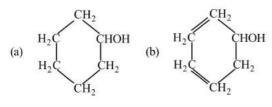
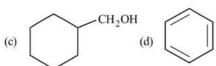
# **ALCOHOLS, PHENOLS AND ETHERS**

# **FACT/DEFINITION TYPE QUESTIONS**

- The characteristic grouping of secondary alcohols is
  - (a) -CH2OH

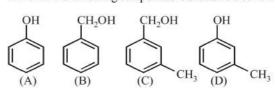
- The compound HOCH<sub>2</sub> CH<sub>2</sub>OH is
  - (a) ethane glycol
- (b) ethylene glycol
- (c) ethylidene alcohol
- (d) dimethyl alcohol
- The structural formula of cyclohexanol is





- Which of the following is dihydric alcohol?
  - (a) Glycerol
- (b) Ethylene glycol
- (c) Catechol
- (d) Resorcinol
- An example of a compound with functional group -O-is:
  - (a) acetic acid
- (b) methyl alcohol acetone
- (c) diethyl ether
  - (d)
  - Butane-2-ol is
    - (a) primary alcohol
- secondary alcohol
- (c) tertiary alcohol
- aldehyde (d)
- Cresol has
  - (a) Alcoholic OH
- (b) Phenolic OH
- (c) -COOH
- -CHO (d)
- How many isomers of C<sub>5</sub>H<sub>11</sub>OH will be primary alcohols?
  - (a) 5
- (b) 4
- (c) 2
- (d) 3

- CH<sub>3</sub> The IUPAC name of CH<sub>3</sub>-CH-CH<sub>2</sub>-C-CH<sub>3</sub> is ÓН ÓН
  - (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
- Number of metamers represented by molecular formula C<sub>4</sub>H<sub>10</sub>O is
  - (a) 4
- (b) 3
- (c) 2
- (d) 1
- Which of the following compounds is aromatic alcohol?



- (a) A, B, C, D
- (b) A, D
- (c) B, C
- (d)
- 12. How many alcohol(s) with molecular formula  $C_4H_{10}O$  are chiral in nature?
  - (a) 1
- (b) 2
- (c) 3
- (d) 4
- Give IUPAC name of the compound given below

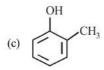
$$\begin{array}{c} \operatorname{CH}_3 - \operatorname{CH} - \operatorname{CH}_2 - \operatorname{CH}_2 - \operatorname{CH} - \operatorname{CH}_3 \\ \stackrel{|}{\operatorname{Cl}} & \operatorname{OH} \end{array}$$

- (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  $CH_3 CH OCH_3$  is  $CH_3$ 
  - (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<sub>6</sub>H<sub>5</sub> CH<sub>2</sub> CH<sub>2</sub>OH
  - (ii) C<sub>6</sub>H<sub>5</sub> − CH<sub>2</sub>OH
  - (iii)  $C_6H_5 CH OH$  $CH_3$
  - (iv)  $C_6H_5 CH_2 CH OH$  $CH_3$
  - (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?







- d) CH(CH<sub>3</sub>)OH
- **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<sub>3</sub>OCH<sub>3</sub>
- 19. Which of the following will not form phenol or phenoxide?
  - (a) C<sub>6</sub>H<sub>5</sub>N<sub>2</sub>Cl
- (b) C<sub>6</sub>H<sub>5</sub>SO<sub>3</sub>Na
- (c)  $C_6H_5Cl$
- (d)  $C_6H_5CO_2H$
- 20. Benzyl alcohol is obtained from benzaldehyde by
  - (a) Fittig's reaction(c) Kolbe's reaction
- (b) Cannizzaro'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

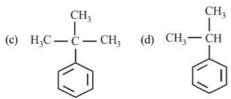
- 23. Ethyl alcohol is industrially prepared from ethylene by
  - (a) Permanganate oxidation
  - (b) Catalytic reduction
  - (c) Absorbing in H<sub>2</sub>SO<sub>4</sub> followed by hydrolysis
  - (d) All the three
- Sodium salt of benzene sulphonic acid on fusion with caustic soda gives
  - (a) Benzene
- (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<sub>2</sub>CO
- (c) RCN
- (d) RCOCI
- 27. Isopropyl alcohol is obtained by reacting which of the following alkenes with concentrated H<sub>2</sub>SO<sub>4</sub> followed by boiling with H<sub>2</sub>O?
  - (a) Ethylene
- (b) Propylene
- (c) 2-Methylpropene
- (d) Isoprene
- Alkenes convert into alcohols by
  - (a) hydrolysis by dil. H<sub>2</sub>SO<sub>4</sub>
  - (b) hydration of alkene by alkaline KMnO<sub>4</sub>
  - (c) hydrolysis by water vapours and conc. HNO<sub>3</sub>
  - (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<sub>2</sub>OH?
  - (i) H<sub>2</sub>/Pd
  - (ii) LiAlH<sub>4</sub>
  - (iii) NaBH<sub>4</sub>
  - (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)
- 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 **42.** by product in the large quantity is





- 34. In the reaction, RNH<sub>2</sub>  $\xrightarrow{\text{HNO}_2}$  ROH + H<sub>2</sub>O + C $\uparrow$ ; C is (where R = C<sub>6</sub>H<sub>5</sub>)
  - (a) NH<sub>3</sub>
- (b) N
- (c) O<sub>2</sub>
- (b) CO<sub>2</sub>
- 35. The correct order of boiling points for primary (1°), secondary (2°) and tertiary alcohol (3°) is
  - (a)  $1^{\circ} > 2^{\circ} > 3^{\circ}$
- (b)  $3^{\circ} > 2^{\circ} > 1^{\circ}$
- (c)  $2^{\circ} > 1^{\circ} > 3^{\circ}$
- (d)  $2^{\circ} > 3^{\circ} > 1^{\circ}$
- 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<sub>3</sub>OH
- (b) C<sub>3</sub>H<sub>7</sub>OH
- (c)  $C_4H_9OH$
- (d) C<sub>10</sub>H<sub>21</sub>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<sub>2</sub>SO<sub>4</sub> 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

  - (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) 
$$CH_2OH$$
 (b)  $OH$  (c)  $CH_2OH$  (d)  $CH_2OH$ 

- **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
- 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
- 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



- methyl ethyl ketone? (a) 2-Propanol (b) 1-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<sub>5</sub> (b) Reduction (c) Oxidation with potassium dichromate (d) Ozonolysis 54. Lucas reagent is (a) Conc. HCl and anhydrous ZnCl<sub>2</sub> (b) Conc. HNO<sub>3</sub> and hydrous ZnCl<sub>2</sub> (c) Conc. HCl and hydrous ZnCl<sub>2</sub> (d) Conc. HNO<sub>3</sub> and anhydrous ZnCl<sub>2</sub> 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-Methyl propan-2-ol 56. When phenol is treated with excess bromine water, it gives: (a) m-Bromophenol (b) o- and p-Bromophenol (d) 2, 4, 6-Tribromophenol (c) 2, 4-Dibromophenol 57. When phenol is heated with CHCl<sub>3</sub> 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 (d) Benzoic acid (c) ZnO + benzene 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  $\xrightarrow{\text{NaOH}}$  (A)  $\xrightarrow{\text{CO}_2+\text{HCl}}$  (B), here B is (a) benzaldehyde (b) chlorobenzene (c) benzoic acid salicylic acid (d) 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 To distinguish between salicylic acid and phenol, one can (a) NaHCO3 solution (b) 5% NaOH solution (c) neutral FeCl<sub>2</sub> (d) bromine water
- 51. Which of the following compounds is oxidised to prepare 64. Ethyl alcohol exhibits acidic character on reacting it with (a) acetic acid (b) sodium metal (c) hydrogen chloride (d) acidic K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> 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 In the following reaction,  $C_2H_5OH \xrightarrow{Conc. H_2SO_4} Z$  identify Z: (b) CH<sub>3</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>3</sub> (a)  $CH_2 = CH_2$ (c) CH<sub>2</sub>CH<sub>2</sub>-HSO<sub>4</sub> (d) (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>SO<sub>4</sub> 67. Chemical name of salol is (a) acetylsalicyclic acid (b) sodium salicylate (c) phenyl salicylate (d) methyl salicylate Aspirin is an acetylation product of (a) p-Dihydroxybenzene (b) o-Hydroxybenzoic acid (c) o-Dihydroxybenzene (d) m-Hydroxybenzoic acid Phenol, when it first reacts with concentrated sulphuric acid and then with concentrated nitric acid, gives (a) 2, 4, 6-trinitrobenzene (b) o-nitrophenol (d) nitrobenzene (c) p-nitrophenol 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? (b) H<sub>3</sub>PO<sub>2</sub> (a) H<sub>3</sub>PO<sub>4</sub> (c) HPO<sub>2</sub> (d) H<sub>3</sub>PO<sub>3</sub> Methanol and ethanol can be distinguished by the following: (a) By reaction with metallic sodium By reaction with caustic soda By heating with iodine and washing soda (d) By heating with zinc and inorganic mineral acid 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 What is the correct order of reactivity of alcohols in the following reaction?  $\xrightarrow{ZnCl_2}$  R - Cl + H<sub>2</sub>O R-OH+HCl-(a)  $1^{\circ} > 2^{\circ} > 3^{\circ}$ (b)  $1^{\circ} < 2^{\circ} > 3^{\circ}$ (c)  $3^{\circ} > 2^{\circ} > 1^{\circ}$ (d)  $3^{\circ} > 1^{\circ} > 2^{\circ}$ 74. CH<sub>2</sub>CH<sub>2</sub>OH can be converted into CH<sub>2</sub>CHO by (a) catalytic hydrogenation (b) treatment with LiAlH<sub>4</sub> (c) treatment with pyridinium chlorochromate (d) treatment with KMnO<sub>4</sub>

Which of the following compounds will react with sodium

(b)  $C_6H_5CH_2OH$ 

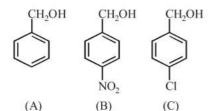
(d)  $C_2H_5OH$ 

hydroxide solution in water?

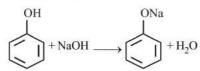
(a)  $C_6H_5OH$ 

(CH<sub>3</sub>)<sub>3</sub>COH

- 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)  $A \le B \le C$
- (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)  $b \le c \le a$
- (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

$$\begin{array}{c}
\text{OH} \\
& \stackrel{\text{Na}_2\text{Cr}_2\text{O}_7}{\longrightarrow} \text{A}
\end{array}$$

Ais



- 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<sub>2</sub>O<sub>3</sub>
  - (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<sub>2</sub>SO<sub>4</sub> followed by hydrolysis
  - (d) All the three
- '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
- The fermentation of starch to give alcohol occurs mainly with the help of
  - (a) O<sub>2</sub>
- (b) air
- (c) CÕ,
- (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<sup>-</sup> in the lungs
  - (c) it increses CO2 content in the blood
  - (d) it is a reduction product of formaldehyde
- 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<sub>3</sub>OH
- (b) Glycerol
- (c)  $C_2H_5OH$
- (d) 2-propanol



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<sub>4</sub> (a foul smelling solid) and pyridine (to give the colour) to make the commercial alcohol unfit for drinking (b) mixing of CuSO<sub>4</sub> (to give the colour) and pyridine (a foul smelling solid) to make the commercial alcohol unfit for drinking (c) mixing of Cu(OAc), and ammonia to make the commercial alcohol unfit for drinking mixing of Cu(OAc), 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 (b) diethyl ether acetone (d) bakelite (c) P.V.C. 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 Wurtz synthesis (b) 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

(a) H-bonding in ethanol H-bonding in dimethyl ether CH<sub>3</sub> group in ethanol (d) CH<sub>2</sub> group in dimethyl ether 103. Ether which is liquid at room temperature is (a) C<sub>2</sub>H<sub>5</sub>OCH<sub>3</sub> (b) CH<sub>2</sub>OCH<sub>2</sub> (c) C<sub>2</sub>H<sub>5</sub>OC<sub>2</sub>H<sub>5</sub> (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? (b) Water (a) Oils and fats (c) NaCl (d) PCl<sub>5</sub> 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<sub>3</sub>OC<sub>2</sub>H<sub>5</sub> (b) C<sub>6</sub>H<sub>5</sub>OCH<sub>3</sub> (c) CH<sub>3</sub>OCH<sub>3</sub> (d) C<sub>2</sub>H<sub>5</sub>OC<sub>2</sub>H<sub>5</sub> 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<sub>4</sub> 113. The major organic product in the reaction,  $CH_3 - O - CH(CH_3)_2 + HI \rightarrow Product is$ (a) ICH2OCH(CH3)2 (b)  $CH_3OC(CH_3)_2$ 

(c) CH<sub>3</sub>I+(CH<sub>3</sub>)<sub>2</sub>CHOH (d) CH<sub>3</sub>OH+(CH<sub>3</sub>)<sub>2</sub>CHI

(b)  $C_6H_5OC_6H_5$ 

(d) Tetrahydrofuran

114. An aromatic ether is not cleaved by HI even at 525 K. The



compound is

(a) C<sub>6</sub>H<sub>5</sub>OCH<sub>3</sub>

(c) C<sub>6</sub>H<sub>5</sub>OC<sub>3</sub>H<sub>7</sub>

ether, due to the presence of

- 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 ethylmagnesiumbromide with 2-pentanone, product formed does not rotate plane polarised light. For this reaction which of the following statement(s) is/are correct?
  - Product formed is achiral.
  - Racemic mixture is formed.
  - Both statements (i) and (ii) are correct.
  - Statement (i) is correct only.
  - Statement (ii) is correct only. (c)
  - (d) Both statements (i) and (ii) are incorrect.
- 120. Which of the following statements are correct?
  - Alcohols react as nucleophiles in the reactions involving cleavage of O-H bond.
  - 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.
  - Alcohols react as electrophiles in the reactions involving C-O bond.
  - (i) only
- (b) (i) and (iv)
- (c) (ii) and (iii)
- (d) (ii) only
- 121. Which of the following are correct statement(s)?
  - Polar nature of O-H bond is responsible for acidic (i) character of alcohols.
    - Acidic strength of alcohols follow the order  $1^{\circ} > 2^{\circ} > 3^{\circ}$ .
    - (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
  - Ethanol on dehydration at 443 K gives ethene
  - 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)
- (b) TFTF
- (c) TTTF
- (d) FTTF
- 123. Which of the following statements are correct?
  - In phenols, the —OH group is attached to  $sp^2$ hybridised carbon of an aromatic ring
  - 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.
  - (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
  - (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.
  - (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 (p) Quinol



(q) Phenol



(r) Catechol

(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 (s) Reaction of alkyl halide to ketone
- 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.

- Assertion is correct, reason is correct; reason is a correct explanation for assertion.
- Assertion is correct, reason is correct; reason is not a correct explanation for assertion.
- 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<sup>3</sup> hybridized carbon atom.

- 129. Assertion: In Lucas test, 3° alcohols react immediately. Reason: An equimolar mixture of anhyd. ZnCl<sub>2</sub> and conc. HCl is called Lucas reagent.
- 130. Assertion: Reimer-Tiemann reaction of phenol with CCl 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<sub>3</sub>. 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.

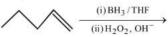
Reason: The reaction occurs by S<sub>N</sub>2 mechanism.

137. Assertion: Ethyl phenyl ether on reaction with HBr form phenol and ethyl bromide.

Reason: Cleavage of C-O bond takes place on ethyloxygen 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<sub>3</sub> C(CH<sub>2</sub>OH) = CH<sub>2</sub>
- 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<sub>4</sub> (alkaline)
  - (b) Osmium tetraoxide (OsO<sub>4</sub>/CH<sub>2</sub>Cl<sub>2</sub>)
  - (c) B<sub>6</sub>H<sub>6</sub> and alk. H<sub>2</sub>O<sub>2</sub>
  - (d)  $O_3/Zn$
- 140. The product of the following reaction is

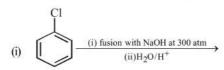


- (a) 1-Pentanol
- (b) 2-Pentanol
- (c) Pentane
- (d) 1,2-Pentanediol
- 141.  $C_6H_5 CH = CHCHO \xrightarrow{X} C_6H_5CH = CHCH_2OH$ . In the above sequence X can be
  - (a) H<sub>2</sub>/Ni
- (b) NaBH<sub>4</sub>
- (c) K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> / H<sup>+</sup>
- (d) Both (a) and (b)

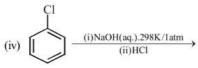




142. Which of the following reactions will yield phenol?



(ii) 
$$\overbrace{ \begin{array}{c} \text{(i)NaNO}_2/\text{HCI} \\ \text{(ii)H}_2\text{O(Warming)} \end{array} }^{\text{NH}_2}$$



- (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<sub>6</sub>H<sub>6</sub>, Cl<sub>2</sub>, hv; Mg.THF; acetone.
  - (ii) C<sub>6</sub>H<sub>6</sub>, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>Cl, AlCl<sub>3</sub>.
  - (iii) C<sub>6</sub>H<sub>6</sub>, CH<sub>3</sub>CHClCH<sub>3</sub>, AlCl<sub>3</sub>.
  - (iv) C<sub>6</sub>H<sub>6</sub>, CH<sub>3</sub>CH<sub>2</sub>Cl, AlCl<sub>3</sub>;
  - (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) CH2=CH-CH(CH3)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
  - Protonation of alkene to form carbocation by electrophilic attack of H<sub>3</sub>O<sup>+</sup>
  - (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(b) B>D>A>C
- (a) D>C>A>B(c) A>B>D>C
- (d) C>B>A>D
- **150.** Arrange the following compounds in order of decreasing acidity:

$$\begin{array}{c|cccc} OH & OH & OH & OH \\ \hline \\ & & \\ \hline \\ CI & CH_3 & NO_2 & OCH_3 \\ (I) & (II) & (III) & (IV) \\ \end{array}$$

- (a) II>IV>I>III
- (b) I>II>III>IV
- (c) III>I>II>IV
- (d) IV>III>I
- **151.** CICH<sub>2</sub>CH<sub>2</sub>OH is stronger acid than CH<sub>3</sub>CH<sub>2</sub>OH 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:

Phenol  $\xrightarrow{\text{Zn dust}}$  X  $\xrightarrow{\text{CH}_3\text{Cl}}$  Anhydrous AlCl<sub>3</sub>  $\xrightarrow{\text{Yn dust}}$  Y

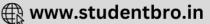
 $\xrightarrow{\text{Alkaline KMnO}_4}$  Z

The product Z is

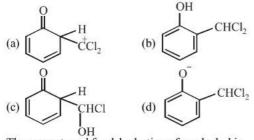
- (a) benzaldehyde
- (b) benzoic acid
- (c) benzene
- (d) toluene







154. When phenol is reacted with CHCl<sub>3</sub> and NaOH followed by acidification, salicylaldehyde is obtained. Which of the following species are involved in the above mentioned reaction as intermediate?



- 155. The reagent used for dehydration of an alcohol is
  - (a) phosphorus pentachloride
  - calcium chloride (b)
  - aluminium oxide (c)
  - sodium chloride (d)
- 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<sub>4</sub>H<sub>10</sub>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 Effect of nitro group.
  - Greater resonance effect of p-nitrophenoxy group
  - 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,

$$CH_3CH_2OH \xrightarrow{P+I_2} A \xrightarrow{Mg} B \xrightarrow{HCHO} B$$

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) <sup>©</sup>OH
- (b)
- (c) <sup>®</sup>OC<sub>6</sub>H<sub>5</sub>
- 161. Which of the following reagents can be used to oxidise primary alcohols to aldehydes?
  - CrO<sub>2</sub> in anhydrous medium.
  - (ii) KMnO<sub>4</sub> 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
  - a mixture of alkene as a major product and ether as a minor product forms.
- 166. In the reaction:

$$\begin{array}{c} CH_3 \\ CH_3 - CH - CH_2 - O - CH_2 - CH_3 + HI & \xrightarrow{Heated} \end{array}$$

Which of the following compounds will be formed?

(b) 
$$CH_3 - CH - CH_2OH + CH_3CH_3$$
  
 $CH_3$ 

-OCH,  $\xrightarrow{HBr}$  the products are 167. In the reaction &

- 168. An aromatic ether is not cleaved by HI even at 525 K. The compound is
  - (a) C<sub>6</sub>H<sub>5</sub>OCH<sub>3</sub>
- (b) C<sub>6</sub>H<sub>5</sub>OC<sub>6</sub>H<sub>5</sub>
- (c)  $C_6H_5OC_3H_7$
- (d) Tetrahydrofuran

# HINTS AND SOLUTIONS

# **FACT/DEFINITION TYPE QUESTIONS**

1. (b) 2. (b)

H-OH 3. (a) or

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

> CH<sub>2</sub>OH CH<sub>2</sub>OH (Ethylene glycol)

- 5. (c) Ethers contain the functional group - O -
- CH<sub>3</sub>CH<sub>2</sub>CH(OH)CH<sub>3</sub> a secondary alcohol 6.
- 7. (b) Cresol has phenolic group - OH
- 8. Four primary alcohols of C<sub>5</sub>H<sub>11</sub>OH are possible. These
  - (i) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH
  - (ii) CH<sub>3</sub>CH<sub>2</sub> CH CH<sub>2</sub>OH CH<sub>3</sub>
  - (iii) CH<sub>3</sub> CH CH<sub>2</sub>CH<sub>2</sub>OH CH<sub>3</sub>

$$\begin{array}{c} \operatorname{CH_3} \\ \text{(iv) CH}_3 - \operatorname{C} - \operatorname{CH_2OH} \\ \operatorname{CH_3} \end{array}$$

CH<sub>3</sub>-CH-CH<sub>2</sub>-C-CH<sub>3</sub> ÓН

2-methyl- 2, 4-pentanediol.

- 10. **(b)**  $C_4H_{10}O:$  **(i)**  $C_2H_5OC_2H_5$  **(ii)**  $CH_3OC_3H_7$ (iii) CH<sub>3</sub>OCH(CH<sub>3</sub>)<sub>2</sub>
- 11. (c) (b)

16.

- 12. (a)
- 13. (c)
- 15. (c)

14. (a)

In this structure -OH group is directly attached to 17. double bonded carbon atom i.e. sp2 hybridized carbon

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

- Benzoic acid (C<sub>6</sub>H<sub>5</sub>COOH) will not form phenol or phenoxide.
- By heating benzaldehyde with conc. NaOH or KOH 20. **(b)** (Cannizzaro reaction).

 $C_6H_5CHO + NaOH -$ Benzaldehyde

> C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>OH + C<sub>6</sub>H<sub>5</sub>COONa Benzyl alcohol Sod. benzoate

Any one of Ni, Pt or Pd can be used in the reduction of aldehydes.

 $CH_2 = CH_2$  $CH_2 - CH_2$ Baeyer's OH OHGlycol

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.

 $H_2C = CH_2 + H_2SO_4 \xrightarrow{100^{\circ}C} C_2H_5HSO_4$ 

 $\rightarrow$  C<sub>2</sub>H<sub>5</sub>OH + H<sub>2</sub>SO<sub>4</sub>

- 25.
- $CH_3MgBr \rightarrow H$ CH<sub>3</sub>

→ H-C-OH CH<sub>3</sub>

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

> $CH_3$   $CHCH_3 \xrightarrow{-H_2O} CH_2 = CHCH_3$ ÓН Isopropyl alcohol





**28. (b)** 
$$CH_2 = CH_2 + H_2O + [O] \xrightarrow{\text{alk. KMnO}_4} \begin{cases} CH_2 - CH_2 \\ OH OH \\ Glycol \end{cases}$$

$$\begin{array}{c} \operatorname{CH}_2 = \operatorname{CH}_2 + \operatorname{H}_2\operatorname{O} \xrightarrow{\quad \operatorname{Conc. \ H}_2\operatorname{SO}_4 \quad} \operatorname{CH}_3 - \operatorname{CH}_2 - \operatorname{OH} \\ \text{Ethanol} \end{array}$$

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).

- 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).

$$RCOOH \xrightarrow{R'OH} RCOOR' \xrightarrow{H_2} RCH_2OH + R'OH$$

- 33. (d)
- 34. (b) A diazonium salt is formed by treating an aromatic primary amine with nitrous acid (NaNO<sub>2</sub> + HCl) at 273-278 K. Diazonium salts are hydrolysed to phenols by warming with water or by treating with dilute acids.

$$\begin{array}{c|c}
NH_2 & \stackrel{\oplus}{N_2} \stackrel{\ominus}{Cl} & OH \\
\hline
NaNO_2 & \stackrel{\oplus}{Warm} & + N_2 + HC
\end{array}$$
Aniline Benzene diazonium chloride

- **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.

- 41. (b) When ethanol dissolves in water then there is emission of heat and contraction in volume.
- **42. (d)**  $C_2H_5OH + 4I_2 + 6NaOH \longrightarrow$

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.

$$R - CH_2 - CH_2 - OH \xrightarrow{Cu} R - CH_2 - CHO + H_2$$
Aldehyde

$$R \xrightarrow{\begin{array}{c} H \\ C \\ C \end{array}} OH \xrightarrow{\begin{array}{c} Cu \\ 300^{\circ}C \end{array}} R - C - R + H_{2}$$

2° alcohol

Ketone

$$R \xrightarrow{CH_3} OH \xrightarrow{Cu} OH \xrightarrow{300^{\circ}C} R - C = CH_2 + H_2O$$

$$CH_3 CH_3$$

3° alcohol

Alkene

$$C_6H_5 - OH \xrightarrow{Cu} No reaction$$

Resonance stabilisation of phenoxide ion (conjugate base of phenol)

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

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



47. (c) 
$$C_6H_5OH + H_2O \rightleftharpoons C_6H_5O^- + H_3O^+$$
Phenoxide ion

The phenoxide ion is stable due to resonance.

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

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<sup>-</sup>)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.

$$\begin{array}{c}
R \\
CHOH \xrightarrow{[O]} R \\
R
\end{array}$$

$$\begin{array}{c}
R \\
C = O \\
R$$
Ketone

**49.** (a) Alcohols are oxidized by removal of H<sub>2</sub> in presence of a heated metal catalyst (Cu)

$$\begin{array}{c} CH_{3}CH_{2}OH \xrightarrow{\quad Cu \quad \quad } CH_{3}CHO + H_{2} \\ \text{1° alcohol} \end{array}$$
 Aldehyde

$$H_3C$$
 $CH$ —OH  $Cu$ 
 $300^{\circ}$   $CH_3CCH_3 + H_2$ 
 $H_3C$ 
 $CH$ 
 $O$ 
 $O$ 
Ketone

- 50. (b)  $C_2H_5OH + CH_3COOH \longrightarrow CH_3COO.C_2H_5 + H_2O$
- 51. (c) Secondary alcohols oxidise to produce kenone.

$$\begin{array}{c} \text{CH}_3\text{CHOHCH}_2\text{CH}_3 \xrightarrow{\quad (O) \quad} \text{CH}_3\text{COCH}_2\text{CH}_3 \\ \text{2-Butanol} \qquad \qquad \text{Ethyl methyl ketone} \end{array}$$

- 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.

$$CH_3CH_2CH_2OH \xrightarrow{[O]}$$
 $n$ -propylalcohal

$$H_3C$$
 CH - OH  $[O]$   $H_3C$  C = C Keton

- 54. (a) Lucas reagent is conc. HCl + anhyd. ZnCl<sub>2</sub>.
- 55. (d) The rates of reaction with lucas reagent follows the

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.

$$CH_{3} - CH_{3} - CH_{3} \longrightarrow CH_{3}$$

2-Methyl-2-propanol

56. (d) OH  $\xrightarrow{3Br_2 \text{ (aq.)}}$  Br  $\xrightarrow{OH}$  Br

2, 4,6-Tribromophenol

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

Reimer-Tiemann reaction.

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

$$\begin{array}{c} OH \\ \hline \\ Phenol \end{array} + Zn \longrightarrow \begin{array}{c} \hline \\ Benzene \end{array}$$



(d) Phenol does not react with NaHCO<sub>3</sub>.

60. (d) 
$$\stackrel{OH}{\bigcirc}$$
  $\stackrel{ONa}{\longrightarrow}$   $\stackrel{ONa}{\bigcirc}$  Phenol

$$\begin{array}{c}
\text{OH} \\
\text{COO}_2 + \text{HCI} \\
140^{\circ} \text{ C}
\end{array}$$
Salicylic acid

61. (d) 
$$CH_3CH_2CHOH \xrightarrow{-H_2O} CH_3$$

$$\begin{aligned} CH_3CH &= CHCH_3 + CH_3CH_2CH = CH_2\\ \text{(Major product)} & \text{(Minor product)} \end{aligned}$$

62. (c) Lucas test is used to distinguish between 1°, 2° and 3° alcohols. Lucas reagent is anhy. ZnCl2 and HCl. 2° alcohol + Lucas reagent ------ turbidity after

1° alcohol + Lucas reagent → No turbidity at room temperature.

- Other options are acids, only Na metal is a base. 64. (b)
- Reactivity increases as the nucleophilicity of the halide 65. ion increases, i.e. I-> Br-> Cl-.
- 66. In presence of acid, alcohols always form carbocations (a) as intermediates.
- 67. (c) 68. (b)
- 69. Phenol on reaction with conc. H<sub>2</sub>SO<sub>4</sub> gives a mixture of o- and p- products (i.e., -SO<sub>3</sub>H group, occupies o-, p- position). At room temperature o-product is more stable, which on treatment with conc. HNO3 will yield o-nitrophenol.

At room temperature o- product is more stable

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

Methanol and ethanol can be distinguished by heating with iodine and washing soda

$$C_2H_5OH \xrightarrow{I_2} CHI_3 + HCOONa$$

$$\xrightarrow{Na_2CO_3} CHI_3 + HCOONa$$

$$(yellow ppt)$$

$$CH_3OH \xrightarrow{I_2} No reaction$$

This is also called iodoform test.

(d) 73. (c) 74. (c) 75. (a) 76. (b) 78. (c) (d)

Electron releasing groups (-CH<sub>3</sub>, -OCH<sub>3</sub>, -NCH<sub>3</sub> 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 (-NO2, -COOH, -CHO etc.) increases

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:)

$$\overrightarrow{B}$$
:+ $\overrightarrow{H}$ - $\overrightarrow{O}$ - $\overrightarrow{O}$ - $\overrightarrow{R}$   $\longrightarrow$   $\overrightarrow{B}$ - $\overrightarrow{H}$ + $\overrightarrow{O}$ - $\overrightarrow{O}$ - $\overrightarrow{R}$ 

Base Acid Conjugate Conjugate

- Oxidation of phenol with chromic acid produces a 81. (b) conjugated diketone known as benzoquinone. In the presence of air, phenols are slowly oxidised to dark coloured mixtures containing quinones.
- 82. Glucose and fructose obtained by hydrolysis of (c) sucrose, are converted into alcohol by enzyme zymase.

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

83. (a) 
$$\underbrace{\text{CO} + \text{H}_2}_{\text{water gas}} + \text{H}_2 \xrightarrow{\text{Cr}_2\text{O}_3 - \text{ZnO}}_{\text{300°C}} \xrightarrow{\text{CH}_3\text{OH}}_{\text{Methanol}}$$

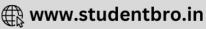
Ethylene is passed into concentrated sulphuric acid at 75-80°C under pressure when a mixture of ethyl hydrogen sulphate and diethyl sulphate is formed.

$$H_2C = CH_2 + H_2SO_4 \xrightarrow{100^{\circ}C} C_2H_5HSO_4$$
  
Ethylene

$$\xrightarrow{\Delta}$$
 C<sub>2</sub>H<sub>5</sub>OH + H<sub>2</sub>SO<sub>4</sub>

85. (b) 86. (a)





$$CH_2 = CH_2 + \overset{+}{H} \overset{-}{H} SO_4 \rightarrow CH_3 - CH_2 - HSO_4$$

$$\text{CH}_3 - \text{CH}_2 \text{HSO}_4 \xrightarrow{\text{H}_2 \text{O}} \text{CH}_3 - \text{CH}_2 - \text{OH} + \text{H}_2 \text{SO}_4$$

Fermentation of sugar

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{Invertase} C_2H_{12}O_6 + C_6H_{12}O_6$$
Glucose Fructose

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

89. (a) 
$$2(C_6H_{10}O_5)_n + nH_2O \frac{Diastase}{\text{(from germinated barley)}}$$

 $n(C_{12}H_{22}O_{11})$ 

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Maltase}} 2C_6H_{12}O_6$$
Glucose

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

- 90. (b)
- 91. (c) Denaturing can also be done by adding 0.5% pyridine, petroleum naptha, CuSO4 etc.
- 92. (c)
- 93. (c) Tonics contain ethyl alcohol.
- 94. (c) Due to presence of methyl alcohol in liquor.
- The quantity of sugar increases and yeast grows on 95. (c) 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 CO2 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. 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) 
$$C_6H_5ONa + C_2H_5I \xrightarrow{\Delta} C_6H_5OC_2H_5 + NaI$$

98. **(b)** 
$$C_2H_5Br + C_2H_5ONa \xrightarrow{-NaBr} C_2H_5 - O - C_2H_5$$
  
Sod. ethoxide

- 99. 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<sub>N</sub>2 mechanism.
- The two components should be (CH<sub>3</sub>)<sub>3</sub>CONa + (CH<sub>3</sub>)<sub>3</sub>CBr. 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<sub>3</sub>OCH<sub>3</sub> and C<sub>2</sub>H<sub>5</sub>OCH<sub>3</sub> are gases while C<sub>2</sub>H<sub>5</sub>OC<sub>2</sub>H<sub>5</sub> (b. p. 308 K) is low boiling liquid.
- 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<sub>6</sub>H<sub>5</sub>OCH<sub>3</sub> undergoes electrophilic substitution reactions.

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

- 111. (a)  $C_6H_5O^- + CH_3I \rightarrow C_6H_5OCH_3 + I^-$
- Ethers are readily cleaved by HI as follows:

$$R-O-R \xrightarrow{H^+} R \xrightarrow{O} R \xrightarrow{D^-} R \xrightarrow{\Gamma^-} ROH + RI.$$

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

$$\begin{array}{c} \text{CH}_{3}\text{O} - \text{CH}(\text{CH}_{3})_{2} + \text{HI} \xrightarrow{\phantom{0}373\text{K}\phantom{0}} \text{CH}_{3}\text{I} + (\text{CH}_{3})_{2}\text{CHOH} \\ \text{Methyl} \\ \text{iodide} \\ \text{slopropyl} \\ \text{iodide} \end{array}$$

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

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

115. (b) 
$$CH_3$$
 CHOCH<sub>3</sub> + HI  $\longrightarrow$  CH<sub>3</sub>I +  $CH_3$  CHOH  $CH_3$  CHOH

- Dehydration of alcohols gives ethers 116. (a)
- $R-O-Ar+HI \longrightarrow Ar-OH+RI$ 117. (d) Aryl-alkyl ether Phenol Alkyl iodide 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.

$$\begin{array}{ccc} O\delta- & & & & \\ & | & & \\ CH_3-C-OCH_3 & & & CH_3-C \equiv N \end{array}$$

$$CH_{3}-\overset{\delta+}{\underset{\delta+}{C}}-OCH_{3} \qquad CH_{3}-\overset{\delta+}{\underset{C}{C}}=\overset{\delta-}{N}$$

$$O\delta-$$

$$CH_{3}-\overset{C}{\underset{\delta+}{C}}-NH_{2} \qquad C_{2}H_{5}-\overset{O}{\underset{\delta-}{C}}-C_{2}H_{5}$$





# 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*

(i) 
$$R - \stackrel{\frown}{\square} - H + \stackrel{\rightarrow}{\triangleright} C - \rightarrow R - \stackrel{\frown}{\square} - \stackrel{\frown}{\square} - R - O - \stackrel{\frown}{\square} - + H^*$$

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

Protonated alcohols as electrophiles

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

$$\overrightarrow{Br^-} + \overrightarrow{CH_2} - \overrightarrow{OH_2}^+ \longrightarrow \overrightarrow{Br} - \overrightarrow{CH_2} + \overrightarrow{H_2O}$$

$$R$$

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

$$R-O: + H-O-H \longrightarrow R-O-H + :OH$$
  
Base Acid Conjugate 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 C H 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<sub>4</sub> (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  $-\ddot{Q}H$ , 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<sub>3</sub>, 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

$$O-R \longrightarrow OH$$

$$+H-X \longrightarrow +R-X$$

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<sub>3</sub>OH) is also known as carbinol. Hence vinyl carbinol is CH<sub>2</sub> = CH - CH<sub>2</sub>OH.
- 139. (c) KMnO<sub>4</sub> (alkaline) and OsO<sub>4</sub> / CH<sub>2</sub>Cl<sub>2</sub> are used for hydroxylation of double bond while O<sub>3</sub> /Zn is used for ozonolysis. Therefore, the right option is (c), i.e.,

$$\begin{aligned} 3\text{CH}_{3}\text{CH} &= \text{CH}_{2} \xrightarrow{\text{BH}_{3} \text{ in THF}} \text{CH}_{3}\text{CH}_{2}\text{CH}_{2})_{3} \text{B} \\ &\xrightarrow{\text{3H}_{2}\text{O}_{2}} \text{NaOH} \rightarrow 3\text{CH}_{3}\text{CH}_{2}\text{CH}_{2}\text{OH} + \text{H}_{3}\text{BO}_{3} \end{aligned}$$

1-propanol

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

$$\begin{array}{c}
\text{(i) BH}_{3}/\text{THF} \\
\text{(ii) H}_{2}\text{O/OH}^{-}
\end{array}$$

1-Pentanol





**141. (b)** NaBH<sub>4</sub> and LiAlH<sub>4</sub> attacks only carbonyl group and reduce it into alcohol group.

$$C_6H_5 - CH = CHCHO \xrightarrow{NaBH_4}$$

- 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<sub>2</sub> = CH OH represents vinylic alcohol. In vinylic alcohols OH group is attached to sp<sup>2</sup> hybridized carbon whereas in allylic alcohols OH group is attached to sp<sup>3</sup> 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  $\rm H_3O^+$ 

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

$$C = C + H - O + H = -C - C + H_2O$$

Step 2: Nucleophilic attack of water on carbocation.

$$-\overset{H}{\overset{\downarrow}{\operatorname{C}}}-\overset{\downarrow}{\overset{\downarrow}{\operatorname{C}}}+\overset{H}{\overset{\downarrow}{\operatorname{H}_2}}O\ \Box\ -\overset{H}{\overset{\downarrow}{\operatorname{C}}}-\overset{H}{\overset{\downarrow}{\operatorname{C}}}-\overset{H}{\overset{\downarrow}{\operatorname{C}}}-\overset{H}{\overset{\downarrow}{\operatorname{C}}}-\overset{H}{\overset{\downarrow}{\operatorname{C}}}$$

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.

-OCH<sub>3</sub> group intensifies -ve charge due to + M effect

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

$$\begin{array}{c|cccc} OH & OH & OH & OH \\ \hline & & & \\ NO_2 & CI & CH_3 & OCH_3 \\ \hline III & I & II & IV \\ (-M,-I) & (-I>+M) & (+I,+HC) & (+M) \end{array}$$

151. (c) CICH<sub>2</sub>CH<sub>2</sub>OH is stronger acid than CH<sub>3</sub>CH<sub>2</sub>OH due to – I effect of Cl.

$$Cl \leftarrow CH_2CH_2OH \longrightarrow Cl \leftarrow CH_2CH_2O^- + H^+$$
Stronger acid

-ve charge on O
dispersed hence
conjugate base, stable

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.



154. (d) Riemer-Tiemann reaction involves electrophilic substitution on the highly reactive phenoxide ring. HCCl<sub>3</sub> + OH<sup>−</sup> → H<sub>2</sub>O + −: CCl<sub>3</sub>

$$\longrightarrow Cl^{-+} : CCl_2$$
Note the C has only a

sextet of electrons

$$\begin{array}{c}
O \\
CCl_2
\end{array}$$

$$\begin{array}{c}
CHCl_2
\end{array}$$

$$O \\
CHCl_2$$

$$OH$$

$$OH$$

$$OH$$

**155.** (c)  $CH_2 = CH_2 \leftarrow \frac{Al_2O_3}{650 \text{ K}} - CH_3CH_2OH - \frac{Al_2O_3}{525 \text{ K}} \rightarrow \frac{Al_2O_3}{525 \text{ K}}$ 

CH3CH2OCH2CH3

**156. (b)** Dehydration of CH<sub>3</sub>OH gives carbene (methylene), an unstable intermediate.

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

**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  $1^\circ$ .

158. (a)

59. (d) 
$$CH_3CH_2OH \xrightarrow{P+I_2} CH_3CH_2I \xrightarrow{Mg} CH_2CH_3$$

$$CH_2CH_3 \xrightarrow{HCHO} H-C-OMgI \xrightarrow{H} (C)$$

$$CH_2CH_3$$

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.

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.

$$\begin{array}{c} CH_{3} \\ H_{3}C - C - CI \\ CH_{3} \end{array} + \begin{array}{c} N_{a}CC_{2}H_{5} \\ \text{sod. cthoxide} \end{array} \longrightarrow$$

tert-butyl chloride

$$\begin{array}{c} CH_2\\ \parallel\\ CH_3-C-CH_3 \end{array} + C_2H_5OH+NaBr$$

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<sub>3</sub>ONa with (CH<sub>3</sub>)<sub>3</sub>C-Br gives exclusively 2-methylpropene.

$$CH_{3}$$

$$CH_{3} - C - Br + \stackrel{+}{Na} \stackrel{-}{\bigcirc} - CH_{3} \longrightarrow$$

$$CH_{3} - C = CH_{2} + NaBr + CH_{3}OH$$

$$CH_{3} - C = CH_{2} + NaBr + CH_{3}OH$$

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

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

67. (d) 
$$CH_3$$
 $CH_3$ 
 $CH_3$ 

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

