Chapter 26. Aldehydes, Ketones and Carboxylic Acids

1. Consider the reactions,

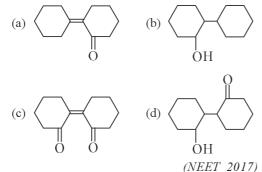
$$\begin{array}{c} X \\ (C_2H_6O) \end{array} \xrightarrow{573 \text{ K}} A \begin{array}{c} A \\ \hline \begin{array}{c} [Ag(NH_3)_2]^{+} \\ \hline \begin{array}{c} OH, \Delta \\ \hline \end{array} \end{array} \xrightarrow{\text{Silver mirror observed}} \\ NH_2NHCONH_2 \end{array} \xrightarrow{Z}$$

Identify A, X, Y and Z.

- (a) A-Methoxymethane, X-Ethanol, Y-Ethanoic acid, Z-Semicarbazide.
- (b) A-Ethanal, X-Ethanol, Y-But-2-enal, Z-Semicarbazone.
- (c) A-Ethanol, X-Acetaldehyde, Y-Butanone, Z-Hydrazone.
- (d) A-Methoxymethane, X-Ethanoic acid, Y-Acetate ion, Z-Hydrazine.

(NEET 2017)

2. Of the following, which is the product formed when cyclohexanone undergoes aldol condensation followed by heating?



3. The correct structure of the product 'A' formed in the reaction

$$\begin{array}{c|c} & H_2 \text{ (gas, 1 atmosphere)} \\ \hline & Pd/\text{carbon, ethanol} \\ & OH \\ & \text{(a)} & \\ \end{array} \begin{array}{c} OH \\ & \text{(b)} \\ \hline \end{array}$$

OH OH (d)
$$\downarrow^+$$
 (NEET-II 2016)

The correct order of strengths of the carboxylic acids

is

- (a) I > II > III
- (b) II > III > I
- (c) III > II > I
- (d) II > I > III

(NEET-II 2016)

- 5. Which of the following reagents would distinguish *cis*-cyclopenta-1-2-diol from the *trans*-isomer?
 - (a) MnO₂
 - (b) Aluminium isopropoxide
 - (c) Acetone
- (d) Ozone

(NEET-I 2016)

- The correct statement regarding a carbonyl compound with a hydrogen atom on its alphacarbon, is
 - (a) a carbonyl compound with a hydrogen atom on its alpha-carbon rapidly equilibrates with its corresponding enol and this process is known as carbonylation
 - (b) a carbonyl compound with a hydrogen atom on its alpha-carbon rapidly equilibrates with its corresponding enol and this process is known as keto-enol tautomerism
 - (c) a carbonyl compound with a hydrogen atom on its alpha-carbon never equilibrates with its corresponding enol
 - (d) a carbonyl compound with a hydrogen atom on its alpha-carbon rapidly equilibrates with its corresponding enol and this process is known as aldehyde-ketone equilibration.

(NEET-I 2016)



(NEET 2013)

- 7. The oxidation of benzene by V_2O_5 in the presence of air produces
 - (a) maleic anhydride (b) benzoic acid
 - (c) benzaldehyde
 - (d) benzoic anhydride.

(2015)

- **8.** Reaction of a carbonyl compound with one of the following reagents involves nucleophilic addition followed by elimination of water. The reagent is
 - (a) hydrazine in presence of feebly acidic solution
 - (b) hydrocyanic acid
 - (c) sodium hydrogen sulphite
 - (d) a Grignard reagent.

(2015)

9. Which one of the following esters gets hydrolysed most easily under alkaline conditions?

(a)
$$H_3CO$$
OCOCH₃
(b) OCOCH₃
(c) OCOCH₃
(d) OoN
(2015)

- 10. An organic compound 'X' having molecular formula C₅H₁₀O yields phenylhydrazone and gives negative response to the iodoform test and Tollens' test. It produces *n*-pentane on reduction. 'X' could be
 - (a) 3-pentanone
- (b) n-amyl alcohol
- (c) pentanal
- (d) 2-pentanone.

(2015, Cancelled)

(2013, Cancelled

11. Which one is most reactive towards nucleophilic addition reaction?

12. The order of stability of the following tautomeric compounds is

- **13.** Reaction by which benzaldehyde cannot be prepared
 - a) + CO + HCl in presence of anhydrous AlCl₃

(b)
$$COOH + Zn/Hg$$
and conc. HCl

(c)
$$CH_3 + CrO_2Cl_2$$
 in CS_2 followed by H_3O^+

14. Predict the products in the given reaction.

(a)
$$CH_2OH$$
 + CH_2COO^-

(b)
$$OH$$
 CH_2OH $+$ OH OH

(c)
$$CH_2OH + COO^-$$
(d) $CH_2OH + OH$
(d) OH
(201)

(2012)

- 15. Acetone is treated with excess of ethanol in the presence of hydrochloric acid. The product obtained is
 - (a) CH₃CH₂CH₂ C CH₂
 - O || (b) CH₃CH₂CH₂ C CH₂CH₂CH₃

 - (d) $(CH_3)_2C < \frac{OC_2H_5}{OC_2H_5}$ (2012)
- **16.** CH₃CHO and C₆H₅CH₂CHO distinguished chemically by
 - (a) Benedict's test
 - (b) Iodoform test
 - (c) Tollen's reagent test
 - (d) Fehling's solution test (2012)
- 17. The correct order of decreasing acid strength of trichloroacetic acid (A), trifluoroacetic acid (B), acetic acid (C) and formic acid (D) is
 - (a) B > A > D > C
- (b) B > D > C > A
- (c) A > B > C > D
- (d) A > C > B > D(2012)
- 18. Consider the following reaction

The product A is

- (a) C₆H₅CHO
- (b) C_6H_5OH
- (c) C₆H₅COCH₃
- (d) C_6H_5Cl

(Mains 2012)

19. Consider the reaction :

 $RCHO + NH_2NH_2 \rightarrow RCH = N - NH_2$

What sort of reaction is it?

- (a) Electrophilic addition-elimination reaction
- (b) Free radical addition-elimination reaction
- (c) Electrophilic substitution-elimination reaction
- (d) Nucleophilic addition-elimination reaction (Mains 2012)
- 20. Which of the following compounds will give a yellow precipitate with iodine and alkali?
 - (a) Acetophenone
- (b) Methyl acetate
- (c) Acetamide
- (d) 2-Hydroxypropane

(Mains 2012)

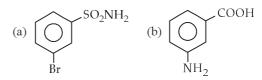
- 21. Clemmensen reduction of a ketone is carried out in the presence of which of the following?

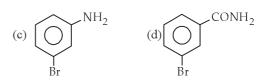
 - (a) Glycol with KOH (b) Zn-Hg with HCl
 - (c) LiAlH₄
 - (d) H2 and Pt as catalyst

(2011)

22. In a set of reactions *m*-bromobenzoic acid gave a product D. Identify the product D.

$$\begin{array}{c}
COOH \\
& \\
Br
\end{array}
\xrightarrow{SOCl_2} B \xrightarrow{NH_3} C \xrightarrow{NaOH Br_2} D$$





(2011)

23. The order of reactivity of phenyl magnesium bromide (PhMgBr) with the following compounds:

$$CH_3$$
 $C=0$, CH_3 $C=0$ and Ph $C=0$
 CH_3 $C=0$ CH_3 CH_3 $C=0$ CH_3 CH

- (b) II > I > III
- (c) I > III > II
- (d) I > II > III

(Mains 2011)



24. Match the compounds given in List-I with List-II and select the suitable option using the code given below.

List-I

List-II

- (A) Benzaldehyde
- (i) Phenolphthalein
- (B) Phthalic anhydride
- (ii) Benzoin condensation
- (C) Phenyl benzoate
- (iii) Oil of
- (D) Mathyl galiaylata
- wintergreen
- (D) Methyl salicylate
- (iv) Fries rearrangement
- (a) (A)-(iv), (B)-(i), (C)-(iii), (D)-(ii)
- (b) (A)-(iv), (B)-(ii), (C)-(iii), (D)-(i)
- (c) (A)-(ii), (B)-(iii), (C)-(iv), (D)-(i)
- (d) (A)-(ii), (B)-(i), (C)-(iv), (D)-(iii)

(Mains 2011)

- **25.** An organic compound *A* on treatment with NH₃ gives *B*, which on heating gives *C*. *C* when treated with Br₂ in the presence of KOH produces ethyl amine. Compound *A* is
 - (a) CH₃COOH
 - (b) CH₃CH₂CH₂COOH

- (d) CH₃CH₂COOH
- (Mains 2011)
- **26.** Which of the following reactions will not result in the formation of carbon-carbon bonds?
 - (a) Reimer-Tiemann reaction
 - (b) Cannizzaro reaction
 - (c) Wurtz reaction
 - (d) Friedel-Crafts acylation

(2010)

- 27. Acetamide is treated with the following reagents separately. Which one of these would yield methyl amine?
 - (a) NaOH-Br₂
- (b) Sodalime
- (c) Hot conc. H₂SO₄
- (d) PCl₅

(2010)

- 28. Among the given compounds, the most susceptible to nucleophilic attack at the carbonyl group is
 - (a) CH₃COOCH₃
- (b) CH₃CONH₂
- (c) CH₃COOCOCH₃
- (d) CH₃COCl

(2010)

29. Which one of the following compounds will be most readily dehydrated?

(Mains 2010)

30. Trichloroacetaldehyde, CCl₃CHO reacts with chlorobenzene in presence of sulphuric acid and produces

(c)
$$CI \longrightarrow CH \longrightarrow CI$$

 CCI_3

$$(d) Cl \xrightarrow{Cl} Cl$$

$$CH_2Cl$$

31. Propionic acid with Br₂/P yields a dibromo product. Its structure would be

(a)
$$H - C - CH_2COOH$$

Br

(b) $CH_2(Br) - CH_2 - COBr$

(d) $CH_2(Br) - CH(Br) - COOH$

(2009)

(2009)

32. Acetophenone when reacted with a base, C₂H₅ONa, yields a stable compound which has the structure

(a)
$$\begin{array}{c} CH_3CH_3 \\ C-C-C \\ OHOH \end{array}$$

$$(b) \begin{picture}(60,0) \put(0.5,0){\line(0,0){100}} \put(0.5,0){\line(0,0)$$

(c)
$$\bigcirc C = CH - C - \bigcirc CH_3$$
 $\bigcirc CH_3$ $\bigcirc CH_3$

- 33. A strong base can abstract an α -hydrogen from
 - (a) ketone
- (b) alkane
- (c) alkene
- (d) amine. (2008)
- **34.** The relative reactivities of acyl compounds towards nucleophilic substitution are in the order of
 - (a) Acid anhydride > Amide > Ester > Acyl chloride
 - (b) Acyl chloride > Ester > Acid anhydride > Amide
 - (c) Acyl chloride > Acid anhydride > Ester >
 - (d) Ester > Acyl chloride > Amide > Acid anhydride. (2008)
- **35.** Reduction of aldehydes and ketones into hydrocarbons using zinc amalgam and conc. HCl is called
 - (a) Cope reduction
 - (b) Dow reduction
 - (c) Wolf-Kishner reduction
 - (d) Clemmensen reduction.

(2007)

- **36.** Which one of the following on treatment with 50% aqueous sodium hydroxide yields the corresponding alcohol and acid?
 - (a) C_6H_5CHO
 - (b) CH₃CH₂CH₂CHO

(d) C₆H₅CH₂CHO

(2007)

- 37. The product formed in Aldol condensation is
 - (a) a beta-hydroxy aldehyde or a beta-hydroxy ketone
 - (b) an alpha-hydroxy aldehyde or ketone
 - (c) an alpha, beta unsaturated ester
 - (d) a beta-hydroxy acid. (2007)
- 38. Consider the following compounds
 - (i) C₆H₅COCl

(ii)
$$O_2N - \bigcirc$$
 COCI

The correct decreasing order of their reactivity towards hydrolysis is

- (a) (i) > (ii) > (iii) > (iv)
- (b) (iv) > (ii) > (i) > (iii)
- (c) (ii) > (iv) > (i) > (iii)
- (d) (ii) > (iv) > (iii) > (i)

(2007)

- **39.** Which of the following represents the correct order of the acidity in the given compounds?
 - (a) FCH₂COOH > CH₃COOH > BrCH₂COOH > CICH₂COOH
 - (b) $BrCH_2COOH > CICH_2COOH > FCH_2COOH > CH_3COOH$
 - (c) FCH₂COOH > CICH₂COOH > BrCH₂COOH > CH₃COOH
 - (d) $CH_3COOH > BrCH_2COOH > CICH_2COOH$ > FCH_2COOH (2007)
- **40.** Nucleophilic addition reaction will be most favoured in
 - (a) CH₃CHO

- (c) $(CH_3)_2C = O$
- (d) CH₃CH₂CHO

(2006)

- 41. A carbonyl compound reacts with hydrogen cyanide to form cyanohydrin which on hydrolysis forms a racemic mixture of α-hydroxy acid. The carbonyl compound is
 - (a) formaldehyde

(c) acetone

CLICK HERE

- (b) acetaldehyde
- (d) diethyl ketone. (2006)



42. In a set of reactions propionic acid yielded a compound D.

$$CH_3CH_2COOH \xrightarrow{SOCl_2} B \xrightarrow{NH_3} C \xrightarrow{KOH} D$$

The structure of D would be

- (a) CH₃CH₂NH₂
- (b) CH₃CH₂CH₂NH₂
- (c) CH₃CH₂CONH₂
- (d) CH₃CH₂NHCH₃ (2006)
- 43. Self condensation of two moles of ethyl acetate in presence of sodium ethoxide yields
 - (a) ethyl propionate
- (b) ethyl butyrate
- (c) acetoacetic ester
- (d) methyl acetoacetate.
- (2006)

44. The major organic product formed from the following reaction:

(b)
$$\longrightarrow$$
 (c) \longrightarrow OH

(c)
$$\rightarrow \frac{\text{HNCH}_3}{\text{OH}}$$

$$(d) \quad \begin{array}{c} \underset{\text{OH}}{\longleftarrow} \\ \end{array}$$

(2005)

45. In a set of reactions acetic acid yielded a product D.

$$CH_{3}COOH \xrightarrow{SOCl_{2}} A \xrightarrow{benzene} B$$

$$\xrightarrow{HCN} C \xrightarrow{HOH}$$

The structure of D would be

(b)
$$\bigcirc CN$$
 $C - CH_3$
OH

(c)
$$CH_2 - C - CH_2$$

(d)
$$OH$$
 $C-COOH$
 CH_3
(2005)

- 46. Which one of the following can be oxidised to the corresponding carbonyl compound?
 - (a) 2-Hydroxypropane
 - (b) ortho-Nitrophenol
 - (c) Phenol
 - (d) 2-Methyl-2-hydroxypropane (2004)
- **47.** In this reaction :

HOH→ CH₃CH(OH)COOH

an asymmetric centre is generated. The acid obtained would be

- (a) D-isomer
- (b) L-isomer
- (c) 50% D + 50% L-isomer
- (d) 20% D + 80% L-isomer (2003)
- **48.** When m-chlorobenzaldehyde is treated with 50% KOH solution, the product(s) obtained

(a)
$$OH$$
 OH OH CH_2OH

$$(d) \qquad \begin{array}{c} OH & OH \\ CH - CH - CH \\ OH \end{array} \qquad (2003)$$

49. A and B in the following reactions are :

$$\begin{array}{ccc}
R - C - R' \xrightarrow{\text{HCN}} A & \xrightarrow{B} & R - C & \text{OH} \\
O & & & & \\
O & & & & \\
CH_2NH_2
\end{array}$$

(a)
$$A = RR'C < \frac{OH}{COOH}$$
, $B = NH_3$

- (b) $A = RR'C < \frac{CN}{OH}$, $B = H_3O^{\oplus}$
- (c) $A = RRCH_2CN$, B = NaOH
- (d) $A = RR'C \stackrel{CN}{\underset{OH}{\longleftarrow}} B = \text{LiAlH}_4$ (2003)

50. In a set of the given reactions, acetic acid

yielded a product
$$C$$
.
 $CH_3COOH + PCl_5 \rightarrow A \xrightarrow{C_6H_6} B \xrightarrow{C_2H_5MgBr} C$

Product C would be

- (a) $CH_3CH(OH)C_2H_5$
- (b) CH₃COC₆H₅
- (c) CH₃CH(OH)C₆H₅

- $\begin{array}{c} C_2H_5\\ |\\ (d) \ CH_3-C(OH)C_6H_5 \end{array}$
- (2003)

51.
$$\overset{\mbox{CH}_2}{\overset{\mbox{CH}_2}{\overset{\mbox{C}}{\overset{\mbox{C}}{\overset{\mbox{H}_3}{\overset{\mbox{C}}{\overset{\mbox{H}_3}{\overset{\mbox{C}}{\overset{\mbox{H}_2}{\overset{\mbox{C}}{\overset{\mbox{C}}{\overset{\mbox{H}_3}{\overset{\mbox{C}}{\overset{\mbox{H}_3}{\overset{\mbox{C}}{\overset{\mbox{H}_3}{\overset{\mbox{C}}{\overset{\mbox{H}_3}{\overset{\mbox{C}}{\overset{\mbox{H}_3}{\overset{\mbox{C}}{\overset{\mbox{C}}{\overset{\mbox{H}_3}{\overset{\mbox{C}}{\overset{\mbox{H}_3}{\overset{\mbox{C}}{\overset{\mbox{C}}{\overset{\mbox{C}}{\overset{\mbox{H}_3}{\overset{\mbox{C}}}}{\overset{\mbox{C}}{\overset{\mbox{C}}}{\overset{\mbox{C}}}{\overset{\mbox{C}}}{\overset{\mbox{C}}{\overset{\mbox{C}}}{\overset{\mbox{C}}}{\overset{\mbox{C}}}{\overset{\mbox{C}}}{\overset{\mbox{C}}}}{\overset{\mbox{C}}}{\overset{\mbox{C}}}{\overset{\mbox{C}}}{\overset{\mbox{C}}}{\overset{\mbox{C}}}{\overset{\mbox{C}}}{\overset{\mbox{C}}}{\overset{\mbox{C}}}{\overset{\mbox{C}}}}}{\overset{\mbox{C}}}{\overset{\mbox{C}}}}}}}}}}}}}}}}}}}}}}}}}$$

- (a) resonating structures
- (b) tautomers
- (c) geometrical isomers
- (d) optical isomers.
- (2002)

52. In the following reaction product
$$P$$
 is $R - C - C1 \xrightarrow{H_2} Pd\text{-BaSO}_4 P$

- (a) RCH₂OH
- (b) RCOOH
- (c) RCHO
- (d) RCH₃ (2002)

53. Which alkene on ozonolysis gives CH₃CH₂CHO and CH₃COCH₃?

(a)
$$CH_3CH_2CH = C < CH_3$$

- (c) $CH_3CH_2CH = CHCH_3$

(d)
$$CH_3 - C = CHCH_3$$
 (2001)

- **54.** Which of the following give positive Fehling solution test?
 - (a) Sucrose
- (b) Glucose
- (c) Fats
- (d) Protein (2001)
- 55. Polarisation in acrolein can be described as

(a)
$$\overset{+\delta}{\text{CH}}_2$$
=CH- $\overset{+\delta}{\text{CHO}}$

(b)
$$\overset{-\delta}{C}H_2 = CH - \overset{+\delta}{C}HO$$

(c)
$$\overset{-\delta}{CH_2}$$
=CH-CHO

(d)
$$^{+\delta}_{CH_2}$$
=CH-CHO

(2000)

- **56.** First product of the reaction between RCHO and NH₂NH₂ is
 - (a) $RCH = NNH_2$
- (b) RCH = NH
- (c) RCH₂NH₂
- (d) RCON₃

(2000)

- 57. Ethyl benzoate can be prepared from benzoic acid by using
 - (a) ethyl alcohol
 - (b) ethyl alcohol and dry HCl
 - (c) ethyl chloride
 - (d) sodium ethoxide.

(2000)

- 58. Reduction by LiAlH₄ of hydrolysed product of an ester gives
 - (a) two alcohols
 - (b) two aldehydes
 - (c) one acid and one alcohol
 - (d) two acids.

(2000)

59. In the reaction $CH_3CN + 2H$

Boiling $H_2O \rightarrow Y$; the term Y is

- (a) acetaldehyde
- (b) ethanamine
- (c) acetone
- (d) dimethylamine

(1999)

- **60.** Aldol condensation will not take place in
 - (a) CH₃COCH₃
- (b) CH₃CHO
- (c) HCHO
- (d) CH₃CH₂CHO

(1999, 1996)

- **61.** Which one of the following compounds will react with NaHCO3 solution to give sodium salt and carbon dioxide?
 - (a) Acetic acid
- (b) n-Hexanol
- (c) Phenol
- (d) Both (b) and (c)

(1999)

- 62. Which one of the following esters cannot undergo Claisen self-condensation?
 - (a) C₆H₅CH₂COOC₂H₅
 - (b) C₆H₅COOC₂H₅
 - (c) CH₃CH₂CH₂CH₂COOC₂H₅
 - (d) $C_6H_{11}CH_2COOC_2H_5$

(1998)

- **63.** An ester (A) with molecular formula, $C_9H_{10}O_2$ was treated with excess of CH3MgBr and the complex so formed, was treated with H2SO4 to give an olefin (B). Ozonolysis of (C) gave a ketone with molecular formula C₈H₈O which shows +ve iodoform test. The structure of (A) is
 - (a) H₃CCH₂COC₆H₅
 - (b) C₂H₅COOC₆H₅
 - (c) $C_6H_5COOC_2H_5$
 - (d) p-H₃CO C₆H₄ COCH₃

(1998)

- **64.** Ketones $[RCOR_1]$ where $R = R_1 =$ alkyl group. It can be obtained in one step by
 - (a) oxidation of tertiary alcohol
 - (b) reaction of acid halide with alcohols
 - (c) hydrolysis of esters
 - (d) oxidation of primary alcohol.

(1997)



- **65.** Phenylmethanol can be prepared by reducing the benzaldehyde with
 - (a) CH₃Br and Na
- (b) CH₃I and Mg
- (c) CH₃Br
- (d) Zn and HCl.

(1997)

- **66.** The oxidation of toluene to benzaldehyde by chromyl chloride is called
 - (a) Etard reaction
 - (b) Riemer-Tiemann reaction
 - (c) Wurtz reaction
 - (d) Cannizzaro's reaction.

(1996)

- **67.** Which of the following compound gives benzoic acid on hydrolysis?
 - (a) Chlorobenzene
- (b) Benzoyl chloride
- (c) Chlorophenol
- (d) Chlorotoluene (1996)
- **68.** The order of reactivity of carbonyl compounds for nucleophilic addition is
 - (a) $Ar_2C = O > R_2C = O > ArCHO > RCHO$ > $H_2C = O$
 - (b) $H_2C = O > R_2C = O > Ar_2C = O > RCHO > ArCHO$
 - (c) $H_2C = O > RCHO > ArCHO > R_2C = O > Ar_2C = O$
 - (d) ArCHO > Ar₂C = O > RCHO > R_2 C = O > H_2 C = O (1995)
- 69. In the reaction

 $CH_3CHO + HCN \rightarrow CH_3CH(OH)CN$,

- a chiral centre is produced. This product is
- (a) dextrorotatory
- (b) racemic mixture
- (c) meso compound
- (d) laevorotatory.

(1995)

70. Which one of the following product is formed when adipic acid is heated?

(c)
$$\begin{array}{c|c} CH_2-CH_2 \\ CH_2-CH_2 \end{array}$$

(d)
$$|_{CH_2-CH_2}^{CH_2-CH_2} C = 0$$
 (1995)

- 71. The oxidation of toluene with CrO₃ in the presence of (CH₃CO)₂O gives a product A, which on treatment with aqueous NaOH produces
 - (a) C₆H₅COONa
 - (b) 2, 4-diacetyl toluene
 - (c) C_6H_5CHO
- (d) $(C_6H_5CO)_2O$.

(1995)

- **72.** Compound A has a molecular formula C₂Cl₃OH. It reduces Fehling's solution and on oxidation, it gives a monocarboxylic acid B. If A is obtained by the action of chlorine on ethyl alcohol, then compound A is
 - (a) methyl chloride
 - (b) monochloro acetic acid
 - (c) chloral
- (d) chloroform.

(1994)

- **73.** Which of the following compound will undergo self aldol condensation in the presence of cold dilute alkali?
 - (a) $CH \equiv C CHO$
- (b) $CH_2 = CHCHO$
- (c) C_6H_5CHO
- (d) CH₃CH₂CHO

(1994)

- **74.** Which of the following compounds will give positive test with Tollen's reagent?
 - (a) Acetic acid
- (b) Acetone
- (c) Acetamide
- (d) Acetaldehyde

(1994)

- **75.** An acyl halide is formed when PCl_5 reacts with an
 - (a) amide
- (b) ester
- (c) acid
- (d) alcohol. (1994)
- 76. Sodium formate on heating yields
 - (a) oxalic acid and H₂
 - (b) sodium oxalate and H₂
 - (c) CO₂ and NaOH
 - (d) sodium oxalate.

(1993)

- 77. $(CH_3)_2C$ CHCOCH₃ can be oxidised to $(CH_3)_2C$ CHCOOH by
 - (a) chromic acid
- (b) NaOI
- (c) Cu at 300°C
- (d) KMnO₄ (1993)
- **78.** In which of the following, the number of carbon atoms does not remain same when carboxylic acid is obtained by oxidation?
 - (a) CH₃COCH₃
- (b) CCl₃CH₂CHO
- (c) CH₃CH₂CH₂OH
- (d) CH₃CH₂CHO

(1992)

- **79.** Benzoic acid gives benzene on being heated with X and phenol gives benzene on being heated with Y. Therefore X and Y are respectively
 - (a) soda-lime and copper
 - (b) Zn dust and NaOH
 - (c) Zn dust and soda-lime
 - (d) soda-lime and zinc dust.

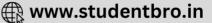
80. Acetaldehyde reacts with

- (a) electrophiles only (b) nucleophiles only
- (c) free radicals only
- (d) both electrophiles and nucleophiles.

(1991)

(1992)





- 81. The reagent (s) which can be used to distinguish acetophenone from benzophenone is (are)
 - (a) 2,4-dinitrophenylhydrazine
 - (b) aqueous solution of NaHSO₃
 - (c) Benedict reagent
 - (d) I2 and NaOH.

(1990)

- 82. Indicate which of the nitrogen compound amongst the following would undergo Hofmann's reaction, i.e., reaction with Br2 and strong KOH to furnish the primary amine $(R - NH_2)$?
 - (a) $R CO NHCH_3$
- (b) $R CO ONH_4$
- (c) $R CO NH_2$
- (d) R CO NHOH.

83.
$$O(CH_2-O)CH_2$$

The above shown polymer is obtained when a carbonyl compound is allowed to stand. It is a white solid. The polymer is

- (a) trioxane
- (b) formose
- (c) paraformaldehyde
- (d) metaldehyde.

(1989)

The given compound describes

a condensation polymer which can be obtained in two ways: either treating 3 molecules of acetone (CH₃COCH₃) with conc. H₂SO₄ or passing propyne (CH₃C \equiv CH) through a red hot tube. The polymer is

- (a) phorone
- (b) mesityl oxide
- (c) deacetonyl alcohol
- (d) mesitylene.

(1989)

85. 3CH₃COCH₃ HCl -3H₂O

$$(CH_3)_2C = CH - CO - CH = C(CH_3)_2$$
(B)

This polymer (B) is obtained when acetone is saturated with hydrogen chloride gas, B can be

- (a) phorone
- (b) formose
- (c) diacetone alcohol
- (d) mesityl oxide.

(1989)

- **86.** The compound formed when malonic acid is heated with urea is
 - (a) cinnamic acid
- (b) butyric acid
- (c) barbituric acid
- (d) crotonic acid.

(1989)

- 87. If formaldehyde and KOH are heated, then we get (b) methyl alcohol
 - (a) methane (c) ethyl formate
- (d) acetylene.
 - (1988)
- 88. Formalin is an aqueous solution of
 - (a) fluorescein
- (b) formic acid
- (c) formaldehyde
- (d) furfuraldehyde. (1988)
- 89. Among the following the strongest acid is

 - (a) CH₂COOH
- (b) CH₂ClCH₂COOH
- (c) CH2ClCOOH
- (d) CH₃CH₂COOH. (1988)

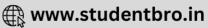
90. Which of the following is the correct decreasing order of acidic strength of

- (i) methanoic acid (iii) propanoic acid
- (ii) ethanoic acid (iv) butanoic acid
- (a) (i) > (ii) > (iii) > (iv)
- (b) (ii) > (iii) > (iv) > (i) (c) (i) > (iv) > (iii) > (ii)
- (d) (iv) > (i) > (iii) > (ii)

(1988)

(Answer Key)

- 1. (b) **5.** (b) 2. 3. (b) 4. (c) 6. (b) 7. 8. 9. (d) **10.** (a) (a) (a) (a)
- 11. 20. (d) 12. (d) 13. (b) 14. (c) 15. (d) 16. (b) 17. (a) 18. (a) 19. (d) 23. 24. (d) 25. 26. (b) 27. 28. **30.** (c) (d) (d) (a) (d) 29. (c) (c)
- **36.** 31. 32. 33. 34. 35. (d) 37. 38. 39. (c) (c) (a) (c) (a) (a) (c) (c) 40. (a)
- 41. (b) **42. 43**. 44. (b) 45. (d) 46. **47. 48**. 49. (d) **50.** (a) (c) (a) (c) (b) (d)
- 51. **52.** (c) 53. 54. (b) 55. (d) **56.** (a) 57. (b) **58. 59**. **60**. (a) (a) (a) (c)
- 61. (a) **62.** (b) **63**. (c) 64. (a) **65**. (d) **66.** (a) **67.** (b) 68. (c) 69. (b) **70.** (a)
- 71. (c) *75*. 77. **78. 79.** 72. **73.** (d) **74.** (d) **76.** (b) (b) (d) 80. (b) (c) (c) (a) 81. 85. **87.** 90. **82.** (c) 83. (a) 84. (d) (a) 86. (c) (b) 88. (c) **89**.



EXPLANATIONS

1. **(b)**: Since, A gives silver mirror test, it must be an aldehyde and aldehydes are formed by oxidation of 1° alcohols. Thus, 'X' is a 1° alcohol, *i.e.*, CH_2CH_2OH .

$$\begin{array}{c} \text{CH}_{3}\text{CH}_{2}\text{OH} \xrightarrow{\text{Cu}, 573 \text{ K}} \xrightarrow{\text{CH}_{3}\text{CHO}} \xrightarrow{\text{Silver mirror}} \\ \text{CH}_{3}\text{CH}_{2}\text{OH} \xrightarrow{\text{Cu}, 573 \text{ K}} \xrightarrow{\text{CH}_{3}\text{CHO}} \xrightarrow{\text{CH}_{2}\text{CHO}} \\ \text{Ethanol} & \text{Ethanal} & \text{Aldol} & \text{condensation} \\ \text{(N)} & \text{OH} & \text{CH}_{2}\text{CHO} \\ \text{CH}_{3} \xrightarrow{\text{CH}} \xrightarrow{\text{CH}} \xrightarrow{\text{CH}} \xrightarrow{\text{CH}} \xrightarrow{\text{CH}} \xrightarrow{\text{CH}} \\ \text{CH}_{3} \xrightarrow{\text{CH}} \xrightarrow{\text{CH}} \xrightarrow{\text{CH}} \xrightarrow{\text{CH}} \xrightarrow{\text{CH}} \\ \text{CH}_{3} \xrightarrow{\text{CH}} \xrightarrow{\text{CH}} \xrightarrow{\text{CH}} \xrightarrow{\text{CH}} \xrightarrow{\text{CH}} \xrightarrow{\text{CH}} \xrightarrow{\text{CH}} \\ \text{CH}_{3} \xrightarrow{\text{CH}} \xrightarrow{\text{CH$$

$$CH_{3}C = \boxed{O + H_{2} \mid N - NH - C - NH_{2}}$$

$$H \qquad \downarrow^{-H_{2}O} \qquad O \qquad | | |$$

$$CH_{3} - CH = N - NH - C - NH_{2}$$

$$Semicarbazone \qquad (Z)$$

2. (a) :

$$\begin{array}{c} O \\ H \\ \hline OH \\ \hline$$

C=C bond is reduced faster than C=O bond with H₂(Pd-C).

4. (b): Acidic strength $\infty - I$ effect

As oxygen is more electron withdrawing (II) and (III) show greater – *I* effect than (I). Thus, (I) is least acidic. Out of (II) and (III), (II) is more acidic than (III) as distance of O increases from —COOH group and acidic strength decreases.

5. (c):

Trans-isomer does not react with acetone.

6. (b): Keto-enol tautomerism :

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

$$\begin{array}{c}
 & C$$

7. (a):

$$+ \frac{9}{2} O_2 \xrightarrow{V_2O_5, 773 \text{ K}} \begin{bmatrix} \text{CHCOOH} \\ || \\ \text{CHCOOH} \end{bmatrix}$$

$$\text{Maleic acid}$$

$$\Delta \downarrow -\text{H}_2\text{O}$$

$$O$$

$$CHC$$

$$|| \\ CHC$$

$$O$$

$$CHC$$

$$|| \\ O$$

$$CHC$$

$$O$$

$$Maleic anhydride$$

8. (a): Carbonyl compounds react with ammonia derivatives in weakly acidic medium as follows:

$$C = O + H_2N - Z \longrightarrow \begin{bmatrix} OH \\ NHZ \end{bmatrix}$$

$$derivative$$

$$H^+ - H_2O$$

$$C = N - Z$$

9. (d): Electron withdrawing groups increase the reactivity towards nucleophilic substitution reaction and $-NO_2$ is a strong electron withdrawing group.

10. (a): Compound 'X' yields phenylhydrazone

$$\begin{array}{c} O \\ \Rightarrow -C - \text{ group.} \\ O \\ \text{II} \\ \text{Negative iodoform test} \Rightarrow CH_3 - C - \text{group is absent} \end{array}$$

Negative Tollens' test \Rightarrow ketone Hence, the compound is 3-pentanone.

$$\begin{array}{c} \text{CH}_3\text{CH}_2 - \begin{array}{c} \text{C} \\ \text{II} \\ \text{CH}_2\text{CH}_2 \\ \text{CH}_3 \end{array} \\ \xrightarrow{\text{3-Pentanone}} \\ \text{(C}_5\text{H}_{10}\text{O)} \\ \text{(X)} \end{array} \quad \begin{array}{c} \text{Reduction} \\ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \\ \text{n-Pentane} \end{array}$$

11. (d): Aromatic aldehydes are more reactive than alkyl aryl ketones. Electron withdrawing group (—NO₂) increases the reactivity towards nucleophilic addition reactions whereas, electron donating group (—CH₃) decreases the reactivity towards nucleophilic addition reactions. Therefore, the order is:

$$\begin{array}{c|c} CHO & CHO & CHO & COCH_3 \\ \hline \bigcirc & > & \bigcirc & > & \bigcirc \\ NO_2 & & CH_3 & \\ \end{array}$$

12. (d):
$$CH_3$$
 C CH_2 CH_3 C

[Enol form (76%) more stable due to intramolecular hydrogen bonding]

- **13. (b)**: Reduction in presence of Zn-Hg and conc. HCl is useful for aldehyde and ketone but carboxylic acid group remains unaffected.
- 14. (c): Aldehyde having no α -hydrogen atoms on heating with concentrated alkali solution (50%) undergo Cannizzaro's reaction.

15. (d):
$$(CH_3)_2C = O + HOC_2H_5 \xrightarrow{HCl_{(g)}} \Delta$$

$$(\mathrm{CH_3})_2\mathrm{C} \underset{\mathrm{Acetal}}{\underbrace{\mathrm{OC_2H_5}}}$$

- **16. (b)**: Acetaldehyde, acetone and methyl ketones having CH_3CO- group undergo haloform reaction. Thus CH_3CHO will give yellow precipitate with I_2 and NaOH but $C_6H_5CH_2CHO$ will not.
- 17. (a): As -I effect increases, COOH group becomes more electron deficient and tendency to loose H^+ ions increases *i.e.*, acid strength increases. As +I effect increases, acid strength decreases. Thus, correct order of acid strength is

$$CF_3COOH > CCl_3COOH > HCOOH > CH_3COOH$$

 $(B) > (A) > (D) > (C)$

O=C-Cl
$$H$$
-C=O

18. (a): H_2
 $Pd/BaSO_4$

It is Rosenmund's reaction.

19. (d)

20. (a,d): This example shows iodoform reaction. The compound with $CH_3 - C$ — group or

iodoform (CHI₃) when react with iodine and alkali.



(Acid derivatives do not give iodoform test)

21. (b): Carbonyl group is reduced to – CH₂ group, when treated with amalgamated zinc and conc. HCl. This process is called Clemmensen's reduction.

23. (d): Greater the number of alkyl groups attached to the carbonyl groups and hence, lower will be its reactivity.

24. (d):

(A) Benzaldehyde

(ii) Benzoin condensation

(B) Phthalic anhydride (i) Phenolphthalein

(C) Phenyl benzoate

(iv) Fries

rearrangement

(D) methyl salicylate

(iii) Oil of

wintergreen

25. (d): The compound will be CH₃CH₂COOH.

$$CH_{3}CH_{2}COOH \xrightarrow{NH_{3}} CH_{3}CH_{2}COONH_{4}$$

$$A \qquad \qquad \downarrow \Delta$$

$$CH_{3}-CH_{2}-NH_{2} \xleftarrow{Br_{2}/KOH} CH_{3}CH_{2}CONH_{2}$$
ethyl amine

26. (b): (a) Reimer-Tiemann reaction :

$$\begin{array}{c}
OH \\
& \downarrow \\
Phenol
\end{array}
+ CHCl_3 \xrightarrow{aq. NaOH} OH \\
Chloroform$$
Salicylaldehyde

(b) Cannizzaro reaction:

(c) Wurtz reaction:

$$H_3C$$
— $I + 2Na + I$ — $CH_3 \rightarrow CH_3$ — $CH_3 + 2NaI$
Methyl iodide Ethane

(d) Friedel-Crafts acylation:

From the above examples it is evident that C—C bond formation does not takes place in Cannizzaro reaction.

27. (a):
$$CH_3CONH_2 + 4NaOH + Br_2 \rightarrow$$
Acetamide
$$CH_3NH_2 + 2KBr + K_2CO_3 + 2H_2O$$
1° Amine

This reaction is called Hofmann Bromamide reaction.

- **28. (d)**: CH₃COC1 is most susceptible to nucleophilic attack. The susceptibility of a substrate towards nucleophilic attack depends on how good a leaving group is attached to it. Cl⁻ is a weak base and therefore a good leaving group.
- **29. (c)**: The ease of dehydration of the given compounds can be explained on the basis of the stability of the carbocation formed. In case of options (a), (b) and (d), a secondary carbocation is formed but the presence of an electron withdrawing

C=O group adjacent to the positively charged carbon, intensifies the charge and hence destabilises the species.

$$H_3C$$
 H_3C
 H_3C
 H_3C
 H_3C
 H_3C
 H_3C
 H_3C
 H_3C
 H_3C
 H_3C

However, in case of option (c), a secondary carbocation is formed, but the electron withdrawing

C=O group is present farther away, as a result, the effect of this group is diminished and hence the carbocation is relatively more stable.



30. (c): It gives D.D.T (*p*,*p*- dichlorodipheny-ltrichloroethane)

$$2C_6H_5Cl + CCl_3CHO \xrightarrow{H_2SO_4} Cl_3CCH$$
—Cl

31. (c): This is Hell-Volhard-Zelinsky reaction. In this reaction, acids containing α -H react with X_2 /red P giving product in which the α -hydrogens are substituted by X.

$$\therefore \text{ CH}_3\text{CH}_2\text{COOH} \xrightarrow{\text{Br}_2/P} \text{CH}_3 - \overset{\text{Br}}{\underset{||}{\text{C}}} - \text{COOH}$$

32. (c): The first step is a simple condensation reaction. The last step is an example of E1cB mechanism and the leaving group is hydroxide, which is unusual. Still this step manages to take place owing to the stability incorporated therein the product, which is a conjugated carbonyl compound.

$$CH_3$$
 CH_2
 CH_3
 CH_3

33. (a): The base (OH⁻) ion removes one of the α -hydrogen atom (which is some what acidic) from aldehyde and ketones to form a carbanion or the enolate ion. The acidity of α -hydrogen is due to reasonance stabilization of enolate anion.

$$(L = X, NH2, O - C - R \text{ or } OR)$$

The relative reactivities of various compounds have been found to be in the following order:

$$\begin{array}{c}
R \\
X
\end{array}
C = O > R - C - O - C - R \\
> R - C \stackrel{O}{\swarrow}_{OR} > R - C \stackrel{O}{\searrow}_{NH}$$

35. (d): Aldehydes and ketones are converted to alkane when treated with zinc amalgam and conc. HCl. This is known as Clemmensen reduction. Here

C = O group is reduced to CH_2 group.

$$R - C - H + 4 [H] \xrightarrow{\text{Zn-Hg}} R - CH_3 + H_2O$$

36. (a): Aldehydes which do not have a-H atom, in presence of 50% NaOH or 50% KOH undergoes disproportionation reaction to produce alcohol and sodium salt of acid. This reaction is known as Cannizzaro reaction. C_6H_5CHO , containing no α -H atom undergoes Cannizzaro reaction to produce benzyl alcohol and sodium benzoate.

$$C_6H_5CHO \xrightarrow{50\% \text{ NaOH}} C_6H_5CH_2OH + C_6H_5COONa$$

- **37.** (a): The aldehydes or ketones containing α -H atom in presence of dilute alkali undergo self condensation reaction to form β -hydroxyaldehyde or β -hydroxyketone. This reaction is known as Aldol condensation.
- **38. (c)**: The ease of hydrolysis depends upon the magnitude of the +ve charge on the carbonyl group. Electron-withdrawing groups increase the magnitude of positive charge and electron donating groups decrease the magnitude of positive charge. Hence, the decreasing order of reactivity towards hydrolysis is

$$OCCI$$
 $OCCI$ $OCCI$

39. (c): FCH₂COOH > ClCH₂COOH > BrCH₂COOH > CH₃COOH

Acidity decreases as the -I effect of the group decreases, F is the most electronegative atom and hence it has highest -I effect among the halogens.



40. (a): The reactivity of the carbonyl group towards the addition reactions depends upon the magnitude of the positive charge on the carbonyl carbon atom. Hence aryl substituent that increases the positive charge on the carbonyl carbon must increase its reactivity towards addition reactions. The introduction of negative group (-I effect) increases the reactivity while introduction of alkyl group (+I effect) decreases the reactivity.

$$H C=O > CH_3 C=O > CH_3 C=O$$

+I effect and steric hind rance increases

41. (b):
$$CH_3CHO + HCN \longrightarrow CH_3 - \stackrel{H}{C} - OH$$

$$\stackrel{H_2O}{\longrightarrow} CH_3 - \stackrel{C}{C} - OH$$

$$COOH$$

42. (a):
$$CH_3CH_2COOH \xrightarrow{SOCl_2} CH_3CH_2COCl_{(B)}$$

$$\xrightarrow{\text{NH}_3} \text{CH}_3\text{CH}_2\text{CONH}_2 \xrightarrow{\text{KOH}} \text{CH}_3\text{CH}_2\text{NH}_2$$

43. (c): Ethyl acetate undergoes Claisen condensation in presence of sodium ethoxide involving α -hydrogen atom in which two molecules of ethyl acetate combine together to form acetoacetic ester.

$$\begin{array}{c} \text{CH}_3\text{COOC}_2\text{H}_5 + \text{CH}_3\text{COOC}_2\text{H}_5 & \xrightarrow{\text{\mathbf{C}_2H}_5\text{ONa}} \\ \text{CH}_3\text{COCH}_2\text{COOC}_2\text{H}_5 + \text{C}_2\text{H}_5\text{OH} \\ \text{Acetoacetic ester} \end{array}$$

44. (b):

$$O \rightarrow CH_3$$
 $O \rightarrow CH_3$
 $O \rightarrow CH_3$

46. (a): Secondary alcohol on oxidation gives a ketone containing the same number of carbon atoms.

$$CH_3 - CHOH \xrightarrow{[O]} CH_3 - CH_3$$

47. (c): Lactic acid $(CH_3CH(OH)COOH)$ is an optically active compound due to the presence of asymmetric carbon atom. It exists in *D*-and *L*-form, the ratio of which is found to be (1:1), *i.e.*, a racemic mixture is obtained.

48. (b):
$$CH_2OH$$
 $COOK$
 CH_2OH COO
 CH_2OH COO
 CH_2OH COO
 CH_2OH COO

The above reaction is known as Cannizzaro's reaction.

49. (d):
$$R - C - R' \xrightarrow{\text{HCN/KCN}} R - C - R'$$
OH
$$\xrightarrow{\text{LiAlH}_4} R - C - R'$$
OH
OH
OH
OH
OH
OH

50. (d):
$$CH_3COOH + PCl_5 \rightarrow CH_3COCI \xrightarrow{C_6H_6}$$
 anhy. $AICl_3$

$$C_6H_5COCH_3 \xrightarrow{C_2H_5MgBr} C_6H_5C - CH_3$$
(B)
OH
(C)



CLICK HERE

51. (a): They are resonating forms because the position of the atomic nuclei remain the same and only electron redistribution has occurred

$$\begin{array}{c} & & \\ & & \\ \text{CH}_2\text{-C-CH}_3 & \longleftrightarrow & \text{CH}_2\text{=C-CH}_3 \\ & & & \\$$

52. (c): This is Rosenmund reaction.

$$R - C - Cl \xrightarrow{\text{H}_2} RCHO$$
O

O

ROBIN PROBLEM 1

BaSO₄ prevents the aldehyde from being reduced and acts as a poison to the palladium catalyst in this reaction.

53. (a): On passing a steam of ozone through a solution of olefin in an organic solvent, an ozonide is obtained.

$$R > C = CR'H + O_3 \longrightarrow R_2C - O - CHR'$$

$$O = O$$
ozonide
ozonide

The ozonide on reduction with Zn and acid or H₂/Ni gives aldehydes and/or ketones.

$$\begin{array}{c|c} R \\ \hline C - O - CHR' \xrightarrow{H_2/N_1} R_2CO + R'CHO \\ \hline O \xrightarrow{O} O \end{array}$$

The nature of these products helps in locating the position of the double bond in olefin.

- **54. (b)** : Glucose reduces Fehling solution because glucose has free -CHO group which is readily oxidised.
- **55.** (d): O-atom is more electronegative than C-atom, therefore O-atom bears partial -ve charge and C-atom to which it is attached bear partial +ve charge

$$CH_2 = CH - CH_2 - CH = C - O$$

$$H$$

$$H$$

$$CH_2 - CH = C - O$$

56. (a): It is a simple condensation reaction which proceeds with elimination of water.

$$R - CH = O + H_2N - NH_2 \xrightarrow{-H_2O} RCH = N - NH_2$$

57. (b): Ethyl benzoate can be prepared by heating benzoic acid with ethyl alcohol in presence of dry HCl or conc. H_2SO_4 . The reaction is called as esterification reaction.

$$\begin{array}{c} {\rm C_6H_5-COOH+C_2H_5-OH} \xrightarrow{\rm dry\ HCl} {\rm C_6H_5COOC_2H_5} \\ {\rm Ethyl\ benzoate} \end{array}$$

58. (a): Reduction of hydrolysed product of ester by LiAlH₄ produces two alcohols.

$$R - COOR' \xrightarrow{\text{H}_2\text{O}} R - COOH + ROH$$

$$\xrightarrow{\text{LiAlH}_4} R - CH_2\text{OH} + ROH$$
59. (a): $CH_3 - C \equiv N + 2H \xrightarrow{\text{ether}} CH_3 - CH \equiv NH$

59. (a):
$$CH_3 - C = N + 2H \xrightarrow{HCl} CH_3 - CH = NH$$

$$CH_3 - CH = NH \xrightarrow{H_2O} CH_3 - CHO + NH_3$$
(1)

- 60. (c): The carbonyl compounds having atleast one α-hydrogen atom undergo condensation reaction in presence of dilute NaOH solution. This reaction is called as aldol condensation reaction. As formaldehyde (HCHO) has no α-hydrogen atom attached to carbonyl group, it does not respond to this test.
- **61.** (a): NaHCO₃ is weakly basic, so it can only react with the acid CH₃COOH. While phenol is weakly acidic and n-hexanol is neutral, they do not react with NaHCO3.

$$CH_3COOH + NaHCO_3 \rightarrow CH_3COONa + CO_2 + H_2O$$

62. (b): The esters having active methylene group (- CH₂ -), show Claisen Condensation reaction. As $C_6H_5 - COOC_2H_5$ has no α -hydrogen atom or active methylene group, so it cannot undergo Claisen-Condensation reaction.

63. (c):
$$C_6H_5 - COOC_2H_5 \xrightarrow{CH_3MgBr}$$

$$C_6H_5 - C - OC_2H_5 \xrightarrow{-Mg(OC_2H_5)Br}$$

$$CH_3$$

$$C_{6}H_{5} - C - CH_{3} \xrightarrow{CH_{3}MgBr} C_{6}H_{5} - C - CH_{3} \xrightarrow{H_{2}O} CH_{5}$$

$$C_{6}H_{5} - \overset{OH}{\overset{1}{\underset{C}{\bigvee}}} - CH_{3} \xrightarrow{\text{conc. } H_{2}SO_{4}} C_{6}H_{5} - \overset{C}{\underset{C}{\longleftarrow}} - CH_{2} \xrightarrow{O_{3}/H_{2}O} CH_{3} \xrightarrow{CH_{3}} \overset{O_{3}/H_{2}O}{\overset{O}{\underset{C}{\bigvee}}} + \overset{O_{3}/H_{2}O}{\overset{O}{\underset{C}{$$

$$C_6H_5 - CO - CH_3 \xrightarrow{I_2/NaOH} CHI_3 + C_6H_5 - COONa$$
 $(C_8H_8O) \xrightarrow{Iodoform}$



64. (a): A tertiary alcohol is difficult to oxidise. But when it is treated with an acidic oxidising agent under some conditions, it is oxidised to ketone and then to acids. Both the ketone and acid contain the lesser number of carbon atoms than the starting alcohol.

65. (d):
$$C_6H_5CHO + 2[H]$$
 Zn/HCl $C_6H_5CH_2OH$

Benzaldehyde Phenylmethanol

(Benzyl alcohol)

66. (a): The oxidation of toluene $(C_6H_5CH_3)$ with chromyl chloride (CrO_2Cl_2) in CCl_4 or CS_2 to give benzaldehyde is called Etard reaction. In this reaction, the chromyl chloride first forms a brown complex, which is separated and then decomposed with H_2O to give benzaldehyde (C_6H_5CHO) .

67. (b):
$$C_6H_5COC1 + H_2O \rightarrow C_6H_5COOH + HC1$$

Benzoyl chloride Benzoic acid

68. (c): With each substitution of hydrogen atom, reactivity of carbonyl compound decreases. This is due to inductive effect in case of alkyl groups and resonance in case of aromatic groups.

69. (b):

$$CH_{3} - CH = O + HCN \longrightarrow CH_{3} - CH = OH \qquad CN$$

$$\longrightarrow CH_{3} - C - OH \qquad + CH_{3} - C - OH$$

$$CN \qquad H$$

70. (c):
$$CH_3$$
 CHO
$$CrO_3$$
 CCH $_3$ CO) $_2$ O

Thus the compound A is chloral.

72. (d): Since CH_3CH_2CHO has α -hydrogen atom, therefore it will undergo aldol condensation in the presence of cold dilute alkali.

73. (d): Acetaldehyde reduces Tollen's reagent to silver mirror.

$$\begin{array}{cccc} CH_{3}CHO & + & 2[Ag(NH_{3})_{2}]^{+} & + & 3OH^{-} \rightarrow \\ (Acetaldehyde) & (Tollen's reagent) & \\ & & CH_{3}COO^{-} + 2H_{2}O + 2Ag & + & 4NH_{3} \\ & & & (Silver mirror) & \end{array}$$

74. (c):
$$3\text{CH}_3\text{COOH} + \text{PCl}_5 \rightarrow 3\text{CH}_3\text{COCl} + \text{POCl}_3$$
Acetic acid Acetyl chloride + HCl

75. (b) : Sodium oxalate and H₂

76. (b):
$$(CH_3)_2C = CHCOCH_3 \xrightarrow{NaOI}$$
 $(CH_3)_2C = CHCOOH + CHI_3$
(NaOH + I) (NaOI is the best suitable reagent for

 $(NaOH + I_2)/NaOI$ is the best suitable reagent for the above reaction.

77. (a): Ketones on oxidation give carboxylic acids with lesser number of carbon atoms *i.e.*, $CH_3COCH_3 \xrightarrow{[O]} CH_3COOH + CO_2 + H_2O$

78. (d):
$$C_6H_5COOH \xrightarrow{Soda-lime} C_6H_6 + ZnO$$

$$C_6H_5OH \xrightarrow{Zn \text{ dust}} C_6H_6 + ZnO$$

X = soda-lime and Y = Zn dust

79. (b) : Acetaldehyde reacts only with nucleophiles. Since the mobile π -electrons of carbon oxygen double bond are strongly pulled towards oxygen, carbonyl carbon is electron-deficient and carbonyl oxygen is electron-rich. Thus, the electron deficient carbonyl carbon is most susceptible to attack by electron rich nucleophilic reagent, *i.e.* by base.

by electron rich nucleophilic reagent, *i.e.* by base.

$$C = \overset{\circ}{\Omega}: + H^{+} \longrightarrow from acidic medium$$

$$C = \overset{\circ}{\Omega}H^{+} \longrightarrow C^{+} = \overset{\circ}{\Omega} - H$$

The nucleophile, then attacks the protonated carbonyl group to form addition product.

$$C = O - H + Z \longrightarrow C$$
Nucleophile

Addition produc

80. (d): Acetophenone reacts with NaOH and I_2 to give yellow ppt. of CHI₃ but benzophenone $(C_6H_5COC_6H_5)$ does not. Hence, it can be used to distinguish between them.

distinguish between them.

$$C_6H_5COCH_3 \xrightarrow{I_2, NaOH} CHI_3 + C_6H_5COONa$$

yellow ppt.





$$R - \text{CONH}_2 \xrightarrow{\text{Br}_2, \text{ KOH}} R\text{NH}_2$$
82. (a): 3HCHO aq. soln.
$$CH_2 \cap CH_2 \cap CH_2$$

Trioxane (metaformaldehyde)

83. (d): Acetone forms mesitylene (1, 3, 5-trimethyl benzene) on distillation with conc. H_2SO_4 .

84. (a):

H₃C C =
$$O + H_2$$
 CH - C - CH $H_2 + O$ = C CH H_3 C C = $O + H_2$ CH - C - CH $H_2 + O$ = C CH $O + H_3$ C C = $O + H_2$ CH - C - CH = $O + H_3$ C CH $O +$

85. (c):
$$CH_2 \subset COOH$$
Malonic acid

 $COOH_2 \hookrightarrow COOH_2 \xrightarrow{\Delta}$
 $COOH_2 \hookrightarrow COOH_2 \xrightarrow{\Delta}$

$$CH_2$$
 $CO - NH$ CO $CO - NH$ CO Barbituric acid

86. (b):HCHO+KOH ^{50%} KOH → HCOOK+CH₃OH The above reaction is called as Cannizzaro's reaction.

87. (c) : 40% HCHO

88. (c): Strongest acid is CH₂ClCOOH. –*I* effect of Cl atom decreases with the increase in distance therefore, CH₂ClCOOH is strongest acid.

89. (a): +I effect of the alkyl group increases from CH₃ to CH₃CH₂ to CH₃CH₂CH₂, resulting the acid character decreases. Therefore, the order is (i) > (ii) > (iii) > (iv).



