.18  Why is carboxyl group in benzoic acid meta directing?

Ans. In benzoic acid the Carboxyl group is meta directing because it is electron-withdrawing

There is +ve charge on ortho acid para positions

Electrophillic substitution takes place at meta-position.

Q.19  Treatment of Benzaldehyde with HCN gives a mixture of two isomers which cannot be separated even by careful fractional distillation. Explain why?

Ans. It is because we get two optical isomers which have same physical properties

Cannot be Separated by Fractional distillation.

\[
\begin{align*}
\text{C}_6\text{H}_5 - \text{C} - \text{H} + \text{HCN} & \rightarrow \text{C}_6\text{H}_5 - \text{C} - \text{CN} \\
\text{H} - \text{C} - \text{OH} & \rightarrow \text{OH} - \text{C} - \text{H} \\
\text{d(+) } & \rightarrow \text{l(-)}
\end{align*}
\]
Q.20 Sodium Bisulphite is used for the purification of aldehydes and Ketones. Explain.

Ans. Aldehydes and Ketones form addition compounds with NaHSO₃ whereas impurities do not.

On hydrolysis we get pure aldehydes and Ketones back.

\[
\text{CH}_3\text{C} = \text{H} + \text{NaHSO}_3 \rightarrow \text{CH}_3\text{CH} - \text{SO}_3\text{Na} \quad \text{H}_2\text{O}
\]

(PURE)

Q.21 Why pH of reaction should be carefully controlled while preparing ammonia derivatives of carbonyl compound?

Ans. In strongly acidic medium ammonia derivatives being basic will react with acids and will not react with carbonyl compound. In basic medium, OH⁻ will attack carbonyl group.

pH of a reaction should be carefully controlled.

Q.22 Why formic acid is stronger acid than acetic acid?

Ans. Due to +I effect, CH₃⁻ group in acetic acid increases e⁻ density on carbon atom which makes it a weak acid.

While in formic acid no such pushing group is present, hence is a more stronger acid than acetic acid.
Q.23   Why is oxidation of alcohols to get aldehydes carried out under controlled conditions?

Ans.   It is because aldehydes get further oxidised to acids, oxidation of alcohols to aldehydes needs to be controlled.

Q.24   Why the oxidation of toluene to benzaldehyde with CrO3 is carried out in the presence of acetic anhydride.

Ans.   If acetic anhydride is not used we will get benzoic acid. Acetic anhydride used to prevent oxidation of benzaldehyde to benzoic acid.

Q.25   Melting point of an acid with even no. of carbon atoms is higher than those of its neighbour with odd no. of carbon atoms.

Ans.   They fit into crystal lattice more readily than odd ones that is why they have higher lattice energy and higher melting point.

Q.26   Why do aldehydes have lower boiling point than corresponding alcohols?

Ans.   Alcohols have lower boiling point as they are not associated with intermolecular whereas alcohols are associated with intermolecular H-bonding. Aldehydes have lower B.p.

Q.27   Why do aldehydes behave like polar compounds?

Ans.   Due to presence of C=O group which is polar.
Q.28  Most aromatic acids are solids while acetic acid and others of this series are liquids. Explain why?

Ans. Aromatic acids have higher molecular weight, More van-der-waals force of attraction as compared to aliphatic acids They are solids.

Q.29  ethers possess a dipole moment even if the alkyl radicals in the molecule are identical. Why?

Ans. It is because ethers are bent molecules, dipole do not get cancelled.

Q.30  Why does acyl chlorides have lower boiling point than corresponding acids?

Ans. Acyl chlorides are not associated with intermolecular H-bonding They have lower boiling point.

Q.31  Why ethers are stored in coloured bottles?

Ans. They are stored in coloured bottles. In presence of sunlight they react with oxygen to form peroxides which may cause explosion.

Q.32  Why formaldehyde cannot be prepared by Rosenmund’s reduction?

Ans. Because the formyl chloride thus formed is unstable at room temperature.

Cannot be prepared by Rosenmund reduction.
Q1. An organic compound (A) \( \{C_8H_{16}O_2\} \) 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 dehyration gives but-1-ene. Identity A, B, C

\[
\text{Ans-: } \text{CH}_3\text{CH}_2\text{CH}_2\text{COOCH}_2\text{CH}_2\text{CH}_2\text{CH}_3 + \text{H}_2\text{O} \xrightarrow{\text{H}_2\text{SO}_4} \begin{array}{l}
\text{(A) Butyl Butanoate} \\
\text{(B)} \\
\text{+} \\
\text{(C)} \\
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} \\
\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} \\
\text{Conc. K}_2\text{Cr}_2\text{O}_7 \\
\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \xrightarrow{\text{K}_2\text{Cr}_2\text{O}_7} \text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} \\
\text{(c)} \\
\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \xrightarrow{\text{Conc. H}_2\text{SO}_4} \text{CH}_3\text{CH}_2\text{CH} = \text{CH}_2 \text{ (bute - 1-ene)}
\]
Q2: An organic compound with the molecular formula C₉H₁₀O forms 2,4 DNP derivative reduces tollens reagent and undergoes cannizaro reaction. On vigorous oxidation, it gives 1,2 benzenecarboxylic acid. Identify the compound.

Ans: -

\[
\begin{align*}
\text{CHO} & \quad \text{CH₂CH₃} \\
\text{H} & \quad \text{C = O} \\
\text{H} & \quad \text{CH₂CH₃} \\
\text{NO₂} & \quad \text{NH₂ - NH - CH₂CH₃} \\
\text{NO₂} & \quad \text{2,4, DNP}
\end{align*}
\]

(2,4, DNP)

\[
\begin{align*}
\text{CHO} & \quad \text{CH₂CH₃} \\
\text{CH = N - NH} & \quad \text{NO₂} \\
\text{CH₂CH₃} & \quad \text{COOH}
\end{align*}
\]

\[
\begin{align*}
\text{CHO} & \quad \text{CH₂CH₃} \\
\text{Hot KMnO₄} & \quad \text{KOH}
\end{align*}
\]
Q3. An organic compound (A) with molecular formula \( \text{C}_8\text{H}_8\text{O} \) forms an orange-red precipitate with 2,4 DNP reagent and gives yellow precipitate on heating with iodine in the presence of sodium hydroxide. It neither reduces tollen’s or fetingil’s reagent, nor does it decolourise bromine water or baeyer’s reagents. On drastic oxidation with chromic acid, it gives a carboxylic acid (B) having molecular formula \( \text{C}_7\text{H}_6\text{O}_2 \). Identify the compounds (A) and (B).

\[
\text{COCH}_3 \quad \text{NO}_2 \\
\text{(A)}
\]

\[
\text{COCH}_3 + \text{NH}_2 - \text{NH} - \text{NO}_2 \\
\text{NO}_2 \quad \text{(2,4,DPN derivative)}
\]

\[
\text{CH}_3 \quad \text{C} = \text{N} \quad \text{NH} - \text{NO}_2 \\
\text{(A)}
\]

\[
\Rightarrow \text{COOH} \\
\text{(B)}
\]

\[
\text{COCH}_3 \quad \text{COONa} \\
\text{(A)} \quad \text{(A)}
\]

\[
\text{H}_2\text{CrO}_4 \quad \text{NaOH} \quad \text{I}_2 \\
\text{COOH} \quad + \text{CHI}_3
\]
Q4. Two moles of organic compound A on treatment with a strong base gives two compounds B and C. Compound B on dehydration with Cu gives A while acidification of C yields carboxylic acid D having molecular formula of CH₂O₂. Identify the compounds A, B, C, D

 Ans:- \[ 2\text{HCHO} \xrightarrow{\text{Conc. KOH}} \text{HCOOK} + \text{CH₃OH} \]  
(A) \hspace{1cm} (C) \hspace{1cm} (B)

\[ \text{CH₃OH} \xrightarrow{\text{Cu, 573 K}} \text{HCHO} \]  
(B) \hspace{1cm} (A)

\[ \text{HCOOK} + \text{HCL} \longrightarrow \text{HCOOH} + \text{KCL} \]  
(c) \hspace{1cm} (D)

Q5. An aliphatic compound A’ with a molecular formula of C₃H₆O reacts with phenylhydrazine to give compound B’. Reaction of A’ with I₂ in alkaline medium on warming gives a yellow precipitate C’. Identify the component A, B, C

 Ans:- \[ \text{CH₃COCH₃} + \text{C₆H₅NH} – \text{NH₂} \longrightarrow \text{CH₃C=N – HN – C₆H₅} \]  
\hspace{1cm} (A) \hspace{1cm} (B)

\[ \text{CH₃C – CH₃} + 3\text{I}_2 + \text{NaOH} \longrightarrow \text{CHI₃} \]  
(A) \hspace{1cm} (Iodoform) \hspace{1cm} (c)
Q6. A component A' with molecular formula C₅H₁₀O gave a positive 2,4-DNP test but a negative tollen’s reagents test. It was oxidised to carboxylic acid B' with molecular formula C₃H₆O₂ when treated with alkalines KMnO₄ under vigorous condition. Sodium salt of B' gave hydrocarbon C' on kolbe electrolysis reduction. Identify A, B, C and D.

Ans:-

\[
\begin{align*}
\text{CH}_3 - \text{CH}_2 - \text{C} - \text{CH}_2 - \text{CH}_3 & \xrightarrow{\text{KMnO}_4} \text{CH}_3\text{CH}_2\text{COOH} \\
(A) & \quad (B) \\
\text{CH}_3 - \text{CH}_2 - \text{C} = \text{O} & \text{NH}_2 - \text{NH} - \text{NO}_2 \\
\text{CH}_2 & \\
\text{CH}_3 &
\end{align*}
\]

\[
\Rightarrow \text{CH}_3 - \text{CH}_2 - \text{C} = \text{O} + \text{NH}_2 - \text{NH} - \text{NO}_2
\]

\[
\Rightarrow \text{CH}_3 - \text{CH}_2 - \text{C} = \text{N} - \text{NH} - \text{NO}_2
\]

\[
\Rightarrow \text{CH}_3\text{CH}_2\text{COONa} \xrightarrow{\text{electrolysis}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 + 2\text{CO}_2
\]

Sodium propanoate (c)
Q7 An organic compound A’ has the molecular formula C₅H₁₀O. It does not reduce Fehling’s solution but forms a bisulphite compound. It also gives a positive iodoform test. What are possible structures of A’? Explain your reasoning.

Ans-: It does not reduce Fehling’s solution but forms bisulphite compound so it is a ketone therefore it gives a positive iodoform test therefore it is methyl ketone.

The possible structures are:

\[
\begin{align*}
\text{O} & \\
\text{CH₃} - \text{C} - \text{CH}_{2} - \text{CH}_{2} \text{CH}_{3} \ & \text{And} \ & \text{CH₃} - \text{C} - \text{CH} - \text{CH}_{3} \\
\text{CH₃} & \\
\end{align*}
\]
Q8. An organic compound A' which has characteristic odour, on treatment with NaOH forms two compounds B' and C'. Compound B' has the molecular formula C\(_7\)H\(_8\)O which on oxidation gives back compound A'. Compound ‘C’ is the sodium salt of an acid which when heated with soda lime yields an aromatic hydrocarbon D’. Deduce A,B,C,D

Ans.

\[
\begin{align*}
\text{CHO} & \quad \rightarrow \quad \text{CH}_2\text{OH} \quad \rightarrow \quad \text{COONa} \\
\begin{array}{c}
\text{(A)} \\
\text{NaOH}
\end{array} & \quad \rightarrow \quad \begin{array}{c}
\text{(B)} \\
\text{Na(OH),CaO}
\end{array} & \quad \rightarrow \quad \begin{array}{c}
\text{(C)} \\
\text{CHO}
\end{array} \\
\text{OXIDATION} & \quad \rightarrow \quad \text{Na}_2\text{CO}_3
\end{align*}
\]
Q9. An organic compound $A'$ is resistant to oxidation forms an oxidation forms a compound $B$ (C$_3$H$_8$O) on reduction. $B'$ reacts with HBr to form a bromide $C'$ which on treatment with alcoholic KOH forms an alkene $D'$ (C$_3$H$_6$). Deduce $A, B, C, D$.

Ans: $\text{CH}_3 - \text{C} - \text{CH}_3 \xrightarrow{\text{LiAlH}_4} \text{CH}_3\text{CH} - \text{CH}_3$

(A)

$\text{CH}_3\text{CH} - \text{CH}_3 + \text{HBr} \rightarrow \text{CH}_3\text{CH} - \text{CH}_3$

(B)

$\text{CH}_3\text{CH} - \text{CH}_3 \text{ alc KOH} \rightarrow \text{CH}_3 - \text{CH} = \text{CH}_2 + \text{KBr}$

(C)

$\text{CH}_3 - \text{C} - \text{CH}_3 \xrightarrow{\text{LiAlH}_4} \text{CH}_3\text{CH} - \text{CH}_3$

(D)

Q10. Etherial solution of an organic compound $A'$ when heated with magnesium gave $B'$ on treatment with ethanal followed by acid hydrolysis gave 2-propanol. Identify the compound $A'$. What is $B'$ known as?

Ans: $\text{CH}_3 \text{ Br} + \text{Mg} \xrightarrow{} \text{CH}_3 \text{ MgBr}$

(a)

$\text{CH}_3\text{CHO} + \text{CH}_3\text{MgBr}$

(b)

$\text{CH}_3 - \text{CH} - \text{CH}_3$

$\text{OH} + \text{Mg (OH)Br}$
Q11. Identify A, B, C, D

\[ A + \text{CH}_3\text{MgBr} \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{CH}_2 - \text{CH} - \text{CH}_3 \]

![Chemical reaction diagram](image)

ANS.

A = CH\(_3\)CH\(_2\)CHO

B = CH\(_3\)CH = CH – CH\(_3\)

C = CH\(_3\) – CH – CH – CH\(_3\)

\[ \text{Br} \quad \text{Br} \]

D = CH\(_3\) – C ≡ C – CH\(_3\)
Q12. Primary alkyl halide $\text{C}_4\text{H}_9\text{Br}$ (A) reacted with alcoholic KOH to give compound (B) is reacted with HBr to give (C) which is an isomer of (A). When (A) is reacted with sodium metal it gives compound (D) $\text{C}_8\text{H}_{18}$ that was different from the compound formed when n-butyl bromide is reacted with sodium. Give the formula of (A) and write equations.

Ans: $\text{CH}_3$ – $\text{CH}$ – $\text{CH}_2\text{Br}$ + alc. KOH $\rightarrow$ $\text{CH}_3$ – $\text{CH}$ – $\text{C}$ = $\text{CH}_2$

$\text{CH}_3$ (A) $\rightarrow$ $\text{CH}_3$ (B)

$\text{CH}_3$ (B) + HBr $\rightarrow$ $\text{CH}_3$ – $\text{C}$ – $\text{CH}_3$

$\text{CH}_3$ (B) $\rightarrow$ (c)

C is the isomer of A

$\text{CH}_3$ – $\text{CH}$ – $\text{CH}_2\text{Br}$ + 2Na $\rightarrow$ $\text{CH}_2\text{Br}$ – $\text{CH}$ – $\text{CH}_3$

$\text{CH}_3$ (D)

$\text{CH}_3$ – $\text{CH}$ – $\text{CH}_2$ – $\text{CH}_2$ – $\text{CH}$ – $\text{CH}_3$

$\text{CH}_3$ (D) $\rightarrow$ (C$_8$H$_{18}$)

Ans:- CH₃CH = CH - CH₃ + H₂O   H₂SO₄ → (B)

(CH₃ - CH - CH₂ - CH₃)

CH₃ - CH - CH₂ - CH₃ + HCL → (CH₃ - CH - CH₂ - CH₃)

ZnCl₂

Cl⁻ (c)

C₂H₅OH-KOH

CH₃ - CH = CH - CH₃ (A)

Q14. An aromatic compound A on treatment with aqueous ammonia and heating forms compound B which on heating with Br₂ and KOH forms a compound C of molecular formula C₆H₇N. Identify A, B, C.

Ans:- COOH

NH₃

Δ

CONH₂

KOH

Br₂

NH₂

(Benzoic acid)  (Benzamide)  (Aniline)
Q15. Two isomeric compound A and B having molecular formula C\(_{15}\)H\(_{11}\)N, both lose N\(_2\) on treatment with HNO\(_2\) and gives compound C and D. C is resistant to oxidation but immediately responds to oxidation to lucas reagent after 5 minutes and gives a positive Iodoform test. Identify A and B.

Ans:-

\[
\begin{align*}
\text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CH}_3 + \text{HNO}_2 & \rightarrow \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CH}_3 \\
\text{NH}_2 (B) & \rightarrow \text{OH} (D) + \text{N}_2 \\
\text{CH}_3 - \text{C} - \text{CH}_3 + \text{HNO}_2 & \rightarrow \text{CH}_3 - \text{C} - \text{CH}_3 \\
\text{NH}_2 & \rightarrow \text{OH} (c) + \text{N}_2
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3 - \text{C} - \text{CH}_3 + \text{CONC. HCl} & \rightarrow \text{CH}_3 - \text{C} - \text{CH}_3 \\
\text{OH} & \rightarrow \text{Cl} (30) \\
\end{align*}
\]

But ‘D’ respond to lucas reagent in 5 minutes.

\[
\begin{align*}
\text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CH}_3 + \text{HCl} & \rightarrow \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CH}_3 \\
\text{OH (D)} & \rightarrow \text{Cl}
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3 - \text{CH(OH)} - \text{CH}_2 - \text{CH}_3 + \text{I}_2 + \text{NaOH} & \rightarrow \text{CH}_3 + \text{CH}_3 - \text{CH}_2 \text{COONa}
\end{align*}
\]
Q16. An organic compound A’ having molecular formula C$_2$H$_5$O$_2$N reacts with HNO$_2$ and gives C$_2$H$_4$O$_3$N$_2$. On reduction A’ gives a compound ‘B’ with molecular formula C$_2$H$_7$N. C’ on treatment with HNO$_2$ gives C’ which gives positive idoform test. Identify A,B,C.

Ans:-

\[
\text{CH}_3\text{CH}_2\text{NO}_2 + \text{HNO}_2 \rightarrow \text{CH}_3 - \text{CH} - \text{NO}_2 \quad \text{(A)}
\]

\[
\text{CH}_3 - \text{CH}_2\text{NO}_2 + \text{SN/HCL} \rightarrow \text{CH}_3 - \text{CH}_2\text{NH}_2 \quad \text{(B)}
\]

\[
\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{I}_2/\text{NaOH} \rightarrow \text{CHI}_3 \quad \text{(iodoform)}
\]

Q17. An organic compound A’ having molecular formula C$_3$H$_5$N on reduction gave another compound B’. The compound B on treatment with HNO$_2$ gave propyl alcohol. B on warming with CHCl$_3$ and alcoholic caustic potash give the offensive smelling C. Identify A,B,C.

Ans:-

\[
\text{C}_2\text{H}_5\text{CN} + 2\text{H}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \quad \text{(A)} \rightarrow \text{(B)}
\]

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2 + \text{CHCl}_3 + 3\text{KOH} \rightarrow \rightarrow \text{CH}_3\text{CH}_2\text{NC} \quad \text{(C)}
\]
Q18. Idomethane reacts with KCN to form a major product A. Compound A' on reduction in presence of LiAlH₄ forms a higher amine 'B'. Compound B on treatment with CuCl₂ forms a blue color complex C. Identify A, B, C

\[
\text{Ans. } \text{M: } \text{CH}_3\text{I + KCN } \rightarrow \text{CH}_3 - \text{CN } \rightarrow \text{CH}_3\text{CH}_2\text{NH}_2 \ (\text{B}) \quad \text{CuCl}_2 \\
\rightarrow [\text{Cu(CH}_3\text{CH}_2\text{NH}_2]_4\text{Cl}_2 \ 	ext{Blue complex}
\]

Q19. An aliphatic compound A with molecular formula C₂H₃Cl on treatment with AgCN gives two isomeric compounds of unequal amount with the molecular formula C₃H₃N. The minor of these two products on complete reduction with H₂ in the presence of Ni gives a compound ‘B’ with molecular formula C₃H₉N. Identify the compounds.

\[
\text{Ans.: } \text{CH}_2 = \text{CH} - \text{Cl } + \text{AgCN } \rightarrow \text{CH}_2 = \text{CH} - \text{CN } + \text{CH}_2 = \text{CH} - \text{N} - \text{C} \\
\text{(A)} \quad \text{(MINOR)} \quad \text{(MAJOR)}
\]

\[
\text{CH}_2 = \text{CH} - \text{C} = \text{N} \quad \text{Ni} \quad \text{H}_2 \quad \text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{NH}_2
\]

B
Q20. A compound ‘X’ having molecular formula C₃H₇NO reacts with Br₂ in presence of KOH to give another compound Y. The compound Y reacts with HNO₂ to form ethanol N₂ gas. Identify X,Y,

Ans:- CH₃CH₂CONH₂ + Br₂ + 4 KOH → CH₃CH₂NH₂

(X) \rightarrow \text{HNO}_2

(Y)

CH₃CH₂OH + N₂ (g)

Q21. A compound A’ of molecular formula C₃H₇O₂N reaction with Fe and conc, HCl gives a compound B’ OF molecular formula C₃H₉N. Compound B’ on treatment with NaNO₂ and HCl gives another compound C’ of molecular formula C₃H₈O. The compound C’ gives effervescences with Na on oxidation with CrO₃. The compound C’ gives a saturated aldehyde containing three carbon atom deduce A,B,C.

Ans:- CH₃CH₂CH₂NO₂ → CH₃CH₂CH₂NH₂ (B)

CH₃CH₂CH₂OH (C)

(Sodium propoxide)

CH₃CH₂CH₂OH \rightarrow \text{CH₃CH₂CHO} (C)
Q22. A Chloro compound $A'$ on reduction with Zn – Cu and alcohol gives the hydrocarbon (B) with five carbon atom. When $A'$ is dissolved in ether and treated with sodium 2,2,5,5 tetramethyl hexhane is formed structure of A and B?

Ans. CH₃

\[
\text{CH}_3 - \text{C} - \text{CH}_2 - \text{Cl} + 2\text{Na (ether)} \rightarrow \text{CH}_3\text{(A)} \\
\text{Zn- CU} \rightarrow \text{CH}_3 - \text{C} - \text{CH}_2 - \text{CH}_2 - \text{C} - \text{CH}_3 \\
\text{CH}_3 - \text{C} - \text{CH}_3 \text{(B)}
\]

**IDENTIFY A,B,C**

Q1. \(\text{CH}_3\text{COOH} \xrightarrow{\Delta} \text{A} \xrightarrow{\text{HCl}} \text{B} \xrightarrow{\text{NaOBr}} \text{C} \)

Q2. \(\text{C}_6\text{H}_5\text{NO}_2 \xrightarrow{\text{Fe/HCl}} \text{A} \xrightarrow{\text{NaNO}_2/\text{HCl}} \text{B} \xrightarrow{\text{H}_2\text{O}/\text{H}} \text{C}^+\)

Q3. \(\text{C}_6\text{H}_5\text{NO}_2 \xrightarrow{\text{Fe/HCl}} \text{A} \xrightarrow{\text{NaNO}_2} \text{B} \xrightarrow{\text{C}_6\text{H}_5\text{OH}} \text{C}\)

Q4. \(\text{CH}_3\text{CH}_2\text{Br} \xrightarrow{\text{KCN}} \text{A} \xrightarrow{\text{LiAlH}_4} \text{B} \xrightarrow{\text{HNO}_2} \text{C}\)
Q5. $C_6H_5N^+\text{Cl}^- \rightarrow A \rightarrow B \rightarrow C$

Q6. $\text{CH}_3\text{CH}_2\text{I} \rightarrow A \rightarrow B \rightarrow C$

Q7. $C_6H_5\text{NH}_2 + (\text{CH}_3\text{CO}_2)_2\text{O} \rightarrow A$

Q8. $C_6H_5\text{N}_2^+\text{Cl}^- \xrightarrow{\text{NaNO}_2/\text{Cu}} \Delta \rightarrow A$

Q9. $A \xrightarrow{\text{NaOH}} B \xrightarrow{\text{HNO}_2} C \xrightarrow{\text{Red p I}_2} D \xrightarrow{\text{I}_2} (\text{CH}_3\text{I})$

Q10. $A \rightarrow B \rightarrow C \rightarrow C_6H_5\text{N}_2\text{Cl}$

Q11. $A \xrightarrow{\text{KOH}} B \xrightarrow{\text{Br}_2} H\text{NO}_2 \rightarrow C \xrightarrow{\text{CH}_3\text{I}} C_2H_5\text{NH}_2$

Q12. $A \xrightarrow{\text{AgCN}} B \xrightarrow{\text{Sn/HCl}} C \xrightarrow{\text{H}^+ / \text{H}_2\text{O}} \text{CH}_3-\text{CH}_2\rightarrow \text{N} \xrightarrow{\text{LiAlH}_4} \text{CH}_3$

Q13. $\text{CH}_3\text{CN} \rightarrow A \rightarrow B$

Q14. $\text{R}_2\text{CO} \xrightarrow{\text{NH}_2} A \xrightarrow{\text{Li/H}_2} B$

Q15. $\text{CH}_2\text{Br} \xrightarrow{\text{CN}} A \xrightarrow{\text{LiAlH}_4} B$

Q16. $\text{NO}_2 \xrightarrow{\text{NaNO}_2/\text{HCl}} O^\circ \rightarrow A \xrightarrow{\text{CuCl}} B$
Q17. \[ \text{NO}_2 \]

\[
\begin{array}{c}
\text{H}_2\text{SO}_4/\text{SO}_3 \\
373\text{K}
\end{array}
\rightarrow
A
\rightarrow
\text{Fe/HCl}
\rightarrow
B
\]

**ANSWERS**

1. \( A = \text{CH}_3\text{CONH}_2 \), \( B = \text{CH}_3\text{NH}_2 \), \( C = \text{CH}_3\text{OH} \)

2. \( A = \text{C}_6\text{H}_5\text{NH}_2 \), \( B = \text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^- \), \( C = \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O} \)

3. \( A = \text{CH}_3\text{CH}_2\text{CN} \), \( B = \text{CH}_3\text{CH}_2\text{-CH}_2\text{NH}_2 \), \( C = \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \)

4. \( A = \text{C}_6\text{H}_5\text{NH}_2 \), \( B = \text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^- \), \( C = \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \)

5. \( A = \text{C}_6\text{H}_5\text{CN} \), \( B = \text{C}_6\text{H}_5\text{COOH} \), \( C = \text{C}_6\text{H}_5\text{CONH}_2 \)

6. \( A = \text{CH}_3\text{CH}_2\text{CN} \), \( B = \text{CH}_3\text{CH}_2\text{CONH}_2 \), \( C = \text{CH}_2\text{CH}_2\text{NH}_2 \)

7. \( A ) \text{ NHCOCH}_3 \)

\[
\begin{array}{c}
\text{NHCOCH}_3
\end{array}
\]

\[
\begin{array}{c}
+ \text{CH}_3\text{COOH}
\end{array}
\]

8. \( \text{C}_6\text{H}_5\text{NO}_2 = A \)

9. \( A = \text{CH}_3\text{CONH}_2 \), \( B = \text{CH}_3\text{NH}_2 \), \( C = \text{CH}_3\text{OH} \)

10. \( A) \text{ OH} \), \( B) \text{ OH} \), \( C) \text{ OH} \)

11. \( A = \text{CH}_3\text{CH}_2\text{COONH}_4 \), \( B = \text{CH}_3\text{CH}_2\text{CONH}_2 \), \( C = \text{CH}_3\text{CH}_2\text{NH}_2 \)
12. \( A = \text{CH}_3\text{Cl} \), \( B = \text{CH}_3\text{NC} \), \( C = \text{CH}_3\text{-CH}_2\text{-NH-CH}_3 \)

13. \( A = \text{CH}_3\text{COOH} \), \( B = \text{CH}_3\text{CH}_2\text{OH} \)

14. \( A = R - C = \text{NH} \), \( B = R - \text{CH} - \text{NH}_2 \)

15. \( \text{CH}_2\text{CN} \) (A) \( \text{CH}_2\text{CH}_2\text{NH}_2 \) (B)

16)

17) \( A = \text{NO}_2 \), \( B = \text{NH}_2 \text{SO}_3\text{H} \)
1 MARK QUESTIONS

Q1. Name the reaction and the reagent used for the conversion of acid chlorides to the corresponding aldehydes.
A. Name: Rosenmund’s reaction Reagent: H₂ in the presence of Pd (supported over BaSO₄) and partially poisoned by addition of Sulphur or quinoline.

\[
\text{O} \quad \text{Pd/BaSO}_4 \quad \text{O} \\
\text{R} - \text{C} - \text{Cl} + \text{H} \quad \xrightarrow{\text{Rosenmund's reaction}} \quad \text{R} - \text{C} - \text{H} + \text{HCl} \\
+ \text{S or quinoline}
\]

Q2. Suggest a reason for the large difference in the boiling points of butanol and butanal, although they have same solubility in water.
A. The b.p. of butanol is higher than that of butanal because butanol has strong intermolecular H-bonding while butanal has weak dipole-dipole interaction. However both of them form H-bonds with water and hence are soluble.

Q3. What type of aldehydes undergo Cannizaro reaction?
A. Aromatic and aliphatic aldehydes which do not contain α-hydrogens.

Q4. Out of acetophenone and benzophenone, which gives iodoform test? Write the reaction involved. (The compound should have CH₃CO-group to show the iodoform test.)
A. Acetophenone (C₆H₅COCH₃) contains the grouping (CH₃CO attached to carbon) and hence given iodoform test while benzophenone does not contain this group and hence does not give iodoform test.

\[
\text{C}_6\text{H}_5\text{COCH}_3 + 3 \text{I}_2 + 4 \text{NaOH} \quad \xrightarrow{\text{I}_2/\text{NaOH}} \quad \text{CHI}_3 + \text{C}_6\text{H}_5\text{COONa} + 3 \text{NaI} + 3 \text{H}_2\text{O}
\]

Q5. Give Fehling solution test for identification of aldehyde gp (only equations). Name the aldehyde which does not give Fehling’s soln. test.
A. R – CHO – 2 Cu²⁺ + 5 OH⁻ \xrightarrow{\text{RCOO}^{-} + \text{Cu}_2\text{O} + 3 \text{H}_2\text{O}}

Benzaldehyde does not give Fehling soln. test. (Aromatic aldehydes do not give this test.)
Q6. What makes acetic acid a stronger acid than phenol?
A. Greater resonance stabilization of acetate ion over phenoxide ion.

Q7. Why HCOOH does not give HVZ (Hell Volhard Zelinsky) reaction but CH₃COOH does?
A. CH₃COOH contains α- hydrogens and hence give HVZ reaction but HCOOH does not contain α-hydrogen and hence does not give HVZ reaction.

Q8. During preparation of esters from a carboxylic acid and an alcohol in the presence of an acid catalyst, water or the ester formed should be removed as soon as it is formed.
A. The formation of esters from a carboxylic acid and an alcohol in the presence of acid catalyst in a reversible reaction.

\[
\text{RCOOH} + \text{R'}\text{OH} \xrightleftharpoons{\text{H}_2\text{SO}_4} \text{RCOOR'} + \text{H}_2\text{O}
\]
Carboxylic acid alcohol Ester

To shift the equilibrium in the forward direction, the water or ester formed should be removed as fast as it is formed.

Q9. Arrange the following compounds in increasing order of their acid strength.
Benzoic acid, 4-Nitrobenzoic acid, 3, 4-dinitrobenzoic acid, 4-methoxy benzoic acid.
A. 4-methoxybenzoic acid < benzoic acid < 4-nitrobenzoic acid <4, dinitrobenzoic acid.

Q10. How is tert-butyl alcohol obtained from acetone?
A. [Diagram of the synthesis process]
2 / 3 MARKS QUESTIONS

1. Arrange the following compounds in increasing order of their boiling points. Explain by giving reasons.
   CH₃CHO, CH₃CH₂OH, CH₃OCH₃, CH₃CH₂CH₃.
   A. The molecular masses of all these compounds are comparable:
      CH₃CHO (44), CH₃CH₂OH (46), CH₃COCH₃ (46), CH₃CH₂CH₃ (44).
      CH₃CH₂OH exists as associated molecule due to extensive intermolecular hydrogen bonding and hence its boiling point is the highest (351 K). Since dipole-dipole interaction are stronger in CH₃CHO than in CH₃OCH₃, hence boiling point of CH₃CHO (293 K) is much higher than that of CH₃OCH₃ (249 K). Further, molecules of CH₃CH₂CH₃ have only weak Vander Waals forces while the molecules of CH₃OCH₃ have little stronger dipole-dipole interactions and hence the boiling point of CH₃OCH₃ is higher (249 K) than that of CH₃CH₂CH₃ (231 K). Thus the overall increasing order of boiling points is:
      CH₃CH₂CH₃ < CH₃OCH₃ < CH₃CHO < CH₃CH₂OH

2. Which acid of each pair shown here would you expect to be stronger?
   CH₃CO₂H or FCH₂CO₂H
   Thus due to lesser electron density in the O — H bond and greater stability of FCH₂COO⁻ ion over CH₃COO⁻ ion FCH₂COOH is a stronger acid than CH₃COOH.

3. Which acid is stronger and why?
   F₃C — C₆H₄ — COOH, CH₃ — C₆H₄ — COOH
   A. CF₃ has a strong (−I) effect.
      It stabilises the carboxylate ion by dispersing the −ve charge.
      Therefore due to greater stability of F₃C — C₆H₄ — COO⁻ (p) ion over CH₃ — C₆H₄COO⁻ (p) ion, F₃C — C₆H₄ — COOH is a much stronger acid than CH₃ — C₆H₄ — COOH.
4. Arrange the following compounds in increasing order of their reactivity towards HCN. Explain it with proper reasoning.

Acetaldehyde, Acetone, Di-tert-butyl ketone, Methyl tert-butyl ketone.
ANS. Addition of HCN to the carboxyl compounds is a nucleophilic addition reaction.
The reactivity towards HCN addition decreases as the + I effect of the alkyl groups increases and/or the steric hindrance to the nucleophilic attack by CN– at the carboxyl carbon increases. Thus the reactivity decreases in the order.

\[
\begin{align*}
\text{Acetaldehyde} & \quad \text{Acetone} & \quad \text{Tert-butyl methyl ketone} & \quad \text{Di-tert-butyl Ketone} \\
\text{H} & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 \\
\quad \text{C} = \text{O} & \quad \text{C} = \text{O} & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 \\
\end{align*}
\]

\[\begin{align*}
\text{-----} & \quad \text{+ I effect increases} & \quad \text{-----} \\
\text{-----} & \quad \text{Steric hindrance increases} & \quad \text{-----} \\
\text{-----} & \quad \text{Reactivity towards HCN addition decreases} & \quad \text{-----} \\
\text{-----} & \quad \text{-----} \\
\end{align*}\]

In other words, reactivity increases in the reverse order, i.e.

\[\text{Ditert-butyl Ketone} < \text{tert-Butyl methyl Ketone} < \text{Acetone} < \text{Acetaldehyde}\]

5. Explain why o-hydroxybenzaldehyde is a liquid at room temperature while p-hydroxybenzaldehyde is a high melting solid.
ANS.
Due to intermolecular H-bonding ortho-hydroxy benzaldehyde exists as discrete molecule whereas due to intermolecular H-bonding, p-hydroxybenzaldehyde exists as associated molecules. To break these intermolecular H-bonds, a large amount of energy is needed. Consequently, p-hydroxybenzaldehyde has a much higher m.p. and b.p. than that of o-hydroxy benzaldehyde. As a result, o-hydroxy benzaldehyde is a liquid at room temperature while p-hydroxy benzaldehyde is a high melting solid.
5 MARKS QUESTIONS

1. Arrange the following compounds in order of their property as indicated-
   i) Acetaldehyde, Acetone, di-tert-butyl ketone, Methyl tert-butyl ketone reactivity towards HCN

   - di-tert-butyl ketone < Methyl tert-butyl ketone < Acetone < Acetaldehyde

   - Aldehydes are more reactive towards nucleophilic addition across the >C=O due to steric and electronic reasons.

   - Sterically, the presence of two relatively large substituents in ketones hinders the approach of nucleophile to carbonyl carbon than in aldehydes having only one such substituent.

   - Electronically, the presence of two alkyl groups reduces the electrophilicity of the carbonyl carbon in ketones.

   ii) CH₃CH₂CHBrCOOH, CH₃CHBrCH₂COOH, (CH₃)₂CHCOOH, CH₃CH₂CH₂COOH acid strength

   - (CH₃)₂CHCOOH < CH₃CH₂CH₂COOH < CH₃CHBrCH₂COOH < CH₃CH₂CHBrCOOH

   - Electron withdrawing groups like –Br increases the acidity of carboxylic aids by stabilizing the conjugate base through delocalisation of negative charge by negative inductive effect. The closer the electron withdrawing group to the –COOH group, greater is the stabilising effect.

   - Electron donating groups decrease the acidity by destabilizing the conjugate base. Greater the number of –CH₃ groups, greater the destabilizing effect and lower the acidity.

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