Alcohols, Phenols and Ethers <u>Multiple Choice Questions (Type-I)</u>

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

(i) *o*-Cresol
(ii) *m*-Cresol
(iii) 2, 4-Dihydroxytoluene
(iv) Benzyl alcohol

Ans. (iv)

Explanation: Monochlorination of toluene in sunlight gives benzyl chloride. On hydrolysis with aq. NaOH, benzyl chloride, shows nucleophilic substitution reaction to give benzyl alcohol.

2. How many alcohols with molecular formula C₄H₁₀O are chiral in nature?

- (i) 1
- (ii) 2
- (iii) 3
- (iv) 4

Ans. (i)

Explanation: If all four group or atoms attached to the carbon atom are different, such a carbon is called asymmetric carbon or chiral carbon.

3. What is the correct order of reactivity of alcohols in the following reaction? $R - OH + HCl \xrightarrow{ZnCl_2} R - Cl + H_2O$

(i) 1° > 2° > 3° (ii) 1° < 2° > 3° (iii) 3° > 2° > 1° (iv) 3° > 1° > 2°

Ans. (iii)

Explanation: This reaction is a type of nucleophilic substitution reaction in which —OH group is replaced by —Cl. The intermediate formed by tertiary alcohol is more stable as 3° carbocation is more stable than primary and secondary carbocation. Thus, the order of reactivity of alcohol will be $3^{\circ} > 2^{\circ} > 1^{\circ}$.

4. CH₃CH₂OH can be converted into CH₃CHO by ______.

- (i) catalytic hydrogenation
- (ii) treatment with LiAlH₄
- (iii) treatment with pyridinium chlorochromate
- (iv) treatment with KMnO₄

Ans. (iii)

Explanation: A better reagent for oxidation of primary alcohols to aldehydes in good yield is pyridinium chlorochromate (PCC), a complex of chromium trioxide with pyridine and HCl.

5. The process of converting alkyl halides into alcohols involves______.

(i) addition reaction

(ii) substitution reaction

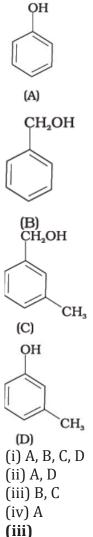
(iii) dehydrohalogenation reaction

(iv) rearrangement reaction

Ans. (ii)

Explanation: The reaction is a type of nucleophilic substitution reaction in which —Cl group is replaced by —OH.

6. Which of the following compounds is aromatic alcohol?



Ans. (iii

Explanation: Phenol is also known as, carbolic acid and it cannot be considered as aromatic alcohol. On the other hand in compound (B) and (C)—OH group is bonded to sp³ hybridized carbon which is bonded to benzene ring.

7. Give IUPAC name of the compound given below.

- (iii) 5-Chlorohexan-2-ol
- (iv) 2-Chlorohexan-5-ol
- Ans. (iii)

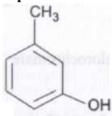
Explanation: —OH group will be given priority.

8. IUPAC name of *m*-cresol is _____.

- (i) 3-methylphenol
- (ii) 3-chlorophenol
- (iii) 3-methoxyphenol
- (iv) benzene-1,3-diol

Ans. (i)

Explanation:



IUPAC name of the compound is 3-methlyphenol.

9. IUPAC name of the compound

 $\begin{array}{c} \operatorname{CH}_{3} \longrightarrow \operatorname{CH} \longrightarrow \operatorname{OCH}_{3} \\ | & & \\ \operatorname{CH}_{3} \end{array}$ is _____.

- (i) 1-methoxy-1-methylethane
- (ii) 2-methoxy-2-methylethane
- (iii) 2-methoxypropane
- (iv) isopropyl methyl ether

Ans. (iii)

Explanation: IUPAC name of the compound is 2-methoxypropane.

10. Which of the following species can act as the strongest base?

(i)
$$^{\Theta}OH$$

(ii) $^{\Theta}OR$
(iii) $^{\Theta}OC_{6}H_{5}$
(iv) $^{\Theta}O$

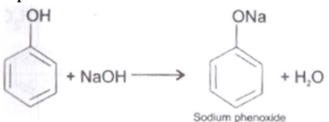
Ans. (ii)

Explanation: Weakest acid has the strongest conjugate base. Among all the four options ROH is the weakest acid.

- **11.** Which of the following compounds will react with sodium hydroxide solution in water?
 - (i) C₆H₅OH (ii) C₆H₅CH₂OH (iii) (CH₃)₃COH (iv) C₂H₅OH

Ans. (i)

Explanation:



12. Phenol is less acidic than ____

(i) ethanol

- (ii) o-nitrophenol
- (iii) *o*-methylphenol
- (iv) *o*-methoxyphenol

Ans. (ii)

Explanation: In substituted phenols, the presence of electron withdrawing group such as nitro group, enhances the acidic strength of phenol. This effect is more pronounced when such a group is present at *ortho* and *para* positons. It is due to the effective delocalisation of negative charge in phenoxide ion. On the other hand, electron releasing groups, such as alkyl groups, in general, do not favour the formation of phenoxide ion resulting in decrease in acid strength. Cresols, for example, are less acidic than phenol.

13. Which of the following is most acidic?

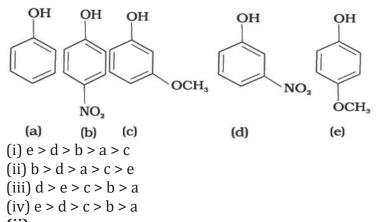
- (i) Benzyl alcohol (ii) Cyclohexanol
- (iii) Phenol

(iv) *m*-Chlorophenol

Ans. (iv)

Explanation: *m*-chlorophenol is most acidic. Alpha carbon of benzyl alcohol and cyclohexanol is *sp*³ hybridized. In *m*-chlorophenol, it is *sp*² hybridized. In *m*-chlorophenol, electron withdrawing group —Cl is present at *meta* position.

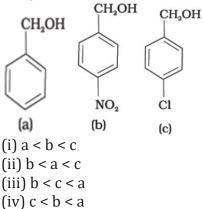
14. Mark the correct order of decreasing acid strength of the following compounds.



Ans. (ii)

Explanation: In substituted phenols, the presence of electron withdrawing group such as nitro group, enhances the acidic strength of phenol. This effect is more pronounced when such a group is present at *ortho* and *para* positons. It is due to the effective delocalisation of negative charge in phenoxide ion. On the other hand, electron releasing groups, such as alkyl groups, in general, do not favour the formation of phenoxide ion resulting in decrease in acid strength. Cresols, for example, are less acidic than phenol.

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



Ans. (iii)

Explanation: It is type of nucleophilic substitution reaction followed by S_N1 mechanism. S_N1 mechanism depends on the stability of carbocation. Presence of electron withdrawing group will decrease the stability of carbocation.

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

Ans. (i)

Explanation: The boiling points of alcohols and phenols increase with increase in the number of carbon atoms (increase in van der Waals forces.). In alcohols, the boiling points decrease with increase of branching in carbon chain (because of decrease in van der Waals forces with decrease in surface area.)

Alcohols, Phenols and Ethers <u>Multiple Choice Questions (Type-II)</u>

<u>Note:</u> In the following questions two or more options may be correct.

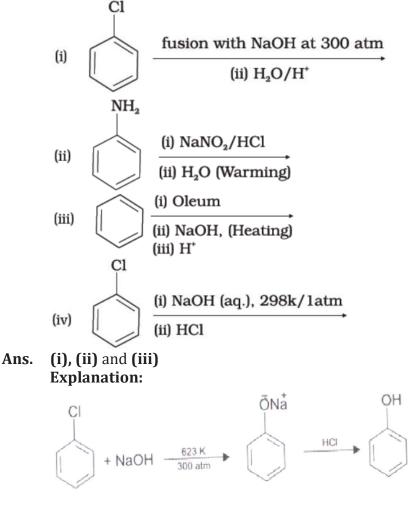
17. Which of the following are used to convert RCHO into RCH₂OH?

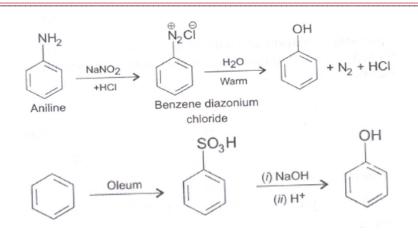
- (i) H₂/Pd
- (ii) LiAlH₄
- (iii) NaBH4
- (iv) Reaction with RMgX followed by hydrolysis

Ans. (i), (ii) and (iii)

Explanation: Aldehydes and ketones are reduced to the corresponding alcohols by addition of hydrogen in the presence of catalysts (catalytic hydrogenation. It is also prepared by treating aldehydes and ketones with sodium borohydride (NaBH₄) or lithium aluminium hydride (LiAlH₄).

18. Which of the following reactions will yield phenol?





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.

Ans. (i), (iii) and (iv)

Explanation: Strong oxidising agents such as acidified potassium permanganate are used for getting carboxylic acids from alcohols directly. CrO₃ in anhydrous medium is used as the oxidising agent for the isolation of aldehydes.

$RCH_2OH \xrightarrow{CrO_3} RCHO$

A better reagent for oxidation of primary alcohols to aldehydes in good yield is pyridinium chlorochromate (PCC), a complex of chromium trioxide with pyridine and HCl.

20. Phenol can be distinguished from ethanol by the reactions with _____.

(i) Br₂/water

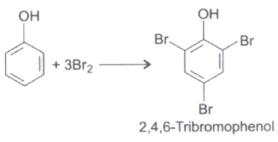
(ii) Na

(iii) Neutral FeCl₃

(iv) All the above

Ans. (i) and (iii)

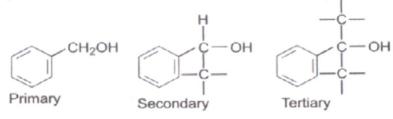
Explanation: Ethanol does not give any reaction with neutral FeCl₃ solution while phenol gives violet color with neutral FeCl₃. When phenol is treated with bromine water, 2,4,6-tribromophenol is formed as white precipitate. Ethanol does not react with bromine water.



21. 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 —CH—OH CH_3 (iv) C_6H_5 — CH_2 —CH—OH CH_3

Ans. (ii) and (iii)

Explanation: Benzylic alcohols: In these alcohols, the —OH group is attached to a sp³-hybridised carbon atom next to an aromatic ring. For example,

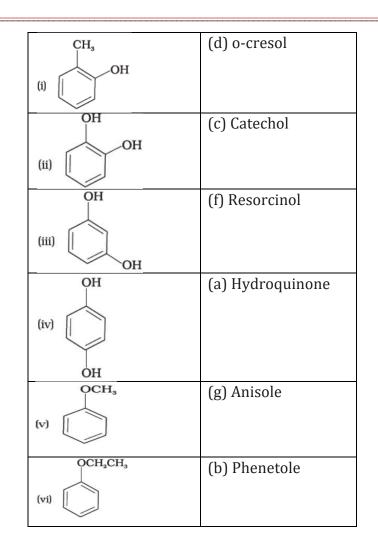


Allylic and benezylic alcohols may be primary, secondary or tertiary.

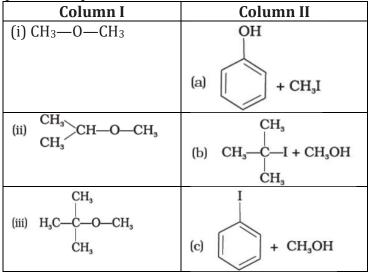
Alcohols, Phenols and Ethers <u>Matching Type</u>

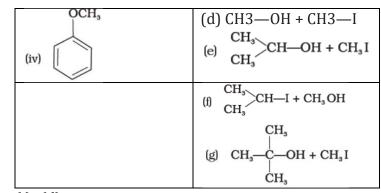
- **<u>Note:</u>** Match the items of Column I and Column II in the following questions.
- 57. Match the structures of the compounds given in Column I with the name of the compounds given in Column II.

	Column I	Column II			
	CH_3	(a) Hydroquinone			
	OH				
	(i) (ii)				
	OH	(b) Phenetole			
	OH				
	(ii)				
	OH				
		(c) Catechol			
	(iii)				
	OH				
	OH	(d) o-Cresol			
	(iv)				
	OH				
	OCH ₃	(e) Quinone			
	(v)				
	OCH ₂ CH ₃	(f) Resorcinol			
		(g) Anisole			
	(vi)				
Ans.	(i) (d)				
Alls.	(i)- (d) (ii) (c)				
	(ii)- (c)				
	(iii)- (f)				
	(iv)-(a)				
	(v)-(g)				
	(vi)-(b)				
	Explantation :				
	Column I	Column II			



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





Ans. (i)- (d)

(ii)- (e)

(iii)- (b)

(iv)- (a)

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

Column I	Column II	
(i) Antifreeze used in car engine	(a) Neutral ferric chloride	
(ii) Solvent used in perfumes	(b) Glycerol	
(iii) Starting material for picric acid	(c) Methanol	
(iv) Wood spirit	(d) Phenol	
(v) Reagent used for detection of	(e) Ethleneglycol	
phenolic group		
(vi) By product of soap industry	(f) Ethanol	
used in cosmetics		

Ans. (i)- (e)

(ii)- (f)

(iii)- (d)

(iv)- (c)

(v)- (a)

(vi)- (b)

Explanation:

(i) Ethleneglycol (IUPAC name of ethylene glycol is ethane-1,2-diol a small percentage of it is used in antifreeze formulation)

(ii) Ethanol (it is less irritating to skin so it is used in perfumes)

(iii) Phenol (by the reaction of phenol with conc. HNO₃ phenol can be converted into picric acid)

(iv) Methanol (methanol is known as wood spirit as it was obtained by destructive distillation of wood)

(v) Neutral ferric chloride (Neutral ferric chloride gives violet colour when treated with phenol)

(vi) Glycerol (it is the by product in soap industry and is used in cosmetics)

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

(i) Methanol	(a) Conversion of phenol to <i>o</i> -hydroxysalicylic acid	
(ii) Kolbe's reaction	(b) Ethyl alcohol	
(iii) Williamson's synthesis	(c) Conversion of phenol to salicylaldehyde	
(iv) Conversion of 2^0 alcohol to ketone	(d) Wood spirit	
(v) Reimer-Tiemann reaction	(e) Heated copper at 573K	
(vi) Fermentation	(f) Reaction of alkyl halide with sodium alkoxide	

Ans. (i)- (d)

(ii)- (a)

(iii)- (f)

(iv)- (e)

(v)- (c)

(vi)- (b)

Explanation:

(i) Methanol Wood spirit (methanol is known as wood spirit as it was obtained by destructive distillation of wood).

(ii) Kolbe's reaction Conversion of phenol to ortho-hydroxyl salicylic acid (reaction of phenol with CO₂ gas gives ortho-hydroxy salicylic acid)

(iii) Williamson' synthesis \rightarrow Reaction of alkyl halide with sodium alkoxide (Reaction of alkyl halide with sodium alkoxide gives ether. It is a very important method for the preparation of ether)

(iv) Conversion of 2^0 alcohol to ketone \rightarrow Heated copper at 573 K (by dehydrogenation of secondary alcohol it is converted into ketone).

(v) Reimer-Tiemann reaction \rightarrow Conversion of phenol to salicylaldehyde (phenol is treated with chloroform in presence of NaOH and salicylaldehyde is formed as the product)

(vi) Fermentation \rightarrow Ethyl alcohol (ethanol is prepared by the fermentation of sugar).

Alcohols, Phenols and Ethers <u>Assertion and Reason Type</u>

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.
- Ans. (ii)

Correct assertion: Addition reaction of water to but-1-ene in acidic medium yields butan-2-01.

Correct reason: Addition of water in acidic medium proceeds through the formation of secondary 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.

Ans. (i)

Explanation: P-nitro phenol is more acidic as nitro group helps in the stabilization of the phenoxide ion by dispersal of negative charge due to resonance.

63. Assertion: IUPAC name of the compound

 $CH_3 - CH - O - CH_2 - CH_2 - CH_3$ is 2-Ethoxy-2-methylethane.

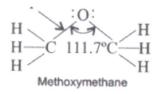
Reason: In IUPAC nomenclature, ether is regarded as hydrocarbon derivative in which a hydrogen atom is replaced by —OR or —OAr group [where R = alkyl group and Ar = aryl group]

Ans. (iv)

Explanation: Correct assertion is the IUPAC name of the compound is 1-(2-propoxy) propane.

- **64. Assertion:** Bond angle in ethers is slightly less than the tetrahedral angle. **Reason:** There is a repulsion between the two bulky (—R) groups.
- Ans. (iv)

Explanation: 141 pm



- **65. Assertion:** Boiling points of alcohols and ethers are high. **Reason:** They can form intermolecular hydrogen-bonding.
- Ans. (ii)

Explanation: Correct assertion: Boiling points of alcohols are higher than that of ethers of comparable molecular mass.

Correct reason: Alcohols can form intermolecular hydrogen bonding while ethers cannot.

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.

Ans. (iv)

Explanation: Bromination of phenol cannot be carried out in presence of Lewis acid.

- **67. Assertion:** *o*-Nitrophenol is less soluble in water than the *m* and *p*-isomers. **Reason:** *m* and *p* Nitrophenols exist as associated molecules.
- Ans. (v)

Explanation: Due to intramolecular hydrogen bonding o-Nitrophenol does not form hydrogen bond with water.

- 68. Assertion: Ethanol is a weaker acid than phenol.Reason: Sodium ethoxide may be prepared by the reaction of ethanol with aqueous NaOH.
- Ans. (iii)

Explanation: Phenoxide ion is stabilized by resonance which is not possible in alkoxide ion.

69. Assertion: Phenol forms 2, 4, 6 – tribromophenol on treatment with Br₂ in carbon disulphide at 273K.

Reason: Bromine polarises in carbon disulphide.

Ans. (ii)

Explanation: Correct assertion: Phenol on treatment with bromine water can form 2,4,6-tribromophenol

Correct reason: In water, phenol gives phenoxide ions which activate the ring towards electrophilic substitution reaction.

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.

Ans. (iv) Explanation: Phenol on treatment with dil. HNO₃ form o-nitrophenol and p-nitrophenol.

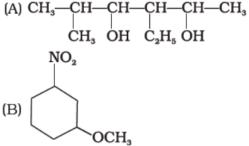
Alcohols, Phenols and Ethers <u>Short Answer Type</u>

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

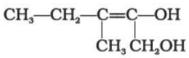
Ans.

CH₂—CH—CH₂ OH OH OH IUPAC name is propane -1,2,3-triol.

23. Write the IUPAC name of the following compounds.



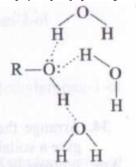
- Ans. (A) 3-Ethyl-5-methylhexan-2,4-diol,(B) 1-Methoxy-3-3nitrocyclohexan
- 24. Write the IUPAC name of the compound given below



Ans. 3-Methylpent-2-ene-1,2-diol

25. Name the factors responsible for the solubility of alcohols in water.

Ans. Solubility of alcohols and phenols in water is due to their ability to form hydrogen bonds with water molecules as shown. The solubility decreases with increase in size of alkyl/aryl (hydrophobic groups).



26. What is denatured alcohol?

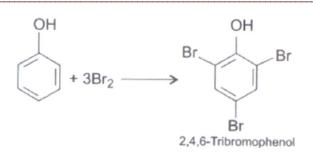
- **Ans.** The commercial alcohol is made unfit for drinking by mixing in it some copper sulphate (to give it a colour) and pyridine (a foul smelling liquid). It is known as denaturation of alcohol.
- 27. Suggest a reagent for the following conversion.



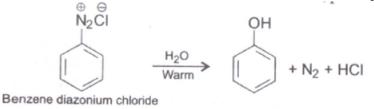
- **Ans.** Pyridinium cholochromate (PCC), a complex of chromium trioxide with pyridine and HCl CH₃—CH—CH—CH₂OH PCC CH₃—CH—CH—CHO
- 28. Out of 2-chloroethanol and ethanol which is more acidic and why?
- **Ans.** The acidic character of alcohols is due to the polar nature of O—H bond. 2-Chloroethanol, is more acidic due to –I effect of chlorine atom. It increases the polarity of O—H bond and increases the acidic strength.
- 29. Suggest a reagent for conversion of ethanol to ethanal.
- **Ans.** A better reagent for oxidation of primary alcohols to aldehydes in good yield is pyridinium chlorochromate (PCC), a complex of chromium trioxide with pyridine and HCl.
- **30.** Suggest a reagent for conversion of ethanol to ethanoic acid.
- **Ans.** Strong oxidizing agents such as acidified potassium permanganate are used for getting carboxylic acids from alcohols directly.
- 31. Out of *o*-nitrophenol and *p*-nitrophenol, which is more volatile? Explain.
- **Ans.** o-nitrophenol, due to intramolecular hydrogen bonding, is more volatile in nature. In *para*-nitrophenol, there is intermolecular hydrogen bonding.

32. Out of *o*-nitrophenol and o-cresol which is more acidic?

- **Ans.** In substituted phenols, the presence of electron withdrawing groups such as nitro group, enhances the acidic strength of phenol. This effect is more pronounced when such a group is present at ortho and para positions. It is due to the effective delocalisation of negative charge in phenoxide ion. On the other hand, electron releasing groups, such as alkyl groups, in general, do not favour the formation of phenoxide ion resulting in decrease in acid strength. Cresols, for example, are less acidic.
- 33. When phenol is treated with bromine water, white precipitate is obtained. Give the structure and the name of the compound formed.
- **Ans.** When phenol is treated with bromine water, 2,4,6 –tribromophenol is formed as white precipitate.



- 34. Arrange the following compounds in increasing order of acidity and give a suitable explanation. Phenol, *o*-nitrophenol, *o*-cresol.
- Ans. Increasing order of acidity will be o-cresol<phenol< o-nitrophenol. Explanation: In substituted phenols, the presence of electron withdrawing groups such as nitro group, enhances the acidic strength of phenol. This effect is more pronounced when such a group is present at ortho and para positions. It is due to the effective delocalization of negative charge in phenoxide ion. On the other hand, electron releasing groups, such as alkyl groups, in general, do not favour the formation of phenoxide ion resulting in decrease in acid strength. Cresols, for example, are less acidic.
- 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.
- **Ans.** Decreasing order of reactivity of sodium metal is: $1^0 > 2^0 > 3^0$
- 36. What happens when benzene diazonium chloride is heated with water?
- Ans. Benzene diazonium chloride when heated with water, phenol is formed.



- 37. Arrange the following compounds in decreasing order of acidity.
- H_2O , ROH, $HC \equiv CH$
- **Ans.** $H_2O>ROH>HC \equiv CH$
- **38.** Name the enzymes and write the reactions involved in the preparation of ethanol from sucrose by fermentation.
- **Ans.** Ethanol, C_2H_5OH , is obtained commercially by fermentation, the oldest method is from sugars. The sugar in molasses, sugarcane or fruits such as grapes is converted to glucose and fructose, (both of which have the formula $C_6H_{12}O_6$), in the presence of an enzyme, invertase.

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

Glucose Fructose

39. How can propan-2-one be converted into *tert*- butyl alcohol?

- **Ans.** Using Grignard reagent.
- 40. Write the structures of the isomers of alcohols with molecular formula C₄H₁₀O. Which of these exhibits optical activity?

Ans.
$$RCOR + R'MgX \rightarrow R - \overset{R'}{\underset{R}{\cup}} - OMgX \xrightarrow{H_2O} R - \overset{R'}{\underset{R}{\cup}} - OH + Mg(OH)X$$

 $CH_3 - CH_2 - CH_2 - CH_2 - OH$ *n*-Butyl alcohol Butan- 1- ol

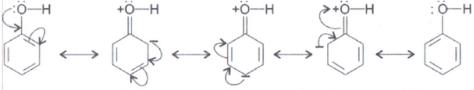
$CH_3 - CH_2 - CH_2 - CH_2 - OH$	n-Butyl alcohol	Butan- 1- ol
$CH_3 - CH - CH_2 - CH_3$	sec-Butyl alcohol	Butan-2-ol
$CH_3 - CH - CH_2 - CH_3$	Isobutyl alcohol	2-Methylpropan-1-ol
$CH_{3} - \bigcup_{\substack{l \\ CH_{3}}}^{CH_{3}} - OH$	<i>tert</i> -Butyl alcohol	2-Methylpropan-2-ol

The asymmetry of the molecule is responsible for the optical activity in a molecule. In the above structures, it is only butan-2-ol which is asymmetric because of the chiral carbon i.e. the carbon atom attached to four different substituents. Hence, it is optically active.

- 41. Explain why is OH group in phenols more strongly held as compared to OH group in alcohols.
- Ans. In phenols, the —OH group is attached to sp² hybridised carbon of an aromatic ring. The carbon- oxygen bond length (136 pm) in phenol is slightly less than that in methanol. This is due to partial double bond character on account of the conjugation of unshared electron pair of oxygen with the aromatic ring whereas in alcohols, the oxygen of the OH group is attached to carbon by a sigma bond formed by the overlap of a sp³ hybridised orbital of carbon with a sp³ hybridised orbital of oxygen. That is why —OH group in phenol is more strongly held as compared to alcohol.

42. Explain why nucleophilic substitution reactions are not very common in phenols.

Ans. The —OH group attached to the benzene ring activates it towards electrophilic substitution reaction. Also, it directs the incoming group to ortho and para positions in the ring as these positions become electron rich due to the resonance effect caused by — OH group. That is why nucleophilic substitution reaction is not common in phenol.



- 43. Preparation of alcohols from alkenes involves the electrophilic attack on alkene carbon atom. Explain its mechanism.
- Ans.

$$>C = C + H_2O \iff >C - C + H_2O \iff >C - C + H_2O \iff >C - C + H_2O + H_2O + H_2O + OH = CH_2 + H_2O \iff >C + CH_2 - CH_2 - CH_2 + CH_2O + C$$

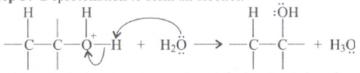
Mechanism: The mechanism of the reaction involves the following three step: Step 1: Protonation of alkene to form carbocation by electrophilic attack of H₃O⁺ $H_2O + H^+ \rightarrow H_2O^+$

$$>C = C < + H - \ddot{O} + H$$

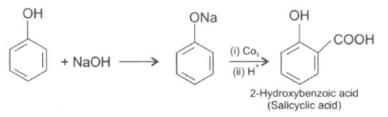
Step 2: Nucleophilic attack of water on carbocation.



Step 3: Deprotonation to form an alcohol.



44. Explain why is O=C=O nonpolar while R—O—R is polar. Ans.



45. Why is the reactivity of all the three classes of alcohols with conc. HCl and ZnCl₂ (Lucas reagent) different?

Reaction with hydrogen halides: Alcohols react with hydrogen halides to form alkyl Ans. halides.

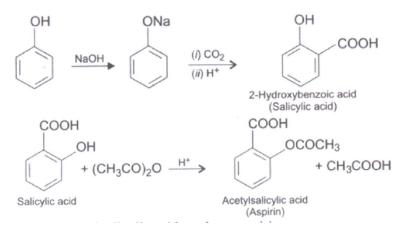
 $ROH+HX \rightarrow R-X+H_2O$

The difference in reactivity of three classes of alcohols with HCl distinguishes them from one another (Lucas test). Alcohols are soluble in Lucas reagent (conc. HCl and ZnCl₂) while their halides are immiscible and produce turbidity in solution. In case of tertiary alcohols, turbidity is produced immediately as they form the halides easily. Primary

alcohols do not produce turbidity at room temperature. The reaction is followed by the formation of carbocation since tertiary carbocation is most stable. Thus, the order of reactivity will be $3^{\circ} > 2^{\circ} > 1^{\circ}$.

46. Write steps to carry out the conversion of phenol to aspirin.

Ans.



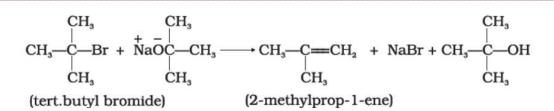
- 47. Nitration is an example of aromatic electrophilic substitution and its rate depends upon the group already present in the benzene ring. Out of benzene and phenol, which one is more easily nitrated and why?
- **Ans.** Phenol will be easily nitrated since the —OH group attached to the benzene ring activates it towards electrophilic substitution. Also, it directs the incoming group to *ortho* and *para* positions in the ring as these positions become electron rich due to the resonance effect caused by —OH group.

48. In Kolbe's reaction, instead of phenol, phenoxide ion is treated with carbon dioxide. Why?

Ans. Phenoxide ion generated by treating phenol with sodium hydroxide is even more reactive than phenol towards electrophilic aromatic substitution. Hence, it undergoes electrophilic substitution with carbon dioxide, a weak electrophile. *Ortho* hydroxybenzoic acid is formed as the main reaction product.

49. Dipole moment of phenol is smaller than that of methanol. Why?

- **Ans.** Due to electron withdrawing effect of phenyl group, the C—O bond in phenol is less polar, whereas in case of methanol the methyl group has electron releasing effect and hence C—O bond in it is more polar. Dipole moment depends upon the polarity of bonds.
- 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.
- **Ans.** In tert-butyl halides, elimination is favoured over substitution, so alkene is the only reaction product and ether is not formed.



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?

Ans. The bond angle in alcohol is slightly less than the tetrahedral angle (109° -28'). It is due to the repulsion between the unshared electron pairs of oxygen. In ethers, the four electron pairs, i.e., the two bond pairs and two lone pairs of electrons on oxygen are arranged approximately in a tetrahedral arrangement. The bond angle is slightly greater than the tetrahedral angle due to the repulsive interaction between the two bulky (—R) groups.

52. Explain why low molecular mass alcohols are soluble in water.

Ans. The low molecular mass alcohols are soluble in water due to the presence of intermolecular hydrogen bonding between their molecules. Polar O-H group favours dissolution process whereas non polar alkyl group does not. As the size of the alkyl group- increases, it overcomes the effect of the polar nature -OH group and the solubility decreases.

53. Explain why *p*-nitrophenol is more acidic than phenol.

- **Ans.** In substituted phenols, the presence of electron withdrawing groups such as nitro groups, enhances the acidic strength of phenol. This effect is more pronounced when such a group is present at *ortho* and *para* positions. It is due to the effective delocalisation of negative charge in phenoxide ion.
- 54. Explain why alcohols and ethers of comparable molecular mass have different boiling points?
- **Ans.** The high boiling points of alcohols are mainly due to the presence of intermolecular hydrogen bonding in them which is lacking in ethers.

55. The carbon-oxygen bond in phenol is slightly stronger than that in methanol. Why?

- **Ans.** C—O bond in phenols has partial double bond character due to resonance and hence is difficult to cleave.
- 56. Arrange water, ethanol and phenol in increasing order of acidity and give reason for your answer.
- **Ans.** phenol>water>ethanol

$$\underset{Base}{R-\ddot{Q}:+H-\ddot{Q}-H\rightarrow R-O_{Conjugate}-H+:\ddot{Q}H}_{Acid}$$

An alkoxide ion is a better proton acceptor than hydroxide ion, which suggests that alkoxides are stronger bases (sodium ethoxide is a stronger base than sodium hydroxide). The reaction of phenol with aqueous sodium hydroxide indicates that phenols are stronger acids than alcohol and water.

The ionisation of an alcohol and a phenol takes place as follows:

$$R - \ddot{Q} - H \rightleftharpoons R - \ddot{Q} = +H^{+}$$

In alkoxide ion, the negative charge is localised on oxygen while in phenoxide ion, the charge is delocalised. The delocalisation of negative charge (structures I-V) makes

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Alcohols, Phenols and Ethers Long Answer Type

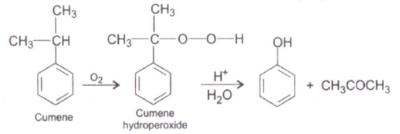
71. Write the mechanism of the reaction of HI with methoxybenzene.

Ans. In case of anisole, methylphenyl oxonium ion, is $C_6H_5 - \overset{+}{O}_{-}CH_3$ formed by protonation of

ether. The bond between O—CH₃ is weaker than the bond between O—C₆H₅ because the carbon of phenyl group is sp² hybridised and there is partial double bond character. Therefore, the attack by I⁻ ion breaks O—CH₃ bond to form CH₃I. Phenols do not react further to give halides because the sp² hybridised carbon of phenol cannot undergo nucleophilic substitution reaction needed for conversion to the halide.

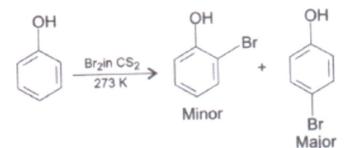
72. (a) Name the starting material used in the industrial preparation of phenol.

Ans. The starting material used in the industrial preparation of phenol is cumene.

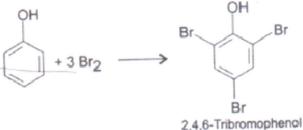


(b) Write complete reaction for the bromination of phenol in aqueous and nonaqueous medium.

Ans.



When phenol is treated with bromine water. 2,4,6-tribromophenol is formed as white precipitate:



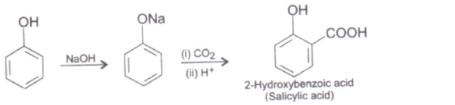
(c) Explain why Lewis acid is not required in bromination of phenol?

Ans. The usual halogenations of benzene takes place in the in presence of a Lewis acid, such as FeBr₃, 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.

73. How can phenol be converted to aspirin?

Ans.



2-hydoxybenzoic acid on treatment with acetic anhydride will give aspirin.

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

Ans. Ethanol, C₂H₅OH, is obtained commercially by fermentation, the oldest method is from sugars. The sugar in molasses, sugarcane or fruits such as grapes is converted to glucose and fructose, (both of which have the formula C₆H₁₂O₆), in the presence of an enzyme, invertase. Glucose and fructose undergo fermentation in the presence of another enzyme, zymase, which if found in yeast.

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

$$Glu \cos e + C_6H_{12}O_6$$

Fructose

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

In wine making, grapes are the source of sugars and yeast. As grapes ripen, the quantity of sugar increases and yeast grows on the outer skin. When grapes are crushed, sugar and the enzyme come in contact and fermentation starts. Fermentation takes place in anaerobic conditions i.e. in absence of air. Carbon dioxide is released during fermentation.