CHAPTER

26

ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

FACT/DEFINITION TYPE QUESTIONS

1. Choose the correct IUPAC name for

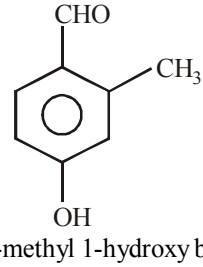
$$CH_3-\underset{\displaystyle CH_2-CH_3}{\overset{\displaystyle |}{CH}}-CHO$$

(a) Butan - 2- aldehyde
(b) 2- methylbutanal
(c) 3- methylisobutyraldehyde
(d) 2- ethylpropanal

2. The IUPAC name of the compound having the molecular formula Cl_3C-CH_2CHO is
(a) 3, 3, 3- trichloropropanal
(b) 1, 1, 1- trichloropropanal
(c) 2, 2, 2- trichloropropanal
(d) Chloral

3. The IUPAC name of $CH_3COCH(CH_3)_2$ is
(a) 2-methyl-3-butanone (b) 4-methylisopropyl ketone
(c) 3-methyl-2-butanone (d) Isopropylmethyl ketone

4. IUPAC name of following will be



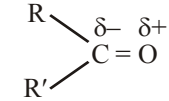
(a) 4-formyl 3-methyl 1-hydroxy benzene
(b) 4-formyl 3-methyl phenol
(c) 4-hydroxy 2-methyl benzaldehyde
(d) 4-hydroxy 2-methyl carbaldehyde

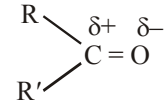
5. IUPAC name of ethyl isopropyl ketone is
(a) 4-methyl pent-3-one (b) 2-methyl pent-3-one
(c) 4-methyl pent-2-one (d) 2-methyl pent-2-one

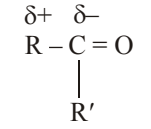
6. In > C = O group sigma bond is formed by
(a) sp^2-p-overlapping (b) sp^3-p-overlapping
(c) sp-p-overlapping (d) s-p-overlapping

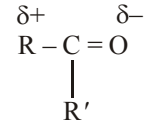
7. The π-bond in carbonyl group is formed by
(a) s-s-overlapping (b) p-p-overlapping
(c) s-p-overlapping (d) p-d-overlapping

8. Which of the following is correct for carbonyl compounds?

(a) 

(b) 

(c) 

(d) 

9. Which of the following contain an aldehyde?
(a) Vanilla beans (b) Meadow sweet
(c) Cinnamon (d) All of these

10. Which of the following have pleasant smell?
(a) Methanal (b) Propanal
(c) Ethanal (d) Hexanal

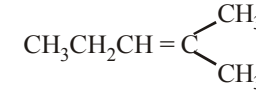
11. Which one of the following can be oxidised to the corresponding carbonyl compound?
(a) 2-hydroxy-propane
(b) Ortho-nitrophenol
(c) Phenol
(d) 2-methyl-2 hydroxy-propane

12. Which one of the following on oxidation gives a ketone ?
(a) Primary alcohol (b) Secondary alcohol
(c) Tertiary alcohol (d) All of these

13. What is formed when a primary alcohol undergoes catalytic dehydrogenation ?
(a) Aldehyde (b) Ketone
(c) Alkene (d) Acid

14. Primary and secondary alcohols on action of reduced copper give
(a) Aldehydes and ketones respectively
(b) Ketones and aldehydes respectively
(c) Only aldehydes
(d) Only ketones

15. Which alkene on ozonolysis gives CH_3CH_2CHO and $CH_3\overset{\displaystyle O}{\overset{\displaystyle ||}{C}}CH_3$

(a) 

(b) $CH_3CH_2CH=CHCH_2CH_3$

(c) $CH_3CH_2CH=CHCH_3$ (d) $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}=CHCH_3$

16. The catalyst used in Rosenmund's reduction is
(a) $HgSO_4$ (b) $Pd/BaSO_4$
(c) anhydrous $AlCl_3$ (d) anhydrous $ZnCl_2$

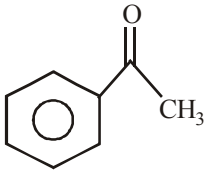
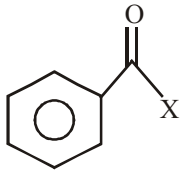
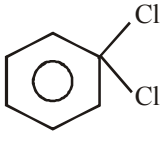
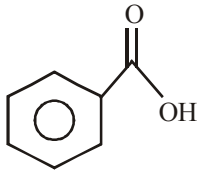
17. $C_6H_5C \equiv N + [H] \xrightarrow{SnCl_2/HCl} C_6H_5CHO + NH_3$.
The above reaction is
(a) Mendius reaction (b) Sandorn's reaction
(c) Rosenmund's reaction (d) Stephen's reaction

18. Benzaldehyde can be prepared by oxidation of toluene by
(a) Acidic $KMnO_4$ (b) $K_2Cr_2O_7/H^+$
(c) CrO_2Cl_2 (d) All of these

19. The oxidation of toluene to benzaldehyde by chromyl chloride is called
(a) Rosenmund reaction (b) Wurtz reaction
(c) Etard reaction (d) Fittig reaction

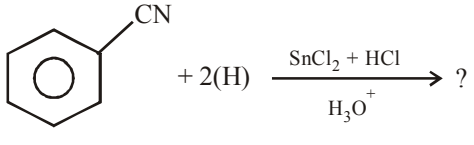
20. An aldehyde group can be present
(a) in between carbon chain
(b) at any position in carbon atom
(c) only at the end of carbon chain
(d) at the second carbon atom of the carbon chain

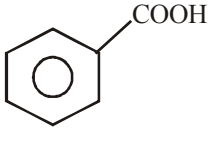
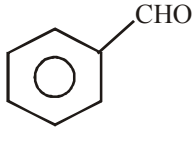
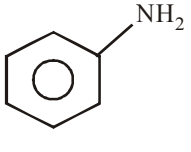
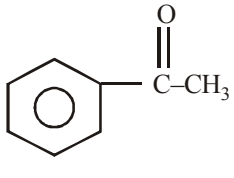
21. Benzaldehyde is obtained from Rosenmund's reduction of

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

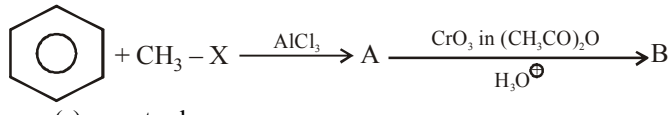
22. Which of the following is not used in the preparation of ketone?
(a) Oxidation of secondary alcohols
(b) Dehydrogenation of 2° alcohol
(c) Pyrolysis of calcium acetate
(d) Acid hydrolysis of alkyl cyanide

23. Product of the following reaction is



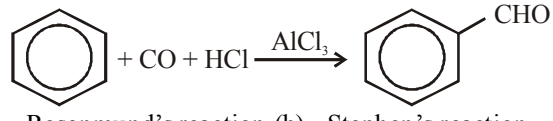
(a) 
(b) 
(c) 
(d) 

24. Find out B in the given reactions



(a) acetophenone
(b) benzaldehyde
(c) cyclohexyl carbaldehyde
(d) benzoic acid

25. The reaction



(a) Rosenmund's reaction (b) Stephen's reaction
(c) Cannizzaro's reaction (d) Gatterman-Koch reaction

26. Which aldehyde cannot be obtained by Rosenmund's reaction?
(a) CH_3CHO (b) HCHO
(c) CH_3CH_2CHO (d) All of these

27. The conversion $PhCN \rightarrow PhCOCH_3$, can be achieved most conveniently by reaction with
(a) CH_3MgBr followed by hydrolysis
(b) $I_2 - NaOH, CH_3I$
(c) Dil. H_2SO_4 followed by reaction with CH_2N_2
(d) $LiAlH_4$ followed by reaction with CH_3I

28. Which of the following is used to prepare ketone from acyl chloride ?
(a) R-MgX (b) R_2Cd
(c) CO + HCl (d) CrO_3

29. Which of the following forces explain the boiling point of aldehydes and ketones?
(a) Hydrogen bonding (b) van der Waal's forces
(c) Dipole-dipole attraction (d) None of these

30. Which is highly soluble in water?
(a) Methanal (b) Propanal
(c) Propanone (d) Butanone

31. Propanal and propanone, both have same molecular formula(C_3H_6O), what do you expect about their boiling points?
(a) Both have same boiling point
(b) Boiling point of propanal is higher than the boiling point of propanone.
(c) Boiling point of propanal is lower than the boiling point of propanone
(d) Nothing can be predicted

32. Less reactivity of ketone is due to
(a) + I inductive effect decrease positive charge on carbonyl carbon atom
(b) steric effect of two bulky alkyl groups
(c) sp^2 hybridised carbon atom of carbonyl carbon atom
(d) Both (a) and (b)

33. Acetaldehyde reacts with
(a) Electrophiles only
(b) Nucleophiles only
(c) Free radicals only
(d) Both electrophiles and nucleophiles

34. Carbonyl compounds undergo nucleophilic addition because of
(a) electronegativity difference of carbon and oxygen atoms
(b) electromeric effect
(c) more stable anion with negative charge on oxygen atom and less stable carbonium ion
(d) None of the above

35. Which of the following statement is false ?
(a) Cannizzaro reaction is given by aldehydes in presence of alkali
(b) Aldol condensation is given by aldehydes in presence of alkali
(c) Aldol condensation is given by aldehydes and ketones in presence of acids
(d) None of the above

36. If formaldehyde and KOH are heated, then we get
(a) methane (b) methyl alcohol
(c) ethyl formate (d) acetylene

37. The reagent which can be used to distinguish acetophenone from benzophenone is
(a) 2,4- dinitrophenylhydrazine
(b) aqueous solution of $NaHSO_3$
(c) benedict reagent
(d) I_2 and Na_2CO_3

38. Benzaldehyde reacts with ethanoic KCN to give
(a) $C_6H_5CHOHCN$ (b) $C_6H_5CHOHCOC_6H_5$
(c) $C_6H_5CHOHCOOH$ (d) $C_6H_5CHOHCHOHC_6H_5$

39. Acetone reacts with iodine (I_2) to form iodoform in the presence of
(a) $CaCO_3$ (b) NaOH
(c) KOH (d) $MgCO_3$

40. $(CH_3)_3C–CHO$ does not undergo aldol condensation due to
(a) three electron donating methyl groups
(b) cleavage taking place between —C— CHO bond
(c) absence of alpha hydrogen atom in the molecule
(d) bulky $(CH_3)_3C$—group

41. Acetaldehyde reacts with semicarbazide and forms semicarbazone. Its structure is
(a) $CH_3CH=NNHCON=CHCH_3$
(b) $CH_3CH=NNHCONH_2$
(c) $CH_3CH=N-\underset{\displaystyle OH}{\underset{|}{N}}-CONH_2$
(d) $CH_3CH=N—CONHNH_2$

42. Iodoform test is not given by
(a) 2-Pentanone (b) Ethanol
(c) Ethanal (d) 3-Pentanone

43. Phenylmethyl ketone can be converted into ethylbenzene in one step by which of the following reagents?
(a) $LiAlH_4$ (b) Zn-Hg/HCl
(c) $NaBH_4$ (d) CH_3MgI

44. When acetaldehyde is heated with Fehling's solution it gives a precipitate of
(a) Cu (b) CuO
(c) Cu_2O (d) $Cu(OH)_2$

45. Aldol condensation would not occur in :
(a) CH_3COCH_3 (b) CH_3CH_2CHO
(c) HCHO (d) CH_3CHO

46. Cannizzaro reaction occurs with
(a) CH_3-CH_2OH (b) C_6H_5CHO
(c) CH_3CHO (d) $CH_3-CO-CH_3$

47. Which of the following compound will show positive silver mirror test ?
(a) HCOOH (b) $CH_3(CHOH)_3CHO$
(c) $CH_3CO(CHOH)CH_3$ (d) Both (a) and (b)

48. Aldehydes and ketones are distinguished by which of the following test ?
(a) Lucas test
(b) Tollen's test
(c) $KMnO_4$ solution (Baeyer's test)
(d) None of these

49. Aldehydes and ketones are generally reduced by :
(a) Clemmensen reduction (b) H_2S
(c) H_2/Ni (d) None of these

50. In which reaction, $>C=O$ can be reduced to $>CH_2$?
(a) Wolf-Kishner reaction (b) Reimer-Tiemann reaction
(c) Wurtz reaction (d) None of these

51. A compound does not react with 2, 4-dinitrophenylhydrazine, the compound is :
(a) Acetone (b) Acetaldehdye
(c) CH_3OH (d) $CH_3CH_2COCH_3$

52. Which gives lactic acid on hydrolysis after reacting with HCN ?
(a) HCHO (b) CH_3CHO
(c) C_6H_5CHO (d) CH_3COCH_3

53. The most appropriate reagent to distinguish between acetaldehyde and formaldehyde is :
(a) Fehling's solution
(b) Tollen's reagent
(c) Schiff's reagent
(d) Iodine in presence of base

54. Aldehydes can be oxidised by :
(a) Tollen's reagent (b) Fehling solution
(c) Benedict solution (d) All the above

55. 2-pentanone and 3-pentanone can be distinguished by :
(a) Cannizaro's reaction (b) Aldol condensation
(c) Iodoform reaction (d) Clemmensen's reduction

56. Cross aldol condensation occurs between
(a) two same aldehydes
(b) two same ketones
(c) two different aldehydes and ketones
(d) None of these

57. Ketone upon treatment with Grignard Reagent gives
(a) primary alcohol (b) secondary alcohol
(c) tertiary alcohol (d) aldehyde

58. When acetaldehyde reacts with alcohol then produce
(a) Acetal (b) Ketal
(c) Acetone (d) None

59. 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

60. 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) $LiAlH_4$ (d) H_2 and Pt as catalyst

61. Which of the following products is formed when benzaldehyde is treated with CH_3MgBr and the addition product so obtained is subjected to acid hydrolysis ?
(a) A secondary alcohol (b) A primary alcohol
(c) Phenol (d) tert-Butyl alcohol

62. During reduction of aldehydes with hydrazine and potassium hydroxide, the first step is the formation of
(a) $R-CH=N-NH_2$ (b) $R-C\equiv N$
(c) $R-\underset{\underset{O}{\|}}{C}-NH_2$ (d) $R-CH=NH$

63. A and B in the following reactions are

$$R-\underset{\underset{O}{\|}}{C}-R' \xrightarrow[KCN]{HCN} A \xrightarrow{B} R-\underset{R'}{\overset{OH}{C}}-CH_2NH_2$$

(a) $A = RR'C(CN)(OH)$, $B = LiAlH_4$
(b) $A = RR'C(OH)(COOH)$, $B = NH_3$
(c) $A = RR'C(CN)(OH)$, $B = H_3O^{\oplus}$
(d) $A = RR'CH_2CN$, $B = NaOH$

64. The product obtained by the reaction of an aldehyde and hydroxylamine is
(a) hydrazone (b) aldoxime
(c) primary amine (d) alcohol

65. Which one gives positive iodoform test ?
(a) $(CH_3)_2CHCH_2OH$
(b) C_6H_5-OH
(c) $CH_3-CH_2-\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}}-CH_2-CH_3$
(d) CH_3CH_2OH

66. The compound that neither forms semicarbazone nor oxime is
(a) HCHO (b) CH_3COCH_2Cl
(c) CH_3CHO (d) $CH_3CONHCH_3$

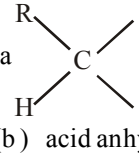
67. Schiff's reagent gives pink colour with
(a) acetaldehyde (b) acetone
(c) acetic acid (d) methyl acetate

68. Benzophenone can be converted into benzene by using
(a) fused alkali
(b) anhydrous $AlCl_3$
(c) sodium amalgam in water
(d) acidified dichromate

69. In the reaction of $NaHSO_3$ with carbonyl compounds to form bisulphite product, the nucleophile is
(a) HSO_3^- (b) SO_3Na
(c) SO_3^{--} (d) None of the above

70. Wolf-Kishner reduction is
(a) reduction of carbonyl compound into alcohol
(b) reduction of carbonyl compound into alkene
(c) reduction of carboxyl compound into alkane
(d) reduction of nitro compound into aniline

71. Tollen's reagent is
(a) ammonical $CuSO_4$
(b) ammonical $AgNO_3$
(c) alkaline solution containing complex of copper nitrate
(d) none of these

72. Compound of general formula  are called
(a) diester (b) acid anhydride
(c) hemiacetal (d) acetal

73. Imine derivatives of aldehyde and ketone is called as
(a) Schiff's reagent (b) Fehling's reagent
(c) Schiff's base (d) Schiff's acid

74. Which reaction is used for detecting the presence of carbonyl group?
(a) Reaction with hydrazine
(b) Reaction with phenyl hydrazine
(c) Reaction with hydroxylamine
(d) All of the above

75. The difference between aldol condensation and Cannizzaro's reaction is that:
(a) the former takes place in the presence of α-H-atom.
(b) the former takes place in the absence of α-H-atom.
(c) the former takes place in the presence of β-H-atom.
(d) none of the above

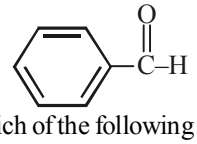
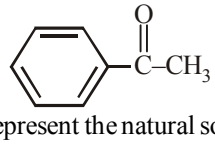
76. $C_6H_5CH=CHCHO \xrightarrow{X} C_6H_5CH=CHCH_2OH$
In the above sequence X can be :
(a) H_2/Ni (b) $NaBH_4$
(c) $K_2Cr_2O_7/H^+$ (d) Both (a) and (b)

77. Which of the following pairs of compounds will undergo aldol and Cannizzaro reaction respectively ?
(i) acetone; benzaldehyde
(ii) acetaldehyde; butan–2–one
(iii) propanone; formaldehyde.
(iv) cyclopentanone, benzaldehyde
(a) (i), (ii) and (iii) (b) (ii) and (iii)
(c) (ii), (iii) and (iv) (d) (iii) and (iv)

78. Two compounds benzyl alcohol and benzoic acid are formed from this compound, when this compound is heated in the presence of conc.NaOH, this compound is.
(a) Benzaldehyde (b) Benzylalcohol
(c) Acetophenone (d) Benzophenone

79. The reagent which does not react with both, acetone and benzaldehyde.
(a) Sodium hydrogensulphite
(b) Phenyl hydrazine
(c) Fehling's solution
(d) Grignard reagent

80. Which of the following compounds will give butanone on oxidation with alkaline $KMnO_4$ solution?
(a) Butan-1-ol (b) Butan-2-ol
(c) Both of these (d) None of these

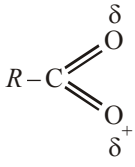
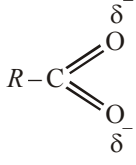
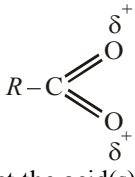
81. Which of the following compounds is most reactive towards nucleophilic addition reactions?
(a) $CH_3-\overset{\overset{O}{\|}}{C}-H$ (b) $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$
(c)  (d) 

82. Which of the following does not represent the natural source of the corresponding acids ?
(a) Formic acid : Red ant
(b) Acetic acid : Vinegar
(c) Butyric acid : Rancid butter
(d) Isobutyric acid : Automobile exhausts

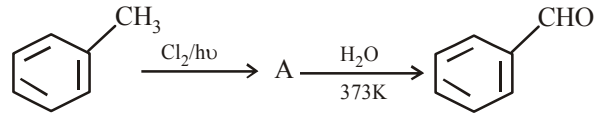
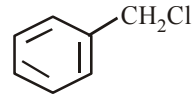
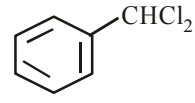
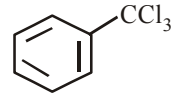
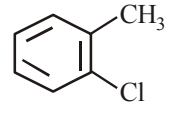
83. Vinegar is a solution of acetic acid which is :
(a) 15 – 20% (b) 20 – 25%
(c) 6 – 8% (d) 2 – 4%

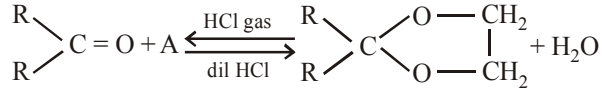
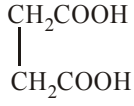
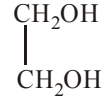
84. Methyl cyanide can be converted into acetic acid by one of the following reactions.
(a) Reduction (b) Hydrolysis
(c) Electrolysis (d) Decarboxylation

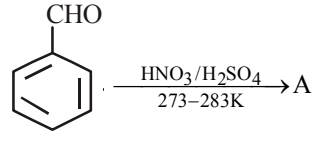
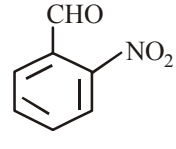
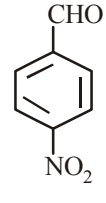
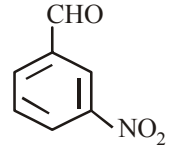
85. Toluene can be oxidised to benzoic acid by
(a) $KMnO_4$ (alk.) (b) $K_2Cr_2O_7$ (alk.)
(c) Both (a) and (b) (d) Neither (a) nor (b)

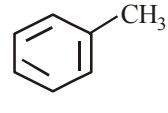
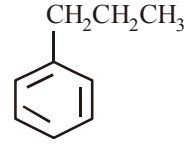
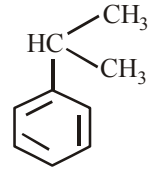
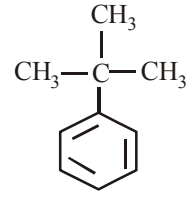
86. Which of the following does the best represent the structure of the carboxylate ion ?
(a)  (b) 
(c)  (d) None of these

87. Select the acid(s) which cannot be prepared by Grignard reagent.
(a) Acetic acid (b) Succinic acid
(c) Formic acid (d) All of the above

88. In the given reaction

A is
(a)  (b) 
(c)  (d) 

89. 
A is
(a) CH_3OH (b) CH_3COOH
(c)  (d) 

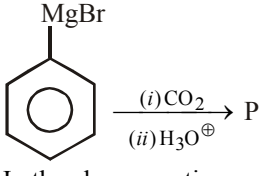
90. In the reaction

Benzaldehyde
A is
(a)  (b) 
(c)  (d) Both (a) and (b)

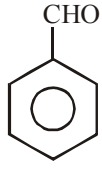
91. Which of the following can not be oxidised to give carboxylic acid?
(a)  (b) 
(c)  (d) 

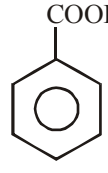
92. Lower carboxylic acids are soluble in water due to
(a) low molecular weight (b) hydrogen bonding
(c) dissociation into ions (d) easy hydrolysis

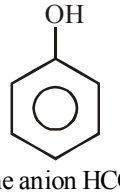
93. Dimerisation of carboxylic acids is due to
(a) ionic bond
(b) covalent bond
(c) coordinate bond
(d) intermolecular hydrogen bond

94. Boiling points of carboxylic acids are
(a) lower than corresponding alcohols
(b) higher than corresponding alcohols
(c) equal to that of corresponding alcohols
(d) None of the above

95. 

In the above reaction product 'P' is
(a) 

(b) 

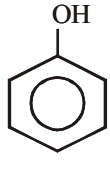
(c) 

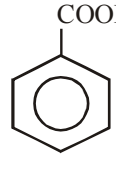
(d) $C_6H_5-\overset{\overset{O}{\|}}{C}-C_6H_5$

96. In the anion $HCOO^-$ the two carbon-oxygen bonds are found to be of equal length. What is the reason for it?
(a) Electronic orbitals of carbon atom are hybridised
(b) The C=O bond is weaker than the C–C bond
(c) The anion $HCOO^-$ has two reasonating structures
(d) The anion is obtained by removal of a proton from the acid molecule

97. Carboxylic acids are more acidic than phenol and alcohol because of
(a) intermolecular hydrogen bonding
(b) formation of dimers
(c) highly acidic hydrogen
(d) resonance stabilization of their conjugate base

98. Which of the following has the maximum acidic strength ?
(a) o- nitrobenzoic acid (b) m-nitrobenzoic acid
(c) p-nitrobenzoic acid (d) p-nitrophenol

99. Which of the following is the weakest acid ?
(a) 

(b) CH_3COOH
(c) HCOOH
(d) 

100. Which of the following acids has the smallest dissociation constant ?
(a) $CH_3CHFCOOH$ (b) FCH_2CH_2COOH
(c) $BrCH_2CH_2COOH$ (d) $CH_3CHBrCOOH$

101. Which one of the following esters is obtained by the esterification of propan-2-ol with ethanoic acid ?
(a) $(CH_3)_2CHCOOCH_3$ (b) $CH_3COOCH_2CH_3$
(c) $CH_3COOCH(CH_3)_2$ (d) $(CH_3)_2CHCOOCH_2CH_3$

102. The major product of nitration of benzoic acid is
(a) 3- Nitrobenzoic acid (b) 4- Nitrobenzoic acid
(c) 2- Nitrobenzoic acid (d) 2, 4- dinitrobenzoic acid

103. Among the following acids which has the lowest pK_a value?
(a) CH_3CH_2COOH (b) $(CH_3)_2CH-COOH$
(c) HCOOH (d) CH_3COOH

104. The correct order of increasing acidic strength is _____
(a) Phenol < Ethanol < Chloroacetic acid < Acetic acid
(b) Ethanol < Phenol < Chloroacetic acid < Acetic acid
(c) Ethanol < Phenol < Acetic acid < Chloroacetic acid
(d) Chloroacetic acid < Acetic acid < Phenol < Ethanol

105. Which reagent can convert acetic acid into ethanol ?
(a) Na + alcohol (b) $LiAlH_4$ + ether
(c) H_2 + Pt (d) Sn + HCl

106. Which is false in case of carboxylic acids?
(a) They are polar molecules
(b) They form H-bonds
(c) They are stronger than mineral acids
(d) They have higher b.p. than corresponding alcohols

107. The elimination of CO_2 from a carboxylic acid is known as
(a) hydration (b) dehydration
(c) decarboxylation (d) carboxylation

108. The reaction of carboxylic acid gives effervescences of CO_2 with $NaHCO_3$. The CO_2 comes from.
(a) $R-COOH$ (b) $NaHCO_3$
(c) Both (a) and (b) (d) None of these

109. Acetic anhydride is obtained by the reaction of
(a) sodium and acetic acid
(b) ammonia and acetic acid
(c) ethanol and acetic acid
(d) P_2O_5 and acetic acid

110. Benzoic acid may be converted to ethyl benzoate by reaction with
(a) sodium ethoxide (b) ethyl chloride
(c) dry HCl—C_2H_5OH (d) ethanol

111. Propionic acid with Br_2/P yields a dibromo product. Its structure would be:
(a) $H-\underset{\underset{Br}{|}}{\overset{\overset{Br}{|}}{C}}-CH_2COOH$ (b) CH_2Br-CH_2-COBr
(c) $CH_3-\underset{\underset{Br}{|}}{\overset{\overset{Br}{|}}{C}}-COOH$ (d) $CH_2Br-CHBr-COOH$

112. The product obtained when acetic acid is treated with phosphorus trichloride is
(a) $CH_3COOPCl_3$ (b) $ClCH_2COCl$
(c) CH_3COCl (d) $ClCH_2COOH$

113. The reaction

$$RCH_2CH_2COOH \xrightarrow[Br_2]{Red\ P} R-CH_2-\underset{\underset{Br}{|}}{CH}-COOH$$

is called as
(a) Reimer- Tiemann reaction
(b) Hell-Volhard Zelinsky reaction
(c) Cannizzaro reaction
(d) Sandmeyer reaction

114. Benzoic acid reacts with conc. HNO_3 and H_2SO_4 to give :
(a) 3-Nitrobenzoic acid
(b) 4-Benzene sulphonic acid
(c) 4-Nitrobenzoic acid
(d) 2-Nitrobenzoic acid

115. In the following reaction

$$RCH_2COOH \xrightarrow{Br_2/P} X \xrightarrow{excess\ NH_3} Y$$

The major compounds X and Y are
(a) $RCHBrCONH_2$; $RCH(NH_2)COOH$
(b) $RCHBrCOOH$; $RCH(NH_2)COOH$
(c) RCH_2COBr ; RCH_2COONH_4
(d) $RCHBrCOOH$; RCH_2CONH_2

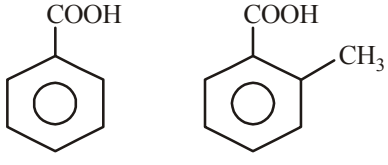
116. The yield of ester in esterification can be increased by

$$CH_3CH_2OH + CH_3COOH \rightleftharpoons CH_3COOCH_2CH_3 + H_2O$$

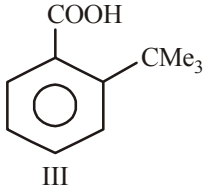
(a) removing water
(b) taking ethanol in excess
(c) taking acetic acid in excess
(d) all the above factors

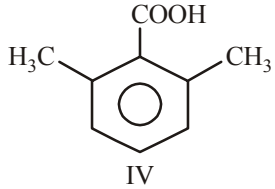
117. A carboxylic acid can best be converted into acid chloride by using
(a) PCl_5 (b) $SOCl_2$
(c) HCl (d) ClCOCOCl

118. Arrange the following four acids in their decreasing order of acidity


I

II


III


IV

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

119. The strongest acid among the following is –
(a) Salicylic acid (b) *m*-hydroxybenzoic acid
(c) *p*-hydroxybenzoic acid (d) Benzoic acid

120. Among the following, the most acidic is :
(a) CH_3COOH (b) $ClCH_2COOH$
(c) $Cl_2CHCOOH$ (d) Cl_2CHCH_2COOH

121. Which of the following is the correct decreasing order of acidic strength of
(i) Methanoic acid (ii) Ethanoic acid
(iii) Propanoic acid (iv) Butanoic acid
(a) (i) > (ii) > (iii) > (iv) (b) (ii) > (iii) > (iv) > (i)
(c) (i) > (iv) > (iii) > (ii) (d) (iv) > (i) > (iii) > (ii)

122. Among the following the strongest acid is
(a) CH_3COOH (b) CH_2ClCH_2COOH
(c) $CH_2ClCOOH$ (d) CH_3CH_2COOH

123. Arrange the following carboxylic acid in their decreasing acidity.

1. $\begin{matrix}COOH\\|\\COOH\end{matrix}$ Oxalic acid
2. $HOOC-CH_2-COOH$ Malonic acid
3. $\begin{matrix}CH_2-COOH\\|\\CH_2-COOH\end{matrix}$ Succinic acid

(a) 3 > 2 > 1 (b) 1 > 2 > 3
(c) 2 > 3 > 1 (d) 2 > 1 > 3

STATEMENT TYPE QUESTIONS

124. Read the following statements and choose the correct option
(i) The carbonyl carbon atom is sp^2 -hybridised
(ii) The carbonyl carbon is an electrophilic (Lewis acid) centre
(iii) The carbonyl oxygen is a nucleophilic (Lewis base) centre
(iv) Carbonyl compounds are non- polar in nature.
(a) (i), (ii) and (iv) are correct
(b) (i), (ii) and (iii) are correct
(c) (ii), (iii) and (iv) are correct
(d) (ii) and (iv) are correct

125. Which of the following statement(s) is/are true regarding preparation of aldehydes and ketones?
(i) Both can be prepared by the oxidation of the concerned alcohol with copper at about 250°C.
(ii) Both can be prepared by the oxidation of the concerned alcohol by Oppenauer oxidation.
(iii) Both can be prepared by the oxidation of respective alcohol with acidic dichromate.
(a) (i) only (b) (ii) and (iii)
(c) (i) and (iii) (d) All the three

126. Which of the following statements are *false*?
(i) No aldehyde can be prepared by the oxidation of primary alcohol with acidic $KMnO_4$.
(ii) Aldehydes having a boiling point less than 100°C can be prepared by the oxidation of primary alcohol with acidic dichromate.
(iii) Secondary alcohols on oxidation with PCC in dichloromethane give carboxylic acids having lesser number of carbon atoms
(iv) Tertiary alcohols can't be oxidised at all
(a) (ii) and (iii) (b) (ii), (iii) and (iv)
(c) (i), (iii) and (iv) (d) (i), (ii) and (iii)

127. Read the following statements and choose the correct option
(i) The boiling points of aldehydes and ketones are lower than those of alcohols of similar molecular masses
(ii) Alcohols show intermolecular hydrogen bonding whereas aldehydes and ketones do not show intermolecular hydrogen bonding.
(iii) The lower members of aldehydes and ketones are miscible with water in all proportions, because they form hydrogen bond with water.
(iv) The solubility of aldehydes and ketones increases rapidly on increasing the length of alkyl chain
(a) TTFF (b) TFFT
(c) FTTT (d) TTTF

128. Aldehydes are generally more reactive than ketones in nucleophilic addition reactions. Which of the following statements accounts for this ?
(i) Sterically, the presence of two relatively large substituents in ketones hinders the approach of nucleophile to carbonyl carbon
(ii) Aldehydes show resonance whereas ketones do not
(iii) Electronically, the presence of two alkyl groups reduce the electrophilicity of the carbonyl carbon more effectively.
(iv) Electronically carbonyl carbon atom in ketones is more electrophilic than in aldehydes
(a) (i) and (iii) (b) (i) and (iv)
(c) (ii) and (iii) (d) (ii) and (iv)

129. $2C_6H_5CHO \xrightarrow[H_2O]{OH^-} C_6H_5CH_2OH + C_6H_5COO^-$
Which of the following statements are correct regarding the above reduction of benzaldehyde to benzyl alcohol?
(i) One hydrogen is coming from H_2O as H^+ and another from C_6H_5CHO as H^-
(ii) One hydrogen is coming from H_2O as H^- and another from C_6H_5CHO as H^+
(iii) One hydrogen from H_2O and another from C_6H_5CHO, both in the form of H^-
(iv) The reduction is an example of disproportionation reaction
(a) (i), (ii) and (iii) (b) (i) and (iv)
(c) (ii), (iii) and (iv) (d) (iii) and (iv)

130. Which of the following statement(s) is/are true regarding esterification of a carboxylic acid with an alcohol ?
(i) It is carried out in presence of a strong acid which acts as a catalyst.
(ii) The strong acid makes the carbonyl carbon more electrophilic, and hence causes the alcohol, a strong nucleophile to attack on the carbonyl carbon.
(iii) The strong acid makes the carbonyl group more electrophilic which is thus attacked easily by an alcohol, a weak nucleophile.
(iv) Esterification can be done even in absence of a strong acid.
(a) (i) and (ii) (b) (i) and (iii)
(c) (i) only (d) (iv) only

MATCHING TYPE QUESTIONS

131. Match the columns

Column-I (Common names)	Column-II (IUPAC names)
(A) Cinnamaldehyde	(p) Pentanal
(B) Acetophenone	(q) Prop-2-enal
(C) Valeraldehyde	(r) 4-Methylpent-3-en-2-one
(D) Acrolein	(s) 3-Phenylprop-2-enal
(E) Mesityl oxide	(t) 1-Phenylethanone

(a) A – (s), B – (t), C – (p), D – (q), E – (r)
(b) A – (p), B – (q), C – (s), D – (t), E – (r)
(c) A – (t), B – (s), C – (p), D – (r), E – (q)
(d) A – (q), B – (t), C – (r), D – (s), E – (p)

132. Match the columns

Column-I	Column-II
(A) $R-CO-CH_3 \xrightarrow{Zn-Hg/HCl} R-CH_2-CH_3$	(p) Friedel-Craft's reaction
(B) $2C_6H_5CHO \xrightarrow{NaOH} C_6H_5COONa + C_6H_5CH_2OH$	(q) Kolbe's reaction
(C) $C_6H_6 + CH_3COCl \xrightarrow[AlCl_3]{Anhyd.} C_6H_5COCH_3$	(r) Clemmensen's reaction
(D) $C_6H_5OH + CO_2 + NaOH \rightarrow HOC_6H_4COONa$	(s) Cannizzaro's reaction

(a) A – (p), B – (q), C – (r), D – (s)
(b) A – (q), B – (p), C – (r), D – (s)
(c) A – (r), B – (s), C – (p), D – (q)
(d) A – (s), B – (r), C – (p), D – (q)

133. Match the columns

Column-I	Column-II
(A) Etard reaction	(p) Alcoholic KOH
(B) Hydroxylation	(q) Anhydrous $AlCl_3$
(C) Dehydrohalogenation	(r) Chromyl chloride
(D) Friedel-Crafts reaction	(s) Dilute alkaline $KMnO_4$

(a) A – (p), B – (q), C – (r), D – (q)
(b) A – (s), B – (r), C – (p), D – (q)
(c) A – (r), B – (s), C – (p), D – (q)
(d) A – (q), B – (p), C – (s), D – (r)

134. Match the columns

Column-I (Reactions)	Column-II (Reagents)
(A) Benzophenone → Diphenylmethane	(p) $LiAlH_4$
(B) Benzaldehyde → 1-Phenylethanol	(q) DIBAL–H
(C) Cyclohexanone → Cyclohexanol	(r) Zn(Hg)/Conc HCl
(D) Phenyl benzoate → Benzaldehyde	(s) CH_3MgBr

(a) A – (p), B – (s), C – (r), D – (q)
(b) A – (q), B – (s), C – (p), D – (r)
(c) A – (s), B – (r), C – (q), D – (p)
(d) A – (r), B – (s), C – (p), D – (q)

135. Match the columns

Column-I	Column-II
(A) $R_2C=NH$	(p) Oxime
(B) $R_2C=NOH$	(q) Semicarbazone
(C) $R_2C=N-NH_2$	(r) Imine
(D) $R_2C=N-NH-\overset{\overset{O}{\|\|}}{C}-NH_2$	(s) Hydrazone

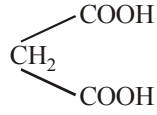
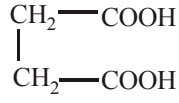
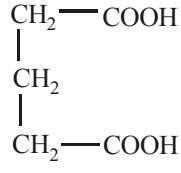
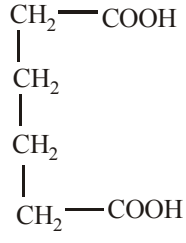
(a) A – (q), B – (s), C – (p), D – (r)
(b) A – (r), B – (p), C– (s), D– (q)
(c) A – (r), B – (s), C – (p), D– (q)
(d) A – (s), B – (r), C – (q), D– (p)

136. Match the acids given in Column-I with their correct IUPAC names given in Column-II.

Column-I (Acids)	Column-II (IUPAC names)
(A) Phthalic acid	(p) Hexane-1, 6-dioic acid
(B) Oxalic acid	(q) Benzene-1, 2-dicarboxylic acid
(C) Succinic acid	(r) Pentane-1, 5-dioic acid
(D) Adipic acid	(s) Butane-1, 4-dioic acid
(E) Glutaric acid	(t) Ethane-1, 2-dioic acid

(a) A – (t), B – (q), C – (r), D – (p), E – (s)
(b) A – (p), B – (s), C – (t), D – (q), E – (r)
(c) A – (q), B – (t), C – (s), D – (p), E – (r)
(d) A – (r), B – (t), C – (p), D – (s), E – (q)

137. Match the columns

Column-I	Column-II
(A) 	(p) Glutaric acid
(B) 	(q) Adipic acid
(C) 	(r) Succinic acid
(D) 	(s) Malonic acid

(a) A – (q), B – (p), C – (s), D – (r)
(b) A – (r), B – (p), C – (s), D – (q)
(c) A – (s), B – (r), C – (p), D – (q)
(d) A – (r), B – (q), C – (s), D – (p)

ASSERTION-REASON TYPE QUESTIONS

Directions : Each of these questions contain two statements, Assertion and Reason. Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes (a), (b), (c) and (d) given below.

(a) Assertion is correct, reason is correct; reason is a correct explanation for assertion.
(b) Assertion is correct, reason is correct; reason is not a correct explanation for assertion
(c) Assertion is correct, reason is incorrect
(d) Assertion is incorrect, reason is correct.

138. **Assertion :** The boiling points of aldehydes and ketones are higher than hydrocarbons and ethers of comparable molecular masses.
Reason : There is a weak molecular association in aldehydes and ketones arising out of the dipole-dipole interactions.

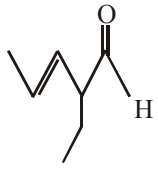
139. **Assertion :** Formaldehyde is a planar molecule.
Reason : It contains sp^2 hybridised carbon atom.

140. **Assertion :** Compounds containing –CHO group are easily oxidised to corresponding carboxylic acids.
Reason : Carboxylic acids can be reduced to alcohols by treatment with $LiAlH_4$.

141. **Assertion :** The molecular mass of acetic acid in benzene is 120 instead of 60.
Reason : The carboxylic acids exist as cyclic dimers in which the two molecules of the acid are held together by two strong hydrogen bonds.

CRITICAL THINKING TYPE QUESTIONS

142. IUPAC name of the following compound is



(a) 2-(2-propenyl) butanal
(b) 2-(1-propenyl) butanal
(c) 4-formyl 4-ethyl but-2-ene
(d) 2-ethyl pent-3-en-l-al

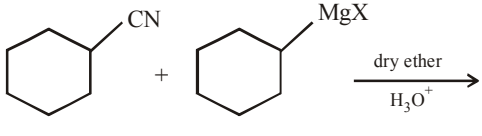
143. Observe the following structures and pick up the correct statement.

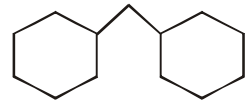
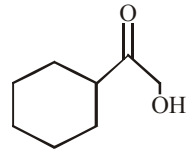
$\underset{\text{I}}{>C=O}$ $\qquad$ $\underset{\text{II}}{>C=\overset{+}{O}H}$

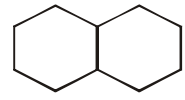
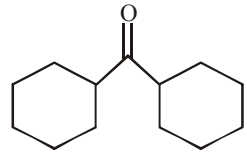
(a) Carbonyl carbon of I is more electrophilic than that of II
(b) Carbonyl carbon of I is less electrophilic than that of II
(c) Carbonyl carbon of both structures have equal electrophilic character
(d) It depends upon the complete structure of the compound

144. The boiling points of aldehydes and ketones lie in between alkanes and alcohols of comparable masses because
(a) alkanes are polar
(b) aldehydes and ketones are non-polar
(c) alkanes are non-polar and aldehydes and ketones contain polar $>C=O$ group and lower alcohols have H-bonding.
(d) alkanes are held together by weak van der Waal's forces (being non-polar), aldehydes and ketones contain polar $>C=O$ group and held together by strong dipole-dipole attraction and lower alcohols have H-bonding, which is stronger than dipole-dipole attraction.

145. Product of the following reaction is



(a)  (b) 

(c)  (d) 

146. Which of the following reagent reacts in different ways with CH_3CHO, HCHO and C_6H_5CHO ?
(a) Fehling solution (b) $C_6H_5NHNH_2$
(c) Ammonia (d) HCl

147. A new carbon - carbon bond is formed in
(i) Aldol condensation (ii) Kolbe's reaction
(iii) Reimer-Tiemann reaction
(iv) Wurtz Fittig reaction
(a) (i) and (iii) (b) (ii) and (iii)
(c) (i), (ii) and (iiv) (d) All the four

148. Which of the following is an example of nucleophilic addition ?

(a) $C_6H_5\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow{NH_2NH_2,H^+} C_6H_5\overset{NNH_2}{\overset{\|}{C}}CH_3$

(b) $C_6H_5\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow{LiAlH_4} C_6H_5\overset{OH}{\overset{|}{C}}HCH_3$

(c) Both (a) and (b)
(d) None of the two

149. Acetal formation is a reversible reaction

$$R\diagdown\!\!\diagup C=O + R'OH \underset{}{\overset{H^+}{\rightleftharpoons}} R\diagdown\!\!\diagup C\overset{OH}{\underset{H}{\diagup\!\!\diagdown}}\overset{OR'}{} \overset{R'OH,\,H^+}{\rightleftharpoons} R\diagdown\!\!\diagup C\overset{OR'}{\underset{H}{\diagup\!\!\diagdown}}\overset{OR'}{} + H_2O$$

Under what conditions, the reaction can be forced to proceed only in right (forward) direction ?
(a) Using excess of alcohol
(b) Using high temperature
(c) Using dilute acid and excess of alcohol
(d) Using dry acid and excess of alcohol

150. In the crossed Cannizzaro reaction involving HCHO as one of the components
(a) HCHO is always oxidised because of electronic effect
(b) HCHO is always oxidised because of steric effect
(c) both of the above statements are true
(d) none of the above statement is true

151. Which of the following acts as a nucleophile in the aldol condensation of ethanal?
(i) OH^- (ii) $H_2\ddot{O}:$
(iii) $^-CH_2CHO$
(a) Only (i) (b) (i) and (ii)
(c) (i) and (iii) (d) All the three

152. Which of the following acts as a nucleophile in the Cannizzaro reaction involving benzaldehyde ?

(i) OH^- (ii) $\bar{C}_6H_4CHO$

(iii) $C_6H_5CH(OH)O^-$ (iv) $H_2\ddot{O}:$

(a) (i) and (iv) (b) (i) and (ii)

(c) (i) and (iii) (d) Only (i)

153. Which of the following undergoes haloform reaction ?

(i) $CH_3CH_2COCH_2Cl$ (ii) $C_6H_5COCH_3$

(iii) $C_6H_5COCHCl_2$ (iv) $CH_3CH_2COCCl_3$

(a) Only (ii) (b) (ii) and (iv)

(c) (i), (ii) and (iv) (d) All the four

154. When ethanal reacts with propanal in the presence of a base, the number of products formed is

(a) 2 (b) 3

(c) 4 (d) 5

155. Aldehydes and ketones will not form crystalline derivatives with

(a) sodium bisulphite

(b) phenylhydrazine

(c) semicarbazide hydrochloride

(d) dihydrogen sodium phosphate.

156. Which of the following compound will undergo self aldol condensation in the presence of cold dilute alkali ?

(a) $CH_2{=}CH-CHO$ (b) $CH{\equiv}C-CHO$

(c) C_6H_5CHO (d) CH_3CH_2CHO.

157. Which of the following is an example of aldol condensation?

(a) $2CH_3COCH_3 \xrightarrow{\text{dil NaOH}} CH_3\overset{CH_3}{\overset{|}{C}}(OH)CH_2COCH_3$

(b) $2HCHO \xrightarrow{\text{dil NaOH}} CH_3OH$

(c) $C_6H_5CHO + HCHO \xrightarrow{\text{dil NaOH}} C_6H_5CH_2OH$

(d) None of the above

158. Identify X,

$$H_3C\diagdown\!\!\diagup C=O \xrightarrow[\text{dry ether}]{CH_3MgI} \text{Intermediate} \xrightarrow{H_2O} X$$
$$H_3C\diagup\!\!\diagdown$$

(a) CH_3OH (b) Ethyl alcohol

(c) Methyl cyanide (d) tert-Butyl alcohol

159. An organic compound of formula, C_3H_6O forms phenyl hydrazone, but gives negative Tollen's test. The compound is

(a) $CH_3CH_2COCH_3$ (b) CH_3CH_2CHO

(c) CH_3COCH_3 (d) Both (a) and (c)

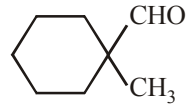
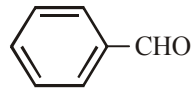
160. $$\begin{matrix}R\\R\end{matrix}\!\!\diagdown\!\!\diagup C=O \xrightarrow{HCN} (A) \xrightarrow{NH_3} (B) \xrightarrow{\text{Hydrolysis}} (C)$$

Compound (C) in above reaction is

(a) α-hydroxy acid (b) α-amino acid

(c) α-amino alkanol (d) α-amino β-hydroxy acid

161. Cannizaro's reaction is not given by _____

(a)  (b) 

(c) HCHO (d) CH_3CHO

162. Benzophenone can be obtained by_____.

(i) Benzoyl chloride + Benzene + $AlCl_3$

(ii) Benzoyl chloride + Diphenyl cadmium

(iii) Benzoyl chloride + Phenyl magnesium chloride

(iv) Benzene + Carbon monoxide + $ZnCl_2$

(a) (i), (ii) and (iii) (b) (ii) and (iii)

(c) (iii) and (iv) (d) (i), (ii) and (iv)

163. Which of the following conversions can be carried out by Clemmensen Reduction ?

(i) Benzaldehyde into benzyl alcohol

(ii) Cyclohexanone into cyclohexane

(iii) Benzoyl chloride into benzaldehyde

(iv) Benzophenone into diphenyl methane

(a) (ii) and (iv) (b) (i) and (iv)

(c) (i) and (iii) (d) (iii) and (iv)

164. Benzaldehyde is less reactive than propanal because

(i) the carbon atom of the carbonyl group of benzaldehyde is less electrophilic as in propanal.

(ii) the carbon atom of the carbonyl group of benzaldehyde is more electrophilic as in propanal.

(iii) carbonyl group in benzaldehyde is more polar due to resonance

(iv) carbonyl group in benzaldehyde is less polar due to resonance

(a) (i) and (iii) (b) (i) and (iv)

(c) (i) only (d) (iv) only

165. Addition of hydrogen cyanide to aldehydes and ketones occurs in presence of a base.The role of base is to

(i) catalyse the reaction

(ii) generate CN^- ion

(iii) slow down the reaction

(iv) to stabilize the cyanohydrins

(a) (i) and (iii) (b) (i) and (ii)

(c) (i) and (iv) (d) (ii) and (iv)

166. Addition of alcohols to aldehydes and ketones takes place in presence of dry HCl gas because it

(i) Protonates the oxygen of the carbonyl compounds

(ii) Increases the electrophilicity of the carbonyl carbon

(iii) Removes the excess moisture from the reaction

(iv) Helps the reaction to move in the forward direction

(a) (i), (ii) and (iv) (b) (i), (ii), (iii) and (iv)

(c) (ii) ,(iii), and (iv) (d) (i), (iii) and (iv)

167. When benzaldehyde and acetaldehyde undergoes reaction with the 2, 4–DNP ?

(a) Benzaldehyde reacts slowly than acetaldehyde

(b) Acetaldehyde reacts slowly than benzaldehyde

(c) Both reacts equally

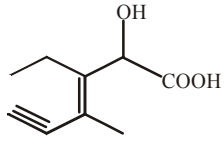
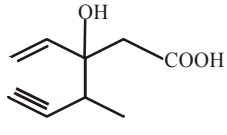
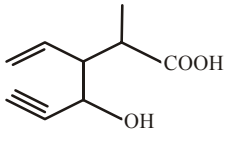
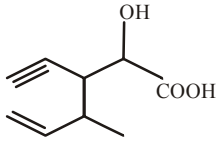
(d) Both do not react with 2, 4-DNP

168. Suppose the reaction of compound containing ketone as functional group is carried in basic medium of NaOH. Which of the following will one use to protect the unwanted reaction due presence of carbonyl moiety.
(a) $NaHSO_3$
(b) HCN
(c) ethylene glycol and HCl
(d) None of these

169. A compound $C_5H_{10}O$ forms orange–red precipitate upon reaction with 2,4–DNP, but does not give positive Tollen's test and iodoform test. Possible compound is
(a) 2, 2–dimethylpropanal (b) 3–methylbutan–2–one
(c) Pentan–3–one (d) None of the above

170. Nitration of the compound is carried out, this compound gives red–orange ppt. with 2,4–DNP, this compound undergoes Cannizzaro reaction but not aldol, than possible product due to nitration is
(a) 3–nitroacetophenone
(b) (2–nitro)–2–phenylethanal
(c) (2–nitro)–1–phenylpropan–2–one
(d) 3–nitrobezaldehyde

171. Structure of the compound whose IUPAC name is 3-ethyl-2-hydroxy-4-methylhex-3-en-5-ynoic acid is :

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

172. The end product *B* in the sequence of reactions,

$$R-X \xrightarrow{CN^-} A \xrightarrow{NaOH} B \text{ is}$$

(a) an alkane
(b) a carboxylic acid
(c) sodium salt of carboxylic acid
(d) a ketone

173. Which is the most suitable reagent for the following conversion?

$$CH_3-CH=CH-CH_2-\overset{\overset{O}{\|}}{C}-CH_3 \longrightarrow CH_3-CH=CH-CH_2-\overset{\overset{O}{\|}}{C}-OH$$

(a) Tollen's reagent (b) Benzoyl peroxide
(c) I_2 and NaOH solution (d) Sn and NaOH solution

174. In the given reaction,

$$(C_6H_5CO)_2O \xrightarrow{H_2O} I$$

$$C_6H_5COOCOCH_3 \xrightarrow{H_2O} II$$

Identify the product(s) formed in the given reaction.

	I	II
(a)	2 molecules of benzoic acid	2 molecules of ethanoic acid
(b)	2 molecules of benzoic acid	1 molecules of benzoic acid and 1 molecule of ethanoic acid
(c)	1 molecule of ethanoic acid	1 molecule of benzoic acid
(d)	1 molecule of benzoic acid	1 molecule of butanoic acid

175. Ethanoic acid can't be obtained by which of the following reaction ?

(i) $C_2H_5Cl \xrightarrow[(ii)\ H_3O^+]{(i)\ KCN}$

(ii) $CH_3Cl \xrightarrow[(ii)\ H_3O^+]{(i)\ AgCN}$

(iii) $CH_3CH=CH_2 \xrightarrow[heat]{KMnO_4 / OH^-}$

(iv) $CH_3Br \xrightarrow[(iii)\ H_3O^+]{(i)\ Mg \ (ii)\ CO_2}$

(a) (iii) and (iv) (b) (i) and (ii)
(c) (ii) and (iii) (d) (i) and (iv)

176. Primary alcohols can be readily oxidised to carboxylic acids by.
(i) $KMnO_4$ in neutral medium.
(ii) $KMnO_4$ in acidic or alkaline medium.
(iii) $K_2Cr_2O_7$ in alkaline medium.
(iv) $K_2Cr_2O_7$ in acidic medium.
(a) (i), (ii) and (iv) (b) (i), (ii) and (iii)
(c) (ii) and (iii) (d) (i) and (iii)

177. Which of the following is correct order of acidity?
(a) $HCOOH > CH_3COOH > ClCH_2COOH > C_2H_5COOH$
(b) $ClCH_2COOH > HCOOH > CH_3COOH > C_2H_5COOH$
(c) $CH_3COOH > HCOOH > ClCH_2COOH > C_2H_5COOH$
(d) $C_2H_5COOH > CH_3COOH > HCOOH > ClCH_2COOH$

178. An organic compound A upon reacting with NH_3 gives B. On heating B gives C. C in presence of KOH reacts with Br_2 to given $CH_3CH_2NH_2$. A is :
(a) CH_3COOH (b) $CH_3CH_2CH_2COOH$
(c) $CH_3-\underset{\underset{CH_3}{|}}{CH}-COOH$ (d) CH_3CH_2COOH

179. The correct order of increasing acid strength of the compounds
(A) CH_3CO_2H (B) $MeOCH_2CO_2H$
(C) CF_3CO_2H (D) $\begin{matrix}Me\\Me\end{matrix}\!\!>\!\!-CO_2H$ is
(a) D < A < B < C (b) A < D < B < C
(c) B < D < A < C (d) D < A < C < B

180. Through which of the following reactions number of carbon atoms can be increased in the chain?

(i) Grignard reaction (ii) Cannizzaro's reaction
(iii) Aldol condensation (iv) HVZ reaction

Choose the correct option.

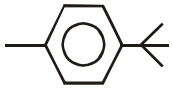
(a) Only (iii) and (i) (b) Only (iii) and (ii)
(c) Only (iii) and (iv) (d) (i), (ii), (iii) and (iv)

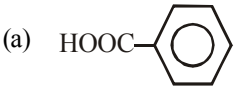
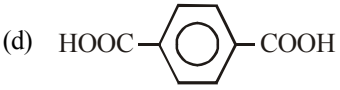
181. In a set of the given reactions, acetic acid yielded a product C.

$$CH_3COOH + PCl_5 \longrightarrow A \xrightarrow[Anh.\,AlCl_3]{C_6H_6} B \xrightarrow[Ether]{C_2H_5MgBr} C$$

Product C would be

(a) $CH_3-\underset{\displaystyle C_2H_5}{\overset{|}{C}}(OH)C_6H_5$ (b) $CH_3CH(OH)C_2H_5$
(c) $CH_3COC_6H_5$ (d) $CH_3CH(OH)C_6H_5$

182.  $\xrightarrow{K_2Cr_2O_7+H_2SO_4}$ Z. Here Z is

(a) 
(b) $(CH_3)_3CCOOH$
(c) Both (a) and (b)
(d) 

183. RCOOH can be reduced to RCH_2OH by

(i) $NaBH_4$ (ii) $LiAlH_4$
(iii) Na/C_2H_5OH (iv) H_2/Catalyst
(a) (ii) and (iv) (b) (i) and (iii)
(c) (i), (ii) and (iv) (d) (i), (iii) and (iv)

184. Kolbe's electrolytic method can be applied on

(i) $\begin{matrix}CH_2COONa\\|\\CH_2COONa\end{matrix}$ (ii) $\begin{matrix}CHCOONa\\\|\\CHCOONa\end{matrix}$

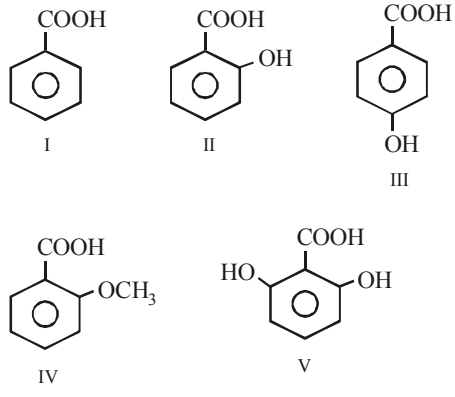
(iii) C_6H_5COOK (iv) CH_3COOK

(a) (i), (ii) and (iv) (b) (i), (ii) and (iii)
(c) (ii), (iii) and (iv) (d) (iii) and (iv)

185. Which of the following represents the correct order of the acidity in the given compounds?

(a) $FCH_2COOH > CH_3COOH > BrCH_2COOH > ClCH_2COOH$
(b) $BrCH_2COOH > ClCH_2COOH > FCH_2COOH > CH_3COOH$
(c) $FCH_2COOH > ClCH_2COOH > BrCH_2COOH > CH_3COOH$
(d) $CH_3\ COOH > BrCH_2COOH > ClCH_2COOH > FCH_2COOH$

186. The correct order for the acidic character of the following carboxylic acids is



(a) IV > I > II > III > V (b) V > II > III > I > IV
(c) V > II > IV > III > I (d) V > II > IV > I > III

HINTS AND SOLUTIONS

FACT/DEFINITION TYPE QUESTIONS

1. (b) $CH_3-\overset{2}{C}H-\overset{1}{C}HO$ with $\overset{3}{C}H_2-\overset{4}{C}H_3$

2. (a)

3. (c) $\overset{1}{C}H_3-\overset{2}{C}(=O)-\overset{3}{C}H(CH_3)-\overset{4}{C}H_3$; 3- methyl-2-butanone

4. (c) **5. (b)** **6. (a)** **7. (b)**

8. (b) O is more electronegative than C.

9. (d) Vanillin -vanilla beans
Salicylaldehyde - meadow sweet
Cinnamaldehyde -from cinnamon.

10. (d) The lower aldehydes have sharp pungent odours. As the size of the molecule increases, the odour becomes less pungent and more fragrant.

11. (a) Carbonyl compounds (aldehydes and ketones) are obtained by the oxidation of 1° and 2° alcohols respectively. Among the given options, only (a) is 2° alcohol hence it can be oxidized to ketone.

$$\underset{\text{2–hydroxypropane}}{H_3CCH(OH)CH_3} \xrightarrow{\text{oxidation}} \underset{\text{Acetone}}{H_3CCOCH_3}$$

12. (b) Secondary alcohols on oxidation give ketones.
Note : Primary alcohols form aldehydes.

$$\underset{\text{Isopropyl alcohol}}{R_2CHOH} \xrightarrow{[O]} \underset{\text{Ketone}}{R_2C=O}$$

13. (a) 1° Alcohols on catalytic dehydrogenation give aldehydes.

$$\underset{1^\circ\text{ alcohol}}{RCH_2OH} \xrightarrow[300^\circ C]{Cu} \underset{\text{Aldehyde}}{RCHO} + H_2$$

14. (a) Alcohols are oxidized by removal of H_2 in presence of a heated metal catalyst (Cu)

$$\underset{1^\circ\text{ alcohol}}{CH_3CH_2OH} \xrightarrow[300^\circ]{Cu} \underset{\text{Aldehyde}}{CH_3CHO} + H_2$$

$$\underset{2^\circ\text{ Alcohol}}{(H_3C)_2CH-OH} \xrightarrow[300^\circ]{Cu} \underset{\text{Ketone}}{CH_3COCH_3} + H_2$$

15. (a)

$$CH_3-CH_2-C(H)(CH_3)=C(CH_3)_2 \xrightarrow{O_3} CH_3-CH_2-C(H)(O)-C(CH_3)_2(O-O) \xrightarrow{(-H_2O)} CH_3-CH_2-CHO + CH_3-C(=O)-CH_3$$

16. (b) Catalyst used in Rosenmund reduction is $Pd/BaSO_4$. Rosenmund reduction is used for reduction of acid chloride.

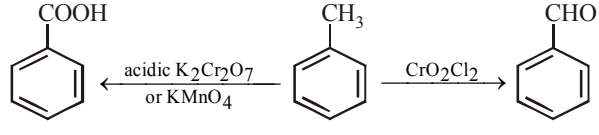
$$R-C(=O)-Cl \xrightarrow{Pd/BaSO_4} R-C(=O)-H$$

17. (d) Phenyl cyanide is reduced into benzaldehyde in the presence of $SnCl_2/HCl$ reagent. This reaction is known as **Stephen's reaction**.

$$C_6H_5C\equiv N + 2[H] \xrightarrow[HCl]{SnCl_2}$$

$$C_6H_5CH=NH \xrightarrow{H_2O/H^+} C_6H_5CHO + NH_3$$

18. (c)



(Etard reaction)

Acidic $KMnO_4$ and $K_2Cr_2O_7$ oxidise toluene to benzoic acid but CrO_2Cl_2 oxidises it to benzaldehyde.

19. (c) **20. (c)** **21. (b)** **22. (d)** **23. (b)**

24. (a) **25. (d)**

26. (b) Formyl chloride is unstable at room temperature.

27. (a) Alkanenitriles (other than methanenitrile) and benzonitrile give ketones with Grignard reagents.

28. (b)

29. (c) $>C=O \longleftrightarrow >\overset{+}{C}-\overset{-}{O}$; the polarity exists in carbonyl group due to resonance.

30. (a) Solubility decreases with increase in mol. wt.

31. (c) Propanone has symmetrical structure.

32. (d)

33. (b) Acetaldehyde reacts only with nucleophiles. Since the mobile p electrons of carbon–oxygen double bond are strongly pulled towards oxygen, carbonyl carbon is electron-deficient and carbonyl oxygen is electron-rich. The electron deficient (acidic) carbonyl carbon is most susceptible to attack by electron rich nucleophilic reagents, that is, by base. Hence the typical reaction of aldehydes and ketones is nucleophilic addition.

34. (c)

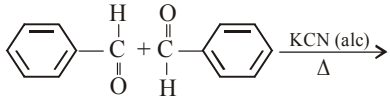
35. (d) Cannizzaro reaction is given by aldehydes having no α-hydrogen atom in the presence of conc. alkali, aldol condensation is given by aldehydes and ketones having at least one α-atom in presence of alkali or in presence of acids

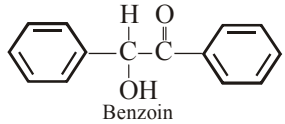
36. (b) Aldehydes containing no α-hydrogen atom on warming with 50% NaOH or KOH undergo disproportionation i.e. self oxidation - reduction known as Cannizzaro's reaction.

$$2\,HCHO \xrightarrow{50\%\,NaOH} HCOONa + CH_3OH$$

37. (d) I_2 and Na_2CO_3 react with acetophenone ($C_6H_5COCH_3$) to give yellow ppt. of CHI_3 but benzophenone ($C_6H_5COC_6H_5$) does not and hence can be used to distinguish between them.

38. (b) When benzaldehyde is refluxed with aqueous alcoholic potassium cyanide, two molecules of benzaldehyde condense together to form benzoin





Benzoin

39. (b) $CH_3COCH_3 + 3I_2 + 4NaOH \longrightarrow$
Acetone

$$CHI_3 + 3NaI + CH_3COONa + 3H_2O$$
Iodoform

Thus acetone reacts with iodine to form iodoform in the presence of NaOH.

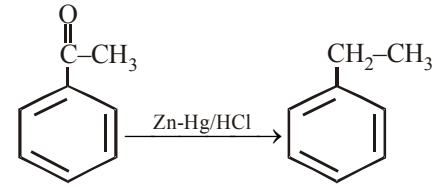
40. (c) Aldol condensation is given by the compounds which contain α hydrogen atom. As the given compound does not contain α hydrogen atom. Hence it does not undergo aldol condensation.

41. (b) $CH_3-\underset{\underset{H}{|}}{C}=O + H_2N-NH-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow{(-H_2O)}$

$$CH_3-CH=N-NH-\overset{\overset{O}{\|}}{C}-NH_2$$
acetaldehyde semicarbazone

42. (d) Iodoform test is exhibited by ethyl alcohol, acetaldehyde, acetone, methyl ketone and those alcohols which possess $CH_3CH(OH)$-group. As 3-pentanone does not contain CH_3CO-group therefore it does not give iodoform test.

43. (b)



Phenyl methyl ketone — Ethyl benzene

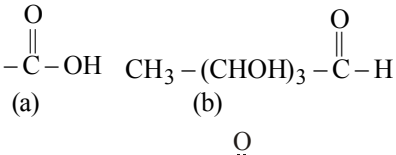
This reaction is known as Clemmensen's reduction.

44. (c) $CH_3CHO + 2Cu^{2+} + OH^- \rightarrow CH_3COOH + Cu_2O\downarrow$
Fehling solution (red)

45. (c) Aldol condensation is given by carbonyl compounds which have α-hydrogen atoms.
$\because$ HCHO does not have any α-hydrogen atom, so it does not give aldol condensation.

46. (b) Cannizzaro reaction is given by aldehydes and ketones which do not have α-hydrogen atom. Benzaldehyde (C_6H_5CHO) does not have α-H atom and hence gives Cannizzaro reaction.

47. (d) Compounds having – CHO group reduce Tollen's reagent to silver mirror. It is called silver mirror test.

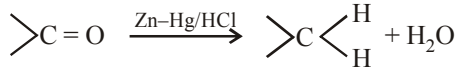


(a) (b)

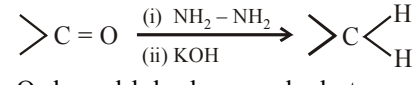
Both (a) and (b) have $-\overset{\overset{O}{\|}}{C}-H$ group so both of them give positive silver mirror test.

48. (b) Tollen's reagent is ammonical $AgNO_3$. Aldehydes form silver mirror with it and ketones do not show any change. So Tollen's reagent is used to distinguish between aldehydes and ketones.

49. (a) Aldehydes and ketones are reduced to alkanes by Clemmensen reduction.

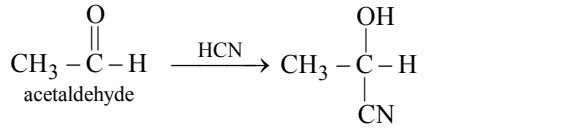


50. (a) Wolf- Kishner reduction

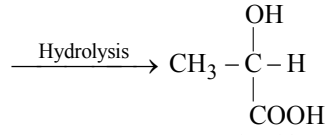


51. (c) Only aldehydes and ketones react with 2, 4-dinitrophenylhydrazine.

52. (b)



acetaldehyde

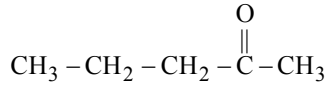


Lactic acid

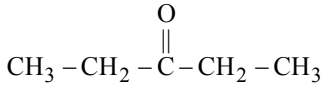
53. (d) HCHO does not undergo iodoform test, while acetaldehyde undergoes iodoform test (I_2 in presence of base) to form yellow precipitate of iodoform.

54. (d) Aldehydes can be oxidised by all the three given reagents.

55. (c) Iodoform test is given by compounds which have CH_3CO group.



2-pentanone



3-pentanone

$\because$ 2-pentanone has CH_3CO group, so it gives iodoform test, while 3-pentanone does not have CH_3CO group, so it does not give iodoform test.

56. (c) In cross aldol condensation aromatic aldehydes or ketones (with or without α-hydrogen) react with aldehydes, ketones or esters having α-hydrogen atoms in the presence of dilute alkali to form a β-unsaturated carbonyl compound.

Example,

(i) $C_6H_5CHO + CH_3CHO \xrightarrow{OH^-}$

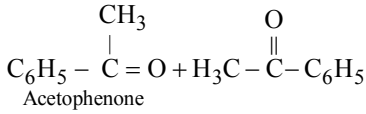
Benzaldehyde Acetaldehyde

$C_6H_5CHOHCH_2CHO$

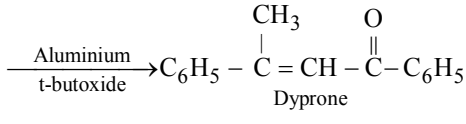
$\downarrow -H_2O$

$C_6H_5CH = CHCHO$

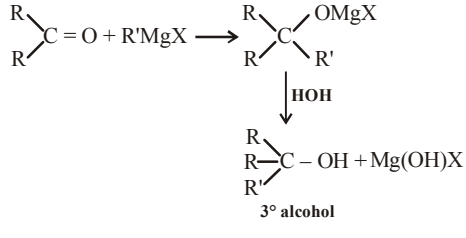
Cinnamaldehyde

(ii) 

Acetophenone

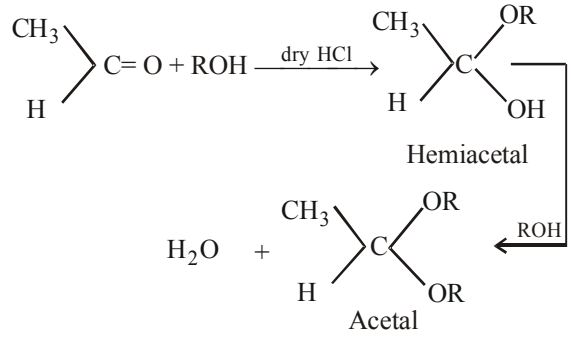


Dyprone

57. (c) 

3° alcohol

58. (a) When acetaldehyde is treated with alcohol in the presence of dry HCl , then acetal is formed

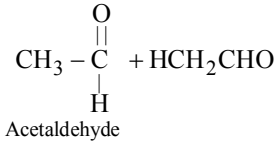


Hemiacetal

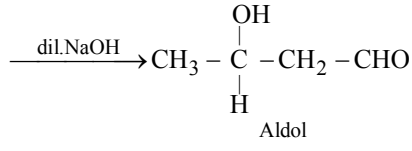
Acetal

Hence, option (a) is correct.

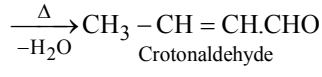
59. (a) Aldehydes and ketones having at least one α-hydrogen atom in presence of dilute alkali give β-hydroxy aldehyde or β-hydroxy ketone



Acetaldehyde

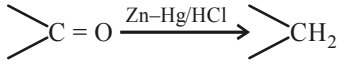


Aldol

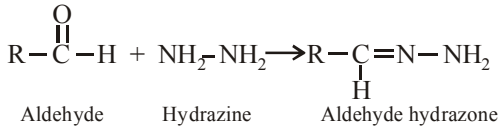


Crotonaldehyde

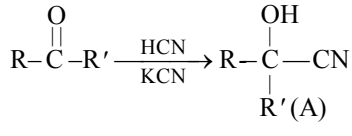
60. (b) Clemmensen reduction is

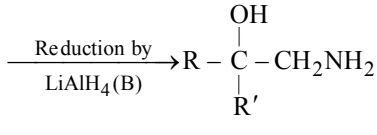


61. (a) Aldehydes, other than formaldehyde, when treated with RMgX give 2° alcohols.

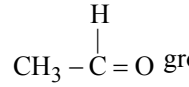
62. (a) 

Aldehyde Hydrazine Aldehyde hydrazone

63. (a) 



64. (b)

65. (d) Iodoform test is given by compounds having CH_3CO– group or secondary alcohols having CH_3– as one of alkyl groups, i.e., CH_3CHOHR or CH_3CH_2OH because it is readily oxidised by halogen (present in reagent) to CH_3CHO which has  group.

66. (d)

67. (a) Aldehydes (e.g. CH_3CHO) restore the pink colour of Schiff's reagent.

68. (a) $C_6H_5COC_6H_5 + KOH \xrightarrow{\text{fusion}}$

$C_6H_6 + C_6H_5COO^-K^+$

69. (c) The nucleophile is SO_3^{--} not HSO_3^-, SO_3Na

70. (c) Wolf-Kishner reduction is reduction of carboxyl compound into alkane.

71. (b) Ammonical $AgNO_3$ is Tollen's reagent.

72. **(d)** **73.** **(c)**

74. **(d)** These reactions lead to replacement of oxygen atom of carbonyl group to form hydrazones and oximes.

75. **(a)** Cannizzaro's reaction is shown by aldehydes lacking α-H-atom. Aldol condensation reactions are shown by aldehydes having α-H-atoms.

76. **(b)** $NaBH_4$ selectively reduces the aldehyde group to alcohol without affecting double bond in a organic compound. So, X is $NaBH_4$.

$$C_6H_5CH=CHCHO \xrightarrow{NaBH_4} C_6H_5CH=CHCH_2OH$$

77. **(a)** All ketones in (i), (ii) and (iii) contain abstractable alpha–proton while all aldehydes do not contain alpha–hydrogen.

78. **(a)** Benzaldehyde undergoes Cannizzaro reaction, which forms benzoic acid and benzylalcohol as the product.

79. **(c)** **80.** **(b)** **81.** **(a)**

82. **(d)** Automobile exhausts are artificial source of isobutyric acid.

83. **(c)** Vinegar is 6 - 8% solution of acetic acid.

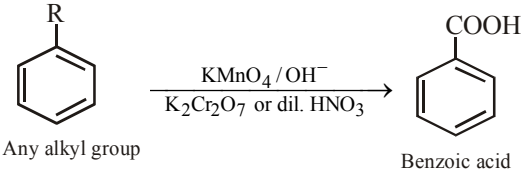
84. **(b)** The overall reaction involved is

$$CH_3CN \xrightarrow{H_2O} CH_3CONH_2 \xrightarrow{H_2O}$$

$$CH_3-COO^{-}\overset{\oplus}{N}H_4 \xrightarrow{HCl} CH_3COOH + NH_4Cl$$

On reduction cyanides yield 1° amines. They do not undergo decarboxylation or electrolysis.

85. **(a)**



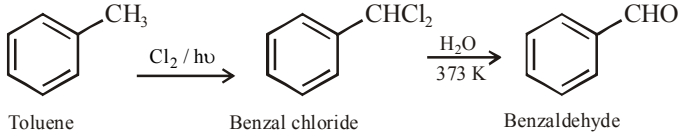
R = Any alkyl group

Benzoic acid

86. **(b)** Both C–O bonds are identical and each O possesses partial negative charge.

87. **(c)** Formic acid cannot be prepared by Grignard reagent.

88. **(b)**



Toluene Benzal chloride Benzaldehyde

89. **(d)**

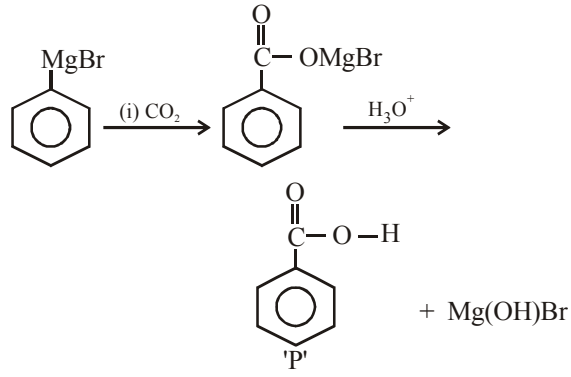
90. **(c)** Carbonyl group acts as a deactivating and metadirecting group.

91. **(d)** Primary and secondary alkyl groups oxidised to give carboxylic acid while tertiary alkyl group remain unaffected.

92. **(b)** **93.** **(d)**

94. **(b)** Due to H-bonding.

95. **(b)** Grignard reagent forms addition product with bubbled carbondioxide which on hydrolysis with HCl yields benzoic acid.



Benzoic acid

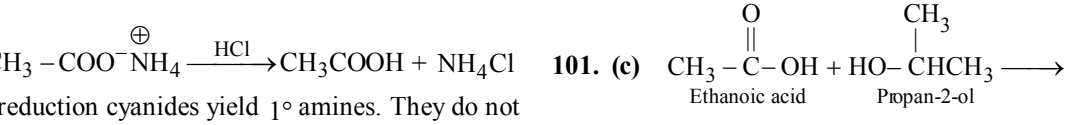
96. **(c)**

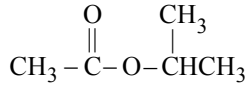
97. **(d)** In carboxylates (conjugate base of carboxylic acids), resonance is more significant because the two resonating structures are similar, while in phenoxide, the resonating structures are not equivalent, alkoxide ions do not show resonance.

98. **(a)** **99.** **(a)**

100. **(c)** Bromine is less electronegative than F, further in $BrCH_2CH_2COOH$, Br is more away from the –COOH group than in $CH_3CHBrCOOH$.

101. **(c)**





102. **(a)**

103. **(c)** $pK_a = -\log K_a$; HCOOH is the strongest acid and hence it has the highest K_a or lowest pK_a value.

104. **(c)**

105. **(b)** $LiAlH_4$ in presence of ether can be used to convert acetic acid into ethanol.

$$CH_3COOH + 3LiAlH_4 \xrightarrow{\text{ether}}$$

acetic acid

$$[CH_3CH_2O]_4AlLi + 2LiAlO_2 + 4H_2$$

$$[CH_3CH_2O]_4AlLi \xrightarrow{H^+} CH_3CH_2OH$$

ethanol

106. **(c)** Carboxylic acids are weak acids.

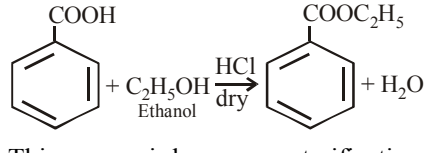
107. **(c)** Removal of CO_2 from carboxylic acid is called decarboxylation.

108. **(b)** It is a test for –COOH gp.;

$$R\text{–}COOH + NaHCO_3 \longrightarrow RCOONa + H_2O + CO_2\uparrow.$$

109. **(d)**

110. **(c)**



This process is known as esterification.

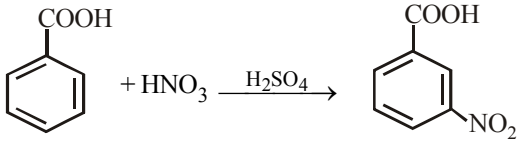
111. (c) This reaction is an example of Hell - Volhard Zelinsky reaction. In this reaction acids containing α – H on treatment with X_2 /P give di-halo substituted acid.

$$CH_3 - CH_2COOH \xrightarrow{Br_2/P} CH_3 - CBr_2 - COOH$$

112. (c) $3CH_3COOH + PCl_3 \longrightarrow \underset{\text{Acetyl Chloride}}{CH_3COCl} + \underset{\text{Phosphorous acid}}{H_3PO_3}$

113. (b)

114. (a) –COOH group when attached to benzene ring deactivates the ring and substitution occurs at m-position. (HNO_3 + H_2SO_4) is a source of $^+NO_2$ (electrophile) which attacks at m-position.



3- nitrobenzoic acid

115. (b) $RCH_2COOH \xrightarrow[\text{HVZ reaction}]{Br_2 / P} R - \underset{\underset{Br}{|}}{CH} - COOH$ 'X'

$\xrightarrow[\text{(Excess)}]{NH_3} R - \underset{\underset{NH_2}{|}}{CH}COOH$ 'Y'

116. (d) The yield of product in a reversible reaction can be increased by (i) removing one of the products, (ii) taking either of the reactant in excess.

117. (d) Use of $SOCl_2$ and ClCOCOCl forms gaseous by-products which can be easily removed, giving better yield of RCOCl. Further, oxalyl chaloride is particularly easy to use becasue any excess of it can be easily evaporated due to its low b.p. (62ºC)

$$R - \overset{\overset{O}{||}}{C} - OH + Cl - \overset{\overset{O}{||}}{C} - \overset{\overset{O}{||}}{C} - Cl \longrightarrow$$

$$R - \overset{\overset{O}{||}}{C} - Cl + HCl\uparrow + CO\uparrow + CO_2\uparrow$$

118. (b)

119. (a) Salicylic acid, because it stabilizes the corresponding salicylate ion by intramolecular H-bonding.

120. (c) $Cl_2CHCOOH$ is most acidic because it has two chlorine at α-position.

121. (a) An electron releasing substituent (+I) intensify the negative charge on the anion resulting in the decrease of stability and thus decreases the acidity of the acid. Hence acid character decreases as the + I-effect of the alkyl group increases as

$CH_3^- < CH_3CH_2^- < CH_3CH_2CH_2^- < CH_3CH_2CH_2CH_2^-$

Hence the order becomes : (i) > (ii) > (iii) > (iv)

122. (c) Chlorine is electron withdrawing group. Further inductive effect is stronger at α position than β-position. i.e.,

$$\overset{\alpha}{CH_2}ClCOOH > \overset{\beta}{CH_2}Cl\overset{\alpha}{CH_2}COOH$$

123. (b)

STATEMENT TYPE QUESTIONS

124. (b) Carbonyl compounds have substantial dipole moments and are polar in nature. The high polarity of the carbonyl group is due to resonance.

125. (a) Primary alcohols on oxidation give carboxylic acids as the final product, of course through aldehydes. Oppenauer oxidation involves oxidation of 2º alcohols to ketones, and not for the oxidation of 1º alcohols.

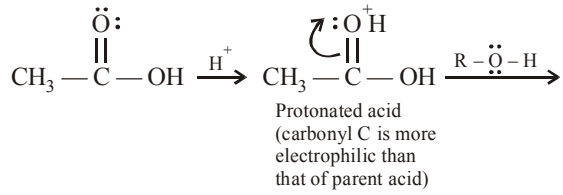
126. (c) If the aldehyde has a boiling point less than 100°C, it can be prepared by the oxidation of 1° alcohols with regular oxidising agents like acidic permanganate or dichromate. Since the aldehyde has a lower boiling point than the alcohol, it is distilled off as soon as it is formed ; so further oxidation to a carboxylic acid is minimized.

127. (d) The solubility of aldehydes and ketones decreases rapidly on increasing the length of alkyl chain.

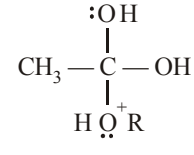
128. (a) Aldehydes are generally more reactive than ketones in nucleophilic addition reactions due to steric and electronic reasons. Sterically, the presence of two relatively large substituents in ketones hinders the approach of nucleophile to carbonyl carbon than in aldehydes having only one such substituent. Electronically, aldehydes are more reactive than ketones because two alkyl groups reduce the electrophilicity of the carbonyl carbon more effectively than in former.

129. (b) The hydrogen atom that is added to the carbonyl carbon of the aldehyde in the reduction is derived directly from the other aldehyde molecule as a hydride ion. The second hydrogen that is added to the negatively charged oxygen is coming from the solvent (consult mechanism of Cannizzaro reaction). Oxidation of one molecule of the compound at the expense of other molecule of the same compound is known as disproportionation.

130. (b) First two steps of the esterification make the question clear



Protonated acid (carbonyl C is more electrophilic than that of parent acid)



MATCHING TYPE QUESTIONS

131. (a) **132. (c)** **133. (b)** **134. (d)** **135. (b)**
136. (c) **137. (c)**

ASSERTION-REASON TYPE QUESTIONS

138. (a) **139. (a)** **140. (b)**

141. (a) The molecular mass of acetic acid in benzene is 120 instead of 60 because the carboxylic acids exists as cyclic dimers in which two molecules of the acid are held together by two strong hydrogen bond.

CRITICAL THINKING TYPE QUESTIONS

142. (d)

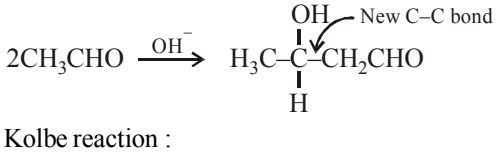
143. (b) In structure II, presence of positive charge on oxygen causes the displacement of π electrons toward oxygen, making carbon more electron deficient than that in unprotonated carbonyl group.

144. (c) It is the reason for the given fact.

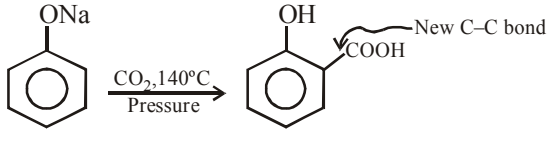
145. (d)

146. (c) With ammonia, HCHO forms hexamethylenetetramine, CH_3CHO gives acetaldehydeammonia addition product, while C_6H_5CHO gives hydrobenzamide.

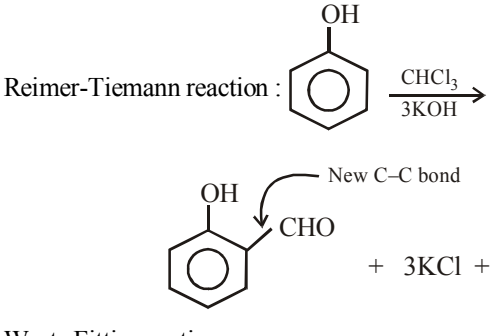
147. (d) Aldol condensation :



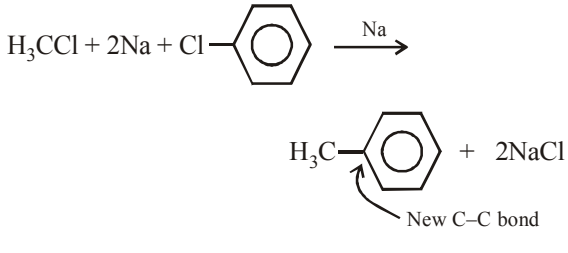
Kolbe reaction :



Reimer-Tiemann reaction :

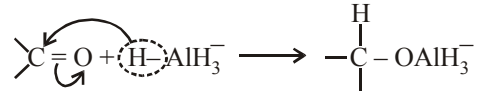


Wurtz Fittig reaction :



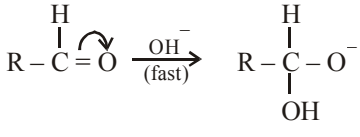
148. (c) (a) $>C=O + H_2NNH_2 \xrightarrow{H^+} >C(OH)NHNH_2 \xrightarrow{H^+} >C=NNH_2$

(b) In the reduction of carbonyl group with $LiAlH_4$ or $NaBH_4$, a hydride ion is transferred from the metal to the carbonyl carbon (nucleophilic addition)

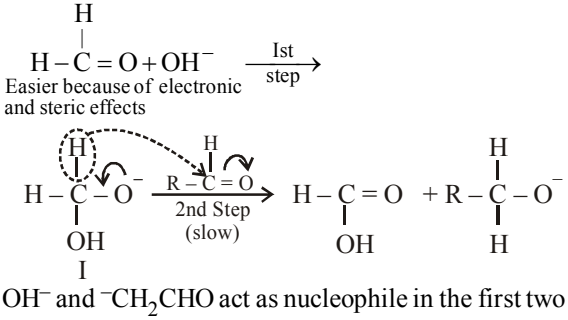


149. (d) Being reversible reaction, the backward reaction i.e. acetal -hemiacetal step can be restricted by minimizing water content, i.e. by using dry HCl. The step hemiacetal - aldehyde can be restricted by using excess of alcohol.

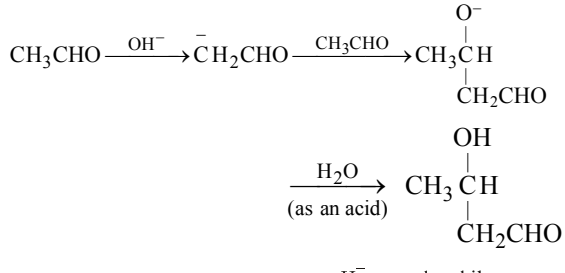
150. (c) First step in Cannizzaro reaction is the nucleophilic addition of OH^- on the carbonyl carbon.



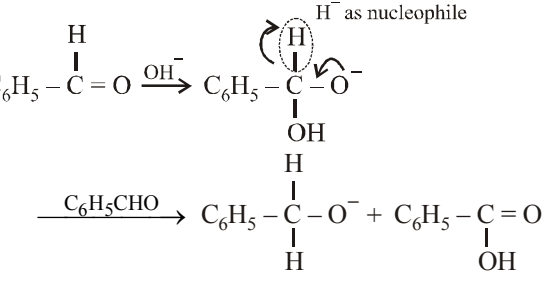
Higher the electron deficiency on cabonyl carbon, more easier will be the attack of the nucleophile (OH^-) on its carbon. Futher, the attack of OH^- on the carbonyl carbon is more easy in case of HCHO because its carbon is least hindered having two hydrogens (steric effect). Thus the intermediate I is formed very easily which donates hydride ion to another aldehyde and thus itself oxidised.



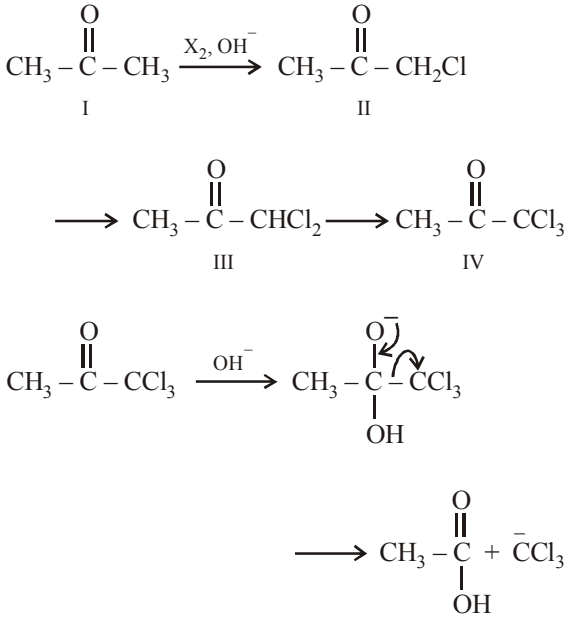
151. (c) OH^- and $^-CH_2CHO$ act as nucleophile in the first two steps.



152. (c)



153. (d) If we observe the haloform reaction carefully, we see that $-COCH_3$ group is first halogenated to the trihalo $-COCX_3$ through monohalogeno and dihalogeno compound. It is the $-COCX_3$ part which then undergoes nucleophilic addition. The product easily loses $-CX_3$ since it is a very good leaving group.



Thus all compounds (I to IV) are ultimately converted to $CHCl_3$ (chloroform).

154. (c) $2CH_3CHO \longrightarrow 1^{st}$ Product,

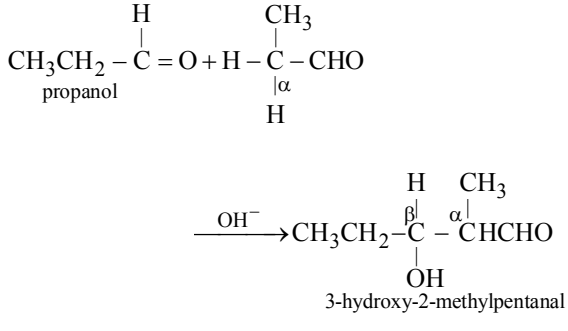
$2\,CH_3CH_2CHO \longrightarrow 2^{nd}$ Product

$CH_3CH_2CHO + \overset{\alpha}{C}H_3CHO \longrightarrow 3^{rd}$ Product;

$CH_3\overset{\alpha}{C}H_2CHO + CH_3CHO \longrightarrow 4^{th}$ Product

155. (d) Dihydrogen sodium phosphate (NaH_2PO_4) does not have a lone pair of electrons on the P atom. As such it can not act as a nucleophile and hence does not react with aldehydes and ketones.

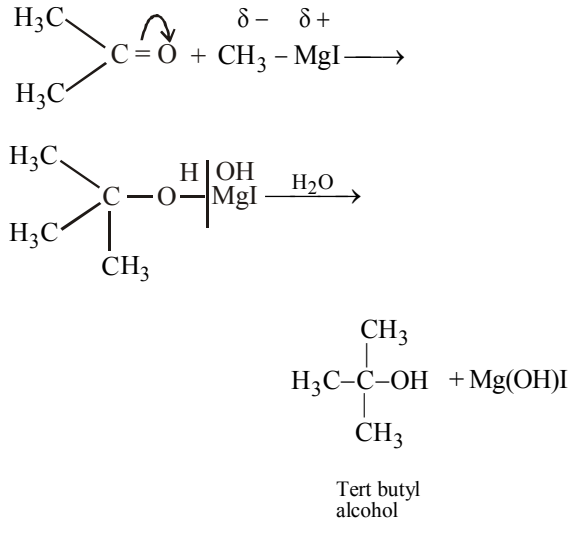
156. (d) Aldehydes which contain a α-hydrogen on a saturated carbon, i.e., CH_3CH_2CHO undergo aldol condensation.



157. (a) Aldol condensation involves an aldehyde or ketone having an α–hydrogen atom. This type of condensation occurs in presence of dilute base (i.e., dil NaOH).

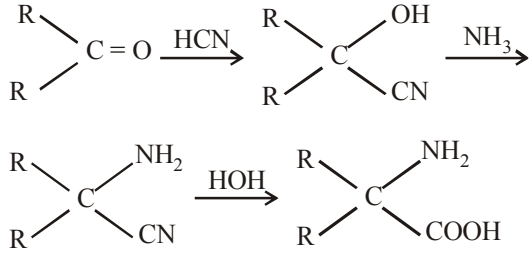
Only CH_3COCH_3 will give aldol condensation (Both HCHO and C_6H_5CHO lack α-hydrogen).

158. (d)



159. (d) Ketones do not respond to Tollen's test. Aldehydes respond to Tollen's test.

160. (b)



161. (d) **162. (a)** **163. (a)**

164. (b) The carbon atom of the carbonyl group of benzaldehyde is less electrophilic than carbon atom of the carbonyl group present in propanal. The polarity of the carbonyl group is reduced in benzaldehyde due to resonance as shown below and hence it is less reactive than propanal.

165. (b) Aldehydes and ketones react with hydrogen cyanide (HCN) to yield cyanohydrins. This reaction occurs very slowly with pure HCN. Therefore, it is catalysed by a base and the generated cyanide ion (CN^-) being a stronger nucleophile readily adds to carbonyl compounds to yield corresponding cyanohydrins

166. (b) Dry hydrogen chloride protonates the oxygen of the carbonyl compounds and therefore, increases the electrophilicity of the carbonyl carbon facilitating the nucleophilic attack by the alcohol molecule. Dry HCl gas also absorbs the water produced in these reactions thereby shifting the equilibrium in the forward direction.

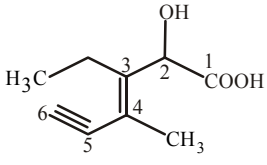
167. (a) Because of resonance in benzaldehyde which is not possible in case of acetaldehyde the positive charge on the carbonyl carbon decreases and hence there is decrease in reactivity.

168. (c) Acetal formed upon reaction of ethylene glycol and HCl, which is unaffected by base hence unwanted reaction does not occur due to presence of carbonyl group.

169. (c) 2, 2-dimethyl propanal gives Tollen's test and 3-methylbutan-2-one gives iodoform test.

170. (d)

171. (a)



IUPAC name of the structure is 3-ethyl-2-hydroxy -4-methylhex-3-en-5-ynoic acid.

172. (c) $R-X \xrightarrow{CN^-} R-CN \xrightarrow{NaOH} RCOONa$

173. (c)

174. (b) $\underset{\text{benzoic anhydride}}{(C_6H_5CO)_2O} \xrightarrow{H_2O} \underset{\text{benzoic acid}}{2C_6H_5-COOH}$

$\underset{\text{bezoyl ethanoic anhydride}}{C_6H_5COOCOCH_3} \xrightarrow{H_2O} \underset{\text{benzoic acid}}{C_6H_5COOH} + \underset{\text{ethanoic acid}}{CH_3COOH}$

175. (b) **176. (a)**

177. (b) Recall that presence of electron-withdrawing group increases, while presence of electron-releasing group decreases the acidity of carboxylic acids.

$\underset{\text{(electron-withdrawing gp.)}}{ClCH_2COOH} > H-\overset{O}{\overset{\|}{C}}-OH > CH_3-\overset{O}{\overset{\|}{C}}-OH >$

(Electron-releasing character increasing from Left to Right)

$C_2H_5-\overset{O}{\overset{\|}{C}}-OH$

178. (d) $A \xrightarrow[(I)]{NH_3} B \xrightarrow[II]{\Delta} C \xrightarrow[KOH,(III)]{Br_2} CH_3CH_2NH_2$

Reaction (III) is a Hofmann bromamide reaction. Now formation of $CH_3CH_2NH_2$ is possible only from a compound $CH_3CH_2CONH_2$(C) which can be obtained from the compound $CH_3CH_2COO^-NH_4^+$(B).

Thus (A) should be CH_3CH_2COOH

$\underset{(A)}{CH_3CH_2-\overset{O}{\overset{\|}{C}}-OH} \xrightarrow{NH_3} \underset{(B)}{CH_3CH_2COO^-NH_4^+} \xrightarrow{\Delta} \underset{(C)}{CH_3CH_2CONH_2}$

$CH_3CH_2NH_2$ (KOH, Br_2)

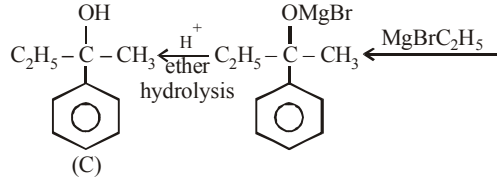
179. (a) The correct order of increasing acid strength

$CF_3COOH > MeOCH_2COOH > CH_3COOH > (Me)_2CH.COOH$

Electron withdrawing groups increase the acid strength and electron donating groups decrease the acid strength.

180. (a) Grignard reagents and nitriles are useful for converting alkyl halide into corresponding carboxylic acids having one carbon atom more than that present in alkyl halides.

181. (a) $CH_3COOH + PCl_5 \rightarrow \underset{[A]}{CH_3COCl} \xrightarrow[Anhyd\,AlCl_3]{C_6H_6}$ Friedle Craft reaction



182. (c) An alkyl group attached to benzene ring can be oxidised only when it contains at least one α-hydrogen atom. Thus here $-CH_3$ group is oxidised and Me_3C- group not. However, Me_3C- group may cause oxidation of the benzene ring to –COOH.

183. (a) **184. (a)**

185. (c) Electron withdrawing substituent (like halogen, $—NO_2$, C_6H_5 etc.) would disperse the negative charge and hence stabilise the carboxylate ion and thus increase acidity of the parent acid. On the other hand, electron-releasing substituents would intensify the negative charge, destabilise the carboxylate ion and thus decrease acidity of the parent acid.

Electronegativity decreases in order

$F > Cl > Br$

and hence –I effect also decreases in the same order, therefore the correct option is

$[FCH_2COOH > ClCH_2COOH > BrCH_2COOH > CH_3COOH]$

186. (d) V is most stable because its anion is stabilized to a greater extent through H – bonding with H atom of OH present on both *ortho*-positions ; followed by II in which one OH group is present. Compound IV comes next to II because here $-OCH_3$ group is present in *ortho* position which although is not capable of forming H–bonding yet more acidic than *p*-HOC_6H_4COOH (III) due to ortho effect. Compound III is less acidic than benzoic acid because of electron-releasing group in the para position. Thus