

CHAPTER -11 ALCOHOLS, PHENOLS AND ETHERS

Alcohols and phenols are hydroxy derivative of aliphatic hydrocarbon and benzene respectively

Type of alcohol

Primary	-OH group is attached to primary Carbon
Secondary	-OH group is attached to secondary Carbon
Tertiary	-OH group is attached to tertiary Carbon
Monohydric	1 -OH group
Dihydric	2 -OH groups
Trihydric	3 -OH groups
Polyhydric	More than 3 -OH groups

Ethers are classified on the basis of groups attached to the oxygen atom. Symmetrical ethers have same alkyl group on either side of the ethereal oxygen group

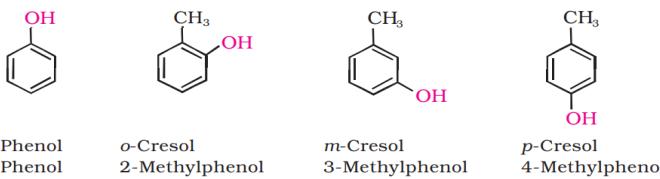
Nomenclature

The name of an alcohol is derived from the name of the alkane from which the alcohol is derived, by substituting 'e' of alkane with the suffix 'ol'. The position of substituents are indicated by numerals

Ethers are named as alkoxy alkane. The larger alkyl group is chosen as the parent hydrocarbon.e.g.

Compound	Common name	IUPAC name
CH ₃ -CH ₂ -CH ₂ -OH	n-Propyl alcohol	Propan-1-ol
CH ₃ -CH(OH)-CH ₃	Isopropyl alcohol	Propan-2-ol
CH ₃ OCH ₃	Dimethyl Ether	Methoxymethane
CH ₃ OCH ₂ CH ₂ CH ₃	Methyl n-propyl ether	1-Methoxypropane

Phenol involves a benzene ring, in its substituted compounds the terms ortho (1,2-disubstituted), meta (1,3-disubstituted) and para (1,4-disubstituted) are often used in the common names.e.g.



Preparation

Alcohols may be prepared (1) by hydration of alkenes (i) in presence of an acid and (ii) by hydroboration-oxidation reaction (2) from carbonyl compounds by (i) catalytic reduction and (ii) the action of Grignard reagents.

Phenols may be prepared by (1) substitution of (i) halogen atom in haloarenes and (ii) sulphonic acid group in aryl sulphonic acids, by -OH group (2) by hydrolysis of diazonium salts and (3) industrially from cumene.

Alcohols and phenols are acidic in nature. **Electron withdrawing groups** in phenol increase its acidic strength and **electron releasing groups** decrease it. Alcohols undergo Nucleophilic substitution with hydrogen halides to yield alkyl halides. Dehydration of alcohols gives alkenes. On oxidation, primary alcohols yield aldehydes with mild oxidizing agents and carboxylic acids with strong oxidizing agents while secondary alcohols yield ketones. Tertiary alcohols are resistant to oxidation.

The presence of -OH group in phenols activates the aromatic ring towards

Uses of methanol, ethanol, phenol and ether:

Methanol is used as a solvent in paints, varnishes and chiefly for making formaldehyde.

- Ethanol is used as a solvent in paint industry and in the preparation of a number of carbon compounds. In industry, phenol is used as a starting material to make plastics, explosives such as picric acid, and drugs such as aspirin. Phenols are widely used in household products and as intermediates for industrial synthesis.

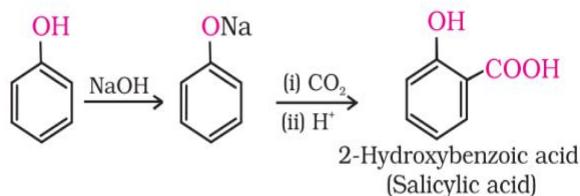
For example, phenol itself is used (in low concentrations) as a disinfectant in household cleaners and in mouthwash. Phenol may have been the first surgical antiseptic.

Vapours of certain ethers are used as insecticides and fumigants for soil.

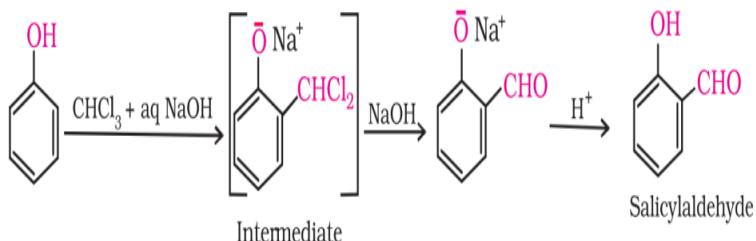
Ethers are also important in medicine and pharmacology, especially for use as anesthetics.

Name Reactions

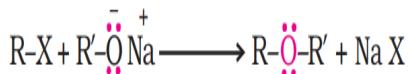
Kolbe's reaction



Reimer-Tiemann reaction



Williamson synthesis



Distinguish test for alcohol and phenols

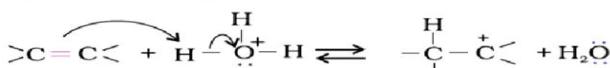
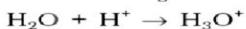
TEST	OBSERVATIONS	RESULT
1. LUCAS REAGENT TEST- Add $\text{ZnCl}_2 + \text{HCl}$ in the given organic compound	-Turbidity appears immediately -Turbidity appears after 5 min -Turbidity appears on heating	3° Alcohol 2° Alcohol 1° Alcohol
2. NEUTRAL FERRIC CHLORIDE TEST- Add Neutral ferric Chloride solution in Organic Compound	-Violet colour appears	- Phenol
3. LITMUS TEST- Add few drops of blue litmus solution in organic compound	-Blue litmus turns red	-Phenol

Mechanisms-

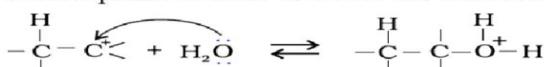
Hydration of alkene

The mechanism of the reaction involves the following three steps:

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



Step 2: Nucleophilic attack of water on carbocation.



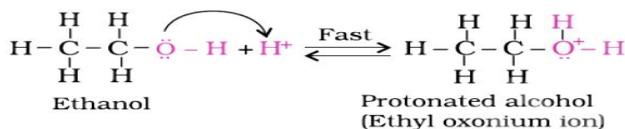
Step 3: Deprotonation to form an alcohol.



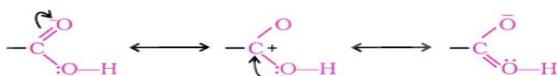
Dehydration of alcohol to give alkene

Mechanism

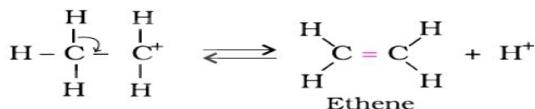
Step 1: Formation of protonated alcohol.



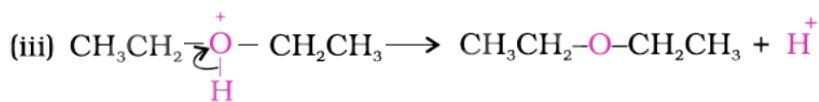
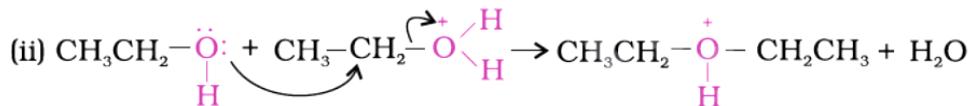
Step 2: Formation of carbocation: It is the slowest step and hence, the rate determining step of the reaction.



Step 3: Formation of ethene by elimination of a proton.



Dehydration of alcohols to give ether



MULTIPLE CHOICE QUESTIONS

- Q1. Which of the following has lowest boiling point?
(a) p-Nitrophenol (b) m-Nitrophenol
(c) o-Nitrophenol (d) Phenol
- Q2. Amongst the following alcohols which would react fastest with conc. HCl and ZnCl₂?
(a) pentan-1-ol (b) 2-methyl butan-1-ol
(c) pentan-2-ol (d) 2-methyl butan-2-ol
- Q3. Rate of dehydration of alcohols follows the order:
(a) $2^\circ > 1^\circ > \text{CH}_3\text{OH} > 3^\circ$ (b) $3^\circ > 2^\circ > 1^\circ > \text{CH}_3\text{OH}$
(c) $2^\circ > 3^\circ > 1^\circ > \text{CH}_3\text{OH}$ (d) $\text{CH}_3\text{OH} > 1^\circ > 2^\circ > 3^\circ$
- Q4. Phenol on heating with CHCl₃ and NaOH gives salicylaldehyde. The reaction is called :
(a) Reimer-Tiemann reaction (b) Gatterman-Koch reaction
(c) Cannizzaro's reaction (d) Hell-Volhard-Zelinsky reaction
- Q5. Which of the following ether cannot be prepared by Williamson's synthesis
(a) Ethyl methyl ether (b) Dimethyl ether
(c) Methyl phenyl ether (d) Di-tert.-butyl ether
- Q6. Which of the following is used for denaturation of commercial alcohol
(a) Copper sulphate (b) Pyridine
(c) Methyl alcohol (d) All of the above
- Q7. The alcohol which is also known as wood spirit is:
(a) Methanol (b) Ethanol
(c) Propanol (d) Butanol
- Q8. Find out correct order of acidic strength among the following
(a) Ethanol > Water > Phenol (b) Ethanol < Water < Phenol
(c) Water < Ethanol < Phenol (d) Phenol > ethanol = Water
- Q9. Monochlorination of toluene in sunlight followed by hydrolysis with aq. NaOH yields.
(a) o-Cresol (b) p-Cresol
(c) 2, 4-Dihydroxytoluene (d) Benzyl alcohol
- Q10. The process of converting alkyl halides into alcohols involves.
(a) addition reaction (b) substitution reaction
(c) dehydrohalogenation reaction (d) rearrangement reaction

ASSERTION AND REASON TYPE QUESTIONS

In the following questions 11 to 20, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices

- (A) Assertion and reason are true and reason is the correct explanation of assertion
(B) Assertion and reason both are true but reason is not correct explanation of the assertion
(C) Assertion is true reason is false
(D) Assertion is false reason is true

Q11. Assertion: Phenols are more acidic than aliphatic alcohols.

Reason: The phenoxide ion is more resonance stabilised than alkoxide ion.

Q12. Assertion: Tertiary alcohols gets converted into an alkene instead of a carbonyl Compounds in the presence of heated metallic copper.

Reason: Tertiary alcohols prefer to undergo dehydrogenation instead of dehydration in the presence of heated copper.

Q13. Assertion: Ethers are non-polar when they are symmetrical.

Reason: Ethers have a bent structure.

Q14. Assertion: n-Butanol has higher boiling point than 2-methyl propan-2-ol.

Reason: Branching increases the strength of van-der-Waal's forces.

Q15. Assertion: It is not possible to prepare anisole from chlorobenzene through Williamson's synthesis.

Reason: The C-Cl bond in chlorobenzene shows partial double bond character due to resonance

Q16. Assertion: Nitro phenol has lower pKa value than phenol.

Reason: The electron withdrawing nature of the nitro group further stabilises the phenoxide ion formed.

Q17. Assertion: Anisole reacts with HI to give phenol and chloromethane.

Reason: The $-\text{OCH}_3$ group in anisole enriches the electron density in the ring through Resonance

Q18. Assertion: It is not possible to purify alcohol beyond 95% purity by simple distillation.

Reason: The intermolecular hydrogen bond in alcohol decreases the boiling point of 95% alcohol.

Q19. Assertion: Ethanol can be distinguished from methanol using iodoform test.

Reason: Methanol has a methyl group attached to a carbon containing hydroxyl groups

Q20. Assertion: Methanol is called wood spirit.

Reason: Methanol can be prepared by the destructive distillation of fresh wood

2 Marks Questions

Q21. Write the mechanism of hydration of ethene to yield ethanol.

Q22. Account for the following:

(i) Propanol has higher boiling point than butane.

(ii) Ortho-nitrophenol is more acidic than ortho-methoxyphenol.

Q23. Di-phenyl ethers can not be synthesised by williamson's ether synthesis. Explain.

Q24. Phenols do not undergo nucleophilic substitution easily.

Q25. Water is more acidic than alcohol. Give reason.

3 Marks Questions

Q26. Out of o-nitrophenol and p-nitrophenol, which is more volatile? Explain.

Q27. Name the reagents used in the following reactions:

(i) Oxidation of a primary alcohol to aldehyde.

(ii) Bromination of phenol to p-bromophenol.

(iii) Butan-2-one to butan-2-ol

Q28. Explain the following with an example.

(i) Kolbe's reaction. (ii) Reimer-Tiemann reaction. (iii) Williamson synthesis.

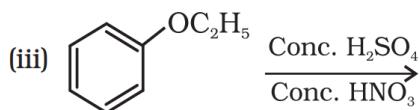
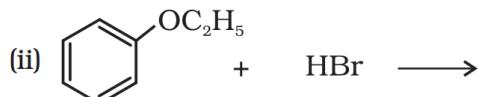
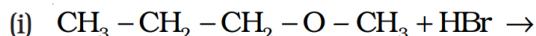
Q29. How do you convert the following?

(i) Phenol to anisole

(ii) Propan-2-ol to 2-methylpropan-2-ol

(iii) Aniline to phenol

Q30. Predict the product of the following reactions.



CASE BASED QUESTIONS

Q 31. Read the given passage and answer the questions that follow:

Alcohols and phenols are most important compounds used in our daily life. Alcohols are prepared by hydration of alkenes, fermentation of glucose, reduction of aldehydes, ketones, carboxylic acids and esters. Alcohols are soluble in water. Boiling points increase with increase in molar mass and decrease with branching. Alcohols on dehydration gives alkene at 443K, follow carbocation mechanism. Excess of alcohol at 413K on dehydration with conc. H_2SO_4 also follow carbocation mechanism but gives diethyl ether. Alcohols undergo nucleophilic substitution reactions, esterification with carboxylic acids and derivatives like amides, acid halides, acid anhydride. Phenol is prepared from cumene, diazonium salts, anisole, chlorobenzene. Phenol is used to prepare salicylaldehyde, salicylic acid, aspirin, methyl salicylate, p-benzoquinone. Phenol undergoes electrophilic substitution reaction at o & p-position. Ethers are functional isomers of alcohols, have low boiling points. Ethers are used as solvents. Unsymmetrical ethers are prepared by Williamson synthesis. Ethers react with HI and undergo SN^1 or SN^2 mechanism depending upon stability of carbocation formed. Aromatic ethers like anisole undergoes electrophilic substitution at o & p-position.

(a) Out of tert- butyl alcohol and n-butanol, which will undergo dehydration faster and why?

(b) Convert phenol to p-benzoquinone.

(c) Why is C—OH bond length in CH_3OH longer than C—OH bond length in phenol?

(d) Why is ROH bond angle in alcohol less than tetrahedral bond angles?

Q,32. Observe the following table showing boiling points of alcohol, molar mass. Study the table and answer the questions based on table and related studied concept.

Compound	pKa
Ethanol	15.9
Phenol	9.98
<i>o</i> -cresol	10.28
<i>p</i> -cresol	10.14
<i>m</i> -cresol	10.08
<i>o</i> -nitro phenol	7.23
<i>p</i> -nitro phenol	7.15
<i>m</i> -nitro phenol	8.40
2, 4-dinitro phenol	4.0
Picric acid	0.71
<i>m</i> -methoxy phenol	9.65
<i>o</i> -methoxy phenol	9.96
<i>p</i> -methoxy phenol	10.21
<i>m</i> -amino phenol	9.87

(a) Which phenolic compound is most acidic?

(b) What is relationship between pKa and acidic character?

(c) Why are cresols weaker acids than phenol?

(d) Why is o-fluoro phenol weakest acid than p-and m-fluoro phenol?

5 Marks Questions

Q33.(a) Give chemical tests to distinguish between the following pairs of compounds.

(i) Pentan-2-ol and Pentan-3-ol

(ii) Methanol and Phenol

(b) o-nitro phenol is more acidic than o-methoxy phenol. Explain why.

(c) Arrange the following sets of compounds in order of their increasing boiling points:

(i) Pentan-1-ol, butan-1-ol, butan-2-ol, ethanol, propan-1-ol, methanol.

(ii) Pentan-1-ol, n-butane, pentanal, ethoxyethane.

Q34. (a) How are the following conversions carried out?

- (i) Propene → Propan-2-ol.
- (ii) Benzyl chloride → Benzyl alcohol.
- (iii) Methyl magnesium bromide → 2-Methylpropan-2-ol.

(b) Give reasons for the following :

- (i) Boiling point of ethanol is higher in comparison to methoxymethane
- (ii) Alcohols are more soluble in water than the hydrocarbons of comparable molecular masses.

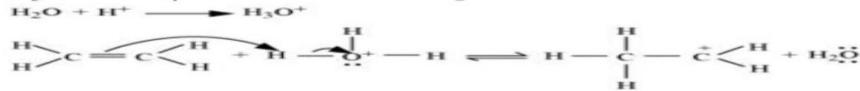
Answer Key

Q1-C	Q2-D	Q3-B	Q4-A	Q5-D
Q6-D	Q7-A	Q8-B	Q9-D	Q10-B
Q11-A	Q12-C	Q13-D	Q14-C	Q15-A
Q16-A	Q17-B	Q18-C	Q19-C	Q20-A

Q21-

The mechanism of the reaction involves the following three step:

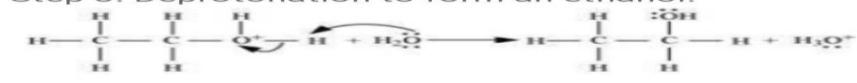
Step 1: Protonation of ethene to form carbocation by electrophilic attack of H_3O^+ .



Step 2: Nucleophilic attack of water on carbocation.



Step 3: Deprotonation to form an ethanol.



Q22(i) This is due to the presence of intermolecular hydrogen bonding. In propanol

(ii) In ortho nitro phenol, electron withdrawing nitro group is present in ortho position decreases the electron density of Oxygen in $-\text{OH}$. As a result it is easier to lose a proton.

Q23. Aryl halide do not undergo nucleophilic substitution easily due to partial double bond character in C-X bond of Aryl halide

Q24. The C – O bond in phenols has some double bond character due to resonance and hence cannot be easily cleaved by nucleophile. So, nucleophilic substitution reactions are not very common in phenols and they give many electrophilic substitution reactions

Q25. Because in alkoxide ion accept proton more easily and shift the equilibrium in backward direction

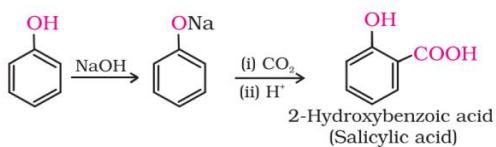
Q26 Ortho nitrophenol is much more volatile in steam due to chelation. Intramolecular hydrogen bonding is present in o-nitrophenol and intermolecular hydrogen bonding in p-nitrophenol.

Q27 (i) $\text{CrO}_3\text{-H}_2\text{SO}_4$

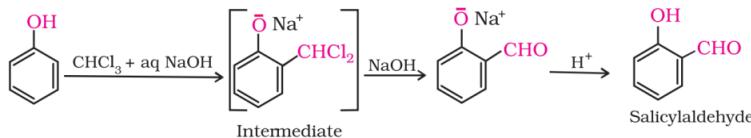
(ii) Br_2 in CS_2

(iii) NaBH_4 or Ni/H_2

Q28 (i) Kolbe's Reaction



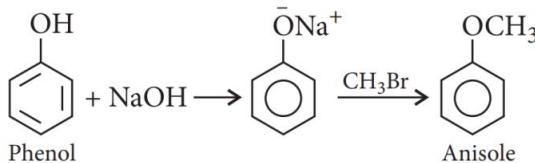
(ii) Reimer-Tiemann reaction



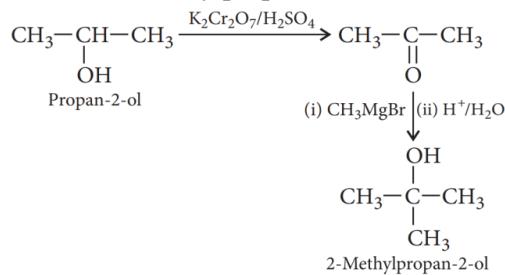
(iii) Williamson synthesis



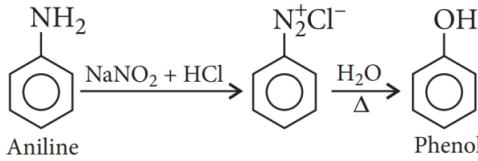
Q.29 (i) Phenol to anisole



(ii) Propan-2-ol to 2-methylpropan-2-ol



(iii) Aniline to phenol



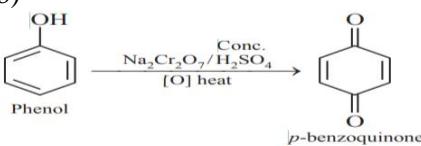
Q.30 (i) $\text{CH}_3\text{CH}_2\text{CH}_3\text{OH}$ & CH_3Br

(ii) $\text{C}_6\text{H}_5\text{OH}$ & $\text{C}_2\text{H}_5\text{Br}$

(iii) $p\text{-NO}_2\text{C}_6\text{H}_4\text{C}_2\text{H}_5$

Q.31 (a) Tertiary butyl alcohol will undergo dehydration faster because 3° carbocation is more stable

(b)



(c) It is due to resonance in phenol, there is double bond character in C—O bond, therefore shorter than single bond in methanol.

(d) It is due to repulsive interaction between two lone pair of electrons in alcohol.

Q32. (a) Picric acid

(b) Lower the pK_a , more will be acidic character.

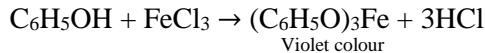
(c) It is because $-\text{CH}_3$ groups are electron releasing, destabilise phenoxide ion

(d) It is because in o-fluoro phenol, there is strong intramolecular H-bonding

Q33. a (i) By Iodoform test-

Pentan-2-ol gives yellow ppt in iodoform test & pentan-3-ol will not respond this test.

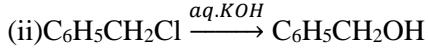
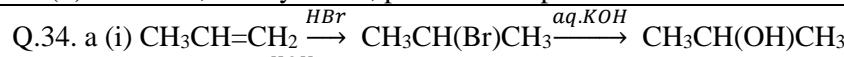
(ii) Phenol with neutral FeCl_3 gives violet colour but methanol does not respond to this test.



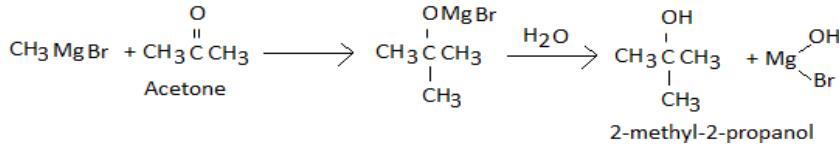
(b) Due to the electron withdrawing nature of nitro group it form stable nitro phenoxide ion as compare to the methoxy phenoxide ion nitrophenol is more acidic.

(c) (i) Methanol, ethanol, propan-1-ol, butan-2-ol, butan-1-ol, pentan-1-ol.

(ii) n-Butane, ethoxyethane, pentanal and pentan-1-ol.



(iii)



b (i) Due to intermolecular hydrogen bonding in ethanol.

(ii) Due to intermolecular hydrogen bonding between alcohol & water molecules.