Chapter 13

Aldehydes, Ketones and Carboxylic Acids

Solutions (Set-1)

Very Short Answer Type Questions:

1. What product is formed when CH₃COOH reacts with PCI₅?

Sol.
$$CH_3COOH \xrightarrow{PCl_5} CH_3COCI + POCl_3 + HCI$$

Sol. 2-Methylcyclohexanone.

Write chemical equation for the following chemical reactions:
 Benzonitrile is converted to benzophenone.

Sol.
$$\bigcirc$$
 Ph—C=N.MgBr COPh
+ PhMgBr \longrightarrow \bigcirc + Mg \bigcirc Rr
NH

4. Draw the structural formula of Hex-2-en-4-ynoic acid.

Sol.
$$CH_3 - C = C - CH = CH - C - OH$$

- 5. Give one chemical test to distinguish between acetaldehyde and benzaldehyde.
- Sol. Acetaldehyde gives positive iodoform reaction while benzaldehyde does not.
- 6. How are formalin and trioxane related to methanal?
- **Sol.** Formalin is 40% aqueous solution of HCHO and trioxane is a trimer of HCHO.
- 7. How can we distinguish formic acid and acetic acid chemically?
- Sol. Formic acid gives silver mirror with Tollen's reagent while acetic acid does not give this test.

8. How can we obtain Propan-2-ol from ethanal?

9. What product is obtained when CH₃COOH reacts with PCI₅?

Sol.
$$CH_3COOH + PCI_5 \longrightarrow CH_3COCI + POCI_3 + HCI$$

Short Answer Type Questions:

11. Arrange the following compounds in increasing order of their boiling points:

Sol. All have comparable molecular masses so deciding factor is their intermolecular forces of interaction, which are strongest in alcohol and weakest in alkane. Therefore

$$\mathsf{CH_3}(\mathsf{CH_2})_3 \mathsf{CH_3} < \mathsf{C_2H_5} - \mathsf{O} - \mathsf{C_2H_5} < \mathsf{CH_3CH_2CH_2CHO} < \mathsf{CH_3}(\mathsf{CH_2})_2 \mathsf{CH_2OH}$$

12. Complete the following equations:

(i)
$$OOOH \xrightarrow{SO_3/H_2SO_4}$$

(ii)
$$CH_3CONH_2 + HNO_2 \longrightarrow$$

(iii)
$$CH_3CHO + C_6H_5NHNH_2 \longrightarrow$$

(ii)
$$CH_3COOH + N_2 + H_2O$$

(iii)
$$CH_3CH = N - NH - C_6H_5 + H_2O$$

acetaldehydephenylhydrazone

- 13. Describe the following reactions:
 - (i) Cannizzaro reaction
 - (ii) Cross aldol reaction
- **Sol.** (i) **Cannizzaro reaction**: Aldehydes which do not contain any α -H atom undergo disproportionation on treatment with conc. alkali in which one molecule is oxidised and another is reduced.

Ex.
$$H$$
 C=0 + C=0 + conc. KOH \longrightarrow CH₃OH + HCOOK

(ii) **Cross Aldol condensation**: When aldol condensation is carried out between two different aldehydes or ketones both containing α -H atom, it is Cross Aldol condensation.

$$CH_{3}CHO + CH_{2}CHO \xrightarrow{dil.} OH \\ CH_{3}-CH-CH_{2}CHO \\ OH \\ CH_{3}-CH-CH-CHO \\ CH_{3} \\ OH \\ CH_{3}CH_{2}-CH-CHO \\ CH_{3} \\ OH \\ CH_{3}CH_{2}-CH-CHO \\ CH_{3} \\ OH \\ CH_{3}CH_{2}-CH-CHO \\ CH_{3} \\ OH \\ CH_{3}CH_{2}-CH-CH_{2}CHO \\ CH_{3}-CH-CH_{2}-CH$$

- 14. Write reactions with conditions for following conversions:
 - (i) Methylbromide to acetic acid
 - (ii) Benzene to toluene

Sol. (i)
$$CH_3Br + KCN(aq) \longrightarrow CH_3CN \xrightarrow{H_2O/H^+} CH_3COOH$$

(ii)
$$\bigcirc$$
 + CH₃Cl $\xrightarrow{\text{anh. AICl}_3}$ \bigcirc CH₃

- 15. Account for the following observations:
 - (i) Oxidation of toluene to benzaldehyde with CrO₃ is carried out in presence of acetic anhydride.
 - (ii) Melting point of an acid with even number of carbon atom is higher than those of its neighbours with odd number of carbon atoms.
- **Sol.** (i) Acetic anhydride is used to stop the reaction at benzaldehyde otherwise the end product must be benzoic acid.
 - (ii) Acids with even no. of carbon atoms fit into crystal lattice more readily than odd ones, hence they have higher lattice energy and higher melting point.
- 16. How can you convert?
 - (i) Acetaldehyde to acetone
 - (ii) Acetylene to acetone

$$\textbf{Sol.} \hspace{0.1cm} \text{(i)} \hspace{0.5cm} \text{CH}_{3} \text{CHO} \xrightarrow{\text{KMnO}_{4}/\text{H}^{+}} \text{CH}_{3} \text{COOH} \xrightarrow{\text{Ca(OH)}_{2}} \text{(CH}_{3} \text{COO)}_{2} \text{Ca} \xrightarrow{\text{dry}} \text{CH}_{3} \text{COCH}_{3} + \text{CaCO}_{3} \text{COOH}_{3} + \text{CaCO}_{3} + \text{CaCO$$

(ii)
$$HC \equiv CH + NaNH_2 \longrightarrow CH \equiv C \longrightarrow Na \xrightarrow{CH_3CI} HC \equiv C \longrightarrow CH_3 \xrightarrow{H_2O/HgSO_4, H_2SO_4} CH_3 \longrightarrow C \longrightarrow CH_3$$

- 17. Arrange the following in order of increasing boiling points:
 - (i) $C_2H_5OC_2H_5$, C_4H_9COOH , C_4H_9OH
 - (ii) C₃H₇CHO, CH₃COC₂H₅, C₂H₅COOCH₃, (CH₃CO)₂O
- **Sol.** (i) $C_2H_5OC_2H_5 < C_4H_9OH < C_4H_9COOH$
 - (ii) $C_3H_7CHO < CH_3COC_2H_5 < C_2H_5COOCH_3 < (CH_3CO)_2O$

- 18. State reasons for the following:
 - Monochloroethanoic acid is a weaker acid than dichloroethanoic acid.
 - Benzoic acid is a stronger acid than ethanoic acid. (ii)

Sol. (i)
$$\begin{array}{c} \text{CI} \leftarrow \text{CH}_2 - \text{C} - \text{OH} < \text{CI} \leftarrow \text{CH} - \text{COOH} \\ \downarrow \\ \text{CI} \end{array}$$

Presence of -I effect and EWG increases the H+ releasing tendency of carboxylic acid.

Benzene ring withdraws electrons towards itself due to resonance and increases its acidic strength while —CH₃ group is electron releasing which decreases its acidic strength.

- How will you obtain an aldehyde by using following process? 19. (a)
 - (i) Dehydrogenation
 - (ii) Catalytic hydrogenation
 - Why do aldehydes behave like polar compounds?

Sol. (a) (i)
$$R - CH_2OH \xrightarrow{Cu} R - CHO + H_2$$

(ii)
$$R - COCI + H_2 \xrightarrow{Pd. BaSO_4} R - CHO + HCI$$

- (b) Due to presence of \supset C=O *i.e.*, carbonyl group aldehyde molecules are polar.
- How will you do the following conversions in not more than two steps?
 - (i) Propanal to butanone
 - (ii) Propanoyl chloride to dipropylamine
 - (iii) Propanoic acid to propenoic acid

$$\text{(ii)} \quad \text{CH}_{3}\text{CH}_{2}\text{COCI} \xrightarrow{\text{CH}_{3}\text{CH}_{2}\text{CH}_{2}\text{NH}_{2}} \\ \text{CH}_{3} \xrightarrow{\text{CH}_{2}\text{CONH}} \\ \text{CH}_{2}\text{CONH} \xrightarrow{\text{CH}_{2}\text{CH}_{2}\text{CH}_{3}} \\ \xrightarrow{\text{conc. HCI}} \\ \text{C}_{3}\text{H}_{7}\text{NHC}_{3}\text{H}$$

$$\begin{array}{c} \text{CI} \\ | \\ \text{(iii)} \quad \text{CH}_{3}\text{CH}_{2}\text{COOH} \xrightarrow{\text{Red P/Cl}_{2}} \text{CH}_{3} \xrightarrow{\text{CH}} \text{COOH} \xrightarrow{\text{alc. KOH}} \text{CH}_{2} = \text{CH} \xrightarrow{\text{COOH}} \\ \end{array}$$

- Draw the structure of a carbonyl group and indicate clearly
 - Hybridised state of carbon
 - (ii) The σ and π bonds present
 - The electrophilic and nucleophilic centres in it.

- **Sol.** (i) C = C + C + C + C = C hybridised state of C is Sp^2
 - (ii) $\sigma C \frac{\sigma}{\pi} O 3\sigma$ bonds and 1π bond on C atom.
 - (iii) CCO Electrophilic centre
 Nucleophilic centre
- 22. Give reasons for the following:
 - (i) Carboxylic acids do not give characteristic reactions of carbonyl group.
 - (ii) Treatment of benzaldehyde with HCN gives a mixture of two isomers which can not be separated even by careful fractional distillation.
 - (iii) Sodium bisulphite is used for the purification of aldehydes and ketones.
- **Sol.** (i) Due to resonance position of carbonyl group is changing

hence these compounds do not give reactions of carbonyl group.

(ii) On nucleophilic addition of HCN to benzaldehyde, it forms two optical isomers which have same physical properties, hence can not be separated by fractional distillation.

(iii) Aldehydes and ketones form addition products with NaHSO₃, whereas impurities don not react and are left behind. Addition products which were earlier crystallised can be easily reconverted to aldehyde and ketone.

$$\begin{array}{c} \text{OH} \\ | \\ \text{CH}_{3}\text{CHO} + \text{NaHSO}_{3} \longrightarrow \text{CH}_{3} - \text{CH} - \text{SO}_{3}\text{Na} \xrightarrow{\text{H}_{3}\text{O}^{+}} \text{CH}_{3}\text{CHO} + \text{NaHSO}_{3} \end{array}$$

23. Complete the following series of reaction:

$$(i) \qquad CH_3CH_2OH \xrightarrow{K_2Cr_2O_7} A \xrightarrow{SOCl_2} B \xrightarrow{NH_3} C \xrightarrow{NaOBr} D$$

$$\text{(ii)} \quad \text{CH}_{3}\text{CH}_{2}\text{CI} \xrightarrow{\text{KCN}} \text{A} \xrightarrow{\text{H}_{2}\text{O}_{2}} \text{B} \xrightarrow{\text{P}_{2}\text{O}_{5}} \text{A}$$

(iii)
$$CH_3COOH \xrightarrow{C_2H_5OH} A \xrightarrow{CH_3MgBr} B \xrightarrow{CH_3MgBr} CH_3O^+$$

$$\text{(ii)} \quad \text{CH}_{3}\text{CH}_{2}\text{CI} \xrightarrow{\text{KCN}} \text{CH}_{3}\text{CH}_{2}\text{C} \equiv \text{N} \xrightarrow{\text{OH}^{-}} \text{CH}_{3}\text{CH}_{2} \xrightarrow{\text{C}} \text{CN}_{4} \xrightarrow{\text{P}_{2}\text{O}_{5}} \text{CH}_{3}\text{CH}_{2} \xrightarrow{\text{P}_{2}\text{O}_{5}} \text{CH}_{3}\text{CH}_{2}\text{CN}$$

$$(iii) \quad CH_{3}COOH \xrightarrow{C_{2}H_{5}OH} CH_{3}COOC_{2}H_{5} \xrightarrow{CH_{3}MgBr} CH_{3} \xrightarrow{C} CH_{3} \xrightarrow{CH_{3}MgBr} CH_{3} \xrightarrow{C$$

- 24. Would you expect benzaldehyde to be more or less reactive in nucleophilic addition reactions than propanal? Explain.
- Sol. Benzaldehyde is considered to be lesser reactive than propanal due to reduced polarity of carbonyl group.

- 25. Write the names of reagents and equations in the conversions of
 - (i) Phenol to salicylaldehyde
 - (ii) Anisole to p-methoxyacetophenone

Sol. (i)
$$OH \rightarrow OH \rightarrow OH \rightarrow CHO$$

Chloroform $CHO \rightarrow CHO \rightarrow CHO$

Salicylaldehyde

It is Reimer Tiemann reaction.

- 26. Give chemical tests to distinguish between following pairs of compounds:
 - (i) Propanoyl chloride and propanoic acid
 - (ii) Benzaldehyde and acetophenone
- Sol. (i) Propanoyl chloride does not give brisk effervescence with NaHCO₃(aq) but propanoic acid does so.
 - (ii) Acetophenone gives yellow ppt of iodoform with 1₂ and NaOH whereas benzaldehyde does not show this reaction.
- 27. Write IUPAC names of the following compounds:

(ii)
$$HOOC - CH_2 - C = CH - COOH$$

 CH_3

- Sol. (i) Methyl 4-bromobenzoate
 - (ii) 3-Methylpent-2-ene-1,5-dioic acid
 - (iii) 6-Bromo-3-hydroxy-5-nitrobenzoic acid
- 28. How will you convert?
 - (i) Ethanal to methane
 - (ii) Ethanol to propanone

$$\textbf{SoI.} \hspace{0.1cm} \textbf{(i)} \hspace{0.5cm} \textbf{CH}_{3}\textbf{CHO} \xrightarrow{[O]} \textbf{CH}_{3}\textbf{COOH} \xrightarrow{\hspace{0.1cm} \textbf{NaOH}} \textbf{CH}_{3}\textbf{COONa} \xrightarrow{\hspace{0.1cm} \textbf{NaOH}, \Delta \\ \hspace{0.1cm} +\textbf{CaO}} \textbf{CH}_{4} + \textbf{Na}_{2}\textbf{CO}_{3}$$

(ii)
$$CH_3CH_2OH \xrightarrow{[O]} CH_3COOH \xrightarrow{Ca(OH)_2} CH_3COO Ca \xrightarrow{dry} CH_3 - CO - CH_3 + CaCO_3$$

- 29. Write chemical equations, for the following reactions:
 - (i) Action of conc. NaOH on 2,2-Dimethyl propanal
 - (ii) Action of dil. NaOH on propanal.

(ii)
$$2 \text{CH}_3 - \text{CH}_2 \text{CHO} \xrightarrow{\text{dil. NaOH}} \text{CH}_3 - \text{CH}_2 - \text{CH} - \text{CH} - \text{CHO}$$

- 30. Write balanced chemical equations for the following reactions:
 - (i) Thionyl chloride reacts with benzoic acid
 - (ii) Acetic acid is treated with Red P and HI
 - (iii) Acetic acid is treated with Zn metal.

Sol. (i)
$$OOOH + SOCI_2 \longrightarrow OOOI + SO_2 + HCI$$

(ii)
$$CH_3COOH + 6HI \xrightarrow{Red P} CH_3 - CH_3 + 3I_2 + 2H_2O$$

(iii)
$$2CH_3COOH + Zn \longrightarrow (CH_3COO)_2Zn + H_2$$

Long Answer Type Questions:

31. Write structures of organic compounds A to F in the following sequence of reactions

- 32. (a) How can the following compounds be obtained?
 - (i) Acetic acid from acetylene
 - (ii) Acetone from acetic acid
 - (iii) Acetaldehyde from acetic acid
 - (b) In what way can acetic acid be distinguished from acetone?

Sol. (a) (i)
$$HC \equiv CH + H_2O \xrightarrow{H_2SO_4} CH_3CHO \xrightarrow{[O]} CH_3COOH$$

$$\text{(ii)} \quad \text{CH}_{3} \text{COOH} \\ \underline{\quad \quad \text{Ca(OH)}_{2}} \\ \text{(CH}_{3} \text{COO)}_{2} \text{Ca} \\ \underline{\quad \quad \text{dry distillation}} \\ \text{CH}_{3} \text{COCH}_{3} \\ \text{+ CaCO}_{3} \\ \\ \text{COOH}_{3} \\ \text{+ CaCO}_{3} \\ \text{- CaCO}_{4} \\ \text{- CaCO}_{5} \\ \text{$$

(iii)
$$CH_3COOH \xrightarrow{LiAlH_4} CH_3CH_2OH \xrightarrow{Cu} CH_3CHO + H_2$$

- (b) Acetone shows iodoform reaction and gives yellow ppt of CHI₃ with NaOH and I₂, acetic acid does not give this reaction.
- 33. Write chemical reactions to show the following conversions:
 - (i) Butanol to butanoic acid
 - (ii) 3-Nitrobromobenzene to 3-Nitrobenzoic acid
 - (iii) 4-Methylacetophenone to Benzene-1,4-dicarboxylic acid
 - (iv) Cyclohexene to Hexane-1,6-dioic acid

Sol. (i)
$$CH_3CH_2CH_2CH_2OH \xrightarrow{CrO_3-H_2SO_4} CH_3CH_2CH_2COOH$$

(ii)
$$NO_2$$
 NO_2 NO

- 34. How will you synthesise the following by using a Grignard reagent?
 - (i) 2,2-Dimethylpentanoic acid
 - (ii) But-3-enoic acid
 - (iii) 2-Phenylpropan-2-ol

$$(ii) \hspace{0.5cm} \mathrm{CH_2} = \mathrm{CH} - \mathrm{CH_2} \mathrm{Br} \xrightarrow{\hspace{0.5cm} \mathrm{Mg} \hspace{0.5cm} \mathrm{CH_2}} \mathrm{CH_2} = \mathrm{CH} - \mathrm{CH_2} \mathrm{MgBr} \xrightarrow{\hspace{0.5cm} (\mathrm{ii}) \hspace{0.5cm} \mathrm{CH_2}} \mathrm{CH_2} = \mathrm{CH} - \mathrm{CH_2} \mathrm{COOH}$$

$$(iii) \quad \bigcirc \stackrel{\mathsf{MgBr}}{\longrightarrow} \stackrel{\mathsf{+CH_3-C-CH_3}}{\longrightarrow} \bigcirc \stackrel{\mathsf{OMgBr}}{\longrightarrow} \stackrel{\mathsf{OH}}{\longrightarrow} \stackrel$$

- 35. (a) Why has monochloroethanoic acid higher pK_a value than dichloroethanoic acid?
 - (b) Give formulas of compounds A and B

$$CH_3MgBr + CO_2 \xrightarrow{dry \text{ ether} \atop H_3O^+} A \xrightarrow{PCI_5} B$$

(c) Identify compounds A and B

$$CH_3COOH \xrightarrow{SOCl_2} A \xrightarrow{LiAIH_4} B$$

Sol. (a) Out of CI—CH₂COOH and CI—CH—COOH, the later one has two —CI atoms and more electron | CI

withdrawing influence hence it is more acidic having lesser pK_a value.

$$\text{(b)} \quad \text{CH}_{3} \text{MgBr} + \text{CO}_{2} \\ \\ \longrightarrow \text{CH}_{3} \\ \\ \text{COOMgBr} \\ \\ \xrightarrow{\text{H}_{3} \\ \text{O}^{+}} \\ \\ \xrightarrow{\text{CH}_{3}} \\ \\ \text{COOH} \\ \xrightarrow{\text{PCI}_{5}} \\ \\ \xrightarrow{\text{CH}_{3}} \\ \\ \text{COOH} \\ \xrightarrow{\text{PCI}_{5}} \\ \\ \xrightarrow{\text{COOH}} \\ \xrightarrow{\text{PCI}_{5}} \\ \\ \xrightarrow{\text{COOH}} \\ \xrightarrow{\text{PCI}_{5}} \\ \xrightarrow{\text{PCI}_{5}}$$

$$\text{(c)} \quad \text{CH$_3$COOH} \underset{\text{A}}{\overset{\text{SOCl}_2}{\longrightarrow}} \text{CH$_3$COCI} \underset{\text{B}}{\overset{\text{LiAIH}_4}{\longrightarrow}} \text{CH$_3$CH$_2$OH}$$

- 36. Which out of each pair is expected to be a stronger acid?
 - (a) CH₃COOH or HCOOH

(f)
$$O_2N$$
 COOH or H_3C COOH

Sol. (a) HCOOH

- (b) CH₃COOH
- (c) HCOOH
- (d) CI-CH2-COOH

37. How will you convert

- (a) Butan-2-ol to 2-methylbutanoic acid
- (b) Propanoic acid to acetic acid
- (c) $(CH_3)_2C = CH-COCH_3$ to $(CH_3)_2C = CH-COOH$

Sol. (a)
$$CH_3CH_2 - CH - CH_3 \xrightarrow{PI_3} C_2H_5 - CH - CH_3 \xrightarrow{Mg/dry} C_2H_5 - CH - CH_3$$

$$C_2H_5 - CH - COOH \xleftarrow{H_2O/H^+}_{-MgI(OH)} C_2H_5 - CHCOOMgI \xleftarrow{CO_2}_{CH_3}$$

$$(b) \quad \text{CH}_3\text{CH}_2\text{COOH} \xrightarrow{\text{NH}_3,\,\Delta} \text{C}_2\text{H}_5\text{CONH}_2 \xrightarrow{\text{Br}_2/\text{KOH}} \text{C}_2\text{H}_5\text{NH}_2 \xrightarrow{\text{HONO}} \text{CH}_3\text{CH}_2\text{OH} \xrightarrow{\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+} \text{CH}_3\text{COOH}_2\text{COOH}_2\text{CH}_2\text{COOH}_2\text{CO$$

(c)
$$(CH_3)_2C = CH - COCH_3 \xrightarrow{+4NaOH + 3I_2} (CH_3)_2C = CH - COONa + CHI_3 + 3NaI + 3H_2O$$

 $(CH_3)_2C = CH - COOH$

38. Give reasoning for the following:

- (a) CH₃COO⁻ ion is more stable than C₂H₅O⁻ ion
- (b) Tertiary butylbenzene does not give benzoic acid when oxidised with KMnO₄
- (c) Carbon oxygen bond lengths in formic acid are different but are the same in sodium formate.
- Sol. (a) In acetate ion there is delocalisation of -ve charge which is not possible in ethoxide ion.

$$CH_3-C \xrightarrow{\circlearrowleft} CH_3-C \xrightarrow{\circlearrowleft} = \begin{bmatrix} CH_3-C \xrightarrow{\circlearrowleft} C \\ O \end{bmatrix} \quad C_2H_5 \Rightarrow \stackrel{\bullet}{O} \stackrel{\bullet}{:}$$

(b) To oxidise the alkyl group attached to benzene ring atleast one α-hydrogen must be present e.g., toluene gets oxidised to benzoic acid but tert butyl group has no α-H hydrogen hence it does not oxidise with KMnO₄.

In formate ion contributing structures for anion are equivalent while these are not the same in formic acid.



Chapter 13

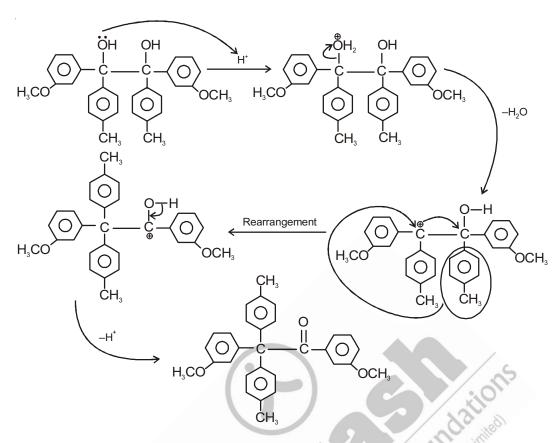
Aldehydes, Ketones and Carboxylic Acids

Solutions (Set-2)

[Aldehydes and Ketones (Preparation and Reactions)]

(3) Both (1) & (2)

Sol. Answer (1)



Migrating power of p-tolyl is more than m-anisyl.

Nucleophile added in this reaction is

(1)
$$AIH_4^-$$

Sol. Answer (4)

$$LiAlH_4 \rightarrow Li^+ + Al^{3+} + 4H^-$$

$$CH_{3} - C - H + H \longrightarrow CH_{3} - C - H \xrightarrow{H_{3}O^{*}} CH_{3} - C - H$$

3. Complete the reaction :
$$Ph - CH = CH - CHO \xrightarrow{PhMgBr (Cu^{2+})} Product$$

Sol. Answer (2)

- 4. $H > C = O \xrightarrow{Nu^{\ominus}} Product$. Product may be
 - (1) Meso
- (2) Racemic
- (3) Inversion
- (4) All of these

Sol. Answer (2)

Product may be recemic, because carbonyl carbon is sp^2 hybridised and has planar shape. So, Nu⁻ attacks on front as well as back side.

5.
$$CH_3 - C - CH_2 - CH_3 \xrightarrow{Conc.} Product$$

The product is

(1) CH₃COOH

(2) CH₂CH₂COOH + HCOOH

(3) CH₃CH₂CH₂COOH

(4) No reaction

Sol. Answer (1)

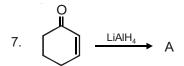
$$\begin{array}{c}
O \\
\parallel \\
CH_3 - C - CH_2 - CH_3 & \xrightarrow{Conc.HNO_3} & 2CH_3COOH
\end{array}$$

According to Popoff's rule, carbonyl group goes with less complex alkyl group.

Sol. Answer (1)

$$\stackrel{\text{SeO}_2}{\longrightarrow} \stackrel{\text{O}}{\longrightarrow} \stackrel{\text{O$$

In this reaction, active methylene group ($-CH_2$) is oxidised to >C=O group.

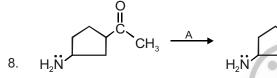


The product predominates is



Sol. Answer (1)

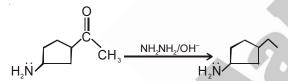
 ${\rm LiAlH_4}$ does not reduce double bond. If double bond is conjugated with phenyl system then double bond is reduced by ${\rm LiAlH_4}$.



A is

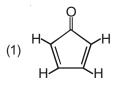
- (1) Zn Hg/HCl
- (2) $NH_2 NH_2/OH$
- (3) Both (1) & (2)
- (4) NaBH

Sol. Answer (2)



In this reaction, ${\rm Zn-Hg/HCl}$ is not used because in acidic medium, ${\rm -NH_2}$ group is affected.

9. Which of the following carbonyl oxygen will form strongest hydrogen bond with H₂O molecule?





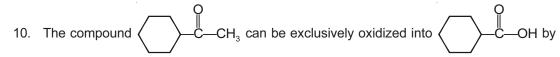




Sol. Answer (2)

forms strongest hydrogen bond with H₂O molecule because in this case carbonyl carbon readily attains

+ve charge due to aromaticity



(1) NaCN followed by hydrolysis

- (2) NaOI followed by H₃O⁺
- (3) KMnO_₄ hot followed by hydrolysis
- (4) K₂Cr₂O₇ followed H₃O⁺

Sol. Answer (2)

$$\begin{array}{c}
O \\
\parallel \\
C - CH_3 \xrightarrow{\text{NaOI}} \\
\end{array}$$

$$\begin{array}{c}
O \\
\parallel \\
C - O^- \text{Na} + CHI_3 \downarrow \\
\end{array}$$

$$\begin{array}{c}
H_3O \\
\Delta
\end{array}$$

$$\begin{array}{c}
O \\
\parallel \\
C - OH
\end{array}$$

The above conversion is known as iodoform reaction.

11. An organic compound [x], C₅H₈O reacts with hydroxylamine to form [y], [y] in the presence of conc. H₂SO₄ gives δ-lactam. [x] neither give Benedicts test nor it respond positively towards haloform test. The compound [x] is

Sol. Answer (3)

$$(x) C_5H_8O$$

$$N - OH$$

$$Conc. H_2SO_4$$

$$Beckmann Rearrangement$$

$$\delta - lactam$$

12.
$$C \rightarrow CH_3 \xrightarrow{PCl_5, 0^{\circ}C} \xrightarrow{(i) \text{ LiNH}_2(3\text{eq})} \xrightarrow{Na / NH_3} [A]$$

(1)
$$CH_2$$
— CH_2 — CH_2 — CH_3 (2) CH_2 — CH_2 — CH_2 — CH_2 — CH_3

Sol. Answer (3)

13.
$$CHO + (x) \longrightarrow_{CH_0COONa} CHOOOH$$

The compound x is

Sol. Answer (3)

14. Trichloroacetaldehyde, CCI₃CHO reacts with chlorobenzene in presence of sulphuric acid and produces

(1)
$$CI \longrightarrow CI$$
 CH_2CI

Sol. Answer (4)

- 15. Which of the following compound will exhibits positive Fehling test as well as iodoform test?
 - (1) Methanal
- (2) Ethanol
- (3) Propanone
- (4) Ethanal

Sol. Answer (4)

16.
$$\bigcirc$$
 CHO (i) conc. NaOH (ii) H_2O/H^* ?

(1) COOH (2) COOH (3) COOH (4) CHO

Sol. Answer (2)

- 17. An aromatic compound 'X' with molecular formula C₉H₁₀O gives the following chemical tests
 - (i) Forms 2,4-DNP derivative
 - (ii) Reduce Tollens reagent
 - (iii) Undergoes Cannizzaro reaction and
 - (iv) On vigorous oxidation, 1,2-benzenedicarboxylic acid is obtained

The compound is

(1)
$$CHO$$
(2) CHO
(3) CHO
(4) CHO
(4) C_2H_5

Sol. Answer (1)

18. The correct order of reactivity of PhMgBr towards given compounds

- (1) (i) > (ii) > (iii)
- (2) (iii) > (ii) > (i)
- (3) (ii) > (iii) > (i)
- (4) (i) > (iii) > (ii)

Sol. Answer (3)

- 19. The increasing order of the rate of HCN addition to compounds A–D is
 - (A) HCHO
- (B) CH₃COCH₃
- (C) PhCOCH₃
- (D) PhCOPh

- (1) A < B < C < D (2) D < B < C < A (3) D < C < B < A (4) C < D < B < A

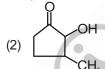
Sol. Answer (3)

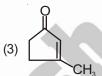
20. CHO + 'X'
$$\xrightarrow{OH^{\bigcirc}}$$
 CH=CH—C—. Identify 'X'

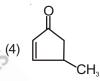
Sol. Answer (3)

21. The diketone $CH_3 - C - (CH_2)_2 - C - CH_3$ on intramolecular aldol condensation gives the final product









Sol. Answer (3)

- 22. Enol content is high test in
 - (1) Acetone
- (2) Acetophenone
- (3) Acetic acid
- (4) Acetyl acetone

Sol. Answer (4)

23.
$$2C_6H_5CHO \xrightarrow{\text{NaOH}} C_6H_5CH_2OH + C_6H_5COONa$$

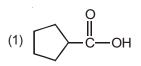
The similar reaction can take place with which of the following aldehyde?

- (1) CH₂CHO
- (2) CH₃CH₂CHO
- (4) CH₃CH₂CH₂CHO

Sol. Answer (3)

[Carboxylic Acids (Preparation and Reactions)]

- $\frac{\text{HBr, Peroxide}}{\text{hv}} > [A] \xrightarrow{\text{(i) Mg/Et}_2O} = [B]. \text{ The final product}$ 24. Consider the following sequence of reaction:
 - [B] in the reaction would be:



Sol. Answer (4)

$$CH_{2} \xrightarrow{HBr, Peroxide} CH_{2} \longrightarrow CH_{2} \longrightarrow CH_{2} \longrightarrow CH_{2} \longrightarrow MgBr$$

$$CH_{2} \xrightarrow{C} C \longrightarrow CH_{2} \longrightarrow$$

25. Which of the following would be the best synthesis of benzoic acid from bromobenzene?

(1)
$$Argan Br + KCN \longrightarrow [A] \xrightarrow{H_3O^+}$$

(2)
$$AgCN \longrightarrow [A] \xrightarrow{H_3O}$$

(3)
$$Rightarrow Br \frac{Mg}{THF} > [A] \frac{(i) CO_2}{(ii) H_3O^+}$$

(4)
$$Rr \frac{Mg}{THF} > [A] \frac{(i) KCN}{(ii) H_3 O^{*}}$$

Sol. Answer (3)

Benzoic Acid

26. Which of the following conversion is known as Stefen's reduction?

(1)
$$C = N \xrightarrow{1. \text{LiAlH}_4} CH_2 - NH_2$$

(2)
$$C = N \xrightarrow{1. \text{SnCl}_2, \text{HCl}} CHO$$

$$(3) \qquad \stackrel{\oplus}{\longleftarrow} \stackrel{\oplus}{\longrightarrow} \stackrel{\ominus}{\stackrel{1. \text{Na, C}_2H_5OH}} \stackrel{-}{\longleftarrow} -\text{NH---CH}_3$$

$$(4) \qquad \begin{array}{c} O \\ C \end{array} \qquad \begin{array}{c} C \\ \end{array} \qquad \begin{array}{c} C \\$$

Sol. Answer (2)

$$C = N \xrightarrow{SnCl_2/HCl} CH = NH \xrightarrow{H_2O} CHC$$

This is known as Stephen's reduction.

Alanine can be obtained from acetaldehyde by the following sequence of reactions 27.

- (1) Reaction with NaCN and NH₄Cl followed by acidic hydrolysis
- (2) Reaction with HCN, acidic hydrolysis and finally reaction with NH₃
- (3) Reaction with HCN, followed by NH₃ and finally acidic hydrolysis
- (4) Reaction with NaHSO₃, followed by NH₃ and finally acidic hydrolysis

Sol. Answer (1)

$$\begin{array}{c} CH_3 \\ CH_3 \\ CH_3 \\ \end{array} > C = O + HCN \longrightarrow \begin{array}{c} CH_3 \\ H \\ \end{array} > C < \begin{array}{c} OH \\ CN \\ \end{array} \longrightarrow \begin{array}{c} NH_3 \\ H \\ \end{array} > C < \begin{array}{c} NH_2 \\ CN \\ \end{array} \longrightarrow \begin{array}{c} H_3O^+ \\ H \\ \end{array} > C < \begin{array}{c} NH_2 \\ COOH \\ \end{array}$$

Acetaldehyde

Alanine

(C – O) bond length designated by α , β , γ and δ are in order (1) $\alpha = \gamma < \beta = \delta$ (2) $\alpha < \beta < \gamma = \delta$ (3) $\alpha < \delta$

(1)
$$\alpha = \gamma < \beta = \delta$$

(2)
$$\alpha < \beta < \gamma = \delta$$

(3)
$$\alpha < \gamma = \delta < \beta$$

(4)
$$\alpha = \beta = \gamma = \delta$$

Sol. Answer (3)

In, H—C due to complete resonance, $\gamma = \delta$, While in H—C partial resonance is present. So, $\alpha < \beta$.

29. Which of the following carboxylic acid is most reluctant to form ester with a given alcohol in the presence of a catalytic amount of concentrated H₂SO₄?

Sol. Answer (1)

 $\begin{array}{c|c} CH_3 & O \\ | & || \\ CH_3 - C - C \\ | & OH \end{array}$ is most reluctant to form ester with alcohol due to presence of bulky group.

30. Which of the following aromatic acids is most acidic?



Sol. Answer (2)

31. Which one of the following orders of acid strength is correct?

(1) $RCOOH > HC \equiv CH > HOH > ROH$

(2) RCOOH > ROH > HOH > HC \equiv CH

(3) $RCOOH > HOH > ROH > HC \equiv CH$

(4) $RCOOH > HOH > HC \equiv CH > ROH$

Sol. Answer (3)

32. The correct order of acidic strength of the carboxylic acid is

(1) Formic acid < Benzoic acid < Acetic acid

(2) Formic acid < Acetic acid < Benzoic acid

(3) Acetic acid < Formic acid < Benzoic acid

(4) Acetic acid < Benzoic acid < Formic acid

Sol. Answer (4)

33.
$$OOOH \xrightarrow{NH_3} A. Identify 'A$$

(1) Benzene

(2) Phthalimide

(3) Benzamide

(4) Acetaldehyde

Sol. Answer (2)

[Acid Derivatives (Preparation and reactions)]

34. Among the given compounds

The order of decreasing acidity is

(1) | || > |V > | > ||

 $(2) | > | \lor > | | > | | |$

 $(3) | | | > | > | \lor > |$

(4) ||| > | > || > |V

Sol. Answer (3)

Due to ortho effect, (III) and (I) are most acidic. If —OH group is present at p-position w.r.t. —COOH group, then it becomes less acidic.

35.
$$CH_3CH_2 - C - O - C_2H_5 \xrightarrow{\text{(i) DIBAL-H (1 eq)}} A + B$$

A and B are respectively

(1) $CH_3CH_2CH_2OH + C_2H_5OH$

(2) $CH_3CH_2CHO + C_2H_5OH$

(3) CH₃CH₂CHO + CH₃CHO

(4) CH₃CH₂CH₂OH + CH₃CHO

Sol. Answer (2)

$$\begin{array}{c} \text{O} \\ \text{II} \\ \text{CH}_3\text{CH}_2 - \text{C} - \text{OC}_2\text{H}_5 \xrightarrow{\text{(i)Di isobutyl}} \text{CH}_3 - \text{CH}_2\text{CHO} + \text{C}_2\text{H}_5\text{OH} \\ \text{(ii) H}_3\text{O}^+ \end{array}$$

36. Consider the following sequence of reactions.

$$C = N \xrightarrow{(i) \text{ PhMgBr}} [A] \xrightarrow{H_2N - C - NH - NH_2} [B]$$

Major product [B] of the given reaction would be

$$(3) \qquad \begin{array}{c} O \\ \parallel \\ NH - C - NH_2 \end{array}$$

Sol. Answer (3)

37. Consider the following sequence of reactions.

$$\begin{array}{c|c}
O \\
C - CI \xrightarrow{Pd/CaCO_3} & [A] \xrightarrow{HO - (CH_2)_3 - OH/H^{\oplus}} [B]
\end{array}$$

The products [A] and [B] are respectively

(1)
$$C = 0$$
 and $C = 0$

(2)
$$C$$
—OH and C — C — C H₂— C H₂

(3)
$$C$$
—OH and C

(4)
$$CH_2$$
 CH_2 CH_2

Sol. Answer (1)

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

$$\begin{array}{c|c}
C \\
C \\
C
\end{array}$$

$$\begin{array}{c|c}
H \\
C \\
C
\end{array}$$

$$\begin{array}{c|c}
H \\
C \\
C
\end{array}$$

$$\begin{array}{c|c}
H \\
C
\end{array}$$

$$\begin{array}{c|c}
C \\
C
\end{array}$$

38. Which reagent or sequence of reagents would best accomplish the following synthesis?

$$\stackrel{\text{OEt}}{\longrightarrow} \stackrel{\text{OEt}}{\longrightarrow}$$

- (1) (i) LiAlH₄ (ii) H⁺, Δ
- (3) (i) Na / NH $_3$ (ii) NaBH $_4$ / H $^+$, Δ

- (2) (i) NaBH₄ (ii) dil. H₂SO₄ (iii) conc.H₂SO₄
- (4) (i) Mg / Et₂O (ii) LiAlH₄ , (iii) H⁺, Δ

Sol. Answer (2)

$$\begin{array}{c|c}
O & OEt \\
\hline
O & NaBH_{*}
\end{array}$$

$$\begin{array}{c}
O & OEt \\
\hline
O & OEt
\end{array}$$

$$\begin{array}{c}
O & OEt \\
\hline
O & OEt
\end{array}$$

- 39. In esterification
 - (1) OH- of acid is replaced by C₆H₅OH
 - (3) OH- of alcohol is replaced by chlorine
- Sol. Answer (4)
- 40. The compound which is not reduced by LiAlH₄ is
 - (1) Cyclohexanone
- (2) 2-Methyl-1-butanol
- (2) H+ of acid is replaced by sodium metal
- (4) OH- of acid is replaced by RO- group
- (3) Ethyl benzoate
- (4) ω-caprolactam

Sol. Answer (2)

Alcohols can't be reduced by ${\rm LiAlH_4}$. Only carbonyl compound, carboxylic acid and acid derivatives are reduced by ${\rm LiAlH_4}$