CHAPTER 25

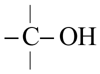
ALCOHOLS, PHENOLS AND ETHERS

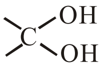
FACT/DEFINITION TYPE QUESTIONS

1. The characteristic grouping of secondary alcohols is

(a) $-CH_2OH$

(b) 

(c)  $-\overset{|}{\underset{|}{C}}-OH$

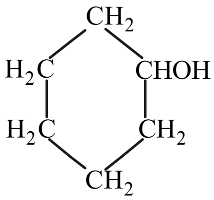
(d) 

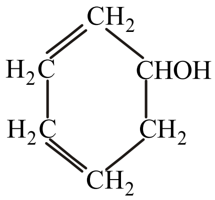
2. The compound $HOCH_2-CH_2OH$ is

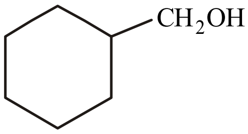
(a) ethane glycol (b) ethylene glycol

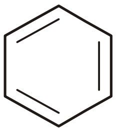
(c) ethylidene alcohol (d) dimethyl alcohol

3. The structural formula of cyclohexanol is

(a) 

(b) 

(c) 

(d) 

4. Which of the following is dihydric alcohol ?

(a) Glycerol (b) Ethylene glycol

(c) Catechol (d) Resorcinol

5. An example of a compound with functional group – O – is :

(a) acetic acid (b) methyl alcohol

(c) diethyl ether (d) acetone

6. Butane-2-ol is

(a) primary alcohol (b) secondary alcohol

(c) tertiary alcohol (d) aldehyde

7. Cresol has

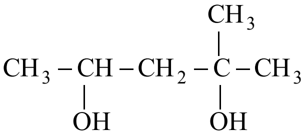
(a) Alcoholic – OH (b) Phenolic – OH

(c) – COOH (d) – CHO

8. How many isomers of $C_5H_{11}OH$ will be primary alcohols ?

(a) 5 (b) 4

(c) 2 (d) 3

9. The IUPAC name of  $CH_3-\underset{OH}{\underset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{\underset{OH}{\underset{|}{C}}}}-CH_3$ is

(a) 1, 1-dimethyl-1, 3-butanediol

(b) 2-methyl-2, 4-pentanediol

(c) 4-methyl-2, 4-pentanediol

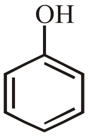
(d) 1, 3, 3-trimethyl-1, 3-propanediol

10. Number of metamers represented by molecular formula $C_4H_{10}O$ is

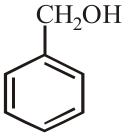
(a) 4 (b) 3

(c) 2 (d) 1

11. Which of the following compounds is aromatic alcohol?



(A)



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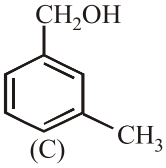

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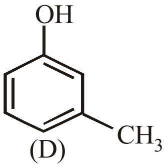


(D)

(a) A, B, C, D (b) A, D

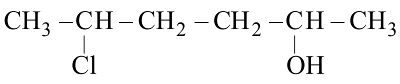
(c) B, C (d) A

12. How many alcohol(s) with molecular formula $C_4H_{10}O$ are chiral in nature?

(a) 1 (b) 2

(c) 3 (d) 4

13. Give IUPAC name of the compound given below



$CH_3-\underset{Cl}{\underset{|}{CH}}-CH_2-CH_2-\underset{OH}{\underset{|}{CH}}-CH_3$

(a) 2-Chloro-5-hydroxyhexane

(b) 2-Hydroxy-5-chlorohexane

(c) 5-Chlorohexane-2-ol

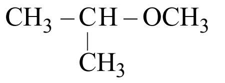
(d) 2-Chlorohexan-5-ol

14. IUPAC name of *m*-cresol is ___________

(a) 2-methylphenol (b) 3-chlorophenol

(c) 3-methoxyphenol (d) benzene-1, 3-diol

15. IUPAC name of the compound



$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}H-OCH_3$ is _______________ .

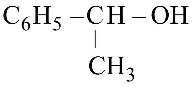
(a) 1-methoxy-1-methylethane
(b) 2-methoxy-2-methylethane
(c) 2-methoxypropane
(d) isopropylmethyl ether

16. Which of the following are benzylic alcohols?

(i) $C_6H_5-CH_2-CH_2OH$

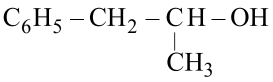
(ii) $C_6H_5-CH_2OH$

(iii)



$C_6H_5-\underset{\displaystyle CH_3}{\underset{|}{C}}H-OH$

(iv)

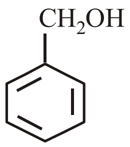


$C_6H_5-CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}H-OH$

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

17. In which of the following structures hydroxyl group is attached to sp^2 carbon atom?

(a)



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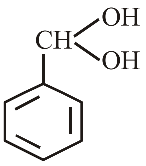

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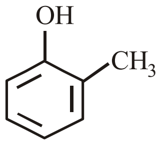

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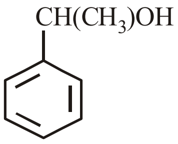


18. Which of the following is an example of unsymmetrical ether?
(a) $C_2H_5OC_2H_5$ (b) $C_6H_5OC_6H_5$
(c) $C_6H_5OC_2H_5$ (d) CH_3OCH_3

19. Which of the following will not form phenol or phenoxide ?
(a) $C_6H_5N_2Cl$ (b) $C_6H_5SO_3Na$
(c) C_6H_5Cl (d) $C_6H_5CO_2H$

20. Benzyl alcohol is obtained from benzaldehyde by
(a) Fittig's reaction (b) Cannizzaro's reaction
(c) Kolbe's reaction (d) Wurtz's reaction

21. In the reduction

$R-CHO+H_2 \longrightarrow RCH_2OH$

the catalyst used is :
(a) Ni (b) Pd
(c) Pt (d) Any of these

22. Ethylene reacts with Baeyer's reagent to give
(a) ethane (b) ethyl alcohol
(c) ethylene glycol (d) None of these

23. Ethyl alcohol is industrially prepared from ethylene by
(a) Permanganate oxidation
(b) Catalytic reduction
(c) Absorbing in H_2SO_4 followed by hydrolysis
(d) All the three

24. Sodium salt of benzene sulphonic acid on fusion with caustic soda gives
(a) Benzene (b) Phenol
(c) Thiophenol (d) Benzoic acid

25. Acid catalyzed hydration of alkenes except ethene leads to the formation of
(a) primary alcohol
(b) secondary or tertiary alcohol
(c) mixture of primary and secondary alcohols
(d) mixture of secondary and tertiary alcohols

26. Ethyl alcohol can be prepared from Grignard reagent by the reaction of :
(a) HCHO (b) R_2CO
(c) RCN (d) RCOCl

27. Isopropyl alcohol is obtained by reacting which of the following alkenes with concentrated H_2SO_4 followed by boiling with H_2O?
(a) Ethylene (b) Propylene
(c) 2-Methylpropene (d) Isoprene

28. Alkenes convert into alcohols by
(a) hydrolysis by dil. H_2SO_4
(b) hydration of alkene by alkaline $KMnO_4$
(c) hydrolysis by water vapours and conc. HNO_3
(d) hydration of alkene by aqueous KOH

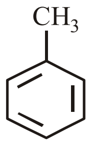
29. Which of the following reacts with NaOH to give an alcohol?
(a) Propene (b) Butene
(c) Ethanal (d) Methanal

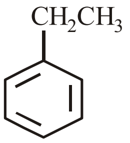
30. By which of the following methods alcohol can be prepared in excellent yield?
(a) From alkenes
(b) By hydroboration-oxidation
(c) From carbonyl compounds
(d) From Grignard reagent

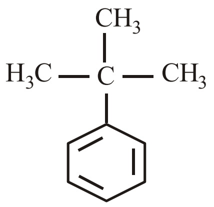
31. Which of the following are used to convert RCHO into RCH_2OH?
(i) H_2/Pd
(ii) $LiAlH_4$
(iii) $NaBH_4$
(iv) Reaction with RMgX followed by hydrolysis
(a) (i) and (ii) (b) (i), (ii) and (iii)
(c) (ii), (iii) and (iv) (d) (i) and (iii)

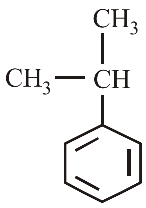
32. Commercially carboxylic acids are reduced to alcohols by converting them to the ______.
(a) esters (b) aldehydes
(c) ketones (d) amines

33. The hydrocarbon which produce phenol and acetone as a by product in the large quantity is

(a) 

(b) 

(c) 

(d) 

34. In the reaction, $RNH_2 \xrightarrow[273-278K]{HNO_2} ROH + H_2O + C\uparrow$;

C is (where $R = C_6H_5$)

(a) NH_3 (b) N_2

(c) O_2 (b) CO_2

35. The correct order of boiling points for primary (1°), secondary (2°) and tertiary alcohol (3°) is

(a) 1° > 2° > 3° (b) 3° > 2° > 1°

(c) 2° > 1° > 3° (d) 2° > 3° > 1°

36. Alcohols of low molecular weight are

(a) soluble in water

(b) soluble in water on heating

(c) insoluble in water

(d) insoluble in all solvents

37. Which of the following has lowest boiling point ?

(a) *p*-Nitrophenol (b) *m*-Nitrophenol

(c) *o*-Nitrophenol (d) Phenol

38. Which statement is not correct about alcohol?

(a) Molecular weight of alcohol is higher than water

(b) Alcohol of less no. of carbon atoms is less soluble in water than alcohol of more no. of carbon atoms

(c) Alcohol evaporates quickly

(d) All of the above

39. Which one of the following alcohols is least soluble in water?

(a) CH_3OH (b) C_3H_7OH

(c) C_4H_9OH (d) $C_{10}H_{21}OH$

40. Methanol and ethanol are miscible in water due to

(a) covalent character

(b) hydrogen bonding character

(c) oxygen bonding character

(d) None of these

41. If ethanol dissolves in water, then which of the following would be observed

(a) absorption of heat and contraction in volume

(b) emission of heat and contraction in volume

(c) absorption of heat and increase in volume

(d) emission of heat and increase in volume

42. Which of the following is correct ?

(a) On reduction of any aldehyde, secondary alcohol is formed

(b) Reaction of vegetable oil with H_2SO_4 gives glycerine

(c) Sucrose on reaction with NaCl gives invert sugar

(d) Alcoholic iodine gives iodoform with NaOH

43. Which of the following is not true in case of reaction with heated copper at 300°C?

(a) Phenol ⟶ Benzyl alcohol

(b) Secondary alcohol ⟶ Ketone

(c) Primary alcohol ⟶ Aldehyde

(d) Tertiary alcohol ⟶ Olefin

44. Phenol is more acidic than alcohol because

(a) phenol is more stable than water

(b) phenol is aromatic and alcohol is aliphatic

(c) phenoxide ion is resonance stabilised

(d) None of these

45. Acidity of phenol is due to

(a) hydrogen bonding

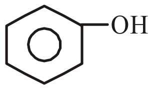
(b) phenolic group

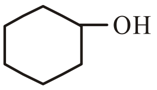
(c) benzene ring

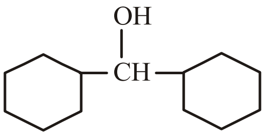
(d) resonance stabilisation of its anion

46. Which one of the following compounds has the most acidic nature?

(a) 

(b) 

(c) 

(d) 

47. The ionization constant of phenol is higher than that of ethanol because :

(a) phenoxide ion is bulkier than ethoxide

(b) phenoxide ion is stronger base than ethoxide

(c) phenoxide ion is stabilized through delocalization

(d) phenoxide ion is less stable than ethoxide

48. Which one of the following on oxidation gives a ketone ?

(a) Primary alcohol (b) Secondary alcohol

(c) Tertiary alcohol (d) All of these

49. 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

50. When ethyl alcohol reacts with acetic acid, the products formed are

(a) Sodium ethoxide + hydrogen

(b) Ethyl acetate + water

(c) Ethyl acetate + soap

(d) Ethyl alcohol + water

51. Which of the following compounds is oxidised to prepare methyl ethyl ketone?
(a) 2-Propanol (b) l-Butanol
(c) 2-Butanol (d) t-Butyl alcohol

52. HBr reacts fastest with
(a) 2-Mehtylpropan-1-ol
(b) 2-Methylpropene-2-ol
(c) propan-2-ol
(d) propan-1-ol

53. *n*-Propyl alcohol and isopropyl alcohol can be chemically distinguished by which reagent?
(a) PCl_5
(b) Reduction
(c) Oxidation with potassium dichromate
(d) Ozonolysis

54. Lucas reagent is
(a) Conc. HCl and anhydrous $ZnCl_2$
(b) Conc. HNO_3 and hydrous $ZnCl_2$
(c) Conc. HCl and hydrous $ZnCl_2$
(d) Conc. HNO_3 and anhydrous $ZnCl_2$

55. The compound which reacts fastest with Lucas reagent at room temperature is
(a) Butan-1-ol (b) Butan-2-ol
(c) 2-Methyl propan-1-ol (d) 2-Methylpropan-2-ol

56. When phenol is treated with excess bromine water, it gives:
(a) *m*-Bromophenol (b) *o*- and *p*-Bromophenol
(c) 2, 4-Dibromophenol (d) 2, 4, 6-Tribromophenol

57. When phenol is heated with $CHCl_3$ and alcoholic KOH when salicyladehyde is produced. This reaction is known as
(a) Rosenmund's reaction (b) Reimer-Tiemann reaction
(c) Friedel-Crafts reaction (d) Sommelet reaction

58. On distilling phenol with Zn dust, one gets :
(a) Toluene (b) Benzaldehyde + ZnO
(c) ZnO + benzene (d) Benzoic acid

59. Phenols do not react with one of the following :
(a) Alkali metals (b) Sodium hydroxide
(c) Potassium hydroxide (d) Sodium bi-carbonate

60. In the reaction

Phenol $\xrightarrow{NaOH}$ (A) $\xrightarrow[140°]{CO_2+HCl}$ (B), here B is

(a) benzaldehyde (b) chlorobenzene
(c) benzoic acid (d) salicylic acid

61. Dehydration of 2-butanol yields
(a) 1-butene (b) 2-butene
(c) 2-butyne (d) Both (a) and (b)

62. Lucas test is done to differentiate between
(a) alcohol and ketone
(b) alcohol and aromatic ketones
(c) 1°, 2° and 3° alcohols
(d) None of these

63. To distinguish between salicylic acid and phenol, one can use
(a) $NaHCO_3$ solution (b) 5% NaOH solution
(c) neutral $FeCl_3$ (d) bromine water

64. Ethyl alcohol exhibits acidic character on reacting it with
(a) acetic acid (b) sodium metal
(c) hydrogen chloride (d) acidic $K_2Cr_2O_7$

65. For the reaction,

$$C_2H_5OH + HX \xrightarrow{ZnCl_2} C_2H_5X + H_2O$$

the order of reactivity is
(a) HBr > HI > HCl (b) HI > HCl > HBr
(c) HI > HBr > HCl (d) HCl > HBr > HI

66. In the following reaction,

$$C_2H_5OH \xrightarrow[443\,K]{Conc.\ H_2SO_4} Z \text{ identify Z:}$$

(a) $CH_2 = CH_2$ (b) $CH_3CH_2OCH_2CH_3$
(c) $CH_3CH_2–HSO_4$ (d) $(CH_3CH_2)_2SO_4$

67. Chemical name of salol is
(a) acetylsalicyclic acid (b) sodium salicylate
(c) phenyl salicylate (d) methyl salicylate

68. Aspirin is an acetylation product of
(a) p-Dihydroxybenzene (b) o-Hydroxybenzoic acid
(c) o-Dihydroxybenzene (d) m-Hydroxybenzoic acid

69. Phenol, when it first reacts with concentrated sulphuric acid and then with concentrated nitric acid, gives
(a) 2, 4, 6-trinitrobenzene (b) *o*-nitrophenol
(c) *p*-nitrophenol (d) nitrobenzene

70. 3 moles of ethanol react with one mole of phosphorus tribromide to form 3 moles of bromoethane and one mole of X. Which of the following is X?
(a) H_3PO_4 (b) H_3PO_2
(c) HPO_3 (d) H_3PO_3

71. Methanol and ethanol can be distinguished by the following:
(a) By reaction with metallic sodium
(b) By reaction with caustic soda
(c) By heating with iodine and washing soda
(d) By heating with zinc and inorganic mineral acid

72. Monochlorination of toluene in sunlight followed by hydrolysis with aq. NaOH yields.
(a) *o*-Cresol (b) *m*-Cresol
(c) 2, 4-Dihydroxytoluene (d) Benzyl alcohol

73. What is the correct order of reactivity of alcohols in the following reaction?

$$R - OH + HCl \xrightarrow{ZnCl_2} R - Cl + H_2O$$

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

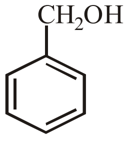
74. CH_3CH_2OH can be converted into CH_3CHO by ________
(a) catalytic hydrogenation
(b) treatment with $LiAlH_4$
(c) treatment with pyridinium chlorochromate
(d) treatment with $KMnO_4$

75. Which of the following compounds will react with sodium hydroxide solution in water?
(a) C_6H_5OH (b) $C_6H_5CH_2OH$
(c) $(CH_3)_3COH$ (d) C_2H_5OH

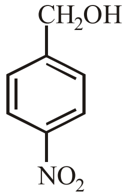
76. Phenol is less acidic than_______________ .
(a) ethanol (b) *o*–nitrophenol
(c) *o*-methylphenol (d) *o*-methoxyphenol

77. Which of the following is most acidic?
(a) Benzyl alcohol (b) Cyclohexanol
(c) Phenol (d) *m*-Chlorophenol

78. Mark the correct increasing order of reactivity of the following compounds with HBr/HCl



(A)



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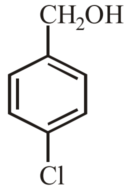
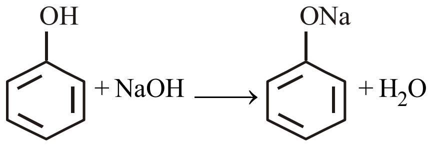


(C)

(a) A < B < C (b) B < A < C
(c) B < C < A (d) C < B < A

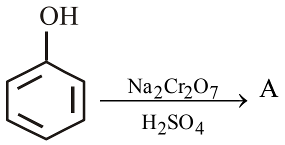
79. Arrange the following in increasing order of their acidity?
o–cresol(a), salicyclic acid(b), phenol(c)
(a) c < a < b (b) b < c < a
(c) a < b < a (d) a < c < b

80. In the reaction

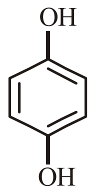


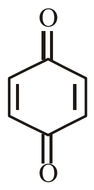
Phenol behaves as
(a) Bronsted base (b) Bronsted acid
(c) Lewis acid (d) Lewis base

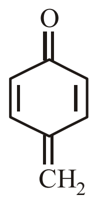
81. In the given reaction

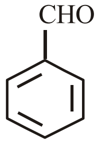


A is

(a) 

(b) 

(c) 

(d) 

82. Which enzyme converts glucose and fructose both into ethanol ?
(a) Diastase (b) Invertase
(c) Zymase (d) Maltase

83. An industrial method of preparation of methanol is :
(a) catalytic reduction of carbon monoxide in presence of $ZnO–Cr_2O_3$
(b) by reacting methane with steam at 900°C with a nickel catalyst
(c) by reducing formaldehyde with lithium aluminium hydride
(d) by reacting formaldehyde with aqueous sodium hydroxide solution

84. Ethyl alcohol is industrially prepared from ethylene by
(a) Permanganate oxidation
(b) Catalytic reduction
(c) Absorbing in H_2SO_4 followed by hydrolysis
(d) All the three

85. 'Drinking alcohol' is very harmful and it ruins the health. 'Drinking alcohol' stands for
(a) drinking methyl alcohol
(b) drinking ethyl alcohol
(c) drinking propyl alcohol
(d) drinking isopropyl alcohol

86. The fermentation reactions are carried out in temperature range of
(a) 20-30°C (b) 30-40°C
(c) 40-50°C (d) 50-60°C

87. Ethanol is prepared industrially by
(a) hydration of ethylene (b) fermentation of sugar
(c) Both the above (d) None of these

88. The fermentation of starch to give alcohol occurs mainly with the help of
(a) O_2 (b) air
(c) CO_2 (d) enzymes

89. In the commercial manufacture of ethyl alcohol from starchy substances by fermentation method. Which enzymes slipwise complete the fermentation reaction
(a) Diastase, maltase and zymase
(b) Maltase, zymase and invertase
(c) Diastase, zymase and lactase
(d) Diastase, invertase and zymase

90. Methyl alcohol is toxic. The reason assigned is
(a) it stops respiratory track
(b) it reacts with nitrogen and forms CN^- in the lungs
(c) it increses CO_2 content in the blood
(d) it is a reduction product of formaldehyde

91. In order to make alcohol undrinkable pyridine and methanol are added to it. The resulting alcohol is called
(a) Power alcohol (b) Proof spirit
(c) Denatured spirit (d) Poison alcohol

92. Wine (alcoholic beverages) contains
(a) CH_3OH (b) Glycerol
(c) C_2H_5OH (d) 2-propanol

93. Tonics in general contain
(a) Ether (b) Methanol
(c) Ethanol (d) Rectified spirit

94. Widespread deaths due to liquor poisoning occurs due to
(a) presence of carbonic acid in liquor
(b) presence of ethyl alcohol in liquor
(c) presence of methyl alcohol in liquor
(d) presence of lead compounds in liquor

95. Select the incorrect statement about the fermentation.
(a) When grapes are crushed, sugar and the enzyme come in contact and fermentation starts
(b) Fermentation takes place in anaerobic conditions
(c) Carbon monoxide is released during fermentation
(d) If air gets into fermentation mixture, the oxygen of air oxidises ethanol to ethanoic acid which in turn destroys the taste of alcoholic drinks

96. Denaturation of alcohol is the
(a) mixing of $CuSO_4$ (a foul smelling solid) and pyridine (to give the colour) to make the commercial alcohol unfit for drinking
(b) mixing of $CuSO_4$ (to give the colour) and pyridine (a foul smelling solid) to make the commercial alcohol unfit for drinking
(c) mixing of $Cu(OAc)_2$ and ammonia to make the commercial alcohol unfit for drinking
(d) mixing of $Cu(OAc)_2$ and pyridine to make the commercial alcohol unfit for drinking

97. Which one is formed when sodium phenoxide is heated with ethyl iodide ?
(a) Phenetole (b) Ethyl phenyl alcohol
(c) Phenol (d) None of these

98. Williamson's synthesis is used to prepare
(a) acetone (b) diethyl ether
(c) P.V.C. (d) bakelite

99. The reaction of sodium ethoxide with ethyl iodide to form diethyl ether is termed
(a) electrophilic substitution
(b) nucleophilic substitution
(c) electrophilic addition
(d) radical substitution

100. Which of the following cannot be made by using Williamson's synthesis?
(a) Methoxybenzene
(b) Benzyl p-nitrophenyl ether
(c) Methyl tertiary butyl ether
(d) Di-tert-butyl ether

101. The reaction given below is known as

$$C_2H_5ONa + IC_2H_5 \longrightarrow C_2H_5OC_2H_5 + NaI$$

(a) Kolbe's synthesis
(b) Wurtz synthesis
(c) Williamson's synthesis
(d) Grignard's synthesis

102. Ethanol and dimethyl ether form a pair of functional isomers. The boiling point of ethanol is higher than that of dimethyl ether, due to the presence of
(a) H-bonding in ethanol
(b) H-bonding in dimethyl ether
(c) CH_3 group in ethanol
(d) CH_3 group in dimethyl ether

103. Ether which is liquid at room temperature is
(a) $C_2H_5OCH_3$ (b) CH_3OCH_3
(c) $C_2H_5OC_2H_5$ (d) None of these

104. Ether can be used
(a) as a general anaesthetic
(b) as a refrigerant
(c) in perfumery
(d) all of the above

105. Which of the following compound is soluble in ether?
(a) Oils and fats (b) Water
(c) NaCl (d) PCl_5

106. An ether is more volatile than an alcohol having the same molecular formula. This is due to
(a) dipolar character of ethers
(b) alcohols having resonance structures
(c) inter-molecular hydrogen bonding in ethers
(d) inter-molecular hydrogen bonding in alcohols

107. Which of the following has strongest hydrogen bonding?
(a) Ethyl amine (b) Ethanal
(c) Ethyl alcohol (d) Diethyl ether

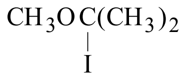
108. Oxygen atom in ether is
(a) very active (b) replaceable
(c) comparatively inert (d) active

109. The ether that undergoes electrophilic substitution reactions is
(a) $CH_3OC_2H_5$ (b) $C_6H_5OCH_3$
(c) CH_3OCH_3 (d) $C_2H_5OC_2H_5$

110. Diethyl ether on heating with conc. HI gives two moles of
(a) ethanol (b) iodoform
(c) ethyl iodide (d) methyl iodide

111. Methylphenyl ether can be obtained by reacting
(a) phenolate ions and methyl iodide
(b) methoxide ions and bromobenzene
(c) methanol and phenol
(d) bromo benzene and methyl bromide

112. Diethyl ether can be decomposed by heating with
(a) HI (b) NaOH
(c) Water (d) $KMnO_4$

113. The major organic product in the reaction,
$CH_3 — O — CH(CH_3)_2 + HI \rightarrow$ Product is
(a) $ICH_2OCH(CH_3)_2$ (b)

$CH_3O\underset{\substack{|\\ I}}{C}(CH_3)_2$
(c) $CH_3I + (CH_3)_2CHOH$ (d) $CH_3OH + (CH_3)_2CHI$

114. An aromatic ether is not cleaved by HI even at 525 K. The compound is
(a) $C_6H_5OCH_3$ (b) $C_6H_5OC_6H_5$
(c) $C_6H_5OC_3H_7$ (d) Tetrahydrofuran

115. When 2-methoxypropane is heated with HI, in the mole ratio 1 : 1, the major products formed are
(a) methanol and 2-iodopropane
(b) methyl iodide and 2-propanol
(c) methyl iodide and 2-iodopropane
(d) methanol and 2-propanol

116. Formation of diethyl ether from ethanol is based on a
(a) dehydration reaction
(b) dehydrogenation reaction
(c) hydrogenation reaction
(d) heterolytic fission reaction

117. The cleavage of an aryl-alkyl ether with cold HI gives :
(a) alkyl iodide and water
(b) aryl iodide and water
(c) alkyl iodide, aryl iodide and water
(d) phenol and alkyl iodide

118. Which of the following compounds is resistant to nucleophilic attack by hydroxyl ions?
(a) Methyl acetate (b) Acetonitrile
(c) Acetamide (d) Diethyl ether

STATEMENT TYPE QUESTIONS

119. When an alcohol is prepared by reaction of ethylmagnesium-bromide with 2–pentanone, product formed does not rotate plane polarised light. For this reaction which of the following statement(s) is/are correct ?
(i). Product formed is achiral.
(ii) Racemic mixture is formed.
(a) Both statements (i) and (ii) are correct.
(b) Statement (i) is correct only.
(c) Statement (ii) is correct only.
(d) Both statements (i) and (ii) are incorrect.

120. Which of the following statements are correct ?
(i) Alcohols react as nucleophiles in the reactions involving cleavage of O–H bond.
(ii) Alcohols react as electrophiles in the reactions involving cleavage of O–H bond.
(iii) Alcohols react as nucleophile in the reaction involving cleavage of C–O bond.
(iv) Alcohols react as electrophiles in the reactions involving C–O bond.
(a) (i) only (b) (i) and (iv)
(c) (ii) and (iii) (d) (ii) only

121. Which of the following are correct statement(s) ?
(i) Polar nature of O–H bond is responsible for acidic character of alcohols.
(ii) Acidic strength of alcohols follow the order 1° > 2° > 3°.
(iii) Alcohols are stronger acids than water.
(iv) Alcohols also react as Bronsted base.
(a) (i), (ii) and (iii) (b) (i), (ii) and (iv)
(c) (ii), (iii) and (iv) (d) (i), (iii) and (iv)

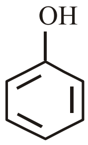
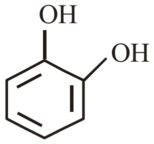
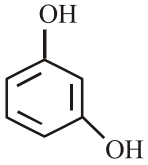
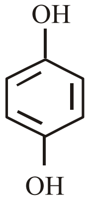
122. Read the following statements and choose the correct option.
(i) Ethanol on dehydration at 443 K gives ethene
(ii) Ethanol on dehydration at 413 K gives diethyl ether
(iii) Only primary alcohols on dehydration give ethers.
(iv) Secondary and tertiary alcohols on dehydration give ethers having 2° and 3° carbon attached with O atom.
(a) TTFF (b) TFTF
(c) TTTF (d) FTTF

123. Which of the following statements are correct ?
(i) In phenols, the —OH group is attached to sp^2 hybridised carbon of an aromatic ring
(ii) The carbon – oxygen bond length (136 pm) in phenol is slightly more than that in methanol
(iii) Partial double bond character is due to the conjugation of unshared electron pair of oxygen with the aromatic ring.
(iv) sp^2 hybridised state of carbon to which oxygen is attached.
(a) (i), (ii) and (v) (b) (i), (ii) and (iii)
(c) (i), (iii) and (iv) (d) (i) and (iv)

124. Which of the following statements are correct ?
(i) Ethanol mixed with methanol is called denatured alcohol.
(ii) Excess of methanol in body may cause blindness.
(iii) In the body methanol is oxidised to methanoic acid.
(iv) A methanol poisoned patient is treated by giving intravenous injections of ethanoic acid.
(a) (i), (ii) and (iii) (b) (ii), (iii) and (iv)
(c) (i) and (v) (d) (i), (iii) and (iv)

MATCHING TYPE QUESTIONS

125. Match the columns

Column-I	**Column-II**
(A) 	(p) Quinol
(B) 	(q) Phenol
(C) 	(r) Catechol
(D) 	(s) Resorcinol

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

126. Match the columns

	Column-I		Column-II
(A)	Methanol	(p)	Conversion of phenol to *o*-hydroxysalicylic acid
(B)	Kolbe's reaction	(q)	Wood spirit
(C)	Williamson's synthesis	(r)	Heated copper at 573 K
(D)	Conversion of 2° alcohol to ketone	(s)	Reaction of alkyl halide with sodium alkoxide

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

127. Match the columns

	Column-I		Column-II
(A)	Antifreeze used in car engine	(p)	Methanol
(B)	Solvent used in perfumes	(q)	Phenol
(C)	Starting material for picric acid	(r)	Ethleneglycol
(D)	Wood spirit	(s)	Ethanol

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

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.

128. Assertion : The bond angle in alcohols is slightly less than the tetrahedral angle.
Reason : In alcohols, the oxygen of –OH group is attached to sp^3 hybridized carbon atom.

129. Assertion : In Lucas test, 3° alcohols react immediately.
Reason : An equimolar mixture of anhyd. $ZnCl_2$ and conc. HCl is called Lucas reagent.

130. Assertion : Reimer-Tiemann reaction of phenol with CCl_4 in NaOH at 340 K gives salicyclic acid as the major product.
Reason : The reaction occurs through intermediate formation of dichlorocarbene.

131. Assertion : Phenol is more reactive than benzene towards electrophilic substitution reaction.
Reason : In the case of phenol, the intermediate carbocation is more resonance stabilized.

132. Assertion : In case of phenol, bromination takes place even in absence of Lewis acid whereas bromination of benzene takes place in presence of Lewis acid like $FeBr_3$.
Reason : – OH group attached to benzene ring is highly deactivating.

133. Assertion : *ter* - Butyl methyl ether is not prepared by the reaction of *ter*-butyl bromide with sodium methoxide.
Reason : Sodium methoxide is a strong nucleophile.

134. Assertion : Ethers behave as bases in the presence of mineral acids.
Reason : Due to the presence of lone pairs of electrons on oxygen.

135. Assertion : With HI, anisole gives iodobenzene and methyl alcohol.
Reason : Iodide ion combines with smaller group to avoid steric hindrance.

136. Assertion : With HI at 373 K, *ter*-butyl methyl ether gives *ter*-butyl iodide and methanol.
Reason : The reaction occurs by S_N2 mechanism.

137. Assertion : Ethyl phenyl ether on reaction with HBr form phenol and ethyl bromide.
Reason : Cleavage of C–O bond takes place on ethyl-oxygen bond due to the more stable phenyl-oxygen bond.

CRITICAL THINKING TYPE QUESTIONS

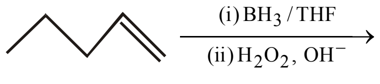
138. Vinyl carbinol is

(a) $HO-CH_2-CH=CH_2$
(b) $CH_3C(OH)=CH_2$
(c) $CH_3-CH=CH-OH$
(d) $CH_3-C(CH_2OH)=CH_2$

139. Propene, $CH_3CH=CH_2$ can be converted into 1-propanol by oxidation. Indicate which set of reagents amongst the following is ideal to effect the above conversion ?

(a) $KMnO_4$ (alkaline)
(b) Osmium tetraoxide (OsO_4/CH_2Cl_2)
(c) B_6H_6 and alk. H_2O_2
(d) O_3/Zn

140. The product of the following reaction is

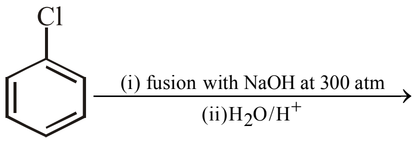


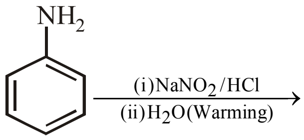
(a) 1-Pentanol (b) 2-Pentanol
(c) Pentane (d) 1,2-Pentanediol

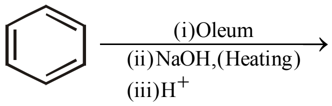
141. $C_6H_5-CH=CHCHO \xrightarrow{X} C_6H_5CH=CHCH_2OH$.
In the above sequence X can be

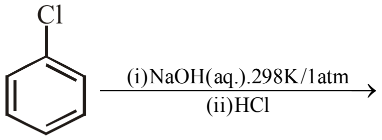
(a) H_2/Ni (b) $NaBH_4$
(c) $K_2Cr_2O_7/H^+$ (d) Both (a) and (b)

142. Which of the following reactions will yield phenol?

(i)


(ii)


(iii)


(iv)


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

143. Hydration of styrene is carried out in presence of acid as catalyst. The major product is.
(a) 1–hydroxy–2–phenylethane.
(b) 1–hydroxy–1–phenylethane.
(c) 2–hydroxy–1–phenylethane.
(d) 2–hydroxy–2–phenylethane.

144. Which of the following reagents can be used for preparation of cumene ?
(i) C_6H_6, Cl_2, hv; Mg.THF; acetone.
(ii) C_6H_6, $CH_3CH_2CH_2Cl$, $AlCl_3$.
(iii) C_6H_6, $CH_3CHClCH_3$, $AlCl_3$.
(iv) C_6H_6, CH_3CH_2Cl, $AlCl_3$;
(a) (i) and (ii) (b) (ii) and (iii)
(c) (i), (ii) and (iii) (d) (ii) and (iv)

145. The hydroboration of an alkene is carried out, then on oxidation with hydrogen peroxide, the alcohol so obtained is achiral. Possible structure of alkene is (are) :
(i) 2, 3– dimethylbut–2–ene.
(ii) 3, 4–dimethylbut –3–ene.
(iii) 2–methyl–but–2–ene.
(iv) 2–methylpropene.
(a) (i) and (iv) (b) (ii) and (iii)
(c) (iii) and (iv) (d) (i) and (iii)

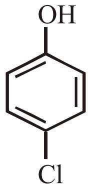
146. Which of the following shows structure of allylic alcohol?
(i) $CH_2=CH-CH_2OH$
(ii) $CH_2=CH-OH$
(iii) $CH_2=CH-CH(CH_3)OH$
(iv) $CH_2=CH-C(CH_3)_2OH$
(a) (i), (iii) and (iv) (b) (i), (ii) and (iv)
(c) (ii), (iii) and (iv) (d) (i), (ii), (iii) and (iv)

147. Mechanism of acid catalysed hydration reaction involves
(i) Protonation of alkene to form carbocation by electrophilic attack of H_3O^+
(ii) Nucleophilic attack of water on carbocation.
(iii) Deprotonation to form alcohol.
(a) (i) and (ii) (b) (i) and (iii)
(c) (i), (ii) and (iii) (d) (ii) and (iii)

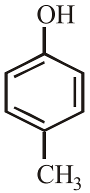
148. Phenol is less acidic than
(a) acetic acid (b) *p*-methoxyphenol
(c) acetylene (d) ethanol

149. The correct order of acid strength of the following compounds :
(A) Phenol (B) *p*–Cresol
(C) *m*–Nitrophenol (D) *p*–Nitrophenol
(a) D > C > A > B (b) B > D > A > C
(c) A > B > D > C (d) C > B > A > D

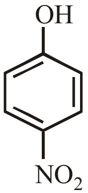
150. Arrange the following compounds in order of decreasing acidity :



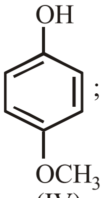
(I) ;



(II) ;



(III) ;



(IV) ;

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

151. $ClCH_2CH_2OH$ is stronger acid than CH_3CH_2OH because of:
(a) – I effect of Cl increases negative charge on O atom of alcohol
(b) – I effect of Cl disperses negative charge on O atom to produce more stable cation
(c) – I effect of Cl disperses negative charge on O atom to produce more stable anion
(d) None of these

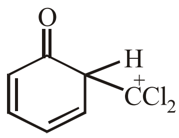
152. Which one of the following compounds will be most readily attacked by an electrophile ?
(a) Chlorobenzene (b) Benzene
(c) Phenol (d) Toluene

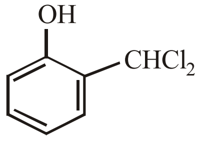
153. Consider the following reaction:

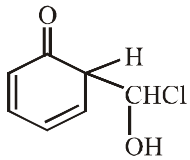
$$\text{Phenol} \xrightarrow{\text{Zn dust}} X \xrightarrow[\text{Anhydrous } AlCl_3]{CH_3Cl} Y \xrightarrow{\text{Alkaline } KMnO_4} Z$$

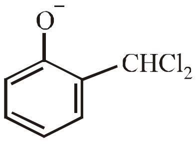
The product Z is
(a) benzaldehyde (b) benzoic acid
(c) benzene (d) toluene

154. When phenol is reacted with $CHCl_3$ and NaOH followed by acidification, salicylaldehyde is obtained. Which of the following species are involved in the above mentioned reaction as intermediate?

(a) 

(b) 

(c) 

(d) 

155. The reagent used for dehydration of an alcohol is
(a) phosphorus pentachloride
(b) calcium chloride
(c) aluminium oxide
(d) sodium chloride

156. The alcohol which does not give a stable compound on dehydration is
(a) ethyl alcohol (b) methyl alcohol
(c) n-Propyl alcohol (d) n-Butyl alcohol

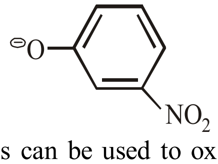
157. A compound of the formula $C_4H_{10}O$ reacts with sodium and undergoes oxidation to give a carbonyl compound which does not reduce Tollen's reagent, the original compound is
(a) Diethyl ether (b) *n*-Butyl alcohol
(c) Isobutyl alcohol (d) *sec*-Butyl alcohol

158. Which of the following fact(s) explain as to why p-nitrophenol is more acidic than phenol?
I. –I Effect of nitro group.
II. Greater resonance effect of p-nitrophenoxy group
III. Steric effect of bulky nitro group
(a) I and II (b) I and III
(c) II and III (d) II alone

159. In the following sequence of reactions,

$$CH_3CH_2OH \xrightarrow{P+I_2} A \xrightarrow[\text{ether}]{Mg} B \xrightarrow{HCHO} C \xrightarrow{H_2O} D$$

the compound D is
(a) propanal (b) butanal
(c) *n*-butyl alcohol (d) *n*-propyl alcohol.

160. Which of the following species can act as the strongest base?
(a) $^{\ominus}OH$ (b) $^{\ominus}OR$
(c) $^{\ominus}OC_6H_5$ (d) 

161. Which of the following reagents can be used to oxidise primary alcohols to aldehydes?
(i) CrO_3 in anhydrous medium.
(ii) $KMnO_4$ in acidic medium.
(iii) Pyridinium chlorochromate.
(iv) Heat in the presence of Cu at 573K.
(a) (i) and (iii) (b) (ii), (iii) and (iv)
(c) (i), (iii) and (iv) (d) (i), (iii) and (iv)

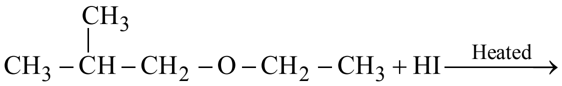
162. Which one of the following will show the highest pH value ?
(a) *m*–nitrophenol. (b) *p*–nitrophenol.
(c) *o*–nitrophenol. (d) Both (b) and (c).

163. Which of the following is most reactive towards aqueous HBr ?
(a) 1-Phenyl-1-propanol
(b) 1-Phenyl-2-propanol
(c) 3-Phenyl-1-propanol
(d) All are equally reactive

164. The major product of the reaction between tert-butyl chloride and sodium ethoxide is
(a) 2-methylprop-1-ene (b) 1-butene
(c) 2-butene (d) ethene

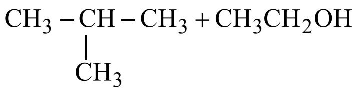
165. In Williamson synthesis if tertiary alkyl halide is used than
(a) ether is obtained in good yield
(b) ether is obtained in poor yield
(c) alkene is the only reaction product
(d) a mixture of alkene as a major product and ether as a minor product forms.

166. In the reaction:

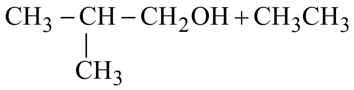


$$CH_3-\underset{}{\overset{CH_3}{\overset{|}{C}H}}-CH_2-O-CH_2-CH_3+HI\xrightarrow{\text{Heated}}$$

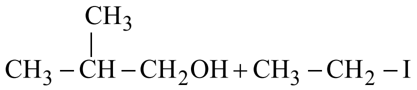
Which of the following compounds will be formed?

(a) 

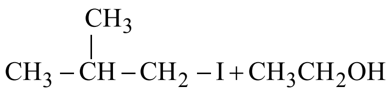
$$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_3+CH_3CH_2OH$$

(b) 

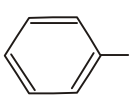
$$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2OH+CH_3CH_3$$

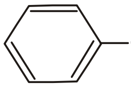
(c) 

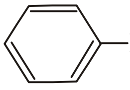
$$CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_2OH+CH_3-CH_2-I$$

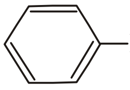
(d) 

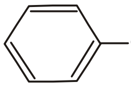
$$CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_2-I+CH_3CH_2OH$$

167. In the reaction  $-OCH_3 \xrightarrow{HBr}$ the products are

(a)  –OBr and CH_4

(b)  –Br and CH_3Br

(c)  –Br and CH_3OH

(d)  –OH and CH_3Br

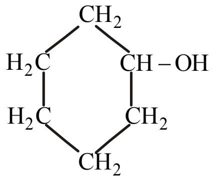
168. An aromatic ether is not cleaved by HI even at 525 K. The compound is
(a) $C_6H_5OCH_3$ (b) $C_6H_5OC_6H_5$
(c) $C_6H_5OC_3H_7$ (d) Tetrahydrofuran

HINTS AND SOLUTIONS

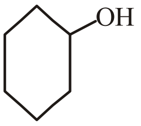
FACT/DEFINITION TYPE QUESTIONS

1. **(b)** **2.** **(b)**

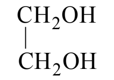
3. **(a)**



or



4. **(b)** Glycols are dihydric alcohols (having two hydroxyl groups). Ethylene glycol is the first member of this series.



$$\begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array}$$

(Ethylene glycol)

5. **(c)** Ethers contain the functional group – O –

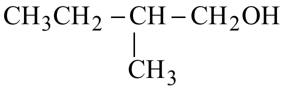
6. **(b)** $CH_3CH_2CH(OH)CH_3$ – a secondary alcohol

7. **(b)** Cresol has phenolic group – OH

8. **(b)** Four primary alcohols of $C_5H_{11}OH$ are possible. These are:

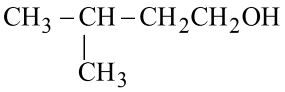
(i) $CH_3CH_2CH_2CH_2CH_2OH$

(ii)



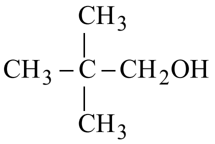
$CH_3CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_2OH$

(iii)



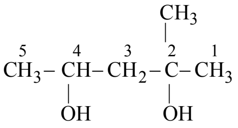
$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2CH_2OH$

(iv)



$CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_2OH$

9. **(b)**



$\overset{5}{CH_3}-\underset{OH}{\underset{|}{\overset{4}{CH}}}-\overset{3}{CH_2}-\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{\overset{2}{C}}}}}-\overset{1}{CH_3}$

2-methyl- 2, 4-pentanediol.

10. **(b)** $C_4H_{10}O$: (i) $C_2H_5OC_2H_5$ (ii) $CH_3OC_3H_7$ (iii) $CH_3OCH(CH_3)_2$

11. **(c)** **12.** **(a)** **13.** **(c)** **14.** **(a)** **15.** **(c)**

16. **(b)**

17. **(c)** In this structure –OH group is directly attached to double bonded carbon atom i.e. sp^2 hybridized carbon atom.

18. **(c)** If two groups attached to the oxygen atom are different then ethers are known as unsymmetrical or mixed ethers.

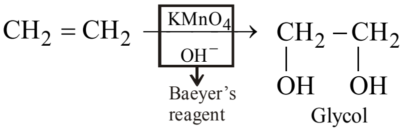
19. **(d)** Benzoic acid (C_6H_5COOH) will not form phenol or phenoxide.

20. **(b)** By heating benzaldehyde with conc. NaOH or KOH (Cannizzaro reaction).

$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} + NaOH \longrightarrow \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} + \underset{\text{Sod. benzoate}}{C_6H_5COONa}$$

21. **(d)** Any one of Ni, Pt or Pd can be used in the reduction of aldehydes.

22. **(c)**



$$CH_2=CH_2 \xrightarrow[OH^-]{\boxed{KMnO_4}} \underset{OH}{\underset{|}{CH_2}}-\underset{OH}{\underset{|}{CH_2}}$$

Baeyer's reagent

Glycol

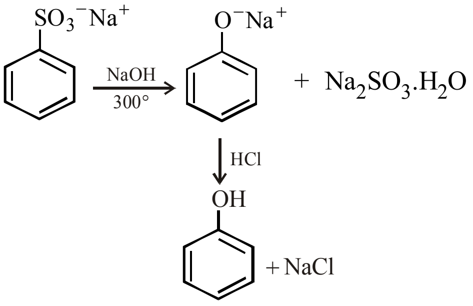
This reaction is known as Baeyer's test for unsaturation.

23. **(c)** Ethylene is passed into concentrated sulphuric acid at 75–80°C under pressure when a mixture of ethyl hydrogen sulphate and diethyl sulphate is formed.

$$\underset{\text{Ethylene}}{H_2C=CH_2} + H_2SO_4 \xrightarrow{100°C} C_2H_5HSO_4$$

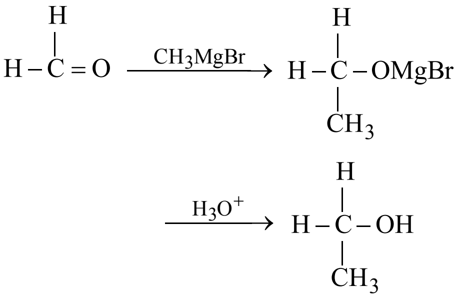
$$\xrightarrow[H_2O]{\Delta} C_2H_5OH + H_2SO_4$$

24. **(b)**



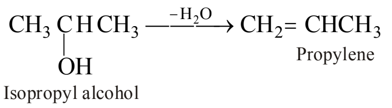
25. **(b)**

26. **(a)**



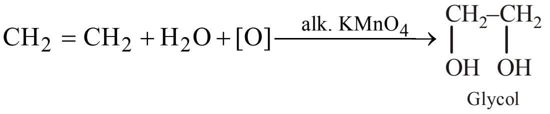
$$H-\overset{H}{\overset{|}{C}}=O \xrightarrow{CH_3MgBr} H-\overset{H}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-OMgBr \xrightarrow{H_3O^+} H-\overset{H}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-OH$$

27. **(b)** Since the compound is formed by hydration of an alkene, to get the structure of alkene remove a molecule of water from the alcohol.



$$\underset{\text{Isopropyl alcohol}}{CH_3\underset{OH}{\underset{|}{C}}HCH_3} \xrightarrow{-H_2O} \underset{\text{Propylene}}{CH_2=CHCH_3}$$

28. **(b)**



$$CH_2=CH_2+H_2O+[O]\xrightarrow{\text{alk. }KMnO_4}\underset{\text{Glycol}}{\underset{OH\quad OH}{CH_2-CH_2}}$$

$$\underset{\text{Ethane}}{CH_2=CH_2}+H_2O\xrightarrow{\text{Conc. }H_2SO_4}\underset{\text{Ethanol}}{CH_3-CH_2-OH}$$

29. **(d)** The aldehydes which do not have α-hydrogen atom react with NaOH when half of molecules are reduced to alcohol and other half of molecules are oxidised to acid (Cannizzaro reaction).

$$\underset{\text{Methanal}}{2\,HCHO}+\xrightarrow{NaOH}\underset{\text{Methyl alcohol}}{CH_3OH}+\underset{\text{Sod. formate}}{HCOONa}$$

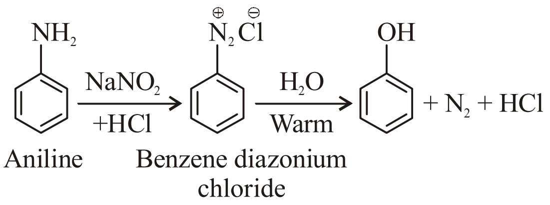
30. **(b)** **31.** **(b)**

32. **(a)** Commercially, acids are reduced to alcohols by converting them to the esters, followed by their reduction using hydrogen in the presence of catalyst (catalytic hydrogenation).

$$RCOOH\xrightarrow[H^+]{R'OH}RCOOR'\xrightarrow[\text{Catalyst}]{H_2}RCH_2OH+R'OH$$

33. **(d)**

34. **(b)** A diazonium salt is formed by treating an aromatic primary amine with nitrous acid ($NaNO_2$ + HCl) at 273-278 K. Diazonium salts are hydrolysed to phenols by warming with water or by treating with dilute acids.



35. **(a)** Among isomeric alcohols surface area decreases from 1° to 2° to 3° alcohols and hence the boiling point.

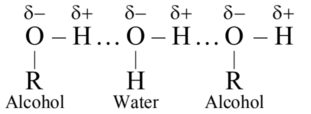
36. **(a)** The lower alcohols are readily soluble in water and the solubility decreases with the increase in molecular weight. The solubility of alcohols in water can be explained due to the formation of hydrogen bond between the highly polarised —OH groups present both in alcohol and water.

37. **(c)** *o*-Nitrophenol has intramolecular H-bonding.

38. **(b)** The solubility of alcohols depend on number of C-atoms of alcohols. The solubility of alcohols in water is decreased by increasing number of C-atoms of alcohol. As resulting molecular weight increases, the polar nature of O – H bond decreases and hence strength of hydrogen bond decreases.

39. **(d)** Solubility of alcohol in water decreases with increase in molecular mass due to increase in water repelling alkyl part in alcohol.

40. **(b)** Hydrogen bonding :



$$\underset{\text{Alcohol}}{\underset{R}{\overset{\delta-}{O}-\overset{\delta+}{H}}}\ldots\underset{\text{Water}}{\underset{H}{\overset{\delta-}{O}-\overset{\delta+}{H}}}\ldots\underset{\text{Alcohol}}{\underset{R}{\overset{\delta-}{O}-\overset{\delta+}{H}}}$$

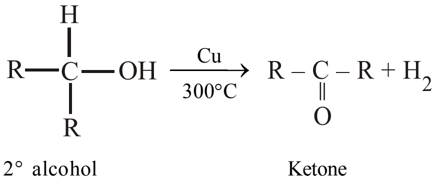
41. **(b)** When ethanol dissolves in water then there is emission of heat and contraction in volume.

42. **(d)** $C_2H_5OH+4I_2+6NaOH\longrightarrow$

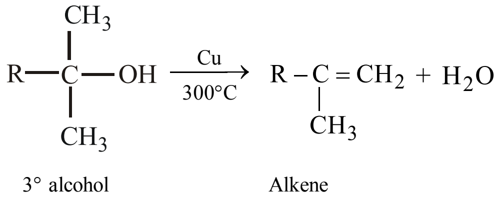
$$\underset{\text{Iodoform}}{CHI_3}\downarrow+HCOONa+5NaI+5H_2O$$

43. **(a)** When primary (1°) alcohols are treated with copper at 300°C, then aldehydes are obtained by dehydrogenation of alcohols. Similarly secondary (2°) alcohols form ketone and alkene is obtained by dehydration of tertiary (3°) - alcohols. But phenol does not respond to this test.

$$\underset{1^\circ\text{ alcohol}}{R-CH_2-CH_2-OH}\xrightarrow[300^\circ C]{Cu}\underset{\text{Aldehyde}}{R-CH_2-CHO}+H_2$$



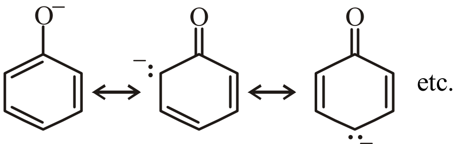
$$\underset{2^\circ\text{ alcohol}}{R-\overset{H}{\underset{R}{C}}-OH}\xrightarrow[300^\circ C]{Cu}\underset{\text{Ketone}}{R-\underset{O}{\overset{}{\underset{\|}{C}}}-R}+H_2$$



$$\underset{3^\circ\text{ alcohol}}{R-\overset{CH_3}{\underset{CH_3}{C}}-OH}\xrightarrow[300^\circ C]{Cu}\underset{\text{Alkene}}{R-\underset{CH_3}{C}=CH_2}+H_2O$$

$$C_6H_5-OH\xrightarrow[300^\circ C]{Cu}\text{No reaction}$$

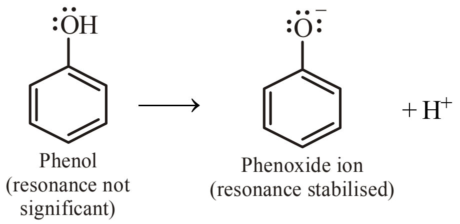
44. **(c)**



Resonance stabilisation of phenoxide ion (conjugate base of phenol)

Conjugate base of ethyl alcohol, i.e., $C_2H_5O^-$ does not show resonance.

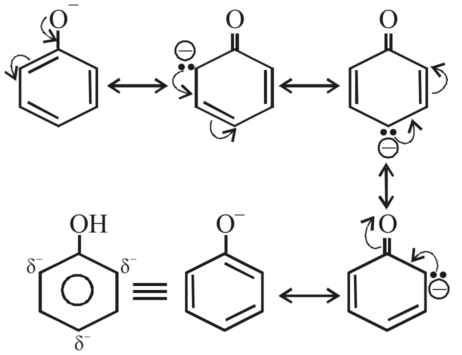
45. **(d)**



46. **(b)** Phenol is most acidic because its conjugate base is stabilised due to resonance, while the rest three compounds are alcohols, hence, their corresponding conjugate bases do not exhibit resonance.

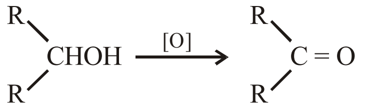
47. **(c)** $C_6H_5OH + H_2O \rightleftharpoons \underset{\text{Phenoxide ion}}{C_6H_5O^-} + H_3O^+$

The phenoxide ion is stable due to resonance.



The negative charge is delocalized in the benzene ring which is a stabilizing factor in the phenoxide ion and because of this reason ionization constant of phenol is higher whereas no resonance is possible in alkoxide ions (RO⁻)derived from alcohol. The negative charge is localized on oxygen atom in case of alcohols.

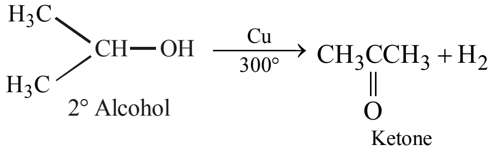
48. **(b)** Secondary alcohols on oxidation give ketones.
Note : – Primary alcohols from aldehydes.



Isopropyl alcohol Ketone

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

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



50. **(b)** $C_2H_5OH + CH_3COOH \longrightarrow CH_3COO.C_2H_5 + H_2O$

51. **(c)** Secondary alcohols oxidise to produce kenone.

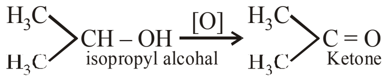
$$\underset{\text{2-Butanol}}{CH_3CHOHCH_2CH_3} \xrightarrow{(O)} \underset{\text{Ethyl methyl ketone}}{CH_3COCH_2CH_3}$$

52. **(b)** Greater the stability of the intermediate carbocation, more reactive is the alcohol. Since 2-methylpropan-2-ol generates 3° carbocation, therefore, it reacts fastest with HBr.

53. **(c)** Primary alcohol on oxidation give aldehyde which on further oxidation give carboxylic acid whereas secondary alcohols give ketone.

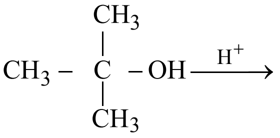
$$\underset{\text{n-propyl alcohal}}{CH_3CH_2CH_2OH} \xrightarrow{[O]}$$

$$CH_3CH_2CHO \xrightarrow{[O]} CH_3CH_2COOH$$



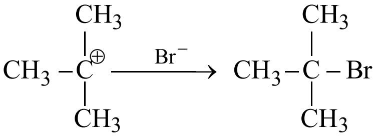
54. **(a)** Lucas reagent is conc. HCl + anhyd. $ZnCl_2$.

55. **(d)** The rates of reaction with lucas reagent follows the order.
3° alcohol > 2° alcohol > 1° alcohol
since carbocations are formed as intermediate, more stable the carbocation, higher will be the reactivity of the parent compound (alcohol). 2-Methylpropan-2-ol generates a 3° carbocation, so it will react fastest; other three generates either 1° or 2° carbocations.



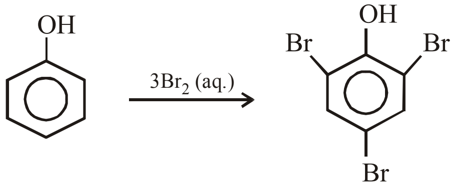
$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH \xrightarrow{H^+}$$

2-Methyl-2-propanol



$$CH_3-\overset{CH_3}{\underset{CH_3}{C^{\oplus}}} \xrightarrow{Br^-} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Br$$

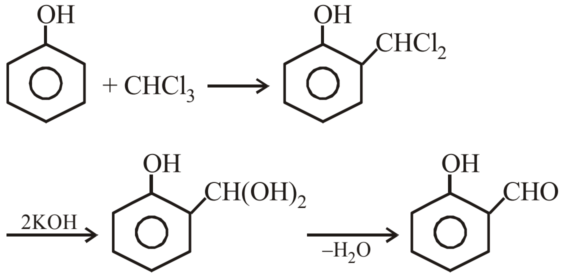
56. **(d)**



2, 4,6-Tribromophenol

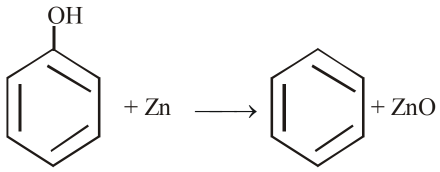
Note : The –OH group in phenol, being activating group, facilitates substitution in the *o*- and *p*-positions.

57. **(b)**



Reimer-Tiemann reaction.

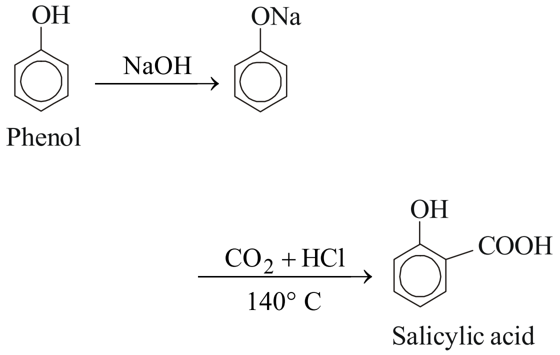
58. **(c)** When phenol reacts with Zinc dust, then benzene and zinc oxide are formed



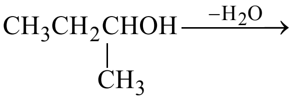
Phenol Benzene

59. **(d)** Phenol does not react with $NaHCO_3$.

60. **(d)**



61. **(d)**



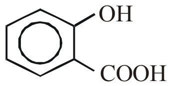
$$\underset{\displaystyle CH_3}{CH_3CH_2\overset{|}{C}HOH} \xrightarrow{-H_2O}$$

$$\underset{\text{(Major product)}}{CH_3CH = CHCH_3} + \underset{\text{(Minor product)}}{CH_3CH_2CH = CH_2}$$

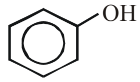
62. **(c)** Lucas test is used to distinguish between 1°, 2° and 3° alcohols. Lucas reagent is anhy. $ZnCl_2$ and HCl.

3° alcohol + Lucas reagent $\longrightarrow$ turbidity immediately
2° alcohol + Lucas reagent $\longrightarrow$ turbidity after 5 minutes
1° alcohol + Lucas reagent $\longrightarrow$ No turbidity at room temperature.

63. **(a)**



Salicylic acid
(evolves CO_2 with $NaHCO_3$)



Phenol
(No reaction with $NaHCO_3$)

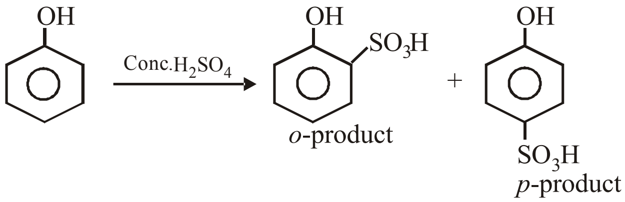
64. **(b)** Other options are acids, only Na metal is a base.

65. **(c)** Reactivity increases as the nucleophilicity of the halide ion increases, i.e. $I^- > Br^- > Cl^-$.

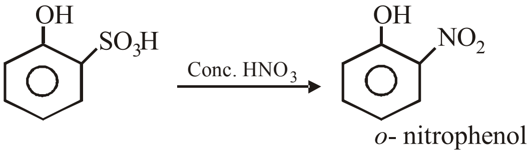
66. **(a)** In presence of acid, alcohols always form carbocations as intermediates.

67. **(c)** **68.** **(b)**

69. **(b)** Phenol on reaction with conc. H_2SO_4 gives a mixture of *o*- and *p*- products (i.e., $-SO_3H$ group, occupies *o*-, *p*- position). At room temperature *o*-product is more stable, which on treatment with conc. HNO_3 will yield *o*-nitrophenol.



At room temperature *o*- product is more stable



70. **(d)** $$3C_2H_5OH + PBr_3 \longrightarrow 3C_2H_5Br + \underset{[X]}{H_3PO_3}$$

71. **(c)** Methanol and ethanol can be distinguished by heating with iodine and washing soda

$$C_2H_5OH \xrightarrow[Na_2CO_3]{I_2} \underset{\substack{\text{Iodoform}\\ \text{(yellow ppt)}}}{CHI_3} + HCOONa + NaI + 2NaOH + H_2O$$

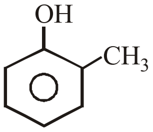
$$CH_3OH \xrightarrow[Na_2CO_3]{I_2} \text{No reaction}$$

This is also called iodoform test.

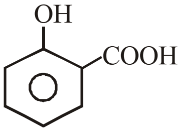
72. **(d)** **73.** **(c)** **74.** **(c)** **75.** **(a)** **76.** **(b)**

77. **(d)** **78.** **(c)**

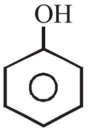
79. **(d)**



o-cresol



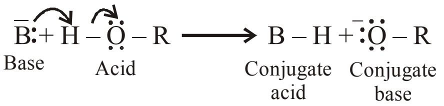
Salicylic acid



Phenol

Electron releasing groups ($-CH_3$, $-OCH_3$, $-NCH_3$ etc) intensify the negative charge of phenoxide ion, i.e., destablises it hence decrease ionization of parent phenol. Therefore decreases acidity while electron donating groups ($-NO_2$, $-COOH$, $-CHO$ etc.) increases acidity.

80. **(b)** Alcohols and phenols are acidic in nature. In fact they are Bronsted acids i.e., they can donate a proton to a stronger base (B:)



81. **(b)** Oxidation of phenol with chromic acid produces a conjugated diketone known as benzoquinone. In the presence of air, phenols are slowly oxidised to dark coloured mixtures containing quinones.

82. **(c)** Glucose and fructose obtained by hydrolysis of sucrose, are converted into alcohol by enzyme zymase.

$$C_6H_{12}O_6 \xrightarrow{\text{zymase}} 2C_2H_5OH + 2CO_2$$

83. **(a)** $$\underbrace{CO + H_2}_{\text{water gas}} + H_2 \xrightarrow[300°C]{Cr_2O_3-ZnO} \underset{\text{Methanol}}{CH_3OH}$$

84. **(c)** Ethylene is passed into concentrated sulphuric acid at 75–80°C under pressure when a mixture of ethyl hydrogen sulphate and diethyl sulphate is formed.

$$\underset{\text{Ethylene}}{H_2C = CH_2} + H_2SO_4 \xrightarrow{100°C} C_2H_5HSO_4 \xrightarrow[H_2O]{\Delta} C_2H_5OH + H_2SO_4$$

85. **(b)** **86.** **(a)**

87. (c) Hydration of alkenes

$$CH_2=CH_2+\overset{+}{H}\,\overset{-}{HSO_4}\rightarrow CH_3-CH_2-HSO_4$$

$$CH_3-CH_2HSO_4\xrightarrow[\text{Boil}]{H_2O}CH_3-CH_2-OH+H_2SO_4$$

Fermentation of sugar :

$$C_{12}H_{22}O_{11}+H_2O\xrightarrow{\text{Invertase}}\underset{\text{Glucose}}{C_6H_{12}O_6}+\underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$\underset{\text{Glucose or Fructose}}{C_6H_{12}O_6}\xrightarrow{\text{Zymase}}2C_2H_5OH+2CO_2$$

88. (d) $\text{Starch}\xrightarrow{\text{Enzymes}}\text{Alcohol}$

89. (a) $$2\underset{\text{Starch}}{(C_6H_{10}O_5)_n}+nH_2O\xrightarrow[\text{(from germinated barley)}]{\text{Diastase}}\underset{\text{Maltose}}{n(C_{12}H_{22}O_{11})}$$

$$C_{12}H_{22}O_{11}+H_2O\xrightarrow[\text{(from yeast)}]{\text{Maltase}}\underset{\text{Glucose}}{2C_6H_{12}O_6}$$

$$C_6H_{12}O_6\xrightarrow[\text{(from yeast)}]{\text{Zymase}}2C_2H_5OH+2CO_2$$

90. (b)

91. (c) Denaturing can also be done by adding 0.5% pyridine, petroleum naptha, $CuSO_4$ etc.

92. (c)

93. (c) Tonics contain ethyl alcohol.

94. (c) Due to presence of methyl alcohol in liquor.

95. (c) The quantity of sugar increases and yeast grows on the outer skin as grapes ripen. When grapes are crushed, sugar and the enzyme come in contact and fermentation starts. Fermentation takes place in anaerobic contidions i.e., in absence of air CO_2 is released during fermentation. If air gets into fermentation mixture the oxygen of air oxidises ethanol to ethanoic acid which in turn destroys the taste of alcoholic drinks.

96. (b) The commercial alcohol is made unfit for drinking by mixing in it some copper sulphate (to give it colour) and pyridine (a foul smelling liquid). It is known as denaturation of alcohol.

97. (a) $$C_6H_5ONa+C_2H_5I\xrightarrow{\Delta}\underset{\text{Phenetole}}{C_6H_5OC_2H_5}+NaI$$

98. (b) $$C_2H_5Br+\underset{\text{Sod. ethoxide}}{C_2H_5ONa}\xrightarrow[-NaBr]{}\underset{\text{diethyl ether}}{C_2H_5-O-C_2H_5}$$

99. (b) Reaction of sodium ethoxide with ethyl iodide to produce diethyl ether is known as Williamson synthesis.

It is a nucleophilic substitution reaction and proceeds via S_N2 mechanism.

100. (d) The two components should be $(CH_3)_3CONa$ + $(CH_3)_3CBr$. However, tert-alkyl halides tend to undergo elimination reaction rather than substitution leading to the formation of an alkene, $Me_2C=CH_2$

101. (c) Preparation of ethers by reacting sodium ethoxide with alkyl halide is called Williamson synthesis.

102. (a) Due to H-bonding, the boiling point of ethanol is much higher than that of the isomeric diethyl ether.

103. (c) CH_3OCH_3 and $C_2H_5OCH_3$ are gases while $C_2H_5OC_2H_5$ (b. p. 308 K) is low boiling liquid.

104. (d) Ether is used (i) as a general anaesthetic, (ii) as refrigerant since it produces cooling on evaporation, (iii) as solvent for oils, fats, resins etc. (iv) for providing inert medium in Wurtz reaction, (v) for preparing Grignard reagent, (vi) in perfumery.

105. (a) Like dissolves like. Oils and fats, being covalent, dissolve in ether, a non-polar solvent.

106. (d) Due to inter-molecular hydrogen bonding in alcohols boiling point of alcohols is much higher than ether.

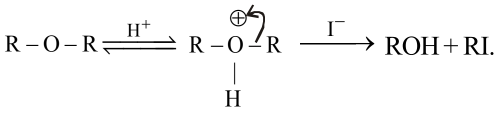
107. (c) **108. (c)**

109. (b) Only alkyl aryl ethers e.g., $C_6H_5OCH_3$ undergoes electrophilic substitution reactions.

110. (c) $C_2H_5OC_2H_5+2\,HI\xrightarrow{\Delta}2\,C_2H_5I+H_2O$

111. (a) $C_6H_5O^-+CH_3I\rightarrow C_6H_5OCH_3+I^-$

112. (a) Ethers are readily cleaved by HI as follows :



$$R-O-R\underset{}{\overset{H^+}{\rightleftharpoons}}R-\underset{\substack{|\\H}}{\overset{\oplus}{O}}-R\xrightarrow{I^-}ROH+RI.$$

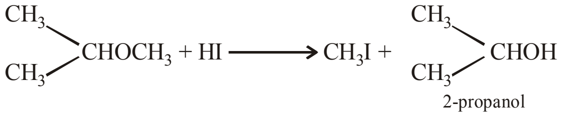
113. (c) In case of unsymmetrical ethers, the site of cleavage depends on the nature of alkyl group e.g.,

$$CH_3O-CH(CH_3)_2+HI\xrightarrow{373K}\underset{\substack{\text{Methyl}\\\text{iodide}}}{CH_3I}+\underset{\substack{\text{Isopropyl}\\\text{alcohol}}}{(CH_3)_2CHOH}$$

The alkyl halide is always formed from the smaller alkyl group.

114. (b) Due to greater electronegativity of sp^2-hybridized carbon atoms of the benzene ring, diaryl ethers are not attacked by nucleophiles like I^-.

115. (b)



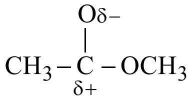
2-propanol

116. (a) Dehydration of alcohols gives ethers

117. (d) $$\underset{\text{Aryl-alkyl ether}}{R-O-Ar}+HI\longrightarrow\underset{\text{Phenol}}{Ar-OH}+\underset{\text{Alkyl iodide}}{RI}$$

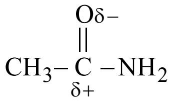
Due to steric hinderance, smaller alkyl group is always attached to iodine.

118. (d) Diethyl ether, being a Lewis base, is not attacked by nucleophiles, while all others contain electrophilic carbon, hence attacked by nucleophiles like OH^- ions.



$$CH_3-\overset{\overset{O\delta-}{|}}{\underset{\delta+}{C}}-OCH_3$$

$$CH_3-\overset{\delta+}{C}\equiv\overset{\delta-}{N}$$



$$CH_3-\overset{\overset{O\delta-}{||}}{\underset{\delta+}{C}}-NH_2$$

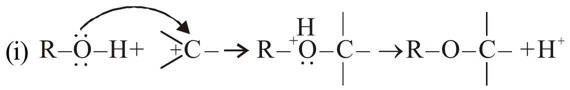
$$C_2H_5-\ddot{\underset{..}{O}}-C_2H_5$$

STATEMENT TYPE QUESTIONS

119. (c) Product formed is 2–methyl–pentan–2–ol hence carbon is attached to four different group therefore the molecule is chiral but because the carbonyl group is planar so attack of methyl group can take place either ways above and below the plane of the of molecule hence equal number of enantiomers are formed and hence the racemic mixture is formed.

120. (b) Alcohols are versatile compounds. They react both as nucleophiles and electrophiles. The bond between O—H is broken when alcohols react as nucleophiles.

Alcohols as nucleophiles

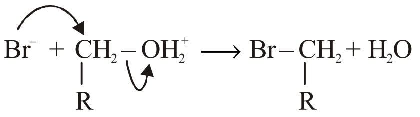


$$\text{(i) } R-\ddot{\underset{..}{O}}-H + \;>\!\overset{+}{C}- \rightarrow R-\overset{+}{\underset{..}{\overset{H}{O}}}-\overset{|}{\underset{|}{C}}- \rightarrow R-O-\overset{|}{\underset{|}{C}}- + H^+$$

(ii) The bond between C — O is broken when they react as electrophiles. Protonated alcohols react in this manner.

Protonated alcohols as electrophiles

$$R-CH_2-OH+\overset{+}{H}\rightarrow R-CH_2-\overset{+}{O}H_2$$



$$Br^- + \underset{R}{\underset{|}{C}}H_2-OH_2^+ \longrightarrow Br-\underset{R}{\underset{|}{C}}H_2 + H_2O$$

121. (b) Alcohols are, weaker acids than water. This can be illustrated by the reaction of water with an alkoxide.

$$R-\ddot{\underset{..}{O}}\!:^- + H-\ddot{\underset{..}{O}}-H \longrightarrow R-O-H + :\ddot{\underset{..}{O}}H^-$$

Base	Acid	Conjugate acid	Conjugate base

This reaction shows that water is a better proton donor (i.e., stronger acid) than alcohol. Also in the above reaction, we note that an alkoxide ion is a better proton acceptor than hydroxide ion, which suggests that alkoxide are stronger bases (sodiumethoxide is a stronger base than sodium hydroxide).

122. (c) The dehydration of secondary and tertiary alcohols to give corresponding ethers is unsuccessful as elimination competes over substitution and as a consequence, alkenes are easily formed.

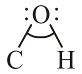
123. (c) The C — O bond length (136 pm) in phenol is slightly less than that in methanol (142 pm).

124. (a) A methanol poisoned patient is treated by giving intravenous injection of ethanol.

MATCHING TYPE QUESTIONS

125. (d) **126. (c)** **127. (b)**

ASSERTION-REASON TYPE QUESTIONS

128. (a) The bond angle  in alcohols is slightly less than the tetrahedral angle (109°-28′). It is due to the repulsion between the unshared electron pairs of oxygen.

129. (b) The correct explanation is : In Lucas test, tertiary alcohols react immediately because of the formation of the more stable tertiary carbocations.

130. (c) The correct reason is : Nucleophilic attack of phenolate ion through the *ortho*-carbon atom occurs on CCl_4 (a neutral electrophile) to form an intermediate which on hydrolysis gives salicylic acid (ArSE reaction).

131. (a) **R** is the correct explanation of **A**. Due to +M effect of $-\ddot{\underset{..}{O}}H$, its intermediate carbocation is more stable than the one in benzene.

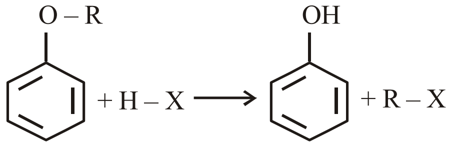
132. (c) The usual halogenation of benzene takes place in the presence of a Lewis acid, such as $FeBr_3$, which polarises the halogen molecule. In case of phenol, the polarisation of bromine molecule takes place even in the absence of Lewis acid. It is due to the highly activating effect of –OH group attached to the benzene ring.

133. (b)

134. (a) **R** is the correct explanation of **A**.

135. (d) **136. (c)**

137. (c) Alkyl aryl ethers are cleaved at the alkyl-oxygen bond due to the more stable aryl-oxygen bond. The reaction yields phenol and alkyl halide



Ethers with two different alkyl groups are also cleaved in the same manner.

$$R-O-R'+HX\rightarrow R-X+R'-OH$$

CRITICAL THINKING TYPE QUESTIONS

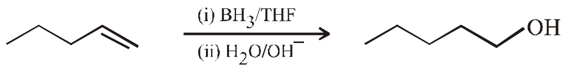
138. (a) Methyl alcohol (CH_3OH) is also known as carbinol. Hence vinyl carbinol is $CH_2=CH-CH_2OH$.

139. (c) $KMnO_4$ (alkaline) and OsO_4 / CH_2Cl_2 are used for hydroxylation of double bond while O_3/Zn is used for ozonolysis. Therefore, the right option is (c), i.e.,

$$3CH_3CH=CH_2 \xrightarrow{BH_3\text{ in THF}} (CH_3CH_2CH_2)_3B$$

$$\xrightarrow[NaOH]{3H_2O_2} \underset{\text{1-propanol}}{3CH_3CH_2CH_2OH} + H_3BO_3$$

140. (a) Hydroboration-oxidation leads to *anti*-Markownikoff's hydration, thus



1-Pentanol

141. (b) $NaBH_4$ and $LiAlH_4$ attacks only carbonyl group and reduce it into alcohol group.

$$\underset{\text{cinnamic aldehyde}}{C_6H_5-CH=CHCHO}\xrightarrow{NaBH_4}\underset{\text{cinnamic alcohol}}{C_6H_5-CH=CH.CH_2OH}$$

142. (a)

143. (b) Carbocation is formed as intermediate which is most stabilized when protonation occurs on terminal carbon.

144. (b) Reaction of 1–chloropropane leads to the formation of the primary carbocation which rearranges to more stable secondary carbocation, hence (ii) and (iii) give similar products.

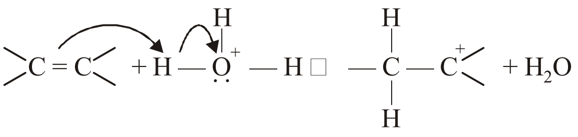
145. (a) In case of (ii) and (iii), the alcohol so obtained contain carbon which is attached to four different groups i.e., chiral carbon while in case of (i) and (iv) achiral alcohol is obtained.

146. (a) $CH_2=CH-OH$ represents vinylic alcohol. In vinylic alcohols –OH group is attached to *sp*^{2} hybridized carbon whereas in allylic alcohols – OH group is attached to *sp*^{3} hybridized carbon.

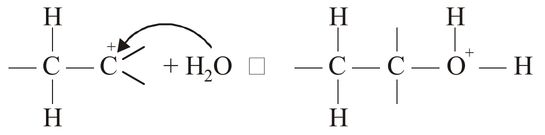
147. (c) The mechanism of the reaction involves the following three steps:

Step 1: Protonation of alkene to form carbocation by electrophilic attack of H_3O^+

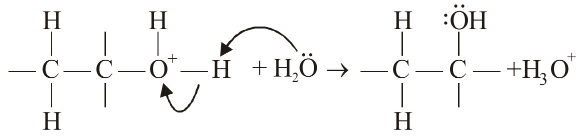
$H_2O + H^+ \rightarrow H_3O^+$



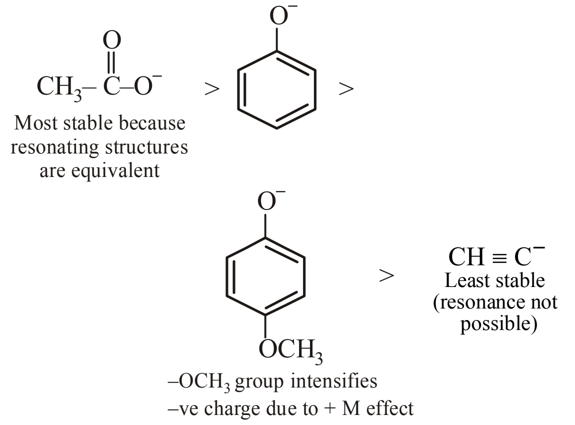
Step 2: Nucleophilic attack of water on carbocation.



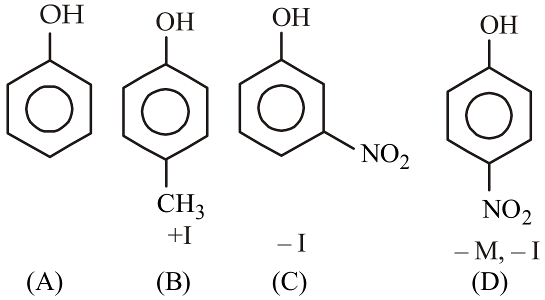
Step 3: Deprotonation to form an alcohol.



148. (a) More the stability of the conjugate base, higher is the acidic character of the parent acid. Stability order of the four conjugate bases is arranged below.

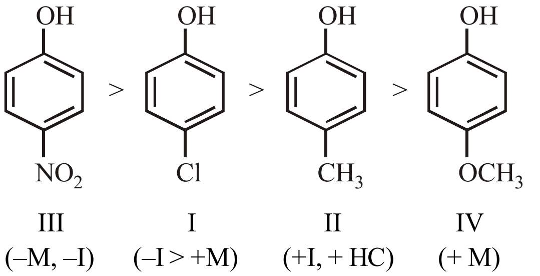


149. (a)



Electron withdrawing substituents increases the acidity of phenols; while electron releasing substituents decreases acidity. Further the particular effect (acidity increasing or decreasing) is more when a substituent is present in o-ortho position to phenolic group. Thus the correct order will be D > C > A > B.

150. (c) Electron withdrawing substituents like –NO_2, Cl increase the acidity of phenol while electron releasing substituents like – CH_3, – OCH_3 decreases acidity. hence the correct order of acidity will be



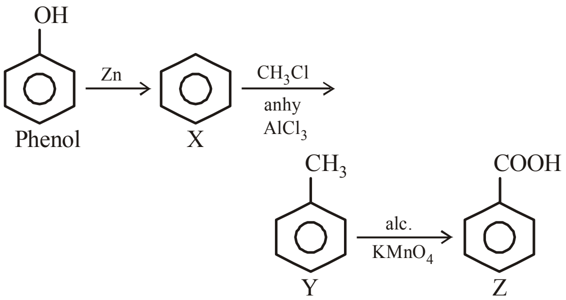
151. (c) $ClCH_2CH_2OH$ is stronger acid than CH_3CH_2OH due to – I effect of Cl.

$$\underset{\text{Stronger acid}}{Cl\leftarrow CH_2CH_2OH}\longrightarrow\underset{\substack{\text{–ve charge on O}\\\text{dispersed hence}\\\text{conjugate base, stable}}}{Cl\leftarrow CH_2CH_2O^- + H^+}$$

$$\underset{\text{Weaker acid}}{CH_3CH_2OH}\longrightarrow\underset{\substack{\text{–ve charge intensified,}\\\text{hence conjugate}\\\text{base unstable}}}{CH_3\rightarrow CH_2O^- + H^+}$$

152. (c) Due to strong electron-donating effect of the OH group, the electron density in phenol is much higher than that in toluene, benzene and chlorobenzene and hence phenol is readily attacked by the electrophile.

153. (b)

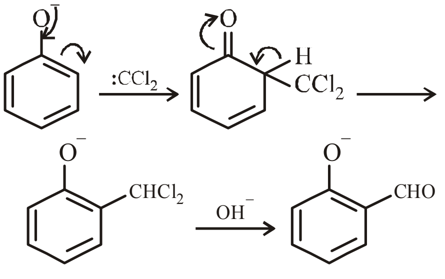


154. (d) Riemer-Tiemann reaction involves electrophilic substitution on the highly reactive phenoxide ring.

$HCCl_3 + OH^- \longrightarrow H_2O + {}^-{:}CCl_3$

$\longrightarrow Cl^- + \;:CCl_2$

Note the C has only a sextet of electrons



A benzal chloride

155. (c) $CH_2=CH_2 \xleftarrow[650K]{Al_2O_3} CH_3CH_2OH \xrightarrow[525K]{Al_2O_3}$

$CH_3CH_2OCH_2CH_3$

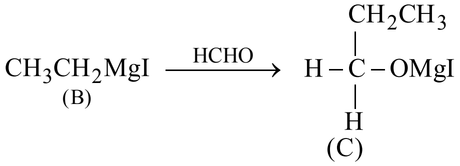
156. (b) Dehydration of CH_3OH gives carbene (methylene), an unstable intermediate.

$CH_3OH \xrightarrow{H_2SO_4} \underset{\text{Carbene}}{[:CH_2]} + H_2O$

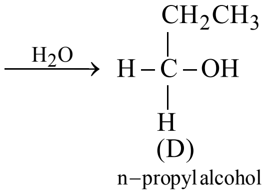
157. (d) Since the compound ($C_4H_{10}O$) react with sodium, it must be alcohol (option *b, c, or d*). As it is oxidised to carbonyl compound which does not reduce Tollen's reagent, the carbonyl compound should be a ketone and thus $C_4H_{10}O$ should be a secondary alcohol, i.e. *sec*-butyl alcohol; other two given alcohols are 1°.

158. (a)

159. (d) $CH_3CH_2OH \xrightarrow{P+I_2} \underset{A}{CH_3CH_2I} \xrightarrow[Ether]{Mg}$



$$\underset{(B)}{CH_3CH_2MgI} \xrightarrow{HCHO} \underset{(C)}{H-\underset{H}{\overset{CH_2CH_3}{C}}-OMgI}$$



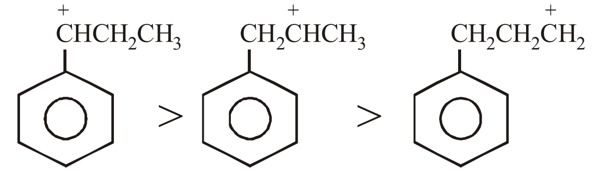
$$\xrightarrow{H_2O} \underset{(D)}{H-\underset{H}{\overset{CH_2CH_3}{C}}-OH}$$

n−propyl alcohol

160. (b) **161. (c)**

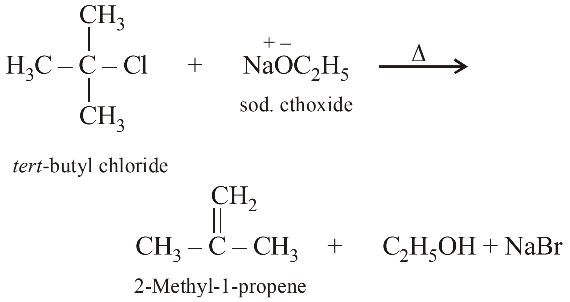
162. (a) In case of *m*–nitrophenol operational effect of nitrogroup is electron withdrawing inductive effect while in case of b and c, both –R and –I effect are operational.

163. (a) Here also, carbocation is formed as an intermediate, hence the species capable of forming most stable carbocation will be most reactive.



Benzyl carbocation 2° carbocation 1° carbocation

164. (a) In Williamson's synthesis the reaction of alkyl halides with sodium alkoxides give ethers. However, if the alkyl halide is 3°, it undergoes elimination to give an alkene.

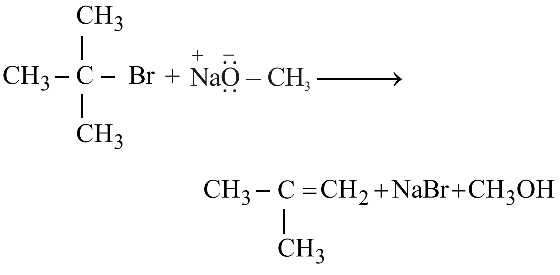


$$\underset{\textit{tert}\text{-butyl chloride}}{H_3C-\underset{CH_3}{\overset{CH_3}{C}}-Cl} + \underset{\text{sod. cthoxide}}{\overset{+\,-}{NaOC_2H_5}} \xrightarrow{\Delta}$$

$$CH_3-\overset{CH_2}{\overset{\|}{C}}-CH_3 + C_2H_5OH + NaBr$$

2-Methyl-1-propene

165. (c) If a tertiary alkyl halide is used, an alkene is the only reaction product and no ether is formed. For example, the reaction of CH_3ONa with $(CH_3)_3C$–Br gives exclusively 2-methylpropene.



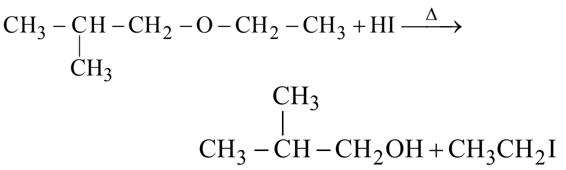
$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Br+\overset{+}{Na}\overset{-}{\ddot{O}}-CH_3 \longrightarrow$$

$$CH_3-\underset{CH_3}{C}=CH_2+NaBr+CH_3OH$$

2-Methylpropene

It is because alkoxides are not only nucleophiles but strong bases as well. They react with alkyl halides leading to elimination reactions.

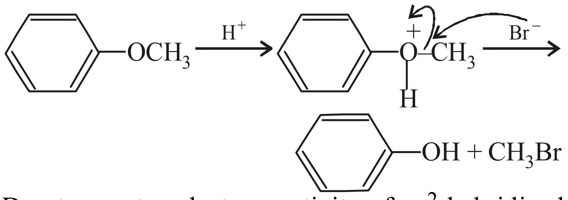
166. (c) In the cleavage of mixed ethers having two different alkyl groups, the alcohol and alkyl iodide that form depend on the nature of alkyl group. When primary or secondary alkyl groups are present, it is the lower alkyl group that forms alkyl iodide therefore



$$CH_3-\underset{CH_3}{CH}-CH_2-O-CH_2-CH_3+HI \xrightarrow{\Delta}$$

$$CH_3-\overset{CH_3}{CH}-CH_2OH+CH_3CH_2I$$

167. (d)



168. (b) Due to greater electronegativity of sp^2-hybridized carbon atoms of the benzene ring, diaryl ethers are not attacked by nucleophiles like I^-.