Aldehydes, Ketones and Carboxylic Acids

 Acetic acid is dissolved in water having oxygen as ¹⁸O. How many ¹⁸O atom will be present in the product molecule?

2.
$$OMe \xrightarrow{(i) \text{ H}^+\text{H}_2\text{O}} Z.$$

$$COOC_2\text{H}_5$$

How many number of sp^2 hybridised carbon atoms are there in the product Z.

3. How many membered ring will be formed in the product P of the following reaction.

$$OH \xrightarrow{(i) \text{ NaBH}_4} F$$

4. Compound A is obtained by following reaction.

$$CH_3COOC_2H_5 \xrightarrow{\quad (i) C_2H_5ONa \\ \quad (ii) H_3O^+ } [A]$$

How many following statement(s) is(are) true about A?

- (i) It gives red colour with blue litmus solution.
- (ii) It decomposes NaHCO₃ solution and evolves CO₂ gas.
- (iii) It decolourises bromine water colour.
- (iv) It reacts with 2,4-dinitrophenyl-hydrazine
- (v) Product A will undergo acid catalysed halogenation.
- 5. How many of the following compound is decarboxylated on heating?

(I)
$$\begin{array}{c} \text{CH}_2\text{COOH} \\ | \\ \text{CH}_2\text{COOH} \end{array}$$

(II) $C_2H_5CH(COOH)_2$

- **6.** How many of the following compounds can be used as an acylating agent?
 - (I) CH₃COCl
- (II) (CH₃CO)₂O
- (III) CH₂COOH
- (IV) CH₂CH₂COCl.
- 7. In the scheme given below, how many number of intramolecular aldol condensation products formed from 'Y'?

$$\begin{array}{c}
1. O_3 \\
2. Zn, H_2O
\end{array}$$
Y
$$\begin{array}{c}
1. \text{NaOH (aq)} \\
2. \text{heat}
\end{array}$$

8. Among the following, how many number of reaction(s) produce(s) benzaldehyde?

II.
$$\frac{\text{CHCl}_2}{\frac{\text{H}_2\text{O}}{100^{\circ}\text{C}}}$$

III.
$$\frac{H_2}{Pd-BasO_4}$$

$$\text{IV.} \qquad \xrightarrow{\begin{array}{c} \text{CO}_2\text{Me} \\ \text{--} & \text{DIBAL-H} \\ \text{--} & \text{Toluene,-78°C} \\ \text{--} & \text{--} & \text{--} \\ \text{--} & \text{--} \\ \text{--} & \text{--} \\ \text{--} & \text{--} & \text{--} \\ \text{--} & \text{--} & \text{--} \\ \text{--}$$

9. Find the number of reactants among the given options which does not undergo Michael addition?

(I)
$$C_6H_5CH = CHCOCH_3 + C_6H_5COCH_3$$

(II)
$$C_6H_5CH = CHCH_2COC_6H_5 + CH_2(COOC_2H_5)_2$$

(III)
$$+$$
 Br $-$ COCH = CH $-$ COCH

(IV)
$$CH_2 = CHCOCH_3 + CH_3COCH_3$$

10. How many number of aldol reaction(s) occurs in the given transformation?

$$CH_3CHO + 4HCHO \xrightarrow{conc. aq. NaOH} HO \xrightarrow{OH} OH$$

11. How many number of organic compounds among the following compounds are present in the reaction mixture after the completion of reactions I and II?

Reaction I:
$$H_3C$$
 CH_3
 CH_3
 CH_3
 CH_3
 CH_3
 CH_3
 CH_3
 CH_3
 CH_3
 CH_3

Reaction II:
$$H_3C$$
 CH_3
 CH_3
 CH_3COOH

$$H_3C$$
 CH_2Br
 CH_3C
 CBr_3
 CBr_3
 CBr_3
 CBr_3

12. Find the total number of product in the given reaction.

$$\overbrace{ \begin{array}{c} \text{i. KOH, H}_2\text{O} \\ \hline \\ \text{ii. H}_{+}^{+} \text{ heat} \end{array} }^{\text{i. KOH, H}_2\text{O}}$$

13. How many steps are there in the mechanism of the following reaction?

- 14. An unknown compound of carbon, hydrogen and oxygen contains 69.77% carbon and 11.63% hydrogen and has a molecular weight of 86. It does not reduce Fehling solution, but forms a bisulphite addition compound and gives a positive iodoform test. How many possible structures can be drawn for the unknown compound?
- **15.** How many total number of ketonic groups are present in compound C and D in the given reaction sequence?

$$\begin{array}{c}
O \\
\hline
C_6H_5CHO \\
\hline
Base
\end{array}
C \xrightarrow{(i) LiAlH_4} D$$

SOLUTIONS

1. (2)
$$CH_3 - C - OH \xrightarrow{H_2O^{18}} CH_3 - C - OH \longrightarrow \\ _{18}O^+H_2$$

$$\xrightarrow{\text{H}_2\text{O}^{18}} \text{CH}_3 \xrightarrow{\text{C}} \text{C} \xrightarrow{\text{O}} \text{H} \xrightarrow{\text{O}} \text{CH}_3 \xrightarrow{\text{C}} \text{C} \xrightarrow{\text{O}} \text{H}$$

2. (1)
$$OMe \xrightarrow{H^+/H_2O} OH \xrightarrow{OH} OH COOH$$

COOH
$$\beta$$
-Keto acid

Remember that β -keto acids undergo decarboxylation on heating.

3. (5)

$$\begin{array}{c}
O \\
O \\
O
\end{array}$$

$$\begin{array}{c}
O \\
O \\
O
\end{array}$$

$$\begin{array}{c}
O \\
O \\
O
\end{array}$$

A γ-hydroxy acid

$$\xrightarrow{\text{H}_3\text{O}^+} \xrightarrow{\text{cyclisation}}$$

4. (4) (I),(III),(IV),(V)

$$CH_3-C-OC_2H_5 \longrightarrow$$

$$\begin{array}{c|c}
O & O^{-} \\
\parallel & | & | \\
-CH_{2} - C - OC_{2}H_{5} \longleftrightarrow CH_{2} = C - OC_{2}H_{5} \\
More stable
\end{array}$$

$$\begin{array}{c} \text{OH} \\ | \\ -\text{H}^+ \\ \text{OH}_2 = \text{C} \\ -\text{OC}_2 \text{H}_5. \end{array}$$

- (3) Dicarboxylic acids having two—COOH groups on the same carbon atom; and β-keto acids are easily decarboxylated on heating.
- 6. (3) Stronger the basic nature of the leaving group, weaker will be its leavability. In CH₃COOH, OH⁻ is a strong base so it can't be removed easily to form CH₃CO required for acetylation (acylation).

7. (1)
$$\underbrace{\begin{array}{c} 1. O_3 \\ 2. Zn, H_2O \end{array}} \xrightarrow{NaOH(aq)}$$

$$\begin{array}{c}
OH \\
-H_2O
\end{array}$$

$$\overbrace{\text{CHCl}_2} \xrightarrow{\text{CHCl}_2} \overbrace{\text{CH}}^{\text{OH}}$$

$$\xrightarrow{-\text{H}_2\text{O}} \text{CHC}$$

9. (2) (II) does not have α , β -unsaturated carbonyl group, while (IV) can't form stable carbanion (from acetone). Remember that cyclopentadiene is quite acidic in nature, because its carbanion is stable due to presence

of conjugated system; hence it functions as the nucleophile required in Michael reaction.

10. (3)
$$^{\alpha}$$
 CH₃ – CHO + HCHO $\xrightarrow{\text{OH}}$ 1st aldol condensation

$$\begin{array}{c} \alpha \\ \mathrm{CH_2-CHO} \\ | \\ \mathrm{CH_2-OH} \end{array} \xrightarrow[\begin{array}{c} \mathrm{OH^-/HCHO} \\ \mathrm{2nd\ aldol} \\ \mathrm{condensation} \end{array} \rightarrow \begin{array}{c} \mathrm{CH_2-OH} \\ \mathrm{CH} - \mathrm{CHO} \\ \mathrm{CH_2-OH} \end{array}$$

$$\frac{\text{OH}^{-}/\text{HCHO}}{\text{3rd aldol} \atop \text{condensation}} + \text{HOCH}_{2} - C - \text{CHO}_{2}$$

$$CH_{2}\text{OH}$$

$$CH_{2}\text{OH}$$

$$\begin{array}{c} \text{CH}_2\text{OH} \\ \text{HOCH}_2 - \begin{array}{c} \text{C} - \text{CH}_2\text{OH} \\ \text{C} - \text{CH}_2\text{OH} \end{array} \\ \begin{array}{c} \text{Cannizzaro} \\ \text{reaction} \end{array}$$

11. (3) Reaction I :
$$CH_3$$
 CH_3 $Br_2(1.0 \text{ mol})$ Na^+OH^-

$$CH_3COONa + CHBr_3 + CH_3 +$$

$$\begin{array}{c} \text{Reaction II}: & \overset{O}{\underset{\text{CH}_{3}}{\bigcup}} & \overset{\text{Br}_{2}(1.0\,\text{mol})}{\underset{\text{CH}_{3}\text{COOH}}{\bigcup}} & \overset{O}{\underset{\text{CH}_{2}\text{Br}}{\bigcup}} & \\ 1.0\,\text{mol} & & & & & & \\ \end{array}$$

12. (2)

$$CH_3 \xrightarrow{KOH, H_2O} CO$$

$$\longrightarrow \bigcup_{\text{(Minor)}}^{\text{CH}_3} \bigcirc \bigcup_{\text{(Major)}}^{\text{CH}_3} \bigcirc \bigcup_{\text{(Major)}}^{\text$$

13. (3)
$$CH_3COCI + AlCl_3 \xrightarrow{step1} CH_3C^+ = O + AlCl_4^-$$

14. (2) Empirical formula can be calculated as

Acetophenone

Element	Percentage	Relative no. of atoms	Simplest ratio
H	11.63	11.63	10
O	18.60	1.16	1

Empirical formula of compound is C₅H₁₀O and empirical formula wt. = 86.

Also molecular wt. = 86.

- ∴ Molecular formula of compound is C₅H₁₀O.
- (ii) Compound forms bisulphite addition compound and thus has carbonyl gp, *i.e.* aldehyde or ketone.
- (iii) It does not reduce Fehling solution and thus it is not an aldehyde but a ketone.
- (iv) It gives positive iodoform test and thus it has unit,

(v) Above facts reveal that the compound is CH₃CH₂CH₂COCH₃ or (CH₃)₂CHCOCH₃ pentan-2-one 3-methylbutan-2-one

15. (1)
$$C_6H_5CHO$$

Base

(C)

 CHC_6H_5

(C)

 CHC_6H_5

(C)

 CHC_6H_5

(D)

There is only one ketonic group in C and zero ketonic group in D.