Solved Problems

Objective

Problem 1: Which of the following compound would be expected to decarboxylates when heated

(a) \( \text{CH}_3 \text{O} = \text{C} = \text{O} \)  
(b) \( \text{CH}_3 \text{CH}_2 = \text{O} \)  
(c) \( \text{CH}_3 \text{C} = \text{O} \)  
(d) \( \text{CH}_3 \text{CH}_2 \text{O} \)

Solution:

\[ \text{CH}_3 \text{O} = \text{C} = \text{O} \xrightarrow{\Delta} \text{H}_3\text{C} = \text{C} = \text{CH}_3 \]

In case of \( \beta \)-keto acid, the ready decarboxylation occurs due to 6-membered low energy transition state formation.

\( \therefore \) (a)

Problem 2:

\[ \text{O} \xrightarrow{\text{CH}_3\text{OH}} \text{A} \]

A is :-

(a) \( \text{CH}_2 - \text{CH} - \text{OH COOCH}_3 \)  
(b) \( \text{CH}_2 - \text{CH} - \text{COOH OCH}_3 \)  
(c) both are correct  
(d) None is correct

Solution:

This bond breaks hence intermediate is

\[ \xrightarrow{\text{CH}_3\text{OH}} \]

\( \therefore \) (a)

Problem 3: End product of the following sequence of reaction is

\[ \text{C} = \text{CH}_3 \xrightarrow{1. \text{I}_2 + \text{NaOH}, \Delta} \xrightarrow{2. \text{H}^+, \Delta} \]

(a) Yellow ppt. of CHI₃, \( \text{COOH} \)  
(b) Yellow ppt. of CHI₃, \( \text{CHO} \)  
(c) Yellow ppt. of CHI₃, \( \text{COOH} \)  
(d) Yellow ppt. of CHI₃, \( \text{COOH COOH} \)
Solution:

Intermediate is

Which loses CO₂ on heating (β-keto acid)

\[ \text{Intermediate is } \quad \begin{array}{c}
\text{O} \\
\text{COOH}
\end{array} \]

\[ \text{Which loses CO}_2 \text{ on heating (β-keto acid)} \]

\[ \therefore \text{(c)} \]

Problem 4: *End product of this conversion* \( \text{CH}_3\text{C}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H} \xrightarrow{1.\text{NaBH}_4, 2.\text{H}_2\text{O,H}^+} \) is

\[ \begin{array}{c}
\text{(a)} \\
\text{(b)} \\
\text{(c)} \\
\text{(d)}
\end{array} \]

**Solution:** NaBH₄ reduces reactant to

\[ \text{CH}_3\text{—CH—CH}_2\text{—CH}_2\text{—CH}_2\text{—CO}_2\text{H} \text{ which forms ester} \]

\[ \begin{array}{c}
\text{OH} \\
\text{OH}
\end{array} \]

\[ \therefore \text{(a)} \]

Problem 5: *When acetic acid reacts with ketene, product formed*

(a) ethyl acetate  (b) aceto-acetic ester

(c) acetic anhydride  (d) no reaction

Solution:

\[ \text{CH}_3\text{COOH} + \text{CH}_2 = \text{C} = \text{O} \xrightarrow{\text{(Ketene)}} \text{acetic anhydride} \]

\[ \therefore \text{(c)} \]

Problem 6: *R—CH₂—CH₂OH can be converted in R—CH₂CH₂COOH. The correct sequence of reagents is*

(a) PBr₃, KCN, H⁺  (b) PBr₃, KCN, H₂

(c) KCN, H⁺  (d) HCN, PBr₃, H⁺

Solution:

\[ \text{RCH}_2\text{CH}_2\text{OH} \xrightarrow{\text{PBr}_3} \text{RCH}_2\text{CH}_2\text{Br} \xrightarrow{\text{KCN}} \text{RCH}_2\text{CH}_2\text{CN} \xrightarrow{\text{H}_2\text{O/H}^+} \text{RCH}_2\text{CH}_2\text{COOH} \]

\[ \therefore \text{(a)} \]

Problem 7: *The pKₐ of acetylsalicylic acid (aspirin) is 3.5. The pH of gastric juice in human stomach is about 2-3 and pH in the small intestine is about 8. Aspirin will be.*

(a) Unionised in the small intestine and in the stomach

(b) Completely ionized in the stomach and almost unionized in the small intestine.

(c) Ionized in the stomach and almost unionized in the small intestine

(d) Ionised in the small intestine and almost unionised in the stomach
Solution: More ionized in basic medium and less ionized in acidic medium, common ion effect  
∴ (d)

Problem 7: On subjecting mesityl oxide to the iodoform reaction, one of the products is the sodium salt of an organic acid. Which acid is obtained?  
(a) (CH₃)₂C=CH—CH₂COOH  
(b) (CH₃)₂CH—COOH  
(c) (CH₃)₂C=CH—COOH  
(d) (CH₃)₂C=CH—CO—COOH

Solution:  
\[
\text{CH}_3\text{C}=\text{CH—C—CH}_3 \xrightarrow{\text{NaOH/I₂}} \text{CH}_3\text{C}=\text{CH—C—OH + CHI}_3
\]

∴ (c)

Problem 8: The ease of alkaline hydrolysis is more for

(a)  
(b)  
(c)  
(d)

Solution:  
Then is more electron deficiency on carbonyl carbon.  
∴ (a)

Problem 9: Which of the following does not undergo Hell - Volhard Zelinsky reaction?  
(a) HCOOH  
(b) CCl₃COOH  
(c) C₆H₅COOH  
(d) All

Solution: None of these contain alpha H atom  
∴ (d)

Subjective

Problem 1: Treatment of 2, 4-pentanenedione with KCN and CH₃COOH, followed by hydrolysis yields two products, (A) and (B). Both (A) and (B) are dicarboxylic acids of formula C₁₅H₁₂O₆. (A) melts at 98°C. When heated, (B) gives first a lactonic acid (C₁₅H₁₀O₅) and finally a dilactone (C₁₅H₈O₄).  
a) What structure must (B) have that permits ready formation of both a monolactone and a dilactone ?  
b) What is the structure of (A) ?
Solution:

\[
\begin{align*}
\text{(A) Meso} & \quad \text{HO} - \text{C} - \text{COOH} \\
\text{(B) Racemic} & \quad \text{HO} - \text{C} - \text{COOH}
\end{align*}
\]

Compound (B) is a racemic modification. It gives monolactone (II), but the remaining —OH and —COOH are cis; (II) can react further to form the dilactone.

\[
\begin{align*}
\text{(B)} & \quad \text{OH} - \text{C} - \text{OH} \\
\text{(II) Monolactone} & \quad \text{O} - \text{C} - \text{C} \\
\text{Dilactone} & \quad \text{O} - \text{C} - \text{O}
\end{align*}
\]

**Problem 2:** An organic compound (A) of formula C₆H₁₀O decolourises Br₂/CCl₄ colour but has no reaction with ammonical cuprous chloride solution. (A) reacts with Schiff’s reagent and also reduces Fehling’s solution. (A) on treatment with silver oxide suspended in aqueous base gives compound (B). C₆H₁₀O₂, which evolves CO₂ from aqueous NaHCO₃ (B) on ozonolysis yields one mole each of propanal and pyruvic acid. What are (A) and (B)?

**Solution:** Compound (A) contains olefinic double bond as it discharges the red colour of Br₂/CCl₄. It also contains —CHO group as it gives positive tests for this group. Since compound (B) liberates CO₂ from NaHCO₃ hence it contains —COOH group. The structure of (B) is determined from its products of ozonolysis as follows:

\[
\begin{align*}
\text{Propanal} & \quad \text{Pyruvic acid}
\end{align*}
\]

Since (B) is obtained by the oxidation of (A) hence (A) is:

\[
\begin{align*}
\text{H} - \text{C} & \quad \text{CHO}
\end{align*}
\]

**Problem 3:** A salt (A) of the formula C₄H₅O₂Ag on refluxing with bromine gives (B), C₃H₅Br. Compound (B) on heating with alcoholic KOH yields (C), C₃H₄, which decolourises Br₂/CCl₄ and cold dilute KMnO₄ solution, but does not react with ammonical AgNO₃ or Cu₂Cl₂. (C) on ozonolysis gives (D), C₃H₄O₄, which on heating eliminates CO₂ to give acetic acid. What are (A) to (D)?
Problem 4: A neutral liquid of formula \( C_7H_{14}O_2 \) is hydrolysed to an acid \( A \), and an alcohol \( B \). Acid \( A \) has a neutralization equivalent of 74. Alcohol \( B \) is not oxidized with an acid solution of \( Na_2Cr_2O_7 \). What is the formula and name of the original compound?

Solution:

\[
\begin{align*}
\text{HOH} & \xrightarrow{\text{H_2SO_4}} \text{H_3C-CH_2-COOH} + \text{H_3C-C-OH} \\
\text{H_3C-C-OH} & \xrightarrow{\text{Na_2Cr_2O_7}} \text{No oxidation}
\end{align*}
\]

Problem 5: An ester of molecular formula \( C_8H_{16}O_2 \) on hydrolysis affords an acid \( A \) and an alcohol \( B \). Oxidation of alcohol \( B \) with \( Na_2Cr_2O_7 \) gives rise to an acid \( C \). Sodium salts of acids \( A \) and \( C \) on fusion with solid \( NaOH \) yield propane in each case. What is the structural formula of the original ester?

Solution:

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_2-\text{C}-\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3 & \xrightarrow{\text{HOH}} \text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} + \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} \\
\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} & \xrightarrow{\text{Na_2Cr_2O_7}} \text{No oxidation}
\end{align*}
\]

Problem 6: Compound \( A, C_3H_7Cl \), reacts with alcoholic KOH to form \( B, C_3H_6 \). Compound \( B \) discharges \( Br_2/CCl_4 \) solution. Reaction of \( A \) with Mg in ether and subsequent treatment with \( CO_2 \) and dilute acid gives \( C \), whose molecular formula is \( C_4H_8O_2 \). When we add compound \( C \) to aqueous \( NaHCO_3 \) solution, bubbles are evolved. What are \( A \) to \( C \)?

Solution:

\[
\begin{align*}
\text{(A)} = \text{H}_3\text{C-CH} & \xrightarrow{\text{Cl}} \text{H}_3\text{C-CH} \\
\text{(B)} = \text{H}_3\text{C-CH} & \xrightarrow{\text{CH}_2} \text{H}_3\text{C-CH} \\
\text{(C)} = \text{H}_3\text{C-CH} & \xrightarrow{\text{CH}_3} \text{H}_3\text{C-CH}
\end{align*}
\]
Problem 7: Compound (A) has a neutralization equivalent of 116. It forms a semicarbazone or phenyl hydrazone, and gives positive iodoform test. Compound (A) reacts with SOCl₂ to give (B) which on Rosenmund’s reduction gives (C). Clemmenson reduction of (C) gives n-pentane. What are (A), (B) and (C)?

Solution:
i) Since (A) forms semicarbazone and phenyl hydrazone, hence it has a >C=O group.

As it also gives iodoform test hence it contains H₃C—C— group in its molecule.

ii) The neutralization equivalent of (A) is 116, hence it also contains a —COOH group. Its formula can be deduced as follows:

\[ 116 - \text{H}_3\text{C} - \text{C} - (+-\text{COOH}) = 116 - (43 + 45) = 28 \]

The value 28 corresponds to two methyl groups. Hence, (A) is

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

Problem 8: An organic acid A, C₃H₄O₃ is catalytically reduced in presence of ammonia to give B, C₃H₇NO₂. B reacts with acetyl chloride, hydrochloric acid and alcohols. It can also react with nitrous acid to give another compound C, C₃H₆O₃, along with the evolution of nitrogen. What are A, B and C. Give reasons?

Solution:

Compound A is acid having one –COOH group only, the remaining part C₂H₃O can be

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

on catalytic reduction keto group is converted into secondary alcohol which with ammonia will give amino acid, i.e.,

\[ \text{CH}_3 - \text{C} - \text{COOH} \xrightarrow{\text{reduction}} \text{CH}_3 - \text{CH} - \text{COOH} \xrightarrow{\text{HNNH}_2, \text{H}_2\text{O}} \text{CH}_3 - \text{CH} - \text{COOH} \]

with nitrous acid, B, react to give
Problem 9: Compound A, $C_5H_8O_3$, when heated with soda lime gives B which reacts with HCN to give C. C reacts with $PCl_3$ to give D which reacts with KCN to form E. E, on alkaline hydrolysis gives a salt which is isolated and heated with soda lime to produce n-butane. A, on careful oxidation with $K_2Cr_2O_7$ gives acetic acid and malonic acid. Give structural formulae of A to E.

Solution:

On Oxidation only two –COOH groups can be introduced, i.e., one to each carbon undergoing C–C fission, but in the resulting products we have three –COOH groups. Hence, one –COOH group is already there in compound A, the remaining portion $C_4H_7O–$, resembles with Keto substituted alkyl group

$$C_4H_7–C–\|–O$$

This indicates that the given organic compound A is Keto substituted acid. To assign position to Keto group in carbon chain, we know that keto acids on careful oxidation undergo C–C bond fission at a place where -C- is situated, further Keto group is also converted into –COOH and remains with acid having small number of carbon atoms. From the above discussion it is clear that acetic acid is formed from.

$$\text{Arrangement } C_3H_7CO – \text{ has } CH_3 – C–CH_2 – CH_2 – \text{ structure and }$$

$$\text{compound A is } CH_3 – C–CH_2 – CH_2 – COOH$$

A, with soda-lime undergoes decarboxylation to give

$$CH_3 – CO – CH_2– CH_3 \text{ (B) }$$

B, being Ketone will give addition product with HCN to form
Problem 10: a) Can the aromatic ring in benzoic acid stabilize the benzoate anion by \(\pi\)-electron delocalization? Illustrate

b) Discuss the electronic effect of the \(p\)-\(NO_2\) group in \(p\)-\(NO_2C_6H_4COO^-\)

Solution: a) The only contributing structure I that delocalizes electron density from PhCOO\(^-\) has a positive charge on an O atom with only six electrons.

The contribution from this extremely high energy resonance structure is nil.

b) There is no direct resonance interaction between \(-COO^-\) and \(-NO_2\). The resonance interaction of the \(NO_2\) with the ring induces some positive charge on the ring C bearing the \(COO^-\) II, from which a strong electron with drawing inductive effect is generated. This effect is base stabilizing and thus acid strengthening.
### Assignments (New Pattern)

#### SECTION – I

<table>
<thead>
<tr>
<th>Single Choice Questions</th>
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<tbody>
<tr>
<td>1. Which of the following carboxylic acids is not reduced to the corresponding 1° alcohol by LiAlH₄?</td>
</tr>
<tr>
<td>(a) CH₃CH(CH₃)COOH</td>
</tr>
<tr>
<td>(c) p-O₂N₆H₄COOH</td>
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<tr>
<td>2. Which of the following dicarboxylic acids gives a cyclic anhydride on heating?</td>
</tr>
<tr>
<td>(a) CH₂(COOH)₂</td>
</tr>
<tr>
<td>(c) HOOC(CH₂)₄COOH</td>
</tr>
<tr>
<td>3. Which of the following dicarboxylic acids gives a linear polymeric anhydride?</td>
</tr>
<tr>
<td>(a) HOOC(CH₂)₃COOH</td>
</tr>
<tr>
<td>(c) HOOC(CH₂)₅COOH</td>
</tr>
<tr>
<td>4. Which of the following orders of reactivity of acid derivatives towards a nucleophile is correct?</td>
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<tr>
<td>(a) acid chloride &gt; anhydride &gt; ester</td>
</tr>
<tr>
<td>(c) acid chloride &gt; ester &gt; anhydride</td>
</tr>
<tr>
<td>5. Which of the following orders regarding the base strength of a leaving group in a reaction of an acid derivative with a nucleophile is correct?</td>
</tr>
<tr>
<td>(a) Cl⁻ &gt; RCOO⁻ &gt; RO⁻</td>
</tr>
<tr>
<td>(c) RO⁻ &gt; RCOO⁻ &gt; Cl⁻</td>
</tr>
<tr>
<td>6. Which of the following orders regarding the base strength of a leaving group in a reaction of an acid with a nucleophile is correct?</td>
</tr>
<tr>
<td>(a) Cl⁻ &lt; RO⁻ &lt; NH₂⁻</td>
</tr>
<tr>
<td>(c) RO⁻ &gt; Cl⁻ &gt; NH₂⁻</td>
</tr>
<tr>
<td>7. The correct sequence regarding the activity of the given acid derivative is</td>
</tr>
<tr>
<td>(a) RCOCl &gt; RCON₃ &gt; (RCO)₂O</td>
</tr>
<tr>
<td>(c) RCON₃ &gt; RCOCl &gt; (RCO)₂O</td>
</tr>
<tr>
<td>8. Which of the following statements is correct?</td>
</tr>
<tr>
<td>(a) 1° amide liberates N₂ when treated with HNO₂</td>
</tr>
<tr>
<td>(b) 2° amide liberates N₂ when treated with HNO₂</td>
</tr>
<tr>
<td>(c) 3° amide liberates N₂ when treated with HNO₂</td>
</tr>
<tr>
<td>(d) None of 1°, 2° and 3° amides produce N₂ when treated</td>
</tr>
<tr>
<td>9. Which of the following amides does not react with HNO₂?</td>
</tr>
<tr>
<td>(a) CH₃CONH₂</td>
</tr>
<tr>
<td>(c) CH₃ CON — CH₃</td>
</tr>
<tr>
<td>C₂H₅</td>
</tr>
</tbody>
</table>
10. The correct sequence of decreasing order of reactivity of hydrolysis of acid chlorides is
(a) PhCOCl > p-O2NC6H4COCl > p-CH3OC6H4COCl
(b) PhCOCl > p-CH3OC6H4COCl > p-O2NC6H4COCl
(c) p-O2NC6H4COCl > PhCOCl > p-CH3OC6H4COCl
(d) p-O2NC6H4COCl > p-CH3OC6H4Cl > PhCOCl

11. Which of the following statements regarding amides is not correct?
(a) Amides do not form salts when treated with aqueous acids
(b) The aqueous solutions of amides are alkaline
(c) Amides are very poor nucleophiles
(d) Amides are considerably less reactive than acid chlorides

12. Which of the following facts is not correct?
(a) As compared to RNH2, RCONH2 is stabilised by delocalisation of the nitrogen lone-pair electrons by the carbonyl group
(b) As compared to RNH3+, RCONH3+ is destabilised because the electron-withdrawing carbonyl group destabilises the positive charge on nitrogen
(c) ΔG° for the conversion of RNH2 → RNH3+ is more than that of the reaction RCONH2 → RCONH3+.
(d) Increased stability of RCONH2 relative to RNH2 and decreased stability of RCONH3+ relative to RNH3+ make amines more basic than amides.

13. The mechanism of nucleophilic acyl substitution in the acyl derivative proceeds as follows which among the following is false?

(a) \[
\begin{align*}
\text{R}^+\text{C}^-\text{G} + \text{H}^- \rightarrow \text{R}^+\text{C}^-\text{G} + \text{H}^+ \\
\text{H}^- + \text{R}^-\text{C}^-\text{G} + \text{H}^+ \rightarrow \text{R}^-\text{C}^-\text{G} + \text{H}^+ \\
\text{R}^-\text{C}^-\text{G} + \text{H}^- \rightarrow \text{R}^-\text{C}^-\text{G} + \text{H}^+ \\
\text{R}^-\text{C}^-\text{G} + \text{H}^- \rightarrow \text{R}^-\text{C}^-\text{G} + \text{H}^+ \\
\end{align*}
\]
(b) \[
\begin{align*}
\text{R}^+\text{C}^-\text{G} + \text{H}^- \rightarrow \text{R}^+\text{C}^-\text{G} + \text{H}^+ \\
\text{H}^- + \text{R}^-\text{C}^-\text{G} + \text{H}^+ \rightarrow \text{R}^-\text{C}^-\text{G} + \text{H}^+ \\
\text{R}^-\text{C}^-\text{G} + \text{H}^- \rightarrow \text{R}^-\text{C}^-\text{G} + \text{H}^+ \\
\text{R}^-\text{C}^-\text{G} + \text{H}^- \rightarrow \text{R}^-\text{C}^-\text{G} + \text{H}^+ \\
\end{align*}
\]
(c) \[
\begin{align*}
\text{R}^+\text{C}^-\text{G} + \text{H}^- \rightarrow \text{R}^+\text{C}^-\text{G} + \text{H}^+ \\
\text{H}^- + \text{R}^-\text{C}^-\text{G} + \text{H}^+ \rightarrow \text{R}^-\text{C}^-\text{G} + \text{H}^+ \\
\text{R}^-\text{C}^-\text{G} + \text{H}^- \rightarrow \text{R}^-\text{C}^-\text{G} + \text{H}^+ \\
\text{R}^-\text{C}^-\text{G} + \text{H}^- \rightarrow \text{R}^-\text{C}^-\text{G} + \text{H}^+ \\
\end{align*}
\]
(d) \[
\begin{align*}
\text{R}^+\text{C}^-\text{G} + \text{H}^- \rightarrow \text{R}^+\text{C}^-\text{G} + \text{H}^+ \\
\text{H}^- + \text{R}^-\text{C}^-\text{G} + \text{H}^+ \rightarrow \text{R}^-\text{C}^-\text{G} + \text{H}^+ \\
\text{R}^-\text{C}^-\text{G} + \text{H}^- \rightarrow \text{R}^-\text{C}^-\text{G} + \text{H}^+ \\
\text{R}^-\text{C}^-\text{G} + \text{H}^- \rightarrow \text{R}^-\text{C}^-\text{G} + \text{H}^+ \\
\end{align*}
\]

14. Kolbe electrolysis of potassium succinate gives CO2 and __________
(a) C2H6 and KOH
(b) C2H2 and KOH
(c) C2H4, KOH and H2
(d) CH4, C2H6 and C2H4.

15. In the following reaction identify compounds A, B, C and D:
\[
P\text{Cl}_3 + \text{SO}_2 \rightarrow A + B;
A + \text{CH}_3\text{COOH} \rightarrow C + \text{SO}_2 + \text{HCl}
2C + (\text{CH}_3)_2\text{Cd} \rightarrow D + \text{CdCl}_2
\]
(a) SOCl2, POCl3, CH3COCl, CH3COCH3
(b) SO2Cl2, HCl, CH3Cl, CH3CHO
(c) SO2, Cl2, C2H5Cl, CH3COCH3
(d) None of these.
16. What are A and B in the following sequence of reactions?

(i) \( \text{CH}_3\text{CH}_2\text{COOH} \xrightarrow{\text{PbBr}_2} \text{A} \)

(ii) \( \text{A} \xrightarrow{(\text{i}) \text{Alc. KOH excess}} \xrightarrow{(\text{ii}) \text{H}^+} \text{B} \)

(a) \( \begin{array}{c}
\text{CH}_3 \xrightarrow{\text{Br}} \text{CH}_2\text{COOH}, \text{CH}_2 = \text{CHCOOH}
\end{array} \)

(b) \( \begin{array}{c}
\text{CH}_3\text{CH}_2\text{COBr}, \text{CH}_2 = \text{CHCOOH}
\end{array} \)

(c) \( \begin{array}{c}
\text{CH}_2\text{CH}_2\text{COOH}, \text{CH}_2 = \text{CHCOOH}
\end{array} \)

(d) \( \begin{array}{c}
\text{H}_3\text{C} \xrightarrow{\text{COOH}, \text{H}_2\text{C}=\text{C} \xrightarrow{\text{COOH}}}
\end{array} \)

17. Acetic acid in the vapour state has a molecular weight of 120 because:
(a) its molecule gets solidified
(b) its molecule gets stabilized by resonance
(c) it undergoes intermolecular H-bonding and exists as the dimmer
(d) it forms anhydride in this condition.

18. Carbonation of alkyl magnesium halide followed by acidification gives:
(a) a carboxylic acid
(b) an alcohol
(c) an anhydride
(d) an aldehyde.

19. Reaction between solid ice and methyl magnesium bromide gives an addition compound which on acidification yields:
(a) ethanoic acid
(b) propanoic acid
(c) ethanal
(d) ethanol.

20. Which reducing agents of the following can be used for the following transformation?
\( \text{CH}_3\text{CH} = \text{CH.COOH} \xrightarrow{\cdot} \text{CH}_3\text{CH} = \text{CH.CH}_2\text{OH}. \)
(a) LiAlH_4
(b) BH_3, THF
(c) H_2/Ni
(d) Na + C_2H_5OH.

21. Which of the following reactions is used to bring about the following conversion?

\( \begin{array}{c}
\text{H}_3\text{C} \xrightarrow{(\text{ii}) \text{NH}_2} \text{H}_3\text{C} \xrightarrow{(\text{i}) \text{N}_2\text{H}} \text{NH}_2
\end{array} \)

(a) Hofmann reaction
(b) Curtius reaction
(c) Ritter reaction
(d) Schmidt reaction.

22. Which one of the following reagents is used to identify acetic acid?
(a) NaOH and I_2
(b) Ceric ammonium nitrate
(c) neutral FeCl_3 solution
(d) Tollens reagent.

23. Consider the following reaction scheme:
\( \begin{array}{c}
\text{CH}_3\text{CH}_2\text{COOH} \xrightarrow{\text{X}} \text{CH}_3\text{CH} \xrightarrow{\text{Y}} \text{COOH} \xrightarrow{\text{Br}} \text{CH}_3\text{CHCOO}^- \xrightarrow{\text{NH}_3\text{O}^-} \text{Alanine}
\end{array} \)

which of the following would be suitable for converting propanoic acid into the amino acid alanine?
24. Which of the following compounds would be expected to decarboxylate when heated

(a) \( \text{CH}_3 \text{OH} \)
(b) \( \text{CH}_3 \text{CH}_2 \)
(c) \( \text{CH}_3 \)
(d) \( \text{CH}_3 \text{COOH} \)

25. \( \text{O} \)

(a) \( \text{CH}_2—\text{CH}—\text{OH} \)
(b) \( \text{CH}_2—\text{CH}—\text{OCH}_3 \)
(c) both are correct
(d) None is correct

SECTION – II

1. Which of the following orders of acid strength is correct?
   (a) \( \text{RCOOH} > \text{ROH} > \text{HOH} > \text{HC} \equiv \text{CH} \)
   (b) \( \text{RCOOH} > \text{HOH} > \text{ROH} > \text{HC} \equiv \text{CH} \)
   (c) \( \text{RCOOH} > \text{HOH} > \text{HC} \equiv \text{CH} > \text{ROH} \)
   (d) \( \text{RCOOH} > \text{HC} \equiv \text{CH} > \text{HOH} > \text{ROH} \)

2. Which of the following orders of base strength is correct?
   (a) \( \text{R}^- > \text{NH}_2 > \text{HC} \equiv \overline{\text{C}} > \text{RCOO}^- \)
   (b) \( \text{R}^- > \text{NH}_2 > \text{RCOO}^- > \text{HC} \equiv \overline{\text{C}} \)
   (c) \( \text{R}^- > \text{RCOO}^- > \text{NH}_2 > \text{HC} \equiv \overline{\text{C}} \)
   (d) \( \text{HC} \equiv \overline{\text{C}} > \text{NH}_2 > \text{RCOO}^- > \text{R}^- \)

3. The relative order of esterification of alcohols is
   (a) \( 1^\circ < 2\circ < 3\circ \)
   (b) \( 1^\circ > 2\circ > 3\circ \)
   (c) \( 1^\circ > 3\circ > 2\circ \)
   (d) \( 1^\circ < 3\circ < 2\circ \)

4. The treatment of \( \text{CH}_3\text{CH}_2\text{COOH} \) with chlorine in the presence of phosphorus gives
   (a) \( \text{CH}_3\text{CH}_2\text{COCl} \)
   (b) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} \)
   (c) \( \text{CH}_3\text{CH}(_2)\text{Cl} \text{COOH} \)
   (d) \( \text{H}_2\text{Cl} \text{CH}_2\text{COOH} \)

5. The treatment of an ester with LiAlH\(_4\) followed by acid hydrolysis produces
   (a) two alcohols
   (b) two acids
   (c) two aldehydes
   (d) one molecule of alcohol and another of carboxylic acid

6. Which of the following reactants produces benzophenone on heating?
   (a) Calcium formate + Calcium benzoate
   (b) Calcium acetate + Calcium benzoate
   (c) Calcium benzoate
   (d) Calcium acetate + Calcium formate
7. Acetic acid differs from formic acid in that
   (a) acetic acid is stable to heat
   (b) formic acid is stable to heat
   (c) acetic acid acts as a reducing agent
   (d) acetic acid shows positive test with Tollens reagent

8. The reaction of formic acid with concentrated H₂SO₄ gives
   (a) CH₃COOH
   (b) CO₂ + H₂O
   (c) CO + H₂O
   (d) HCHO

9. Which of the following reagent/solution can be used to distinguish between methanoic acid and ethanoic acid?
   (a) Tollens reagent
   (b) FeCl₃ solution
   (c) NaOH solution
   (d) Na₂CO₃ solution

10. Which of the following reactants would produce acetophenone on heating?
    (a) Calcium acetate + Calcium formate
    (b) Calcium formate + Calcium benzoate
    (c) Calcium acetate + Calcium benzoate
    (d) Calcium acetate

11. The Hell-Volhard-Zelinsky reaction is used in the synthesis of
    (a) aldehydes
    (b) α-haloacids
    (c) acid halides
    (d) ketones

12. Which of the following sequences of rate of alkaline hydrolysis of esters is correct?
    (a) CH₃CH₂COOCH₃ < (CH₃)₂CHCOOCH₃ < (CH₃)₃CCOOCH₃
    (b) CH₃CH₂COOCH₃ > (CH₃)₂CHCOOCH₃ > (CH₃)₃CCOOCH₃
    (c) CH₃CH₂COOCH₃ > (CH₃)₂CHCOOCH₃ < (CH₃)₃CCOOCH₃
    (d) CH₃CH₂COOCH₃ < (CH₃)₂CHCOOCH₃ > (CH₃)₃CCOOCH₃

13. When propionic acid is treated with aqueous sodium bicarbonate, CO₂ is liberated. The C from CO₂ comes from
    (a) methyl group
    (b) carboxylic acid group
    (c) methylene group
    (d) Bicarbonate

14. Which of the following reducing agents can be used to reduce RCOOH to RCH₂OH?
    (a) NaBH₄
    (b) Na/EtOH
    (c) LiAlH₄
    (d) H₂/Catalyst

15. Which of the following carboxylic acids is not reduced to the corresponding 1° alcohol by BH₃/THF?
    (a) CH₃CH(CH₃)CH₂COOH
    (b) p-CH₃COC₆H₄COOH
    (c) m-O₂NC₆H₄COOH
    (d) (Z)-CH₃CH=CHCH₂COOH

16. Which does not react with Fehling’s solution?
    (a) CH₃CHO
    (b) C₆H₅CHO
    (c) C₆H₁₂O₆
    (d) HCOOH.
17. Which does not form a phenyl hydrazone?
   (a) \( \text{CH}_3\text{C} = \text{C.OOH} \)  
   (b) \( \text{H}_3\text{C} = \text{C} = \text{CH}_2\cdot\text{CH}_3 \)  
   (c) \( \text{H}_3\text{C} = \text{C.OH} \)  
   (d) \( \text{H}_3\text{C} = \text{C} = \text{H} \).

18. Which does not have a carbonyl group?
   (a) benzoic acid  
   (b) ethanoic acid  
   (c) picric acid  
   (d) aspirin.

19. Which of the following compounds is not an aliphatic acid?
   (a) stearic acid  
   (b) palmitic acid  
   (c) oleic acid  
   (d) p-nitro benzoic acid.

20. The acid in which \(-\text{COOH}\) is not present is:
   (a) ethanoic acid  
   (b) picric acid  
   (c) lactic acid  
   (d) palmitic acid.

21. \((\text{CH}_3)_2\text{C} = \text{CHCOCH}_3\) can be oxidized to \((\text{CH}_3)_2\text{C} = \text{CHCOOH}\) by:
   (a) chromic acid  
   (b) \(\text{NaOH}\) and \(\text{I}_2\)  
   (c) \(\text{Cu}\) at 300°C  
   (d) \(\text{KMnO}_4\).

22. Which of the following is used to perform following transformation?
   \[
   \text{H}_3\text{C} = \text{CHCOCH}_3 \rightarrow \text{H}_3\text{C} = \text{CHCOOH}
   \]
   (a) \(\text{SOCl}_2\)  
   (b) \(\text{PCl}_3\)  
   (c) \(\text{PCl}_3\)  
   (d) \(\text{SO}_2\text{Cl}_2\).

23. Which of the following does not give iodoform?
   (a) pyruvic acid  
   (b) lactic acid  
   (c) actophenone  
   (d) propionic acid.

24. One can distinguish between \(\text{HCOOH}\) and \(\text{CH}_3\text{COOH}\) with:
   (a) \(\text{NaHCO}_3\)  
   (b) \(\text{H}_2\text{SO}_4\)  
   (c) Tollens reagent  
   (d) Fehling’s solution.

25. Which of the following decarboxylates readily in the temperature range 100–150°C?
   (a) \(\text{CH}_2=\text{CH.CH}_2\text{COOH}\)  
   (b) \(\text{O}_2\text{NCH}_2\text{COOH}\)  
   (c) \(\text{NC—CH}_2\text{COOH}\)  
   (d) \(\text{CH}_3\text{COCH}_2\text{COOH}\).
When the following three different types of esters are hydrolysed in basic medium,

\[
\begin{align*}
\text{Carboxylate} & : \quad R \text{C}^\circ \text{O}^\circ \text{OR} \\
\text{Sulphonate} & : \quad \text{Ar} \text{S}^\circ \text{O}^\circ \text{OR} \\
\text{Phosphate} & : \quad \text{R} \text{O}^\circ \text{P}^\circ \text{OH}
\end{align*}
\]

The hydroxide anion attacks the acyl carbon in carboxylates while it attacks the alkyl carbon in sulphonates leading to a difference in the site of cleavage. More interestingly, phosphate esters lie somewhat in between carboxylates and sulphonates in that cleavage can occur in either direction.

In acidic solution, all the three types of phosphates (monoalkyl, dialkyl and trialkyl) are hydrolysed to phosphoric acid, while in basic solution only trialkyl phosphates undergo hydrolysis and only one alkoxy group is removed.

1. Which of the following factor explains the difference in attack of the nuceophile, \( \text{OH}^- \) on carboxylates and sulphonates?
   (a) sulphonate anions are weakly basic and hence good leaving groups.
   (b) Carboxylate anions are strongly basic and hence poor leaving groups
   (c) both (a) and (b)
   (d) None of the two

2. Competition between phosphorus and alkyl carbon to nucleophilic attack is due to the fact that
   (a) Phosphorus can accept an additional pair of electrons
   (b) Phosphoric acid lies between carboxylic acid and sulphonic acid
   (c) Both (a) and (b)
   (d) None of the two

3. The rate of hydrolysis of monoalkyl phosphates tends to ............ with increase in pH.
   (a) Decrease      (b) Increase
   (c) Remains unaffected      (d) None of these

4. In an aqueous solution, a monoalkylphosphate ester can exist as
   (a) A neutral ester
   (b) A monoanion and dianion
   (c) A monoanion, dianion and protonated ester
   (d) A monoanion, dianion, protonated ester and neutral ester

Write-up II

Menthanoic acid, the first member of carboxylic acid series, when warmed with concentrated sulphuric acid decompose in the following way and evolve carbon monoxide.

\[
\begin{align*}
\text{H} & \text{C} \text{O} \text{H}_2 \quad \text{H} \text{C} \text{OH}_2 \quad \text{H} \text{C} \text{O}^\circ \text{H}_2 \quad \text{H} \text{C} \text{O}^\circ \text{H}_2
\end{align*}
\]

The driving force for this reaction lies in the fact that the \( \text{HC} \equiv \text{O}^+ \) ion is very unstable acid and thus easily loses \( \text{H}^+ \).
5. Formic acid on heating with conc. H₂SO₄ gives
   (a) CO₂ + H₂  (b) CO + H₂O
   (c) CO        (d) H₂O

6. What happens when acetic acid is treated with conc. H₂SO₄?
   (a) CO + H₂O  (b) CH₄ + CO₂
   (c) CO + CH₄  (d) No reaction

7. If acetic acid is replaced by triphenylacetic acid, the products formed will be
   (a) (C₆H₅)₃CH + CO  (b) (C₆H₅)₃CH + CO₂
   (c) (C₆H₅)₃COH + CO  (d) No reaction

8. If formic acid is replaced by benzoyleformic acid, C₆H₅COCOOH the product formed will be
   (a) C₆H₅COOH + CO + CO₂  (b) C₆H₅COOH + CO₂
   (c) C₆H₅COOH + CO  (d) C₆H₅CHO + CO₂

Write-up III

Amides undergo hydrolysis to yield carboxylic acid plus amine on heating in either aqueous acid or aqueous base. The conditions required for amide hydrolysis are more severe than those required for the hydrolysis of esters, anhydrides or acid chlorides, but the mechanism is similar (nucleophilic acyl substitution). Nucleophilic acyl substitutions involve a tetrahedral intermediate, hence these are quite different from alkyl substitution (RCH₂Br → NaCN → RCH₂CN) which involves a pentavalent intermediate or transition state.

One of the important reactions of esters is their reaction with two equivalent of Grignard reagent to give tertiary alcohols.

9. The mechanism involved during the hydrolysis of acid derivatives is:
   (a) elimination-addition  (b) addition-elimination
   (c) nucleophilic addition elimination  (d) electrophilic addition elimination

10. Which of the following constitutes the best substrate during the acidic hydrolysis of amides?
    (a) O
        R—C—NH₂
        OH⁺
    (b) O
        R—C—NH₃
    (c) O
        R—C—NH₂
    (d) O
        R—C—NH₃

11. For which functional derivative of carboxylic acids, acidic hydrolysis is avoided?
    (a) Acid chlorides  (b) Acid amides
    (c) Acid anhydrides  (d) Esters

12. When is treated with two equivalent of methyl magnesium iodide and the product acidified the final product will be
Write-up IV

Compounds that contain two strong electron withdrawing groups on a carbon atom are more acidic than compounds without such groups and are easily converted to their enolate ion. These enolate ions act as stronger nucleophiles and also undergo nucleophilic addition as well as substitution.

\[ \text{if } G \text{ is leaving group} \]

\[
\begin{align*}
\text{Z} & \text{Z} + :B \rightarrow \text{BH} + \text{HC}^{-} \\
\text{HC}^{-} & \text{Z} + R^+G \rightarrow \text{Z} \text{R} \text{O}^{-} \text{G}^{-}
\end{align*}
\]

\[ \text{if } G \text{ is also alkyl group} \]

\[
\begin{align*}
\text{Z} & \text{Z} \text{O}^{-} \text{G} + \text{H}^{-} \rightarrow \text{Z} \text{OH} \text{R}^{-}
\end{align*}
\]

13. Predict the final product ‘B’ in the following sequence of reaction:

\[
\begin{align*}
\text{H}_2\text{C} & \text{O} \rightarrow \text{CH}_3 \rightarrow A \xrightarrow{\text{Al-Hg}} B:
\end{align*}
\]

(a) \[ \text{H}_2\text{C} \text{O} \text{CH}_3 \]

(b) \[ \text{H}_2\text{C} \text{O} \text{CH}_3 \]

(c) \[ \text{H}_2\text{C} \text{O} \text{CH}_3 \]

(d) \[ \text{H}_2\text{C} \text{O} \text{CH}_3 \]

14. Predict the product in the following reaction:

\[
\begin{align*}
1,6 - \text{dibromobutane} + \text{CH}_2(\text{COOEt})_2 \xrightarrow{\text{EtONa} \text{EtOH} \Delta} X \xrightarrow{\text{H}_2\text{O}^+} X
\end{align*}
\]

(a) \[ \text{HO} \text{CO}_2 \text{O} \text{HO} \]

(b) \[ \text{HO} \text{CO}_2 \text{O} \text{HO} \]

(c) \[ \text{COOH} \text{COOH} \]

(d) \[ \text{COOEt} \text{COOEt} \]
15. Predict the product:

\[
\begin{align*}
&\text{(a)} \quad \begin{array}{c}
\text{Cl} \\
\text{OMe}
\end{array} \\
&\text{(b)} \quad \begin{array}{c}
\text{Cl} \\
\text{OMe}
\end{array} \\
&\text{(c)} \quad \begin{array}{c}
\text{Cl} \\
\text{OMe}
\end{array} \\
&\text{(d)} \quad \begin{array}{c}
\text{Cl} \\
\text{OMe}
\end{array}
\end{align*}
\]

\[
\begin{align*}
\text{i) } & \quad \text{aq. OH} \\
\text{ii) } & \quad \text{CH Cl Y} \\
\end{align*}
\]

16. Predict the product Y:

\[
\begin{align*}
&\text{(a)} \quad \begin{array}{c}
\text{H}_3\text{C} \\
\text{O}
\end{array} \\
&\text{(b)} \quad \begin{array}{c}
\text{H}_3\text{C} \\
\text{O}
\end{array} \\
&\text{(c)} \quad \begin{array}{c}
\text{H}_3\text{C} \\
\text{O}
\end{array} \\
&\text{(d)} \quad \begin{array}{c}
\text{H}_3\text{C} \\
\text{O}
\end{array}
\end{align*}
\]

\[
\begin{align*}
\text{i) } & \quad \text{BuLi} \\
\text{ii) } & \quad \text{Me-Br EtOH}
\end{align*}
\]

\[
\begin{align*}
\text{H}_3\text{C}_2
\end{align*}
\]

\[
\begin{align*}
\text{N CH}_3
\end{align*}
\]

Write-up V

\[
\begin{align*}
\text{COOAg} \\
\text{CCl}_4
\end{align*}
\]

17. The rearrangement from C to D is called
   (a) Curtius   (b) Hoffmann
   (c) Beckmann   (d) Lossen

18. In C to D type of rearrangement, without any Catalyst following will undergo self rearrangement.
   (a) Oxime of cyclohexanone
   (b) Benzene sulphonic ester of oxime of benzo phenone
   (c) Oxime of aceto phenone
   (d) Oxime of acetone

19. From ‘B’ to ‘C’ can be brought up by following reagent
   (a) N\textsubscript{3}H   (b) PhSO\textsubscript{2}Cl
   (c) CH\textsubscript{2}N\textsubscript{2}   (a)NaN\textsubscript{3}

20. ‘D’ is
   (a) \textomega- Amino caproic acid   (b) Pentane 1, 5 dioic acid
   (c) Hexane 1, 6 dioic acid   (d) Perlon
SECTION – IV
Subjective Questions

LEVEL – I

1. Two isomeric carboxylic acids H and I, C₆H₈O₂, react with H₂/Pd giving compounds C₆H₁₀O₂. H gives a resolvable product and I gives a non-resolvable product. Both isomers can be oxidized to C₆H₅COOH. Give the structure of H and I.

2. Identify the products (A), (B), (C) and (D) in the following sequence:

\[
\begin{align*}
C_{15}H_{31}COOH & \xrightarrow{\text{LiAlH₄}} (A) \xrightarrow{\text{HCl}} (B) \xrightarrow{(i)\text{Mg, ether}} (C) \xrightarrow{(ii)\text{KMnO₄, conc. H}_2\text{SO}_4} (D)
\end{align*}
\]

3. A neutral liquid (Y) has the molecular formula C₆H₁₂O₂. On hydrolysis it yields an acid (A) and an alcohol (B). Compound (A) has a neutralization equivalent of 60. Alcohol (B) is not oxidized by acidified KMnO₄, but gives cloudiness immediately with Lucas reagent. What are (Y), (A) and (B) ?

4. Esterification does not take place in the presence of ethyl alcohol and excess of concentrated H₂SO₄ at 170°C. Explain.

5. Why does carboxylic acid functions as bases though weak ones?

6. Which ketone of the formula C₅H₁₀O will yield an acid on haloform reaction?

7. Highly branched carboxylic acids are less acidic than unbranched acids. Why?

8. A carboxylic acid does not form an oxime or phenyl hydrazone. Why?

9. Formic acid reduce Tollen’s reagent. Why?

10. The K₂ for fumaric acid is greater than maleic acid. Why.

LEVEL – II

1. Complete the following equations:

\[
\begin{align*}
i) \quad & \text{CH₃CH₂CH₂CH₂Br} \xrightarrow{\text{CN}^-} ? \xrightarrow{\text{H₂O/H}^+} ? \\
\text{H₂C} & \text{-C-} \text{Br + CN}^- \xrightarrow{\text{Cold conc. H}_2\text{SO}_₄} ? \xrightarrow{\text{HOH}} ? \xrightarrow{\text{SOCl₂}} ? \xrightarrow{\text{Mg, ether}} ? \xrightarrow{(i)\text{CO₂}} ? \xrightarrow{(ii)\text{H}^+} ? \\
\end{align*}
\]

2. Compound (A) C₅H₈O₂ liberated carbon dioxide on reaction with sodium bicarbonate. It exists in two forms neither of which is optically active. It yields compound (B) C₅H₁₀O₂ on hydrogenation. Compound (B) can be separated into two enantiomorphs. Write the structural formulae of (A) and (B) giving reason.

3. Give structures of compounds:

\[
\begin{align*}
\text{Acetylene} + \text{CH₃MgBr} & \xrightarrow{-\text{CH₄}} (G) \xrightarrow{\text{CO₂}} (H) \xrightarrow{\text{H₂O/H}^+} (I) (C₃H₂O₂) \\
\text{H₂O, H}_2\text{SO}_₄ & \xrightarrow{\text{H}_2\text{SO}_₄} (J) (C₃H₄O₃) \xrightarrow{\text{KMnO₄}} \text{CH₂(COOH)₂}
\end{align*}
\]
4. An ester $\text{C}_6\text{H}_{12}\text{O}_2$ was hydrolysed with water, an acid (A), and an alcohol (B), were obtained. Oxidation of (B) with chromic acid produced A. What is the structure of the original ester? Write equations for all the reactions.

5. Complete the following equation:
$$\text{RCO}_2\text{H} \xrightarrow{\text{SOCl}_2} ? \xrightarrow{\text{Na}_2}\text{D} \xrightarrow{\text{inert solvent}} ? \xrightarrow{\text{Hydrolysis}} ?$$

6. Acid halides of formic acid are unstable. Why?

7. What is the product of the following reaction?
$$\begin{align*}
\text{H}_3\text{C} &\xrightarrow{\text{(i) Silver oxide in aq. base}} \text{C} &\xrightarrow{\text{(ii) H}^+} \text{CHO} \\
\text{CH}_3 &\xrightarrow{\text{(iii) H}^+} \text{?}
\end{align*}$$

8. An unsaturated acid (A) of molecular formula $\text{C}_5\text{H}_6\text{O}_4$ eliminates $\text{CO}_2$ easily and gives another unsaturated acid (B) of formula $\text{C}_4\text{H}_6\text{O}_2$. By saturation with $\text{H}_2/\text{Pt}$ (B) gives butanoic acid. Neither (A) nor (B) shows cis-trans isomerism. What are (A) and (B)?

9. A pleasant smelling optically active ester (F) has M.W. = 186. It does not react with Br$_2$ in CCl$_4$. Hydrolysis of (F) gives two optically active compounds, (G) soluble in NaOH and (H). (H) gives a positive iodoform test and on warming with conc. $\text{H}_2\text{SO}_4$ gives (I) (Saytzeff-product) with no geometrical isomers. (H) on treatment with benzene sulfonyl chloride gives (J), which on treatment with NaBr gives optically active (K). When the Ag$^+$ salt of (G) is treated with Br$_2$ racemic (K) is formed. Give structures of (F) to (K) and explain your choices.

10. Two moles of an ester (A) are condensed in the presence of sodium ethoxide to give a β-keto ester (B) and ethanol. On heating in an acidic solution (B) gives ethanol and β-keto acid (C). On decarboxylation (C) gives 3-pentanone. Identify (A), (B) and (C) with proper reasoning. Name the reaction involved in the conversion of (A) to (B).

LEVEL – III (Judge yourself at JEE level)

1. Acetophenone on reaction with hydroxylamine-hydrochloride can produce two isomeric oximes. Write structures of the oximes.

2. An organic acid (A), $\text{C}_5\text{H}_{10}\text{O}_2$ reacts with Br$_2$ in the presence of phosphorus to give (B). Compound (B) contains an asymmetric carbon atom and yields (C) on dehydrobromination. Compound (C) does not show geometric isomerism and on decarboxylation gives an alkene (D) which on ozonolysis gives (E) and (F). Compound (E) gives a positive Schiff’s test but (F) does not. Give structures of (A) to (F) with reasons.

3. An liquid (X) having molecular formula $\text{C}_6\text{H}_{12}\text{O}_2$ is hydrolysed with water in presence of an acid to give a carboxylic acid (Y) and an alcohol (Z). Oxidation of (Z) with chromic acid gives (Y). What are (X), (Y) and (Z)?

4. An acidic compound (A), $\text{C}_4\text{H}_8\text{O}$ loses its optical activity on strong heating yielding (B). $\text{C}_4\text{H}_8\text{O}_2$ which reacts readily with KMnO$_4$. (B) forms a derivative (C) with SOCl$_2$, which on reaction with (CH$_3$)$_2$NH gives (D). The compound (A) on oxidation with dilute
chromic acid gives an unstable compound (E) which decarboxylates readily to give (F), C₃H₆O. The compound (F) gives a hydrocarbon (G) on treatment with amalgamated Zn and HCl. Give structures of (A) to (G) with proper reasoning.

5. The sodium salt of a carboxylic acid, (A) was produced by passing a gas (B) into aqueous solution of caustic alkali at an elevated temperature and pressure (A) on heating in presence of sodium hydroxide followed by treatment with sulphuric acid gave a dibasic acid (C). A sample of 0.4g of (C) on combustion gave 0.08 g of H₂O and 0.39 g of CO₂. The silver salt of the acid, weighing 1.0 g, on ignition yielded 0.71 g of Ag as residue. Identify (A), (B) and (C).

6. An organic compound (A) on treatment with ethyl alcohol gives a carboxylic acid (B) and compound (C). Hydrolysis of (C) under acidic conditions gives (B) and (D). Oxidation of (D) with KMnO₄ also gives (B). (B) on heating with Ca(OH)₂ gives (E) (Molecular formula C₃H₆O) (E) does not gives Tollen’s test and does not reduce Fehling solution but forms 2, 4–dinitrophenylhydrazone. Identify (A) to (E).

7. Two mole of an ester (A) are condensed in presence of sodium ethoxide to give a B-keto ester (B) and ethanol. On heating in an acidic solution (B) gives ethanol and aβ-keto acid (C). On decarboxylation (C) gives 3-pentanone. Identify (A), (B) and (C) with proper reasoning and give reactions.

8. Compound (A) (C₆H₁₂O₂) on reduction with LiAlH₄ yielded two compounds (B) and (C). The compound (B) on oxidation gave (D). 2 moles of (B) on treatment with alkali (aqueous) and subsequent heating furnished (E). The later on catalytic hydrogenation gave (C). The compound (D) was oxidized further to give (F) which was found to be monobasic acid (m.wt.60.0). Deduce structures of (A) to (E).

9. Compound (A) C₅H₈O₂ liberated CO₂ on reaction with sodium bicarbonate. It exists in two forms neither of which is optically active. It yielded compound (B), C₅H₁₀O₂ on hydrogenation. Compound (B) can be separated into enantimorphs. Write structures of (A) and (B).

10. An organic compound (A) on treatment with acetic acid in presence of sulphuric acid produces an ester (B). (A) on mild oxidation gives (C). (C) with 50% KOH followed by acidification with dilute HCl generates (A) and (D). (D) with PCl₅ followed by reaction with ammonia gives (E). (E) on dehydration produces hydrocyanic acid. Identify (A) to (E).

SECTION – V

Miscellaneous Questions

The following questions (to) consists of two statements, one labelled as ASSERTION (A) and REASON (R). Use the following key to chose the correct appropriate answer.
(a) If both (A) and (R) are correct, and (R) is the correct explanation of (A).
(b) If both (A) and (R) are correct, but (R) is not the correct explanation of (A).
(c) If (A) is correct, but (R) is incorrect.
(d) If (A) is incorrect, but (R) is correct.

1. **Assertion:** Acetic acid does not undergo haloform reaction.
   **Reason:** Acetic acid has no alpha hydrogens.
True / False type questions

2. Hydrolysis of an ester in the presence of a dilute acid is known as saponification.

3. The boiling point of propionic acid is more than that of n-butyl alcohol, an alcohol of comparable molecular weight.

4. Read the following statement and explanation and answer as per the options given below:
   **Statement:** acetate ion is more basic than the methoxide ion.
   **Explanation:** The acetate ion is resonance stabilized.
   (a) Both S and E are true and E is the correct explanation of S.
   (b) Both S and E are true but E is not the correct explanation of S.
   (c) S is true but E is false
   (d) S is false but E is true
Answers to Assignments

SECTION - I

| 1. (c) | 6. (a) | 11. (b) | 16. (a) | 21. (d) |
| 2. (b) | 7. (a) | 12. (c) | 17. (c) | 22. (c) |
| 3. (d) | 8. (a) | 13. (b) | 18. (a) | 23. (c) |
| 4. (a) | 9. (c) | 14. (c) | 19. (a) | 24. (a) |
| 5. (c) | 10. (c) | 15. (a) | 20. (a) | 25. (a) |

SECTION - II

| 1. (b) | 8. (c) | 15. (d) | 22. (a), (b), (c) |
| 2. (a) | 9. (a) | 16. (b) | 23. (d) |
| 3. (b) | 10. (c) | 17. (c) | 24. (c), (d) |
| 4. (c) | 11. (b) | 18. (c) | 25. (a), (d) |
| 5. (a) | 12. (b) | 19. (d) |
| 6. (c) | 13. (d) | 20. (b) |
| 7. (a) | 14. (c) | 21. (b) |

SECTION - III

| 1. (c) | 6. (d) | 11. (a) | 16. (c) |
| 2. (a) | 7. (c) | 12. (b) | 17. (c) |
| 3. (a) | 8. (c) | 13. (c) | 18. (b) |
| 4. (d) | 9. (c) | 14. (b) | 19. (a) |
| 5. (b) | 10. (c) | 15. (d) | 20. (a) |

SECTION - IV

LEVEL – I

1. The uptake of 2 H atoms shows the presence of one >C = C< along with C₆H₅— and —COOH, which accounts for the 6° unsaturation. Furthermore H and I are monosubstituted benzene derivatives. H is C₆H₅ – C(COOH) = CH₂ giving H₃C.CHC₆H₅COOH with one asymmetric carbon atom. I is C₆H₄CH = CH.COOH, giving C₆H₄CH₂CH₂COOH with no asymmetric carbon.

\[
\text{H}_3\text{C} \text{CH} = \text{CH} \text{COOH} \xrightarrow{\text{Pd}} \text{H}_3\text{C} \text{CH} = \text{CH} \text{CH}_2\text{COOH}
\]

2. (A) = C₁₅H₃₁CH₂OH, (B) = C₁₅H₃₁CH₂Cl, (C) = C₁₅H₃₁CH₂CH₂CH₂OH, (D) = C₁₅H₃₁CH₂CH₂CH₂COOH.
3. (Y) is an ester because it is hydrolysed to acid and alcohol. Since the alcohol is not oxidized by acidified KMnO₄ and gives cloudiness at once with Lucas reagent, hence it is a t-alcohol.

\[
\begin{align*}
\text{HOH} & \xrightarrow{\text{HOH}} \text{CH}_3\text{COCC}_3\text{H}_3 \quad \text{(Y)} \\
\text{CH}_3 & \xrightarrow{\text{HOH}} \text{H}_3\text{C-C-OH} + \text{CH}_3\text{C-OH} \\
\text{(A)} & \quad \text{(B)}
\end{align*}
\]

4. This is because C₂H₅OH undergoes dehydration to form C₂H₄ at 170°C in presence of excess of conc. H₂SO₄.

\[
\text{CH}_3\text{CH}_2\text{OH} \xrightarrow{\text{H}_2\text{SO}_4 \text{ (conc.)}} \xrightarrow{170^\circ\text{C}} \text{H}_2\text{O} + \text{CH}_2 = \text{CH}_2
\]

5. In the presence of strong acids, the H⁺ is captured by the carboxylic acid and the following equilibrium is established:

\[
\begin{align*}
\text{R-C-} & \xrightarrow{\text{H}_2\text{SO}_4} \text{R-C-} \\
\text{OH} & + \text{H}_2\text{SO}_4 & \text{OH} & + \text{H}_2\text{SO}_4
\end{align*}
\]

6. 

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

7. It is because the carboxylate group (—COO⁻) of the branched acid is more shielded from the solvent molecules, therefore, it cannot be stabilized effectively by solvation.

8. It is because carboxylic group does not have a true carbonyl group due to resonance.

\[
\text{Due to resonance } >\text{C} = \text{O} \text{ bond of } —\text{COOH } \text{develops partial double bond character and cannot show reactions with hydroxylamine, phenyl hydrazine, etc.}
\]

9. It is because formic acid combines the properties of both an aldehyde and an acid.

\[
\text{Aldehyde}
\]

\[
\text{HCOOH} + 2[\text{Ag(NH}_3)_2]^+\text{OH}^- \xrightarrow{\Delta} \text{HCOONH}_4 + 3\text{NH}_3 + \text{H}_2\text{O} + 2\text{Ag} \downarrow
\]

or 

\[
\text{HCOOH} + \text{Ag}_2\text{O} \xrightarrow{} \text{CO}_2 + \text{H}_2\text{O} + 2\text{Ag} \downarrow
\]

10. Both these unsaturated acids have two ionisable hydogens. After the release of first hydrogen, second hydrogen of maleate ion is involved in H-bonding, whereas no H-bonding is possible in fumarate ion.
Due to the formation of H-bond in maleate ion more energy is required to remove $\text{H}^+$ from it than from fumarate ion, in which $\text{H}^+$ release is easy comparatively. Thus, K₂ for fumaric acid is more than maleic acid.

**LEVEL – II**

1. i) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br} \xrightarrow{\text{CN}^-/\text{H}^+} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CN}$

   $\xrightarrow{\text{21OH}^-/\text{H}^+} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}$

   (n-Pentanoic acid)

   ii)

   $\text{H}_3\text{C} \xrightarrow{\text{CN}/\text{H}^-} \text{H}_3\text{C} \xrightarrow{\text{H}_2\text{SO}_4/\text{H}_2\text{O}} \text{H}_3\text{C} \xrightarrow{\text{HOH}} \text{H}_3\text{C} \xrightarrow{\text{MgCl}_2/\text{Et}_2\text{O}} \text{H}_3\text{C} \xrightarrow{\text{CO}_2/\text{H}_2\text{O}} \text{H}_3\text{C} \xrightarrow{\text{MgBr}_2} \text{H}_3\text{C} \xrightarrow{\text{H}_2\text{SO}_4/\text{H}_2\text{O}} \text{H}_3\text{C} \xrightarrow{\text{Cl}} \text{H}_3\text{C} \xrightarrow{\text{CH}_3\text{COOH}}$

2. (A) Geometrical isomers

   C₃H₅—C—COOH or HOOC—C—C₃H₅

   (B)

3. $\text{H} \xrightarrow{H^+} \text{H} \xrightarrow{\text{H}_2\text{SO}_4/\text{H}_2\text{O}} \text{H} \xrightarrow{\text{CO}_2/\text{H}_2\text{O}} \text{H} \xrightarrow{\text{Kmno}_4} \text{H}_2\text{C} \xrightarrow{\text{COOH}}$

4. $\text{CH}_3\text{CH}_2\text{C—OCH}_2\text{CH}_2\text{CH}_3 \xrightarrow{\text{H}_2\text{O}/\text{H}^+} \text{CH}_3\text{CH}_2\text{COOH} + \text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$

   $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \xrightarrow{\text{Chromic acid}} \text{CH}_3\text{CH}_2\text{CHO} \xrightarrow{\text{H}_2\text{SO}_4/\text{H}_2\text{O}} \text{CH}_3\text{CH}_2\text{COOH}$
5. \[ \text{RCO}_2\text{H} \xrightarrow{\text{SOCl}_2} \text{RCOCl} \xrightarrow{\text{NaN}_3} \text{RCON}_3 \xrightarrow{\text{D}} \text{RNCO} \xrightarrow{\text{Hydrolysis}} \text{RNH}_2 \]

6. \( \text{C} = \text{O} \) bond is very stable due to large \( \Delta H_f \) of CO; so the decomposition reaction
\[ \text{H} \xrightarrow{} \text{C} = \text{Cl} \xrightarrow{} \text{C} = \text{O} + \text{HCl} \] is favoured. Formly chloride is not stable above \(-60^\circ\text{C}\).

7. An extremely mild but selective oxidizing agent for aldehydes is silver oxide suspended in aqueous base. An unsaturated acid is obtained with this reagent because the \( >\text{C} = \text{C}< \) remains untouched by this reagent.

8. \[ \text{C}_5\text{H}_6\text{O}_4 \xrightarrow{\Delta} \text{C}_4\text{H}_6\text{O}_2 \xrightarrow{\text{B}_2} \text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} \]
\[ \text{H}_2\text{C} \xrightarrow{\Delta} \text{CH}_2 = \text{CH} \xrightarrow{\text{B}_2/\text{Ni}} \text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} \]

9. Is a saturated monoester with M.W = 186
\[ \text{F} = \text{H}_3\text{C} \xrightarrow{\text{CH}_3} \text{O} \xrightarrow{\text{CH}_3} \text{OH} \]
\[ \text{H} = \text{H}_3\text{C} \xrightarrow{\text{CH}_3} \text{O} \xrightarrow{\text{CH}_3} \text{OH} \]
\[ \text{J} = \text{H}_3\text{C} \xrightarrow{\text{OSO}_2\text{C}_6\text{H}_5} \text{CH}_3 \]
\[ \text{G} = \text{H}_3\text{C} \xrightarrow{\text{H}_3} \text{OH} \]
\[ \text{I} = \text{H}_3\text{C} \xrightarrow{\text{Br}} \text{CH}_3 \]
\[ \text{K} = \text{H}_3\text{C} \xrightarrow{\text{Br}} \text{CH}_3 \]

10. (A) \( \text{C}_2\text{H}_5\text{COOC}_2\text{H}_5 \)  (B) \( \text{C}_2\text{H}_5\text{CO}-(\text{CH}_2\text{H}_3)\text{COOC}_2\text{H}_5 \)
(C) \( \text{C}_2\text{H}_5\text{COCH}(\text{CH}_3)\text{COOH} \)

---

**LEVEL – III**

1. \[ \text{H}_5\text{C}_6 \xrightarrow{\text{NH}_2\text{OH}} \text{H}_3\text{C} \xrightarrow{\text{B}} \text{H}_5\text{C}_6 \]
\[ \text{N} \xrightarrow{\text{OH}} \text{N} \xrightarrow{\text{OH}} \text{OH} \]
\[ \text{ syn } \] and  \[ \text{ anti (isomers) } \]
2. A = \begin{align*}
&\text{H}_3\text{C} \\
&\text{H}_3\text{C} \\
&\text{OH}
\end{align*}

B = \begin{align*}
&\text{H}_3\text{C} \\
&\text{H}_3\text{C} \\
&\text{O} \\
&\text{Br}
\end{align*}

C = \begin{align*}
&\text{H}_3\text{C} \\
&\text{H}_3\text{C} \\
&\text{OH}
\end{align*}

D = \begin{align*}
&\text{H}_3\text{C} \\
&\text{H}_3\text{C}
\end{align*}

E = HCHO

3. X = \begin{align*}
&\text{H}_3\text{C} \\
&\text{O} \\
&\text{CH}_3
\end{align*}

propyl propionate

Y = \begin{align*}
&\text{H}_3\text{C} \\
&\text{O} \\
&\text{OH}
\end{align*}

propionic acid

Z = \begin{align*}
&\text{H}_3\text{C} \\
&\text{OH}
\end{align*}

propan-1-ol

4. A = \begin{align*}
&\text{H}_2\text{O} \\
&\text{CH}_3 \\
&\text{O}
\end{align*}

B = \begin{align*}
&\text{H}_2\text{OH} \\
&\text{O} \\
&\text{CH}_3
\end{align*}

C = \begin{align*}
&\text{H}_2\text{Cl} \\
&\text{O} \\
&\text{O}
\end{align*}

D = \begin{align*}
&\text{D} \\
&\text{N}
\end{align*}

E = \begin{align*}
&\text{H}_3\text{C} \\
&\text{O} \\
&\text{O}
\end{align*}

F = \begin{align*}
&\text{H}_3\text{C} \\
&\text{O}
\end{align*}

G = \begin{align*}
&\text{H}_3\text{C} \\
&\text{CH}_3
\end{align*}

5. (A) HCOOH  (B) CO  (C) COOH.CO OH

6. (A) (CH₃CO)₂O (Acetic anhydride)
    (B) CH₃COOH (Ethanoic acid)
    (C) CH₃COOC₂H₅ (Ethyl ethanoate)
    (D) C₃H₅ OH (Ethanol)
    (E) CH₃COCH₃

7. (A) CH₃CH₂COOC₂H₅ (Ethyl propanoate)
    (B) CH₃.CH₂.CO.CH.COOC₂H₅ (Ethyl (2-methyl, 3-ketopentanoate)
    \begin{align*}
    &\text{CH}_3
    \end{align*}
    (C) CH₃.CH₂.CO.CH.COOC₂H₅ (2-methyl, 3-ketopentanoic acid)
    \begin{align*}
    &\text{CH}_3
8. 
(A) CH₃CH₂CH₂CH₂OOCCH₂CH₃ or CH₃COOCH₂CH₂CH₂CH₃ 
(B) C₂H₅OH 
(C) CH₃CH₂CH₂CH₂OH 
(D) CH₃CHO 
(E) CH₃CH==CH.CHO 
(F) CH₃COOH 

9. 
(A) \[
\begin{array}{c}
\text{CH₃–C–COOH} \\
\text{CH₃–C–H} \\
\text{Cis}
\end{array}
\quad \begin{array}{c}
\text{CH₃–C–COOH} \\
\text{H–C–CH₃} \\
\text{Trans}
\end{array}
\]

(B) \[
\begin{array}{c}
\text{CH₃CH₂C*–COOH} \\
\text{CH₃}
\end{array}
\] (2-methylbutanoic acid) 

10. 
A = CH₂OH (Methanol) 
B = CH₃COCH₃ (Methyl ethanoate) 
C = HCHO (Methanal) 
D = HCOOH (Methanoic acid) 
E = HCONH₂ (Formamide or methanamide) 

SECTION - V 

1. (c) 
2. False 
3. True 
4. (d)