Unit 111 ALCOHOLS, PHENOLS AND ETHERS

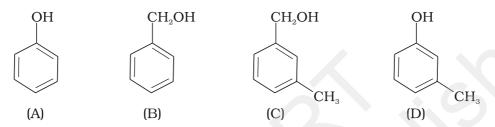
I. Multiple Choice Questions (Type-I)

1.	Monochlorination of toluene in sunlight followed by hydrolysis with aq. NaOl
	yields.

- (i) o-Cresol
- (ii) m-Cresol
- (iii) 2, 4-Dihydroxytoluene
- (iv) Benzyl alcohol
- **2.** How many alcohols with molecular formula $C_4H_{10}O$ are chiral in nature?
 - (i)
 - (ii) 2
 - (iii) 3
 - (iv) 4
- **3.** What is the correct order of reactivity of alcohols in the following reaction?

- (i) $1^{\circ} > 2^{\circ} > 3^{\circ}$
- (ii) $1^{\circ} < 2^{\circ} > 3^{\circ}$
- (iii) $3^{\circ} > 2^{\circ} > 1^{\circ}$
- (iv) $3^{\circ} > 1^{\circ} > 2^{\circ}$
- **4.** CH₃CH₂OH can be converted into CH₃CHO by _____
 - (i) catalytic hydrogenation
 - (ii) treatment with LiAlH₄

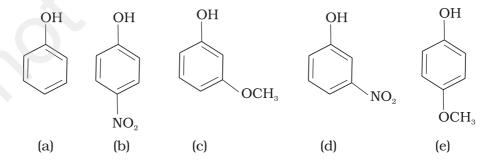
- (iii) treatment with pyridinium chlorochromate
- (iv) treatment with KMnO₄
- **5.** The process of converting alkyl halides into alcohols involves_____
 - (i) addition reaction
 - (ii) substitution reaction
 - (iii) dehydrohalogenation reaction
 - (iv) rearrangement reaction
- **6.** Which of the following compounds is aromatic alcohol?



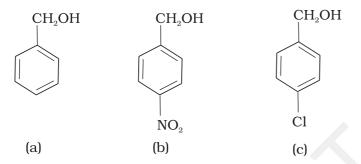
- (i) A, B, C, D
- (ii) A, D
- (iii) B, C
- (iv) A
- **7.** Give IUPAC name of the compound given below.

- (i) 2-Chloro-5-hydroxyhexane
- (ii) 2-Hydroxy-5-chlorohexane
- (iii) 5-Chlorohexan-2-ol
- (iv) 2-Chlorohexan-5-ol
- **8.** IUPAC name of *m*-cresol is ______.
 - (i) 3-methylphenol
 - (ii) 3-chlorophenol
 - (iii) 3-methoxyphenol
 - (iv) benzene-1,3-diol
- **9.** IUPAC name of the compound CH_3 —CH— OCH_3 is _______. CH_3
 - (i) 1-methoxy-1-methylethane
 - (ii) 2-methoxy-2-methylethane

- (iii) 2-methoxypropane
- (iv) isopropylmethyl ether
- **10.** Which of the following species can act as the strongest base?
 - (i) [⊖]OH
 - (ii) [⊖]OR
 - (iii) ${}^{\ominus}$ O C_6H_5
 - (iv) [⊖]O NO
- **11.** Which of the following compounds will react with sodium hydroxide solution in water?
 - (i) C_6H_5OH
 - (ii) $C_6H_5CH_2OH$
 - (iii) $(CH_3)_3 COH$
 - (iv) C_2H_5OH
- **12.** Phenol is less acidic than ______.
 - (i) ethanol
 - (ii) o-nitrophenol
 - (iii) o-methylphenol
 - (iv) *o*-methoxyphenol
- 13. Which of the following is most acidic?
 - (i) Benzyl alcohol
 - (ii) Cyclohexanol
 - (iii) Phenol
 - (iv) *m*-Chlorophenol
- **14.** Mark the correct order of decreasing acid strength of the following compounds.



- (i) e > d > b > a > c
- (ii) b > d > a > c > e
- (iii) d > e > c > b > a
- (iv) e > d > c > b > a
- **15.** Mark the correct increasing order of reactivity of the following compounds with HBr/HCl.



- (i) a < b < c
- (ii) b < a < c
- (iii) b < c < a
- (iv) c < b < a
- **16.** Arrange the following compounds in increasing order of boiling point.

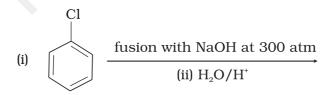
Propan-1-ol, butan-1-ol, butan-2-ol, pentan-1-ol

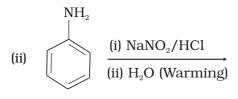
- (i) Propan-1-ol, butan-2-ol, butan-1-ol, pentan-1-ol
- (ii) Propan-1-ol, butan-1-ol, butan-2-ol, pentan-1-ol
- (iii) Pentan-1-ol, butan-2-ol, butan-1-ol, propan-1-ol
- (iv) Pentan-1-ol, butan-1-ol, butan-2-ol, propan-1-ol

II. Multiple Choice Questions (Type-II)

Note: In the following questions two or more options may be correct.

- 17. Which of the following are used to convert RCHO into RCH₂OH?
 - (i) H_2/Pd
 - (ii) LiAlH₄
 - (iii) NaBH
 - (iv) Reaction with RMgX followed by hydrolysis
- **18.** Which of the following reactions will yield phenol?





(iii)
$$\overbrace{ \begin{array}{c} \text{(i) Oleum} \\ \text{(ii) NaOH, (Heating)} \\ \text{(iii) } \text{H}^{\scriptscriptstyle +} \end{array} }$$

- **19.** Which of the following reagents can be used to oxidise primary alcohols to aldehydes?
 - (i) CrO₃ in anhydrous medium.
 - (ii) KMnO₄ in acidic medium.
 - (iii) Pyridinium chlorochromate.
 - (iv) Heat in the presence of Cu at 573K.
- **20.** Phenol can be distinguished from ethanol by the reactions with _____
 - (i) Br₂/water
 - (ii) Na
 - (iii) Neutral FeCl₃
 - (iv) All the above
- **21.** Which of the following are benzylic alcohols?
 - (i) C_6H_5 — CH_2 — CH_2 OH
 - (ii) C_6H_5 — CH_2OH

(iii)
$$C_6H_5$$
— CH — OH
 CH_3

(iv)
$$C_6H_5$$
— CH_2 — CH — OH
 CH_3

III. Short Answer Type

22. What is the structure and IUPAC name of glycerol?

23. Write the IUPAC name of the following compounds.

(A)
$$CH_3$$
— CH — CH — CH — CH — CH_3

$$CH_3$$
 OH C_2H_5 OH

24. Write the IUPAC name of the compound given below.

- **25.** Name the factors responsible for the solubility of alcohols in water.
- **26.** What is denatured alcohol?
- **27.** Suggest a reagent for the following conversion.

- 28. Out of 2-chloroethanol and ethanol which is more acidic and why?
- **29.** Suggest a reagent for conversion of ethanol to ethanal.
- **30.** Suggest a reagent for conversion of ethanol to ethanoic acid.
- **31.** Out of *o*-nitrophenol and *p*-nitrophenol, which is more volatile? Explain.
- **32.** Out of *o*-nitrophenol and o-cresol which is more acidic?
- **33.** When phenol is treated with bromine water, white precipitate is obtained. Give the structure and the name of the compound formed.
- **34.** Arrange the following compounds in increasing order of acidity and give a suitable explanation.

Phenol, o-nitrophenol, o-cresol

- **35.** Alcohols react with active metals e.g. Na, K etc. to give corresponding alkoxides. Write down the decreasing order of reactivity of sodium metal towards primary, secondary and tertiary alcohols.
- **36.** What happens when benzene diazonium chloride is heated with water?
- **37.** Arrange the following compounds in decreasing order of acidity.

$$H_2O$$
, ROH, $HC \equiv CH$

- **38.** Name the enzymes and write the reactions involved in the preparation of ethanol from sucrose by fermentation.
- **39.** How can propan-2-one be converted into *tert* butyl alcohol?
- **40.** Write the structures of the isomers of alcohols with molecular formula $C_4H_{10}O$. Which of these exhibits optical activity?

- **41.** Explain why is OH group in phenols more strongly held as compared to OH group in alcohols.
- **42.** Explain why nucleophilic substitution reactions are not very common in phenols.
- **43.** Preparation of alcohols from alkenes involves the electrophilic attack on alkene carbon atom. Explain its mechanism.
- **44.** Explain why is O=C=O nonpolar while R—O—R is polar.
- **45.** Why is the reactivity of all the three classes of alcohols with conc. HCl and ZnCl₂ (Lucas reagent) different?
- **46.** Write steps to carry out the conversion of phenol to aspirin.
- **47.** Nitration is an example of aromatic electrophilic substitution and its rate depends upon the group already present in the benzene ring. Out of benzene and phenol, which one is more easily nitrated and why?
- **48.** In Kolbe's reaction, instead of phenol, phenoxide ion is treated with carbon dioxide. Why?
- **49.** Dipole moment of phenol is smaller than that of methanol. Why?
- **50.** Ethers can be prepared by Williamson synthesis in which an alkyl halide is reacted with sodium alkoxide. Di-*tert*-butyl ether can't be prepared by this method. Explain.
- **51.** Why is the C—O—H bond angle in alcohols slightly less than the tetrahedral angle whereas the C—O—C bond angle in ether is slightly greater?
- **52.** Explain why low molecular mass alcohols are soluble in water.
- **53.** Explain why p-nitrophenol is more acidic than phenol.
- **54.** Explain why alcohols and ethers of comparable molecular mass have different boiling points?
- **55.** The carbon-oxygen bond in phenol is slightly stronger than that in methanol. Why?
- **56.** Arrange water, ethanol and phenol in increasing order of acidity and give reason for your answer.

IV. Matching Type

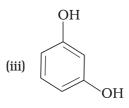
Column I

Note: Match the items of Column I and Column II in the following questions.

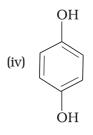
57. Match the structures of the compounds given in Column I with the name of the compounds given in Column II.

Column II

(b) Phenetole



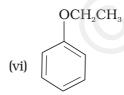
(c) Catechol



(d) o-Cresol



(e) Quinone



(f) Resorcinol

(g) Anisole

58. Match the starting materials given in Column I with the products formed by these (Column II) in the reaction with HI.

Column I

Column II

(ii)
$$CH_3$$
 CH—O—CH $_3$

(b)
$$CH_3$$
 CH_3 CH_3 CH_3 CH_3 CH_3

$$\begin{array}{c|c} OCH_3 \\ \hline \\ \text{(iv)} \end{array}$$

(d)
$$CH_3 - OH + CH_3 - I$$

(e)
$$CH_3$$
 CH $OH + CH_3I$

(f)
$$CH_3$$
 CH + CH_3 OH

$$\begin{array}{c} \operatorname{CH_3} \\ \mid \\ \operatorname{C} - \operatorname{OH} + \operatorname{CH_3} \operatorname{I} \\ \mid \\ \operatorname{CH_3} \end{array}$$

59. Match the items of column I with items of column II.

Column I

Column II

- (i) Antifreeze used in car engine
- (ii) Solvent used in perfumes
- (iii) Starting material for picric acid
- (iv) Wood spirit
- (v) Reagent used for detection of phenolic group
- (vi) By product of soap industry used in cosmetics

- (a) Neutral ferric chloride
- (b) Glycerol
- (c) Methanol
- (d) Phenol
- (e) Ethleneglycol
- (f) Ethanol
- **60.** Match the items of column I with items of column II.

Column I

Column II

(i) Methanol

(a) Conversion of phenol to o-hydroxysalicylic acid

(ii) Kolbe's reaction Ethyl alcohol (b) Conversion of phenol to (iii) Williamson's synthesis salicylaldehyde (iv) Conversion of 2° alcohol to ketone Wood spirit (d) (v) Reimer-Tiemann reaction Heated copper at 573K (e) (vi) Fermentation (f) Reaction of alkyl halide with sodium alkoxide

V. Assertion and Reason Type

Note: In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(i) Assertion and reason both are correct and reason is correct explanation of assertion.

(ii) Assertion and reason both are wrong statements.

(iii) Assertion is correct statement but reason is wrong statement.

(iv) Assertion is wrong statement but reason is correct statement.

(v) Both assertion and reason are correct statements but reason is not correct explanation of assertion.

61. Assertion : Addition reaction of water to but-1-ene in acidic medium yields butan-1-ol

Reason: Addition of water in acidic medium proceeds through the formation of primary carbocation.

62. Assertion : *p*-nitrophenol is more acidic than phenol.

Reason: Nitro group helps in the stabilisation of the phenoxide ion by dispersal of negative charge due to resonance.

63. Assertion : IUPAC name of the compound

 $\mathrm{CH_3-\!CH-\!O-\!CH_2-\!CH_2-\!CH_3}$ is 2-Ethoxy-2-methylethane. $\mathrm{CH_3}$

Reason: In IUPAC nomenclature, ether is regarded as hydrocarbon derivative in which a hydrogen atom is replaced by —OR or —OAr group [where R = alkyl group and Ar = aryl group]

64. Assertion : Bond angle in ethers is slightly less than the tetrahedral angle.

Reason: There is a repulsion between the two bulky (—R) groups.

65. Assertion : Boiling points of alcohols and ethers are high.

Reason: They can form intermolecular hydrogen-bonding.

66. Assertion : Like bromination of benzene, bromination of phenol is also

carried out in the presence of Lewis acid.

Reason: Lewis acid polarises the bromine molecule.

67. Assertion : o-Nitrophenol is less soluble in water than the m- and

p-isomers.

Reason : m- and p- Nitrophenols exist as associated molecules.

68. Assertion : Ethanol is a weaker acid than phenol.

Reason : Sodium ethoxide may be prepared by the reaction of ethanol

with aqueous NaOH.

69. Assertion : Phenol forms 2, 4, 6 – tribromophenol on treatment with Br.

in carbon disulphide at 273K.

Reason: Bromine polarises in carbon disulphide.

70. Assertion : Phenols give *o*- and *p*-nitrophenol on nitration with conc.

HNO₃ and H₂SO₄ mixture.

Reason : —OH group in phenol is o–, p– directing.

VI. Long Answer Type

71. Write the mechanism of the reaction of HI with methoxybenzene.

72. (a) Name the starting material used in the industrial preparation of phenol.

(b) Write complete reaction for the bromination of phenol in aqueous and non aqueous medium.

(c) Explain why Lewis acid is not required in bromination of phenol?

73. How can phenol be converted to aspirin?

74. Explain a process in which a biocatalyst is used in industrial preparation of a compound known to you.

ANSWERS

I. Multiple Choice Questions (Type-I)

1. (iv)	2. (i)	3. (iii)	4. (iii)	5. (ii)	6. (iii)
7. (iii)	8. (i)	9. (iii)	10. (ii)	11. (i)	12. (ii)
13. (iv)	14. (ii)	15. (iii)	16. (i)		

II. Multiple Choice Questions (Type-II)

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17. (i), (ii), (iii) 18. (i), (ii), (iii) 19. (i), (iii), (iv) 20. (i), (iii) 21. (ii), (iii)
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III. Short Answer Type

22.
$$CH_2$$
— CH — CH_2 ; Propane-1,2,3-triol OH OH OH

- 23. (A) 3-Ethyl-5-methylhexane-2,4-diol, (B) 1-Methoxy-3-nitrocyclohexane
- 24. 3-Methylpent-2-ene-1,2-diol
- 25. (i) Hydrogen bonding (ii) Size of alkyl/aryl group.
- 26. Alcohol is made unfit for drinking by mixing some copper sulphate and pyridine in it. This is called denatured alcohol.
- 27. CrO₃, pyridine and HCl. (Pyridinium chlorochromate)
- 28. 2-Chloroethanol, due to –I effect of chlorine atom.
- 29. CrO₃, Pyridine and HCl (Pyridinium chlorochromate)
- 30. Any strong oxidising agent e.g., acidified KMnO₄ or K₂Cr₂O₇.
- 31. Ortho nitrophenol, [**Hint**: intramolecular hydrogen bonding in *o*-nitrophenol and intermolecular hydrogen bonding in *p*-nitrophenol.]
- 32. *o*-Nitrophenol, [**Hint**: CH₃ group is electron releasing]

34. Increasing order of acidity:o-cresol < phenol < o-nitrophenol

[**Hint:** In substituted phenols, the presence of electron withdrawing groups, enhance the acidic strength of phenol whereas, electron releasing groups decrease the acidic strength of phenol.]

35. Decreasing order of reactivity of sodium metal is:

 $1^{\circ} > 2^{\circ} > 3^{\circ}$

- 36. **[Hint:** It gives phenol]
- 37. [**Hint**: $H_2O > ROH > HC \equiv CH$]
- 38. See NCERT textbook for Class XII
- 39. [Hint: Using Grignard reagent]
- 40. See NCERT textbook for Class XII
- 41. See NCERT textbook for Class XII
- 42. See NCERT textbook for Class XII
- 43. See NCERT textbook for Class XII
- 44. See NCERT textbook for Class XII
- 45. An alcohol reacts with conc. HCl and $ZnCl_2$ (Lucas reagent) to give carbocation. More stable is the carbocation, faster is the reaction.

46.

OH ONa OH

COOH

NaOH

(i)
$$CO_2$$

(ii) H^+

(CH₃CO)₂O

(Salicylic acid)

CH₃COOH

CH₃COOH

(Aspirin)

- 47. Phenol is more easily nitrated than benzene as the presence of —OH group in phenol increases the electron density at ortho and para positions in benzene ring by +R effect. The nitration, being an electrophilic substitution reaction is more facile where the electron density is more.
- 48. Phenoxide ion is more reactive than phenol towards electrophilic aromatic substitution and hence undergoes electrophilic substitution with carbondioxide which is a weak electrophile.
- 49. In phenol, C—O bond is less polar due to electron-withdrawing effect of benzene ring whereas in methanol, C—O bond is more polar due to electron-releasing effect of —CH₃ group.
- 50. In *tert*-butyl halides, elimination is favoured over substitution, so alkene is the only reaction product and ether is not formed.

(tert.butyl bromide)

(2-methylprop-1-ene)

- 51. See NCERT textbook for Class XII.
- 52. See NCERT textbook for Class XII.
- 53. See NCERT textbook for Class XII.
- 54. See NCERT textbook for Class XII.
- 55. This is due to the fact that—
 - (i) In phenol, conjugation of unshared electron pair over oxygen with aromatic ring results in partial double bond character in carbonoxygen bond.
 - (ii) In phenol, oxygen is attached to a sp^2 hybridised carbon atom while in methanol, it is attached to a sp^3 hyrbidised carbon atom. The bond formed between oxygen and sp^2 hybridised carbon is more stable than that formed between oxygen and sp^3 hybridised carbon.
- 56. Increasing order of acidity is ethanol < water < phenol. The phenoxide ion obtained after the removal of a proton is stabilised by resonance whereas the ethoxide ion obtained after the removal of a proton is destabilised by '+I' effect of $-C_2H_5$ group. Therefore phenol is stronger acid than ethanol. On the other hand ethanol is weaker acid than water because electron releasing $-C_2H_5$ group in ethanol inreases the electron density on oxygen and hence the polarity of O—H bond in ethanol decreases which results in the decreasing acidic strength. Hence acidic strength increases in the order given above.

IV. Matching Type

58. (i)
$$-$$
 (d), (ii) $-$ (e), (iii) $-$ (b), (iv) $-$ (a)

60. (i)
$$-$$
(d), (ii) $-$ (a), (iii) $-$ (f), (iv) $-$ (e); (v) $-$ (c), (vi) $-$ (b)

V. Assertion and Reason Type

61. (ii)	62. (i)	63. (iv)	64. (iv)	65. (ii)	66. (iv)
67. (v)	68. (iii)	69. (ii)	70. (iv)		

VI. Long Answer Type

- 71. Consult NCERT textbook for Class XII.
- 72. Consult NCERT textbook for Class XII.
- 73. Consult NCERT textbook for Class XII.
- 74. Consult NCERT textbook for Class XII.