

CHAPTER - 11

ALCOHOLS, PHENOLS AND ETHERS

Alcohols \rightarrow R-OH Phenols - OH Ethers \rightarrow R-O-R Monohydric alcohols \rightarrow compounds containing C_{sp3}-OH bond \rightarrow

Primary alcohol (R-CH₂-OH), secondary alcohol (R₂CH-OH), tertiary alcohol (R₃C-OH)

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Allylic alcohols

Benzylic alcohol

Depending on the number of hydroxyl groups attached, alcohols can be classified into three types.

- **Monohydric alcohols:** They contain one -OH group. Example, CH₃CH₂-OH
- **Dihydric alcohols:** They contain two -OH groups. Example, 1,2-Ethandiol.
- **Trihydric alcohols:** They contain three -OH groups. Example 1,2,3-Propantriol.

сн _а — сн ₂ —сн ₂ но	сн,- но	-сн₂ но		сн₂— но	сн₂—сн₂ но
Propanol	1, 2-Eti	nandiol		1, 3 -P	ropandiol
сн₂— сн — сн₂ но но но		сн,– но	-сн- но	-сң — но	CH2
1, 2, 3-Propantriol		1	, 2, 3-B	utantriol	

Depending on the number of carbon atoms which are directly attached to the carbon that is bonded with the -OH group, alcohols can be classified into three types.

Primary alcohol - Primary alcohols are those alcohols where the carbon atom of the hydroxyl group (OH) is attached to only one single alkyl group. Some examples of these primary alcohols include Methanol (propanol), ethanol, etc. The complexity of this alkyl chain is unrelated to the classification of any alcohol considered as primary. The existence of only one linkage among –OH group and an alkyl group and the thing that qualifies any alcohol as a primary.

Secondary alcohol - Secondary alcohols are those where the carbon atom of the hydroxyl group is attached to two alkyl groups on either side. The two alkyl groups present may be either structurally identical or even different.

Tertiary Alcohol - Tertiary alcohols are those which feature a hydroxyl group attached to the carbon atom which is connected to 3- alkyl groups. The physical properties of these alcohols mainly depend on their structure. The presence of this -OH group allows the alcohols in the formation of hydrogen bonds with their neighbouring atoms. The bonds formed are weak, and this bond makes the boiling points of alcohols higher than its alkanes.



In phenols -Or group is connected to sp² hybridised carbon. It can also be monohydric, dihydric etc. dihydric phenol into ortho, meta or para derivative.



In allylic alcohols, -OH group is attached to sp^3 hybridised carbon but close to C = C bond.

CH₂ = CH-CH₂OH, Benzylic alcohol (C₆H₅CH₂OH)

Nomenclature of Alcohols

Alcohols are of three major classes. They are:

Mono	hvdı	ic A	co	hol
1.10110				

Dihydric Alcohol

Trihydric Alcohol

We will now discuss the nomenclature of these alcohols.

(1) Monohydric Alcohol

Monohydric alcohols have the general formula $C_nH_{2n+1}OH$ where n = 1, 2, etc. We can also represent them as R-OH where R describes an alkyl group. There are three systems for the nomenclature of Monohydric Alcohol.

<u>**Common System</u>**: In this system, we name the monohydric alcohols as Alkyl Alcohol. We get their names by adding the name alcohol after the name of the alkyl group present in the molecule.</u>

Example

The compound CH₃-OH has one methyl group with an alcohol group. Hence, we call it Methyl Alcohol.

<u>Carbinol System</u>: In this system, methyl alcohol (CH₃OH) gets the name Carbinol while other alcohols get their names

as alkyl or aryl derivatives of carbinol. Example: CH₃-CH₂-OH is methylcarbinol and CH₃-CH₂-CH₂-OH is Ethylcarbinol.

IUPAC System: In IUPAC nomenclature, we term the alcohols as Alkanols. We get the name of any alcohol by replacing the last 'e' from the name of the corresponding alkane by the suffix '-ol'. Then, we select the longest carbon chain containing the OH group as the parent chain. We, then, number the longest chain in such a way that the carbon atom carrying the OH group gets the smaller number. After this, we show the position of the substituents by suitable numbers allotted to their respective carbon atom.

Example

The compound CH3-OH is Methyl Alcohol but in the IUPAC, we call it as Methanol. Here, we replace the last 'e' of the methane by 'ol' which indicates the presence of an alcohol group. In the naming of the Cyclic monohydric alcohols prefix, 'cyclo' is used in writing the common or the IUPAC names of the straight chain alcohols

2) Dihydric Alcohol

Dihydric alcohols have the general formula of $(CH_2)_n(OH)_2$, where n= 2,3,4.... etc. Because of their sweet taste, we refer to them as Glycols. Depending upon the relative position of the two hydroxyl group, we can classify them as α , β , Υ ω glycols, etc. Let us look at the system of their nomenclature.

Common System: In common system, we name the α -glycols by adding the word Glycol after the name of the alkene. In contrast β , Υ ... ω – glycols get their names as the corresponding polymethylene glycols. Example:

HO-CH₂CH₂CH₂-OH

HO-CH₂CH₂CH₂CH₂CH₂-OH

Trimethylene glycol (Aβ-glycol)

pentamethylene glycol

IUPAC system: In this system, we name the glycols as Diols and their class name is Alkanediols. We use Arabic numerals to indicate the two hydroxyl group positions.



3) Trihydric Alcohol

The general formula of trihydric alcohols is $(CH_2)_n(OH)_3$ where n = 3, 4, 5 ...etc. In this system, we do not have any general rule of nomenclature. So, there is only one IUPAC rule. In this IUPAC system of trihydric alcohol, we call them as Alakanetriols. We use Arabic numerals to indicate the position of the OH group.

Compound	Common name	IUPAC name
$\begin{array}{l} \mathbf{CH}_3-\mathbf{OH}\\ \mathbf{CH}_3-\mathbf{CH}_2-\mathbf{CH}_2-\mathbf{OH}\\ \mathbf{CH}_3-\mathbf{CH}-\mathbf{CH}_3\\ \mathbf{I} \end{array}$	Methyl alcohol n-Propyl alcohol Isopropyl alcohol	Methanol Propan-1-ol Propan-2-ol
$CH_3 - CH_2 - CH_2 - CH_2 - OH$ $CH_3 - CH - CH_2 - CH_3$	n-Butyl alcohol sec-Butyl alcohol	Butan-1-ol Butan-2-ol
OH CH ₃ – CH – CH ₂ – CH ₃ I OH	Isobutyl alcohol	2-Methylpropan-1-ol
$CH_{3} - C - OH$ I $CH_{3} - C - OH$	<i>tert-</i> Butyl alcohol	2-Methylpropan-2-ol
$\begin{array}{ccc} CH_2-CH-CH_2\\ I&I\\ OH&OH&OH \end{array}$	Glycerol	Propane -1, 2, 3-triol

Nomenclature of Phenols

The simplest derivative of benzene is Phenol. It is the common name as well as an accepted IUPAC name. Both in the common and in the IUPAC system, we name the substituted phenols as the derivatives of phenols.

In the common system, we indicate the substituent position present on the benzene ring with respect to -OH group by adding the prefix such as ortho (o-) for 1:2, meta (m-) for 1,3 and para (p-) for 1,4.

However, in the IUPAC system, we use Arabic numerals to indicate the position of the substituent w.r.t –OH group. The carbon carrying the OH group gets the number 1. The phenols having a carbonyl group such as aldehyde, ketonic, carboxyl or an ester group get their names as hydroxyl derivatives of the parent aromatic compound.

Structure	Common name	IUPAC name
o-	Phenol	Phenol (Benzenole)
OH CH ₃	o-cresol	2-methylphenol
OH CH ₃	m-cresol	3-methylphenol
OH → → → → → → → → → → → → →	p-cresol	4-methylphenol
ОНОН	Catechol	2-hydroxyphenol



Nomenclature of Ethers

Common System: We get the common names of ethers by naming the two alkyl or aryl groups linked to the oxygen atom as separate words in alphabetical order and adding the word ether. In case of symmetrical ethers, we use the prefix di before the name of the alkyl or the aryl group.

IUPAC system: In the IUPAC system, ethers are Alkoxyalkanes. The ethereal oxygen is taken with the smaller alkyl group and forms a part of the alkoxy group. On the other hand, the larger alkyl group is taken to be the part of the alkane.

Compound	Common name	IUPAC name
CH3OCH3	Dimethyl ether	Methoxymethane
$C_2H_5OC_2H_5$	Diethyl ether	Ethoxyethane
CH ₃ OCH ₂ CH ₂ CH ₃	Methyl n-propyl ether	1-Methoxypropane
C ₀ H ₅ OCH ₃	Methyl phenyl ether (Anisole)	Methoxybenzene (Anisole)
C ₆ H ₅ OCH ₂ CH ₃	Ethyl phenyl ether (Phenetole)	Ethoxybenzene
$C_6H_5O(CH_2)_6-CH_3$	Heptyl phenyl ether	1-Phenoxyheptane
CH ₃ O-CH-CH ₃ I CH ₃	Methyl isopropyl ether	2-Methoxypropane
$C_{e}H_{3}$ -O-CH ₂ -CH ₂ -CH ₂ -CH ₃	Phenyl isopentyl ether	3- Methylbutoxybenzene
$CH_{3^{-}} O - CH_2 - CH_2 - OCH_3$	_	1,2-Dimethoxyethane
H _s C CH _s OC ₂ H _s	_	2-Ethoxy- -1,1-dimethylcyclohexane



Sol. (i) 4-Chloro-2,3-dimethylpentan-1-ol (ii) 2-Ethoxypropane (iii) 2,6-Dimethylphenol (iv) 1-Ethoxy-2-nitrocyclohexane

Alcohol Preparation

(i) From alkenes

Q.

By acid catalysed hydration in accordance with Markownikoff law.



Mechanism: There are three steps in the mechanism of acid catalysed hydration of an alkene to form corresponding alcohol.

Step 1: Carbocation formation and carbocation is formed by attack of H_3O^+ .

Step 2: Nucleophile H₂O attacks on carbocation.

Step 3: Deprotonation to form alcohol H⁺ will be eliminated.



By hydroboration-oxidation



Propan-1-ol

(ii) From carbonyl compounds By reduction of aldehydes and ketones

$$\begin{array}{c} R-CHO \xrightarrow{H_2/(Ni \text{ or } Pt)} R-CH_2OH \\ \text{Aldehyde} \xrightarrow{LiAlH_4/NaBH_4} R^- CH_2OH \\ \end{array}$$

$$CH_3 - CHO \longrightarrow CH_3 - CH_2OH$$

Ethanal

Ethanol

Aldehydes produce the primary alcohol while ketones provide the secondary alcohol, when reduced.

By reduction of carboxylic acids and esters

$$\begin{array}{c} 0 \\ R = C - OH \\ \hline 2. \quad Dilute sulfuric acid \\ \hline 2. \quad Dilute sulfuric acid \\ \hline 3. \quad Dilute sulfur cache \\$$

If we take secondary alcohol than secondary alcohol potassium halide and traces of alkenes is formed.

Example: If we take tertiary alkyl halide then on reacting with KOH we get alkene as major product and potassium halide.

$$CH_3 C(CH_3)_2Br + (aq.)KOH \rightarrow CH_2-CH_2-CH_3 + KBr | CH_3 C(CH_3)_2Br + (aq.)KOH \rightarrow CH_2-CH_3 + CH_3 + CH$$

(iv) Preparation from Grignard reagent

(a) The Grignard reagent reacts with formaldehyde to form primary alcohol.



Please remember whenever Grignard reagent reacts with formaldehyde it forms primary alcohol. When Grignard reagent reacts with any other alcohol it forms secondary alcohol

(v) Hydrolysis of ethers



(vi) From the primary amines - by treatment with nitrous acid



Industrial preparation of alcohol is by two methods: Hydration of alkene and fermentation of sugar (used in breweries)

Fermentation - Breakdown of complex substance into simple substance by action of enzymes released by anaerobic bacteria.

By this method we can prepare only ethanol.

In this firstly the sugarcane juice and water are mixed and heated to form sweet liquid called molasses.

Then in presence of yeast and enzyme invertase it breaks in to glucose and fructose and then further glucose and fructose break into further simpler substances called ethanol and carbon dioxide. This method is generally carried out in breweries.

Sugarcane juice + H₂O —keer→, molasses

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

(Sucrose) (invertase) (Glucose) fructose

 $C_6H_{12}O_6 \rightarrow C_2H_5OH + Co_2$

(zymase) (Ethanol)

Preparation of Phenols (i) From haloarenes



(ii) From Benzene sulphonic acid



(iii) From diazonium salts





Physical properties of alcohol

•	They are	usually	liquid at ro	oom temperature.	
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- They do not emit smoke when they are burning.
- They are flammable and produce a blue flame.
- They usually give off a pleasant aroma without glycerol and a few alcoholic beverages.
- Alcohol is colourless.

State of existence: Lower members are colourless liquids with characterize smell. Higher members with more than 12 carbons are solid.

Boiling point: They have high boiling points due to hydrogen bonding.

If we compare their boiling points with hydrocarbons they will possess higher boiling point because of existence of hydrogen bonds in them due to which they occur at associated molecules.



Note

Boiling point increase with increase in carbons in chain: As no. of carbon atoms increases Vander wall force increases hence boiling point increases

Example

$CH_3CH_2CH_2OH < CH_3CH_2CH_2CH_2OH$

The Second compound will definitely have the higher boiling point as it has more number of carbon atoms.

Boiling point decreases with branching: as surface area gets reduced therefore Vander wall force decrease and boiling point also decreases.

Example: The one degree will have higher boiling point as it has more surface area.

С

CH₃

CH₃CH₂OH

CH3

Solubility: They are soluble in water due to formation of hydrogen bonds in them .However solubility decreases with increase in number of carbon atoms in chain as non-polar part increases therefore solubility decreases.



The second one will have lower solubility because the nonpolar part is more in it.

Physical properties of phenols

(1) The Boiling Point of Phenols

Phenols generally have higher boiling points in comparison to other hydrocarbons with equal molecular masses. The main reason behind this is the presence of intermolecular hydrogen bonding between hydroxyl groups of phenol molecules. In general, the boiling point of phenols increases with increase in the number of carbon atoms.

(2) The Solubility of Phenols

The hydroxyl group determines the solubility of phenol in water. The hydroxyl group in phenol is responsible for the formation of intermolecular hydrogen bonding. Thus, hydrogen bonds form between water and phenol molecules which make phenol soluble in water.

(3) The Acidity of Phenols

Phenols react with active metals such as sodium, potassium etc. and give the corresponding phenoxide. These reactions of phenols indicate its acidic nature. In phenol, the sp2 hybridized carbon of the benzene ring attached directly to the hydroxyl group acts as an electron withdrawing group.

Thus, it decreases the electron density of oxygen. Due to the delocalization of negative charge in the benzene ring, phenoxide ions are more stable than alkoxide ions. Therefore, we can say phenols are more acidic than alcohols.

Chemical reaction of alcohol

Alcohol is most versatile organic compound. They can behave in different manner to give different reaction. Three type of reaction we will study

- Alcohol behaves as nucleophiles They are electron rich species
 R-O-H → RO⁻ + H (Acidic character is also shown) alkoxide
- Alcohols behave as electrophile Electron deficient Carbocation is formed R-OH → R⁺ + OH⁻

Acidity of alcohols and phenols

Reaction with metals: Alcohols and phenols react with active metals such as sodium, potassium and aluminium to yield corresponding alkoxides/phenoxides and hydrogen. In addition to this, phenols react with aqueous sodium hydroxide to form sodium phenoxides.

$$2R-O-H + 2Na \longrightarrow 2R-O-Na + H_{2}$$
Sodium
alkoxide
$$6 \text{ CH}_{3} - \stackrel{C}{\underset{C}{\text{C}-OH}}_{1} + 2Al \longrightarrow 2 \left(\stackrel{C}{\underset{C}{\text{CH}_{3}}}_{2} \stackrel{C}{\underset{C}{\text{C}-O}}_{2} \stackrel{C}{\underset{C}{\text{H}_{3}}}_{3} Al + 3H_{2}$$
tert- Butyl alcohol Aluminium
tert- butoxide
$$0H$$

$$2 \stackrel{O}{\underset{C}{\text{H}_{3}}}_{2} \stackrel{O}{\underset{C}{\text{H}_{3}}}_{2} \stackrel{O}{\underset{C}{\text{H}_{3}}}_{2} \stackrel{O}{\underset{C}{\text{H}_{3}}}_{2} + 2Na \longrightarrow 2 \stackrel{O}{\underset{C}{\text{H}_{3}}}_{2} \stackrel{O}{\underset{C}{\text{H}_{3}}}_{2} + H_{2}$$



Sodium phenoxide

This reaction shows that alcohols and phenols can donate H⁺ ions so they are acidic.

Acidity of alcohols: The acidity of alcohol decreases in the order of primary alcohol > secondary alcohol > tertiary alcohol as shown below. This decreases in acidity is because of the more inductive effect of alkyl group (electron releasing group) in tertiary alcohol than secondary and primary alcohol that increases the electron density on oxygen thereby decreasing the polarity of O-H bond and therefore its acidity.



Alcohols, however, are weaker acids than water as shown by the reaction below. If the alcohols were stronger acids than water, the reaction given below will not occur in forward direction since water (H-O-H) will not be able to donate H to alkoxide.

R-Ö: +	н-ё-н—	\rightarrow R-O-H	+ :ÖН
Base	Acid	Conjugate	Conjugate
		acid	base

why phenols are more acidic than alcohols?

Phenols react with aqueous sodium hydroxide to produce phenoxide ions. This indicates that the acidity of phenols is higher in comparison to the alcohols. The phenoxide ion is stabilized by the delocalization of negative charge due to the resonance in the benzene ring.

Alcohols following the elimination of H⁺ create an alkoxide ion which is the conjugate base of alcohol. The negative charge existing on oxygen atoms in alkoxide ion increases due to the +I inductive effect of the alkyl group connected to it and this destabilises the conjugate base and makes alcohol less acidic.

- In the case of phenols, the negative charge on the oxygen atom is delocalized around the ring by resonance, resulting in phenoxide ions. The negative charge on oxygen is thereby delocalized to the ortho and para carbon atoms, and the phenoxide ion is transformed into a stable resonant structure. This stabilises the phenoxide ion and renders phenol more acidic than alcohol.



Note

in resonating structure of phenoxide ion -ve charge is present at ortho and paraposition. So -ve charge stabilising groups can increase stability of substituted phenoxide ion. Thus is can increase the acidity



Esterification: Alcohols and phenols react with carboxylic acids, acid chlorides and acid anhydrides to form esters.

$$Ar/RO - H + R' - COOH \stackrel{H^*}{\longleftarrow} Ar/ROCOR' + H_2O$$
$$Ar/R - OH + (R'CO)_2O \stackrel{H^*}{\longleftrightarrow} Ar/ROCOR' + R'COOH$$
$$R/ArOH + R'COCI \stackrel{Pyridine}{\longrightarrow} R/ArOCOR' + HCI$$

The reaction with carboxylic acid and acid anhydride is carried out in the presence of a small amount of concentrated sulphuric acid. The reaction is reversible, and therefore, water is removed as soon as it is formed. The reaction with acid chloride is carried out in the presence of a base (pyridine) so as to neutralise HCl which is formed during the reaction. It shifts the equilibrium to the right-hand side. The introduction of acetyl (CH₃CO) group in alcohols or phenols is known as acetylation. Acetylation of salicylic acid produces aspirin.



SALICYLIC ACID

ACETYLSALICYLIC ACID ACETIC ACID

Cleavage of carbon-oxygen bond in alcohols: Reaction with HX: $R-OH + HI \rightarrow RI + H_2O$

Reaction with SOCl₂/PCl₃/PCl₅:



Dehydration: alcohols undergo dehydration to form alkenes on treating with a protic acid e.g., concentrated H_2SO_4 or H_3PO_4 or catalyst such as anhydrous zinc chloride or alumina

$$C_2H_5OH \xrightarrow{H_2SO_4} CH_2 = CH_2 + H_2O$$

Secondary and tertiary alcohols are dehydrated under milder conditions.

$$CH_{3}CHCH_{3} \xrightarrow{85\% H_{3}PO_{4}} CH_{3}- CH = CH_{2} + H_{2}O$$

$$CH_{3}-C-OH \xrightarrow{20\% H_{3}PO_{4}} CH_{3}-C-CH_{3} + H_{2}O$$

$$CH_{3}-C-OH \xrightarrow{20\% H_{3}PO_{4}} CH_{3}-C-CH_{3} + H_{2}O$$

Relative ease of dehydration follows the order as: Tertiary > secondary > primary

Mechanism:

Dehydration of alcohols follows a three-step mechanism.

Formation of protonated alcohol Formation of carbocation Formation of alkenes

1.Formation of protonated alcohol:

In this step, the alcohol is acted upon by a protic acid. Due to the lone pairs present on the oxygen atom it acts as a Lewis base. Protonation of alcoholic oxygen takes place which makes it a better leaving group. It is a reversible step which takes place very quickly.

2. Carbocation formation:

In this step, the C-O bond breaks generating a carbocation. This step is the slowest step in the mechanism of dehydration of an alcohol. Hence, the formation of the carbocation is considered as the rate-determining step.

3. Alkene formation:

This is the last step in the dehydration of alcohol. Here the proton generated is eliminated with the help of a base. The carbon atom adjacent to the carbocation breaks the existing C-H bond to form C=C. Thus, an alkene is formed.

Dehydrogenation and rehydrogenation reactions are reversible and the reagents and components are recyclable as a result of which the device can be used more efficiently as a hydrogen supply network technology compared to other hydrogen storage materials.

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 ethane by elimination of a proton.



Oxidation of alcohols: Oxidation of alcohols involves the formation of a carbon-oxygen double bond with cleavage of an O-H and C-H bonds.



In this primary alcohols give aldehydes in presence of oxidizing agent acid

Acidified K₂Cr₂O₇, CrO₃, Collins-reagent, CrO₃ pyridine,PCC (pyridinium chlorochromate), PDC (Pyridium dichromate). CH₃CH₂OH $\xrightarrow{\text{K2CR2O7}[0]}$ CH₃CHO \rightarrow CH₃COOH



If we want to stop the reaction at stage of aldehyde, we can use mild oxidizing agent. It is to be noted that primary alcohols give aldehyde and secondary alcohols give ketones.



Secondary alcohols gives ketones but under drastic conditions like use of potassium dichromate it gives carboxylic acid with less number of carbon atom than in alcohol.



Secondary alcohol

Tertiary alcohols give alkene because they do not have H atom so oxidation is not possible and they show elimination reaction.



(aldehvde)

Dehydrogenation - removal of Hydrogen. $CH_3 CH_2 OH (1^0) \xrightarrow{CU}{573 k} CH_3 CHO$

ethanol

$$CH_3$$
 CH_3 CH_3

2 -propanol

$$CH_3 - CH_3 \xrightarrow[]{CH_3}{CH_3} - CH_3 \xrightarrow[]{CU}{S73 k} CH_3 - CH_3 (alkene)$$

2 methyl 2-propanol

Note

 $C_2H_5OH\ is\ used\ for\ drinking\ purpose\ are\ beverage\ but$

 CH_3 OH is not good to consume. When in C_2H_5OH , CH_3OH is added it becomes denatured alcohol if it is consumed by anyone it causes death. It hits the nervous system and can cause blindness.

Reactions of phenols

(a) Electrophilic substitution reaction: Electrophilic aromatic substitution reactions are the reactions where an electrophile replaces one or more hydrogen atoms attached to the aromatic ring. Phenols are highly prone to electrophilic substitution reactions due to rich electron density. The hydroxyl group attached to the aromatic ring in phenol facilitates the effective delocalization of the charge in the aromatic ring. Thus, it stabilizes the arenium ion through resonance. The hydroxyl group also acts as ortho para directors.

Nitration: The -OH group present in phenols activates the ring to such extent that some phenols can be nitrated even with dilute nitric acid at low temperature.



Q. Why ortho-nitrophenol is more volatile than para-nitrophenol?

Sol. O-Nitrophenol forms intramolecular H bond whereas molecules of P-Nitrophenol get associated through intermolecular H bond. During boiling, the strong intermolecular H bonding increases the boiling point but intramolecular H bonding cannot do so. Therefore, O-Nitrophenol is more steam volatile than P-Nitrophenol.

Sulphonation: Phenol's can be sulphonated readily at O-(ortho) and P(para) positions by the action of concentrated sulphuric acid.



(b) Kolbe reaction: When phenol is treated with sodium hydroxide, phenoxide ion is generated. The phenoxide ion generated is more reactive than phenol towards electrophilic aromatic substitution reaction. Hence, it undergoes electrophilic substitution reaction with carbon dioxide, which is a weak electrophile. Ortho-

hydroxybenzoic acid (salicylic acid) is formed as the primary product. This reaction is popularly known as Kolbe's reaction.



(c) Reimer-Tiemann reaction: The Reimer Tiemann reaction is an organic chemical reaction where phenol is converted into an ortho hydroxy benzaldehyde using chloroform, a base, and acid workup. This reaction can also be described as the chemical reaction used for the ortho-formylation of phenols.



Reaction of Phenol with zinc dust:



Oxidation of phenol:



Benzoquinone

Preparation of Ethers

(a) Alcohol dehydration:



Mechanism: The formation of ether is a nucleophilic bimolecular reaction (SN₂) involving the attack of alcohol molecule on a protonated alcohol, as indicated below:

(i)
$$CH_{s}-CH_{2}-\overset{\circ}{O}-H + H' \rightarrow CH_{s}-CH_{2}-\overset{\circ}{O}-H$$

(ii) $CH_{s}CH_{2}-\overset{\circ}{O}: + CH_{3}-\overset{\circ}{C}H_{2}-\overset{\circ}{O} \overset{+}{H} \rightarrow CH_{s}CH_{2}-\overset{\circ}{O}-CH_{2}CH_{3} + H_{2}O$
(iii) $CH_{3}CH_{2}\overset{\circ}{\xrightarrow{O}} - CH_{2}CH_{3} \rightarrow CH_{3}CH_{2}-O-CH_{2}CH_{3} + H^{\dagger}$
(iii) $CH_{3}CH_{2}\overset{\circ}{\xrightarrow{O}} - CH_{2}CH_{3} \rightarrow CH_{3}CH_{2}-O-CH_{2}CH_{3} + H^{\dagger}$

(b) Williamsons synthesis: It is used for the preparation of simple as well as mixed ethers. Alkyl halide is heated with alcoholic sodium or potassium alkoxide to form corresponding ethers.

Thus, methyl iodide, on heating with alcoholic sodium methoxide forms dimethyl ether.

CH₃-O-CH₂CH₃ + Nal Ethyl methyl ether

Mechanism:

Step 1: Alcohol reacts with sodium metal to form the conjugate base sodium alkoxide and realeases hydrogen gas.



Step 2: Sodium alkoxide is added to primary alkyl halide to form the desired ether along with sodium halide.



(c) In aryl ethers, sodium phenoxide reacts with RX



ou. phenoxide

Physical properties of ethers

Existence: Lower members are gases and higher members may be liquids or solid due to increase in the Vander wall force.

Dipole moment: Ethers have higher dipole moments because of electro negativity difference and structure is bent. They have larger bond angles than alcohol. Alcohol have one hydrogen and ether there are two bulky groups so, repulsion between bulky groups are more therefore Bond angle will increase.

More the bulky group's, lower is the value of dipole moments. $CH_3 - O - CH_3 (1.3 D) C_2H_5OC_2H_5 (1.18 D)$ **Boiling point**: Ethers have low boiling point because of less polarity.

 $CH_3 CH_2 O CH_2 CH_3 CH_3 CH_2 CH_2 CH_2 OH$

Boiling point – 307.6k boiling point – 390k (more polarity)

Solubility: lower members are more soluble.

Example – $C_2 H_5 OH$ $CH_3 OCH_3$] same solubility

But as number of Carbon atoms increase, solubility decrease because non polar part increase.

Chemical properties

(a) Cleavage of CO bond in ethers: The order of reactivity of halogen acids towards this reaction is:

HI > HBr > HCl > Hl

The HI bond is broken easily but HF bond can't be broken .The reaction involved is

Ether cleavage with strong acid

 $\text{R-o-R'} \xrightarrow{\text{HI}} \text{R-OH} + \text{I-R'}$

First step is protonation.

Second step is cleavage of a C-O bond

Can proceed through SN1 or SN2 depending on substrate If 'excess' HI is present, the alcohol product will be coverted to an alkyl iodide.



Mechanism:

The reaction of an ether with concentrated HI starts with protonation of ether molecule.

Step 1:

$$CH_3 - \overset{\frown}{O} - CH_2CH_3 + H - 1 \rightleftharpoons CH_3 - \overset{\frown}{O} - CH_2CH_3 + \Gamma$$

Step 2:

Iodide is a good nucleophile. It attacks the least substituted carbon of the oxonium ion formed in step 1 and displaces an alcohol molecule by $S_N 2$ mechanism. Thus, in the cleavage of mixed ethers with two different alkyl groups, the alcohol and alkyl iodide formed, depend on the nature of alkyl groups. When primary or secondary alkyl groups are present, it is the lower alkyl group that forms alkyl iodide ($S_N 2$ reaction).

$$\overbrace{\Gamma + CH_3 - \overset{H_1}{\odot} - CH_3CH_3} \xrightarrow{} \left[\underset{I \cdots CH_3 \cdots \overset{H_1}{\odot} \overset{H_1}{\odot} \cdots CH_2CH_3}{\overset{H_1}{\odot} - CH_3-I} + CH_3CH_2-OH \right]$$

When HI is in excess and the reaction is carried out at high temperature, ethanol reacts with another molecule of HI and is converted to ethyl iodide.

Step 3:

$$CH_{3}CH_{2} - \bigcup_{i=1}^{G} -H_{i} + H_{i} - I \implies CH_{3}CH_{2} - \bigcup_{i=1}^{G} H_{i} + I$$

$$CH_{3}CH_{2} - \bigcup_{i=1}^{G} H_{i} + I \xrightarrow{i=1}^{G} CH_{3}CH_{2} + H_{2}O$$

However, when one of the alkyl group is a tertiary group, the halide formed is a tertiary halide as shown below. It is because in step 2 of the reaction, the departure of leaving group (HO-CH₃) creates a more stable carbocation [(CH₃)₃C⁺], and the reaction follows SN1 mechanism.

$$\begin{array}{c} CH_{3} & CH_{3} \\ CH_{3}-\overset{I}{C}-\overset{I}{O}-CH_{3}+HI \longrightarrow CH_{3}\overset{OH}{OH}+CH_{3}-\overset{I}{C}-I \\ CH_{3} & CH_{3} \end{array}$$

(b) Electrophilic Substitution: The alkoxy group (-OR) is ortho, para directing and activates the aromatic ring towards electrophilic substitution in the same way as in phenol. The ortho, and para directing nature can be seen from it's resonance structure as shown below.



(Major) (minor)

Friedel-Crafts reaction (addition of alkyl and acyl group):





Uses of ethers

- Ethers are used as a refrigerant.
- They are used as industrial solvent for fat and oils.
- When mixed with alcohol they make alcohol denatured.
- They are used in Perfumery like:
- In aniseeds Anethol is present which is a phenyl ether.
- In clove oil Eugenol is present.
- In vanilla extract vanillin is present.
- In mint Thymol is present.



- (i) On the basis of the number of hydroxyl groups
- (ii) According to the hybridization of the carbon atom, sp3 or sp2 to which the -OH group is attached. Ethers are classified on the basis of groups attached to the oxygen atom.

Alcohols may be prepared

- (1) By hybridization of alkenes
 - (i) In presence of an acid
 - (ii) By hydroboration-oxidation reaction
- (2) From carbonyl compounds by
 - (i) Catalytic reduction
 - (ii) The action of Grignard reagents.

Phenols may be prepared by

- (1) Substitution of
 - (i) Halogen atom in haloarenes
 - (ii) Sulphonic acid group in aryl sulphonic acids, by -OH group
- (2) By hydrolysis of diazonium salt
- (3) Industrially from cumene

Alcohols have higher boiling point than other classes of compounds, namely hydrocarbons, ethers and haloakanes of comparable molecular masses. The ability of alcohols, phenols and ethers to form intermolecular hydrogen bonding with water makes them soluble in it. Alcohols and phenols are acidic in nature. Electron withdrawing groups in phenols 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 oxidising agents and carboxylic acids with strong oxidising agents while secondary alcohols yield ketons. Tertiary alcohols are resistant to oxidation.

The presence of -OH group in phenols activates the aromatic ring towards electrophilic substitution and directs the incoming group to ortho and para positions due to resonance effect. Reimer-Tiemann reaction of phenol yields salicylaldehyde. In presence of sodium hydroxide, phenol generates phenoxide ion which is even more reactive than phenol. Thus, in alkaline medium, phenol undergoes Kolbe's reaction.

Ether may be prepared by (i) Dehydration of alcohols (ii) Williamson synthesis

The boiling points of ethers resemble those of alkanes while their solubility is comparable to those of alcohols having same molecular mass. The C-O bond in ethers can be cleaved by hydrogen halides. In electrophilic substitution, the alkoxy group activates the aromatic ring and directs the incoming group at ortho and para positions.





due to low reactivity

QUESTIONS FOR PRACTICE

1.	The heating of phenyl met	hyl ether with HI produces		(c) NaBH ₄	(d) all of these
	(a) lodobenzene (c) Benzene	(b) Phenol (d) Ethyl chloride	11	Which of the following r primary alcohols to alde	eagents can be used to oxidise hydes?
2.	Among the following se produces anisole? (a) CH ₃ CHO; RMgX (b) C ₆ H ₅ OH; NaOH, CH ₃ I	ts of reactants which one		 (a) CrO₃ in anhydrous m (b) KMnO₄ in acidic med (c) Pyridinium chloroch (d) Heat in the presence 	edium. ium. romate. of Cu at 573K.
	(c) C_6H_5OH , neutral FeCl ₃ (d) C_6H_5 —CH ₃ ; CH ₃ COCl;	AlCl ₃	12	One mole of ethyl acetat LiAlH ₄ in dry ether a	e on tatment with an excess of and subsequent acidification
3.	Monochlorination of tolu hydrolysis with aq. NaOH (a) o-Cresol (c) 2, 4-Dihydroxytoluene	ene in sunlight followed by yields. (b) m-Cresol (d) Benzyl alcohol		produces (a) 1 mole acetic acid + 2 (b) 1 mole ethyl alcohol (c) 2 moles of ethyl alcohol (d) 1 mole of 2 hyterrol	l mole ethyl alcohol + 1 mole methyl alcohol nol
4.	CH ₃ CH ₂ OH can be convert (a) Catalytic hydrogenatio (b) Treatment with LiAlH4 (c) Treatment with pyridi (d) Treatment with KMnO	ed into CH3CHO by n 4 nium chlorochromate 4	13	(d) I hole of 2-butation Which of the following stable carbocation durin (a) 2-methyl-1-propano (c) 1-Butanol	alcohols will give the most g dehydration? (b) 2-methyl-2-propanol (d) 2-Butanol
5.	The correct order of bo secondary (2°) and tertian (a) $1^\circ > 2^\circ > 3^\circ$ (c) $2^\circ > 1^\circ > 3^\circ$	iling point of primary (1°), y (3°) alcohols is (b) 3° > 2° > 1° (d) 2° > 3° > 1°	14	A compound X with the be oxidised to another formulae is C ₃ H ₆ O ₂ . The (a) CH ₃ CH ₂ OCH ₃	molecular formula C ₃ H ₈ O can compound Y whose molecular compound X may be (b) CH ₃ CH ₂ CHO (d) CH ₂ CHOHCH ₂
6.	Which compound is pr phenol is allowed to read medium? (a) Picric acid (c) 2 4 6-Tribromopheno	edominantly formed when ct with bromine in aqueous (b) O-Bromophenol	15	(c) chischizerizioni Order of esterification o (a) 3° > 1° > 2° (c) 1 ° > 2° > 3°	f alcohols are (b) 2°> 3° > 1° (d) None of these
7.	 (c) 2, 1, 0 Tribiomopheno Phenols are more acidic th (a) Phenoxide ion is stabil (b) Phenols are more solu (c) Phenoxide ion does no (d) Alcohols do not lose H 	nan alcohols because ised by resonance ble in polar solvents t exhibit resonance atoms at all	16	What happens when te over heated copper at 3 (a) Secondary butyl alco (b) 2-methylpropene is (c) 1-butene is formed (d) Butanol is formed	rtiary butyl alcohol is passed 00°C? hol is formed formed
8.	Which of the following a distinguish between phen (a) FeCl ₃ (c) Br ₂ /CCl ₄	reagents cannot be used to ol and benzyl alcohol? (b) Litmus soln (d) All of these	17	What would be the react 2, 4-dimenthyl pentan-3 (a) Propanal and propyl (b) 3-methylbutanal and	ant and reagent used to obtain -ol? magnesium bromide 2-methyl magnesium iodide
9.	1-propanol and 2-propan by	ol can be best distinguished		(c) 2-dimethylpropano odide (d) 2-methylpropanal ar	d iconropyl magnesium iodide
	 (a) Oxidation with KMnO₄ followed by reaction with Fehling solution. (b) Oxidation with acidic dichromate followed by reaction with Fehling solution. (c) Oxidation by heating with copper followed by reaction with Fehling solution. (d) Oxidation with concentrated H₂SO₄ followed by reaction with Fehling solution 	18	The decreasing order of	boiling point of the following	
			(a) 3-methylbuan-2-ol> 1-ol	2-methylbutan-2-ol > pentan-	
			 (b) Pentan-1-ol>3-meth 2-ol (c) 2-methylbutan-2-ol 	ylbutan-2-ol> 2-methylbutan-	
10	Which of the following ar RCH ₂ OH? (a) H ₂ /Pd	e used to convert RCHO into (b) LiAlH4		(d) 2-methylbutan-2-ol2-ol	> pental-1-ol> 3-methylbutan-

- **19** Acid catalysed dehydration of t-butanol is faster than that of n-butanol because
 - (a) tertiary carbocation is more stable than primary carbocation
 - (b) primary carbocation is more stable than tertiary carbocation
 - (c) t-butanol has a higher boiling point
 - (d) rearrangement takes place during dehydration of t- butanol
- - (a) butan-1-ol,
 - (b) butan-2-ol
 - (c) 2-methylpropan-1-ol
 - (d) 2,2-dimethylbutynal-1-oI
- 21 Vapours of an alcohol X when passed over hot reduced copper, produce an alkene, the alcohol is
 - (a) primary alcohol
 - (b) secondary alcohol
 - (c) tertiary alcohol
 - (d) dihydric alcohol
- 22 Picric acid is a yellow coloured compound. Its chemical name is
 - (a) m-nitrobenzoic acid
 - (b) 2, 4, 6-trinitrophenol
 - (c) 2, 4, 6-tribromophenol
 - (d) p-nitrophenol
- **23** Ortho-nitrophenol is less soluble in water than, p- and m- nitrophenols because
 - (a) o-nitrophenol shows intramolecular H-bonding
 - (b) o-nitrophenol shows intermolecular H-bonding
 - (c) melting point of o-nitrophenol is lower than those of m- and p-isomers
 - (d) o-nitrophenol is more volatile in steam than those of m- and p-isomers
- 24 The best reagent to convert pent-3-en-2-ol into pent-3en- 2-one is
 - (a) acidic permanganate
 - (b) acidic dichromate
 - (c) chromic anhydride in glacial acetic acid
 - (d) pyridiriium chlorochromate
- **25** Tertiary butyl alcohol gives tertiary butyl chlorideon treatment with
 - (a) Conc HCl/anhydrous ZnCl₂
 - (b) KCN
 - (c) NaOCl
 - (d) Cl₂
- 26 Conversion of phenol to salicyclic acid and to salicyaldehyde are known as (respectively)(a) Reimer-Tiemann reaction and Kolbe's reaction

(b) Williamson's synthesis and Hydrobrationoxidation
(c) Kolbe's reaction and Williamson's synthesis
(d) Kolbe's reaction and Reimer-Tiemann reaction
Which of the following is phenol?
(a) Cresol (b) Catechol
(c) Benzenol (d) All of these
Benzoquinone is prepared by reaction of phenol with
(a) Na₂Cr₂O₇, H₂SO₄ (b) KMnO₄, H₂SO₄
(c) Na₂CrO₄, HCl (d) K₂MnO₄, H₂SO₄

27

28

- 29 The major product obtained on interaction of phenol with sodium hydroxide and carbon dioxide is

 (a) benzoic acid
 (b) salicyaldehyde
 (c) salicylic acid
 (d) phthalic acid
- **31** In the reduction $R - CHO + H_2 \rightarrow RCH_2OH$ the catalyst used is : (a) Ni (b) Pd (c) Pt (d) All of these
- 32 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
- 33 Ethyl alcohol can be prepared from Grignard reagent by the reaction of :
 (a) R₂CO
 (b) HCHO
 - (c) RCN (d) RCOCl
- **34** Isopropyl alcohol is obtained by reacting which of the following alkenes with concentrated H₂SO₄ followed by boiling with H₂O?
 - (a) Ethylene(b) Propylene(c) 2-Methylpropene(d) Isoprene
- 35 Ethyl alcohol is industrially prepared from ethylene by(a) Permanganate oxidation(b) Catalytic reduction
 - (c) Absorbing in H2SO4 followed by hydrolysis
 - (d) All the three
- 36 Sodium salt of benzene sulphonic acid on fusion with caustic soda gives(a) Benzene(b) Phenol
 - (c) Thiophenol (d) Benzoic acid
- Which of the following reacts with NaOH to give an alcohol?(a) Propene(b) Butene
 - (c) Ethanal (d) Methanal

- **38** Which of the following compounds is oxidised to prepare methyl ethyl ketone?
 - (a) 2-Propanol(b) l-Butanol(c) 2-Butanol(d) t-Butyl alcohol
- **39**HBr reacts fastest with
(a) 2-Mehtylpropan-1-ol
(c) propan-2-ol(b) 2-Methylpropan-2-ol
(d) propan-1-ol
- 40 n-Propyl alcohol and isopropyl alcohol can be chemically distinguished by which reagent?
 (a) PCl₅
 (b) Reduction

 - (c) Oxidation with potassium dichromate
 - (d) Ozonolysis
- **41** Lucas reagent is
 - (a) Conc. HCl and anhydrous ZnCl₂
 - (b) Conc. HNO_3 and hydrous $ZnCl_2$
 - (c) Conc. HCl and hydrous ZnCl₂
 - (d) Conc. HNO_3 and anhydrous $ZnCl_2$
- 42 Chloro-Ethane reacts with Which of the Following to Give Diethyl Ether?
 (a) NaOH
 (b) H₂SO₄
 (c) C U ONa
 (d) Na S O
 - (c) C_2H_5ONa (d) $Na_2S_2O_3$
- - (c) Alcohol (d) Ester
- 44Dehydration of Alcohol is an Example of _____
(a) addition reaction
(c) substitution reaction(b) elimination reaction
(d) redox reaction
- **45** In the following compounds:



- (c) II > I > III > IV (d) IV > III > I > IIThe III PAC name of the other $CH_0 = CH_0 CH_0 O$
- 46The I.U.P.A.C. name of the ether CH2 = CH-CH2O CH3 is
(a) Allyl methyl ether(b) l-Methoxy-2-propene
(d) Vinyl dimethyl ether
- 47.

The ether

()-0-CH2-()

when treated with HI produces



48.



49 Which of the following alcohols reacts most readily with Lucas reagent?

(a)
$$CH_{3}CH_{2}CH_{2}OH$$

(b) $CH_{3} - CH - CH_{3}$
(c) $CH_{3} - CH_{3}$
(c) $CH_{3} - C - OH_{1}$
(d) $CH_{3} - CH - CH_{3}OH_{2}$
(d) $CH_{3} - CH - CH_{3}OH$

50 Identify the final product of the reaction sequence.

 $\bigcup \xrightarrow{Zn} X \xrightarrow{CH_3COCl} Y$ distillation X AlCl₃

(a) Benzophenone(b) Acetophenone(c) Diphenyl(d) Methyl salicylate

ASSERTION AND REASONING

- Q1. Assertion: Lucas reagent is a mixture of anhydrous ZnCl₂ and concentrate HCl.
 Reason: Primary alcohol produce ppt. with Lucas reagents.
 - (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
 - (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
 - (c) If the Assertion is correct but Reason is incorrect.
 - (d) If both the Assertion and Reason are incorrect.
- Q2. Assertion: Conc. HCl and anhydrous ZnCl₂ in 1:1 mixture is called Lucas reagent.
 Reason: Generally 3⁰ alcohols give immediate white turbidity with HCl/ZnCl₂. Conc. HCl and anhydrous
 - ZnCl₂ in 1:1 mixture is called Lucas reagent.(a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
 - (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
 - (c) If the Assertion is correct but Reason is incorrect.
 - (d) If both the Assertion and Reason are incorrect.
- Q3. Assertion: In Lucas test, 3º alcohols react immediately.

Reaso : An equimolar mixture of anhyd. ZnCl₂ and conc. HCl is called Lucas reagent.

- (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
- (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
- (c) If the Assertion is correct but Reason is incorrect.
- (d) If both the Assertion and Reason are incorrect.
- Q4. Assertion: Reimer-Tiemann reaction of phenol with CCl₄ in NaOH at 340 K gives salicyclic acid as the major product.

Reason: The reaction occurs through intermediate formation of dichlorocarbene.

(a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.

- (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
- (c) If the Assertion is correct but Reason is incorrect.
- (d) If both the Assertion and Reason are incorrect.

TRUE/FALSE

Q1. Ether is soluble in water. (a) True (b) False

Ethers are insoluble in cone. H₂SO₄ while alkanes are Q2. soluble. (a) True (b) False

Diethyl ether and 1-butanol have the same solubility in Q3. water.

(b) p-Cresol

(d) Resorcinol

(a) True (b) False

Q9. Which of the following phenols is not dihydric?

HOMEWORK

- **Q1.** Glucose and fructose are converted to ethanol in the presence of _ (a) reductase (b) invertase (c) zymase (d) oxidase Which of the following compounds is not used in the Q2. denaturation of alcohol? (a) Ethyl alcohol (b) Copper sulphate (c) Methyl alcohol (d) Pyridine **Q3.** What is the common name of Butan-2-ol? (a) tert-Butyl alcohol (b) n-Butyl alcohol (c) sec-Butyl alcohol (d) Isobutyl alcohol Q4. How many carbon atoms are present in the parent chain of tert-Butyl alcohol? (a) 2 (b) 3 (c) 4 (d) 5 Q5. What is the IUPAC name of Isopropyl alcohol? (a) 2-Methylpropan-2-ol (b) Propan-1-ol (d) 2-Methylpropan-1-ol (c) Propan-2-ol **Q6.** Which of the following is not a polyhydric alcohol? (a) Benzene-1,2-diol (b) Cyclohexanol (d) Propylene glycol (c) Ethylene glycol Identify the correct IUPAC name for the given Q7. compound. $CH_3 - CH - CH_2 - CH_2$ OH OH (a) Butane-1,4-diol (b) Butane-diol (c) Butylene glycol (d) Butane-1,3-diol **Q8.** Which of the following is an incorrect name for the compound with aromatic ring having hydroxyl groups at para positions? (a) Quinol (b) Hydroquinone (c) Benzene-1,4-diol (d) Resorcinol
 - **Q10.** What is the correct IUPAC name of the following phenol? OH

(a) Quinol

(c) Catechol



- (a) 1,2,4-Triphenol (b) Benzene-1,2,4-triol (c) 1,2,4-Benzenetriol (d) Benzene-1,2,4-triphenol
- **Q11.** What is the correct common name of 2-Bromophenol? (a) 2-Hydroxybromobenzene
 - (b) 2-Bromophenol
 - (c) m-Bromophenol
 - (d) o-Bromophenol
- **Q12.** Which of the following is given highest preference while naming when present in the same structure? (a) Halogen group (b) Hydroxyl group (c) Nitro group
 - (d) Triple bond
- **Q13.** Which of the following compounds is ethoxyethane? (a) $C_2H_5OC_3H_7$ (b) CH₃OCH₃ (c) $CH_3OC_2H_5$ (d) $C_2H_5OC_2H_5$
- **Q14.** What is the IUPAC name of CH₃-O-CH₂-CH₂-OCH₃? (a) 1,4-Dimethoxypropane (b) 1,2-Dimethoxyethane (c) 1,3-Dimethoxybutane (d) 2,3-Dimethoxyethane
- **Q15.** What is the IUPAC name of $CH_3(CH_2)_6$ -OC₆H₅? (a) Phenyl heptyl ether (b) Heptyl phenyl ether (c) 1-Phenoxyheptane (d) 1-Hepoxybenzene

Q16. How many lone pairs of electrons does 0 atom have in methanol?

(a) 4	(b) 0
(c) 1	(d) 2

- Q17. Which of the following is not a correct reason for the C-O bond length in phenol to be less than that in methanol?
 - (a) Repulsion between the electron lone pairs of oxygen

0

- (b) Partial double bond character of C-O bond
- (c) Conjugation of lone pair of electrons with the aromatic ring
- (d) sp2 hybridised sate of carbon of C-O bond

Q18. If the dipole moment of methanol is 1. 71D, predict the dipole moment of phenol. (b) 1.54D (a) 1.96D (c) 1.71D (d) 1.89D

Q19. If the C-O bond length in methanol is 142pm, what will be the C-O bond length in the given compound?



- (b) 96pm (d) 141pm
- **Q20.** How are alcohols prepared from haloalkanes? (a) By treating with Mg metal
 - (b) By treating with concentrated H₂SO₄
 - (c) By heating with aqueous NaOH
 - (d) By treating with a strong reducing agent
- **Q21.** Which of the following process do not yield alcohols? (a) Free radical halogenation of alkanes
 - (b) Acid catalysed hydration of alkenes
 - (c) Hydroboration-oxidation of alkenes
 - (d) Reduction of aldehydes
- Q22. Identify the catalyst in the hydration of alkenes to produce alcohols.

(a) Ni	(b) HCl
(c) FeCl ₃	(d) Pt

Q23. Propene when reacted with water in the presence of H₂SO₄ gives

(a) 2-Methylpropan-2-ol	(b) Propan-1-ol
(c) Propan-2-ol	(d) 2-Methylpropan-1-ol

- **Q24.** Identify the nucleophile that attacks the carbocation in the second step of acid catalysed hydration of alkenes? (a) H_3O^+ (b) OH-(c) H_2O (d) H+
- **Q25.** Name the following step from the mechanism of acid catalysed hydration of ethene.



(a) Deprotonation	(b) Protonation
(c) Electrophilic attack	(d) Nucleophilic attack

- Q26. Which compound reacts with propene to form tripropyl borane? (a) Sodium borohydride (b) Borane
 - (c) Diborane (d) Boric acid
- Q27. Which of the following is not required for the conversion of trialkyl borane to an alcohol? (a) Diborane (b) Water
 - (c) Sodium hydroxide
 - (d) Hydrogen peroxide
- **Q28.** What happens when an aldehyde is treated with lithium aluminium hydride?
 - (a) No reaction
 - (b) Primary alcohol is formed
 - (c) Secondary alcohol is formed
 - (d) Tertiary alcohol is formed
- Q29. Which carbonyl compound yields secondary alcohols when treated with LiAlH4?
 - (a) Ester (b) Aldehyde (c) Ketone
 - (d) Carboxylic acid
- **Q30.** Which of the following aldehydes can produce 1° alcohols when treated with Grignard reagent?
 - (a) Butanal (b) Methanal (c) Ethanal

(d) Propanal

ASSERTION AND REASONING

- 01. Assertion: Phenol is more reactive than benzene towards electrophilic substitution reaction. Reason: In the case of phenol, the intermediate carbocation is more resonance stabilized.
 - (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
 - (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
 - (c) If the Assertion is correct but Reason is incorrect.
 - (d) If both the Assertion and Reason are incorrect.
- Q2. 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. Like bromination of benzene, bromination of phenol is also carried out in the presence of Lewis acid.

- (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
- (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
- (c) If the Assertion is correct but Reason is incorrect.
- (d) If both the Assertion and Reason are incorrect.
- (e) Assertion is wrong reason is correct.

Q3. Assertion: Ethers behave as bases in the presence of mineral acids.

Reason: Due to the presence of lone pairs of electrons on oxygen.

- (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
- (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
- (c) If the Assertion is correct but Reason is incorrect.
- (d) If both the Assertion and Reason are incorrect.
- (e) Assertion is wrong reason is correct.
- **Q4.** Assertion: Ethanol is a weaker acid than phenol. **Reason:** Sodium ethoxide may be prepared by the reaction of ethanol with aqueous NaOH.
 - (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
 - (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
 - (c) If the Assertion is correct but Reason is incorrect.
 - (d) If both the Assertion and Reason are incorrect.
 - (e) Assertion is wrong reason is correct.
- **Q5.** Assertion: o-Nitrophenol is less soluble in water than the m- and p-isomers.

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

- (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
- (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
- (c) If the Assertion is correct but Reason is incorrect.
- (d) If both the Assertion and Reason are incorrect.
- (e) Assertion is wrong reason is correct.

TRUE/FALSE

- **Q1.** All alcohols are equally miscible with water. (a) True (b) False
- Q2. Phenols are stronger acids than alcohols. (a) True (b) False
- Q3. An electron withdrawing group present at o- and p-positions increases the acidic strength of a phenol.(a) True(b) False
- Q4. Chlorophenols are stronger acids than phenol. (a) True (b) False

SOLUTIONS

S1. (b) The heating of phenyl-methyl ether with HI produces phenol. Step I :

$$C_6H_5 - \dddot{O} - CH_3 + HI \rightleftharpoons C_6H_5 - \dddot{O} - CH_3 + I$$

Step II :

н

$$I + CH_3 - C_6H_5 \rightarrow CH_3I + C_6H_5OH$$

S2. (b) The above reaction is the preparation of Anisole phenol+NaOH+CH₃I gives anisole. C₆H₅OH, NaOH, CH₃I is the correct answer.



S3. (d) Monochlorination of toluene in sunlight gives benzyl chloride. On hydrolysis with aq. NaOH, benzyl chloride shows nucleophilic substitution reaction to give benzyl alcohol.



S4. (c) Pyridinium chlorochromate (PCC), a complex of chromium trioxide with pyridine and HCl gives good yield of aldehydes and prevents further oxidation to carboxylic acids.

$$CH_3CH_2OH \xrightarrow{PCC} CH_3CHO$$

S5. (a) The presence of -OH groups in a compound leads to Hydrogen-bonding which greatly increases its boiling. Generally, the more 'exposed' the -OH group, the better it can participate in intermolecular H-bonding and thus, the boiling point will elevate. By that logic, primary alcohols will have the highest boiling point while tertiary alcohols will have the lowest boiling point. 1°>2°>3°

S6. (c)

S7. (a) Phenol is more acidic than alcohols due to stabilisation of phenoxide ion through resonance. Presence of electron withdrawing group increases the acidity of phenol by , stabilising phenoxide ion while presence of electron

releasing group decreases the acidity of phenol by destabilising phenoxide ion

- S8. (a) Ferric chloride can be used to distinguish between phenol and benzyl alcohol. This is because, phenols react with neutral ferric chloride solution to give blue, violet or green colouration whereas alcohols do not react.
- S9. (a) When 1-propanol is heated with copper, it is oxidized to aldehyde which on passing through Fehling's solution gives red ppt. whereas 2-propanol on heating with copper, get oxidized to ketone which doesn't react with Fehling's solution.
- S10. (d) 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).

 $\operatorname{RCHO} \xrightarrow{H_2 + Catalyst} \operatorname{RCH}_2\operatorname{OH}$

RCHO LIAIH4 or NaBH4 RCH2OH

The reaction of RMgX with any aldehyde other than methanal gives secondary alcohols not the primary alcohols.

$$RCHO + RMgX \rightarrow R - CH(OMgX) - R \xrightarrow{Hydrolysis} R - CH(OH) - R$$

- S11. (b) KMnO₄ in acidic medium cannot be used to oxidize primary alcohols to aldehydes. The oxidation will not stop at aldehyde stage. It will further continue to carboxylic acid. To stop oxidation at aldehyde stage, we need mild oxidising agent such as PCC or PDC is used.
- **S12.** (c) Ethyl Acetate on treatment with LiAlH4 undergo reductions gives 2 moles of ethyl alcohol.

$$CH_{3}COOC_{2}H_{5} \xrightarrow{LiAlH_{4}/H_{3}O^{+}} CH_{3}CH_{2}OH + C_{2}H_{5}OH$$

S13. (b) The tertiary carbocation formed during dehydration of 2-methyl-2-propanol is most stable.



(3° carbocation, most stable)

S14. (c) By molecular formula, it can be concluded that, it is an alcohol and terminal alcohols can undergo oxidation.

 $CH_3CH_2CH_2OH \xrightarrow{\text{oxidation}} CH_3CH_2COOH$

- **S15.** (c) The relative order of esterification of alcohols is $1^{0}>2^{0}>3^{0}$. Thus as the steric hinderance (or bulkiness) increases from primary to secondary to tertiary alcohol, the order of esterification decreases.
- **S16.** (b) Tertiary alcohol when passed over Cu at 300° C is dehydrated to alkene.

$$\begin{array}{c} CH_{3} = \overset{CH_{3}}{\underset{C}{\text{H}_{3}}} = OH & \overset{Cu, 300^{0}C}{\longrightarrow} CH_{3} = \overset{CH_{2}}{\underset{CH_{3}}{\text{H}}} \\ t = butyl \ alcohol & \overset{Cu, 300^{0}C}{\longrightarrow} 2 = methyl \ propene \end{array}$$

S17. (d)

$$16.(d): CH_3 - CH - CH - CH = O + (CH_3)_2 CHMgI \longrightarrow$$

$$I = O + (CH_3)_2 CHMgI \longrightarrow$$

$$CH_3$$
2-Methylpropanal Isopropyl magnesium

$$(CH_3)_2CH = \begin{array}{c} H \\ I \\ CH_3)_2CH = \begin{array}{c} H \\ CH_3 \\ CH$$

2,4-dii

S18. (b) The boiling point of alcohol is determined by the ease and extent of H-bonding among the alcohol molecules.

Therefore the order of boiling point is primary alcohol > secondary alcohol > tertiary alcohol as: Pentan-1-ol > 3-methylbutan-2-ol > 2methylbutan-2-ol.

- **S19.** (a) Alcohol + $H_2SO_4 \rightarrow Alkene$
 - The dehydration reaction is an elimination reaction that goes via carbocation formation. Since tertiary carbocations are most stable due to + Inductive effect of alkyl groups, then is the secondary and least stable is primary.

Therefore the reactivity of alcohol is governed by the stability of carbocation that follows the order as

Tertiary > secondary > primary

Hence, acid catalysed dehydration of t-butanol is faster than that of n-butanol because tertiary carbocation formed by t-butanol is more stable than primary carbocation formed by n-butanol.

$$\begin{array}{c} \text{CH}_{3} \longrightarrow \text{CH}_{2}\text{CH}_{2}\text{CH}_{3} \xrightarrow{\text{conc. H}_{3}\text{SO}_{4}} \rightarrow \text{CH}_{3}\text{CH} \longrightarrow \text{CH}_{3}\text{CH}_{3} \\ \downarrow & \downarrow \\ \text{OH} & \downarrow \\ \text{OH} & \downarrow \\ (X) \\ \text{Butan-2-ol} & \text{CH}_{3}\text{CHO} + \text{CH}_{3}\text{CHO} \\ & \text{CH}_{3}\text{CHO} + \text{CH}_{3}\text{CHO} \\ & \text{CH}_{3}\text{CHO} + \text{CH}_{3}\text{CHO} \\ \end{array}$$

S20. (b)

- Given: $X(ROH)+Cu(hot) \rightarrow alkene primary alcohol$ S21. (c) passed over Cu at 300°C is dehydrogenated to aldehydes and hydrogen gas liberates secondary alcohols are dehydrogenated to ketones with liberation of hydrogen gas tertiary alcohol is dehydrated to alkene. This method can therefore be used to distinguish between primary, secondary and tertiary alcohol. Thus X should be a tertiary alcohol
- Picric acid is a yellow coloured compound. Its S22. (b) chemical name is 2,4,6 -trinitrophenol.



S23. (a) Due to intramolecular H-bonding, -OH group is not available to form a hydrogen bond with water. Hence o-nitrophenol is sparingly soluble in water while m- and p-nitrophenol are soluble due to intermolecular H-bonding with water.



S24. (c) Only suitable reagent is chromic anhydride in glacial acetic acid. Other will also effect (C=C) bond.

$$\begin{array}{c} \operatorname{CH}_{3} - \operatorname{CH}^{2^{*}} - \operatorname{CH} = \operatorname{CH} - \operatorname{CH}_{3} \longrightarrow \\ & | \\ & \operatorname{OH} \\ & \operatorname{CH}_{3} - \operatorname{C} - \operatorname{CH} = \operatorname{CH} - \operatorname{CH}_{3} \\ & | \\ & | \\ & | \\ & | \\ & 0 \end{array}$$

C(me)₃-Cl <u>C(CH</u>₃)₃-OH S25. (a)

This is Lucas reagent

- S26. (d) Phenol on reaction with carbon dioxide in the presence of a base like NaOH gives Salicylic acid. It is Kolbe's Reaction
 - Phenol on reaction with chloroform in the presence of a base like NaOH gives Salicylaldehyde. It is Reimer-Tiemann reaction.



S27. (d) Compounds containing —OH group directly attached to benzene ring are called phenolic compounds.



S28. (a) Phenol to benzoquinone is an oxidation reaction where a strong oxidising agent dichromate in acidified medium is used.



S29. (c)



S30. (d) RCH₂OH→RCHO

It's an oxidation reaction.

Pyridinium chlorochromate is amild oxidising agent that oxidises primary alcohol to aldehydes and secondary alcohols to ketones. It does not effect any other functional group and therefore have high selectivity for oxidation of alcohols. Whereas acidic permanganate, acidic dichromate, chromic anhydride in glacial acetic acid are strong oxidising agents and can do further oxidation to carboxylic acid.

The most suitable reagent for $RCH_2OH \rightarrow RCHO$ is pyridinium chlorochromate (PCC)

- S32. (d) Tertiary alcohol reacts fastest with Lucas reagent at room temperature.2-methyl propan-2-ol is a tertiary alcohol, thus reacts immediately with Lucas reagent.
- **S33.** (b) Ethyl alcohol can be prepared by reaction of Grignard reagent with formaldehyde. $CH_3-MgBr + H-CO-H \rightarrow CH_3CH_2-OMgBr \rightarrow CH_3CH_2OH$

$$CH_3 - CH = CH_2 + H_2O \xrightarrow[Markownikoffstule]{CmcH_2SO_4} CH_3 - CH_1 - CH_3$$

$$H_{\text{Isopogratisated}}$$

S34. (b)

$$CH_{2} = CH_{2} \xrightarrow{H \cdot SO_{4}} CH_{3} - CH_{2} - HSO_{4} \xrightarrow{H \cdot SO_{4}} CH_{3} CH_{2} - OH + H_{2}SO_{4}$$

S35. (c)

S36. (b)

S37.

(d) HCHO + HCHO
$$\xrightarrow{\text{NaOH}}$$
 CH₃OH + HCOONa

$$CH_3 - CH - CH_2 - CH_3 \xrightarrow{[O]} CH_3 - \overset{O}{C} - CH_2CH_3$$

- S38. (c)
- **S39.** (b) Reactivity of alcohol with HBr is $3^0 > 2^0 > 1^0$

 $\begin{array}{c} CH_3-CH_2-CH_2OH \xrightarrow{[0]} CH_3-CH_2-CHO \xrightarrow{[0]} K_2Cr_2O_7/H_2SO_4 \\ \text{propionaldehyde} \end{array} \xrightarrow{CH_2-CHO} \frac{[0]}{K_2Cr_2O_7/H_2SO_4} CH_3-CH_2-COOH \\ \text{alcohol} \end{array}$

$$\begin{array}{c} \text{CH}_3 - \text{CH}_2 - \text{CH}_3 \xrightarrow{[0]} \text{CH}_3 - \text{C} - \text{CH}_3 \\ \downarrow \\ \text{OH} \\ \text{OH} \\ \text{isopropyl alcohol} \\ \end{array} \xrightarrow{(0)} \text{CH}_3 - \text{C} - \text{CH}_3 \\ \begin{array}{c} \text{CH}_3 - \text{C} - \text{CH}_3 \\ \text{OH} \\ \text{$$

S41. (a) Lucas' reagent is a solution of anhydrous Zinc Chloride in concentrated HCl.

This solution is used to classify alcohols of low molecular weight. The reaction is a substitution in which the chloride replaces a hydroxyl group. The best results for this test are observed in tertiary alcohols, as they form the respective alkyl halides fastest due to higher stability of the intermediate tertiary carbocation.

The Lucas test in alcohols is a test to differentiate between Primary, secondary, and Tertiary Alcohols. It is based on the difference in reactivity of the three classes of alcohols with hydrogen halides via an SN_1 reaction.

Since, the Lucas reagent is Anhydrous ${\rm ZnCl}_2$ and Conc. HCl.

S31. (d)

S42. (c) Chloroethane reacts with X to give diethyl ether. The compound X is NaOEt (sodium ethanolate). It is an example of Williamson ether synthesis in which alkyl halide reacts with sodium alkoxide to form an ether.



S43. (b) (b)Primary alcohols get dehydrogenated with reduced copper at 573K, to give corresponding aldehydes.

$$\mathbf{R} - \mathbf{CH}_2\mathbf{OH} \xrightarrow{\mathbf{Cu. 573 K}} \mathbf{R} - \mathbf{CHO} + \mathbf{H}_2$$

Primary alcohul

S44. (b) Dehydration of alcohol is an example β -elimination. It involves the loss of two atoms/groups from adjacent carbon atoms.

 $C_{H_3}^{\beta}C_{H_2}^{\alpha}OH \xrightarrow{alcKOH} CH_2 = CH_2$

- S45. (d)
- **S46.** (a) $CH_2=CH-CH_2^-$ is called ally 1 radical. Therefore, its-name is allyl methyl ether.
- S47. (a)
- S48. (b)
- S49. (c)
- S50. (b)

ASSERTION AND REASONING

- S1. (c) Lucas reagent is a mixture of anhydrous ZnCl₂ and conc. HCl is used for the distinction of monohydric alcohol. Tertiary alcohols on addition produce a precipitate immediately while secondary alcohols produce ppt. after 5 minutes. Primary alcohols do not produce any precipitate. Therefore, assertion is true but reason is false.
- S2. (b)
- **S3.** (b) Both assertion and reason are true but reason is not the correct explaination of assertion.
 - (1) Lucas test is carried out to distinguish between 1°, 2° and 3° alcohols.
 - (2) Lucas reagent is a solution of anhydrous ZnCl₂ and concentrate HCl.
 - (3) With 3° alcohols it gives turbidity immediately. This is because 3° cation is very stable and the reaction takes place quickly.
 - (4) With 2° alcohols it does not give turbidity immediately, it takes 2-5 minutes. This is

because 2° cation is less stable as compared to 3° cation.

- (5) With 1° alcohols, it does not give turbidity. This is because at room temperature Lucas reagent doesn't react with 1° alcohols.
- S4. (c) Nucleophilic attack of phenolate ion through the ortho-carbon atom occurs on CCl₄ to form an intermediate which on hydrolysis gives salicylic acid.

TRUE/FALSE

S1. (a) Lower ethers such as dimethyl ether or diethyl ethers are fairly soluble in water due to the presence of hydrogen bonding with water. But higher ethers do not form H-bonds with water so they are not soluble to much extent. H-bonding between ethers and $H_2O \rightarrow$

> R^{δ⁻δ⁺} Ο:----H R', Λ.Ο. Η

Hydrogen Bond

- S2. (b) The C-O bonds in ethers are polar whereas alkanes are non-polar molecules. Due to the polar nature of ethers, they are very soluble in concentrated acids like H2SO4. Their solubility in conc. H2SO4 is due to the formation of oxonium ions.
 - $R-O-R + H_2SO_4 \rightarrow R_2OH^+ HSO_4^-$

Dialkyl oxonium hydrogen sulphate

S3. (a) The miscibility of ethers with water resembles those of alcohols of the some molecular mass. Both diethyl ether and 1-butanol are miscible to almost the same extent i.e. 7.5 and 9 g/ 100 mL water. This is due to the fact that just like alcohols, oxygen of ether can also form hydrogen bonds with water molecule as shown:



HOMEWORK

- **S1.** (c) Glucose and fructose undergo fermentation in the presence of an enzyme called zymase, which is found in yeast.
- S2. (a) Ethyl alcohol is drinkable and is made unfit to drink to avoid misuse in industries. This is done by adding some methanol, copper sulphate (to give it colour) and pyridine (to make it foul smelling). This is known as denaturation of alcohol.
- S3. (c) Butan-2-ol has a parent chain of 4 carbon atoms and the OH group at the second carbon. Such configurations have the prefix sec- in the common name.
- S4. (b) The IUPAC name of tert-Butyl alcohol is 2methylpropan-2-ol, which has two substituent groups at the C-2 position, namely one methyl and one hydroxyl group.
- **S5.** (c) Isopropyl alcohol has a parent chain of three carbon atoms with the hydroxyl group at the second carbon, hence propan-2-ol.
- S6. (b) Polyhydric alcohols have two or more hydroxyl groups in their structure and are named as either glycols in the common system or as diols and triols in the IUPAC system.
- **S7.** (d) This is a dihydric alcohol with OH groups at the first and third carbon positions. Butylene glycol is also the correct name but in the common system.
- S8. (d) Resorcinol is the common name for the dihydric phenolic compound with the OH groups at meta positions or 1, 3 positions.
- S9. (b) m-Cresol is a monohydric phenol with a methyl group at meta position with respect to OH. Its IUPAC name is 3-Methylphenol.
- S10. (b) Polyhydric phenols are named as hydroxy derivatives of benzene in the IUPAC system. The positions 1,2,4 comply with the lowest set of locants rule.
- **S11. (d)** Phenol is used as the common as well as the IUPAC name and haloarenes with hydroxy groups are named as halo derivatives of phenols.

- **S12. (b)** Functional groups are given the highest preference while naming compounds according to the IUPAC system.
- **S13. (d)** Ethoxyethane is an ether which is a derivative of ethane with one hydrogen atom replaced by ethoxy group (OC₂H₅).
- **S14. (b)** The base hydrocarbon is ethane, in which one hydrogen of each carbon atom is replaced by a methoxy group, making it a dimethoxy ether.
- **S15. (c)** Since heptane is a larger group than benzene, it is chosen as the parent hydrocarbon and the compound is named as an aryloxy derivative of heptane.
- S16. (d) The oxygen atom in methanol is sp³ hybridised. One of the sp3 orbitals overlaps with 1s orbital of hydrogen (of OH group) and one sp³ orbital overlaps with sp3 orbital of C atom. The remaining two sp3 orbitals contain one lone pair of electrons each.
- **S17. (a)** The two lone pairs of electrons of oxygen are present in OH groups of both phenol and methanol and has an effect on the C-O-H bond angle and not the C-O bond length.
- **S18. (b)** Phenol has a smaller dipole moment than methanol because the C-O bond in phenols is polar due to the electron withdrawing effect of the aromatic ring.
- **S19. (d)** The shown compound in methoxymethane which is an ether. The C-O bond length in ethers is almost the same as that in alcohols.
- **S20. (c)** Haloalkanes when heated with aqueous NaOH or KOH give respective alcohols. This is a nucleophilic substitution reaction where the halide group is replaced by the OH nucleophile.
- **S21. (a)** Alkanes on free radical halogenation produce a mixture of haloalkanes and not alcohols. Alcohols can be prepared from alkenes by acid catalysed hydration and hydroboration-oxidation or from reduction of aldehydes.

- **S22. (b)** Alkenes react with water in the presence of a mineral acid as a catalyst to form alcohols. The H+ ion from the acid helps to form a carbocation for nucleophilic attack.
- **S23. (c)** Since propene is an unsymmetrical alkene, the given hydration reaction takes place in accordance to Markovnikov's rule, to form propan-2-ol. The double bond is broken and the OH group attaches at the second carbon.
- **S24. (c)** Nucleophiles are electron rich species that attack the part of the structure that is electron deficient. In this step, the H_2O nucleophile attacks the carbocation forming a protonated alcohol.
- **S25. (a)** In this step, the electron pair of water attack the protonated alcohol, resulting in the loss of H+ from oxygen (deprotonation) to form an alcohol.
- S26. (c) Diborane (B₂H₆) reacts with alkenes to give trialkyl boranes as a product of successive addition. Firstly, CH₃CH₂CH₂(BH₂) is formed which reacts with propene to give (CH₃CH₂CH₂)₂BH, which further reacts with propene to finally give (CH₃CH₂CH₂)B, which is tripropyl borane.
- **S27. (a)** Trialkyl boranes are oxidised by hydrogen peroxide in the presence of aqueous NaOH to form alcohols. Diborane is not required for this conversion but is essential in the production of trialkyl boranes.
- **S28. (b)** LiAlH₄ acts as a reducing agent which reduces an aldehyde by adding hydrogen atoms to it result in the formation of a primary alcohol.
- **S29. (c)** Ketones react with reducing agents LiAlH₄ or NaBH₄ to get reduced to alcohol where the OH group is formed at the C of the C-O group. This results in the C being bonded to two alkyl groups apart from the OH and H atom.
- **S30. (b)** Methanal on treatment with Grignard reagent forms an adduct which has only one alkyl group attached to the C atom along with two hydrogens and one O-Mg-X (X=halogen) group. This on hydrolysis will form a primary alcohol where the OH group will replace the O-Mg-X group.

ASSERTION AND REASONING

S1. (a) Phenol is more reactive than benzene towards electrophilic substitution reaction. The donation of the oxygen's lone pair into the ring system increases the electron density around the ring. That makes the ring much more reactive than it is in benzene. The intermediate carbocation is more resonance stabilized.



S2. (e)



Lewis acid is not recognised as –OH group polarises the Br2 molecule. Hence, assertion is wrong statement.

Bromine molecule in the presence of Lewis acid, Br2 gets polarised to form ar+. Br-Br + FeBr₃ \rightarrow Br⁺ + FeBr₄-

Hence reason is correct.

S3. (a) Because of the presence of lone pairs of electrons, the ether can act as a base in presence of mineral acid.

$$C_2H_5 \longrightarrow C_2H_5 + HCl \longrightarrow C_2H_5 \longrightarrow 0 - C_2H_5Cl$$

H
Diethly oxonium chloride
(stable oxonium salt)

- S4. (b) EtOH is weaker acid than phenol because it is tough to remove H⁺ ion from EtOH whereas phenol readily gives H⁺ to form phenoxide ion (highly stable due to resonance).
 - \rightarrow However, Sodium ethoxide may be prepared by the reaction of EtOH with NaOH but the reason is not the correct explanation for Assertion
- **S5.** (b) Intramolecular H-bonding is present in nitrophenol. It does not form hydrogen bonds with water, thus is less soluble in water.



m-nitrophenol and p-nitrophenol forms intermolecular hydrogen bonds with water. Hence, assertion is a correct statement. Also, mnitrophenol and p-nitrophenol exist as associated molecules due to formation of H-bonds with water. Thus reason is also correct, but is not a correct explanation for assertion.

TRUE/FALSE

- S1. (b) Miscibility decreases with increase in molecular mass and increases with branching of chains. Because the relative proportion of the hydrocarbon part in alcohols increases with increasing molecular weight which outweighs the effect of hydrogen bond formation with water and decreases solubility.
- **S2. (a)** Phenols are stronger acids than alcohols is due to delocalization of negative charge stabilises the phenoxide ions due to resonance in benzene ring.

PhOH \rightleftharpoons PhO⁻+H⁺, where PhO⁻ is known as phenoxide ion,

Phenol gives phenoxide anion as a product. Due to resonance stabilization of phenoxide ion the acidity of phenol is stronger than alcohol.

- **S3. (a)** An electron withdrawing group present at ortho and para positions increase the acidic strength of a phenol because of delocalization of negative charge will be more effecting the phenoxide ion. The negative charge in dispersed and thus leads to higher acidic strength of phenol.
- S4. (a) Chlorophenol are stronger acids than phenol. As we know chlorine is an electron withdrawing group and consist -I effect (minus inductive effect) and +R effect (plus resonance effect). Thus due to electron withdrawing nature chlorophenols can easily remove its protons than phenol. Hence, higher will be the acidity of chlorophenols than phenol.