

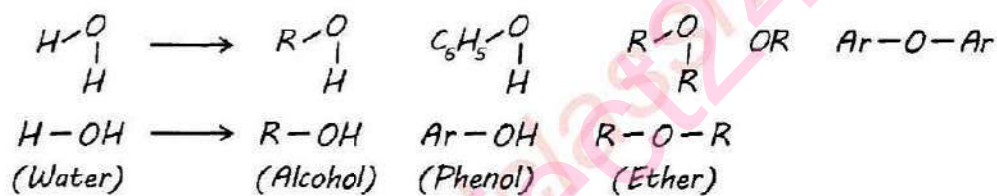
CHAPTER

18

ALCOHOLS, PHENOLS & ETHERS

Introduction:

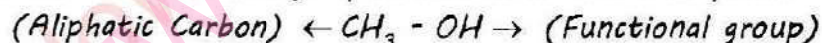
Alcohols, phenols and ethers are very close to each other in structures. These are thought to be the derivatives of water. Their structures are just like water. In case of alcohols one hydrogen atom of water is replaced by an alkyl group. In phenol one hydrogen atom of water is replaced by an aromatic ring whereas in ether both hydrogen atoms have been replaced by alkyl groups/aryl groups.



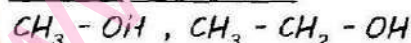
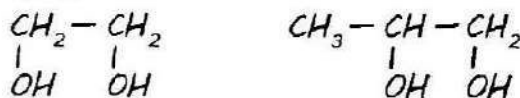
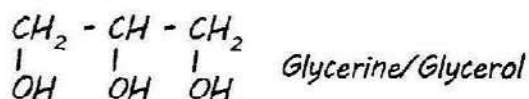
Q1: Define alcohol. Explain various types of alcohols. How alcohols are named by common and IUPAC system?

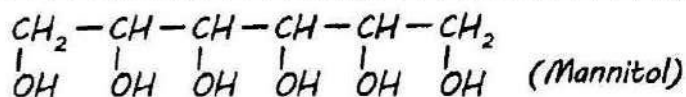
Ans: Alcohols:

"The hydroxy derivatives of aliphatic hydrocarbons are called alcohols." The general formula of alcohols is $\text{R}-\text{OH}$. Its general formula is also written as $\text{C}_n\text{H}_{2n+1}\cdot\text{OH}$. The functional group of alcohols is $-\text{OH}$. Example is:



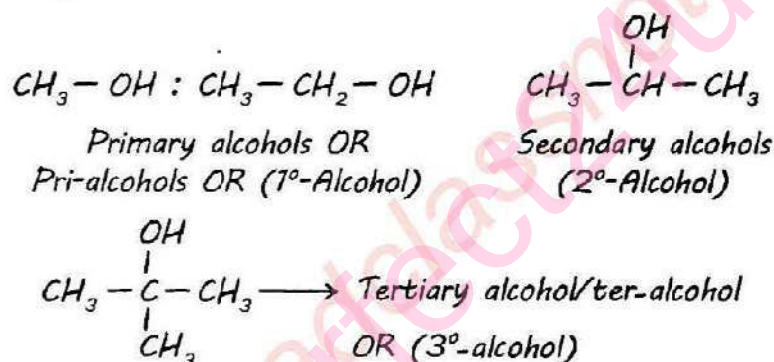
On the basis of number of hydroxyl groups alcohols are of three types:

1. Monohydric alcohols:2. Dihydric alcohols:3. Polyhydric alcohols:



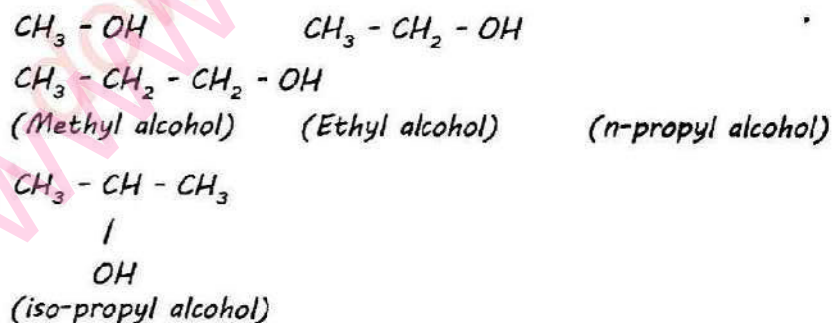
Monohydric alcohols are of three types. It depends upon whether -OH group is bonded to primary carbon, secondary carbon or tertiary carbon.

- When -OH group is bonded to primary carbon atom such alcohols are called primary alcohols.
- When -OH group is bonded to secondary carbon atom such type of alcohols are called secondary alcohols.
- When -OH group is bonded to tertiary carbon then it is called tertiary alcohol.

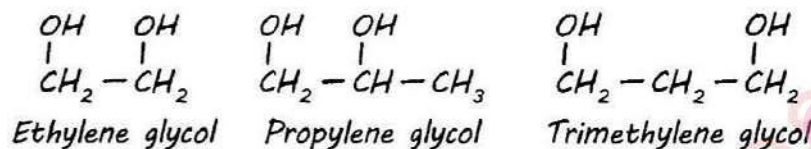
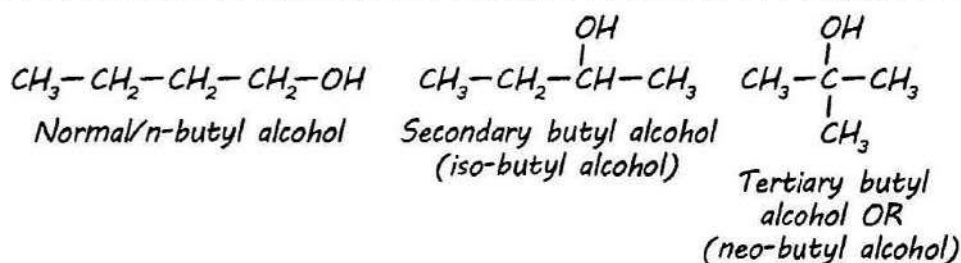


Common System for Naming Alcohols:

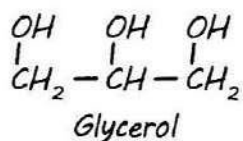
The common system depends upon the simplest monohydric alcohols. In this system R-OH is named as alkyl alcohol. First write the name of alkyl group, then the word alcohol. Examples are:



For higher members, it becomes necessary to indicate, whether a particular alcohol is primary (n-) secondary (iso-) or tertiary (neo-) alcohol.



The smallest trihydric alcohol is named as glycerol.



IUPAC System for Naming Alcohols:

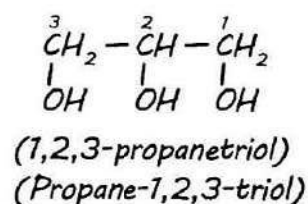
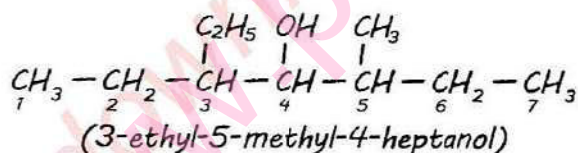
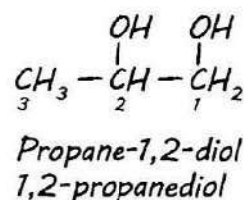
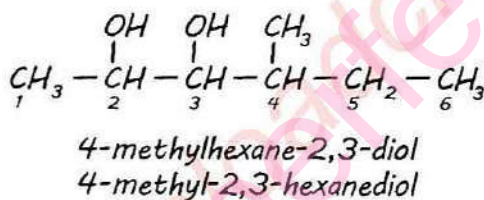
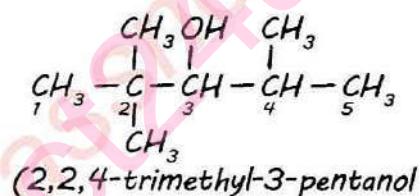
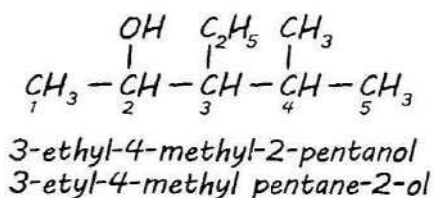
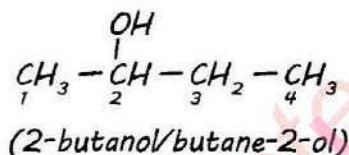
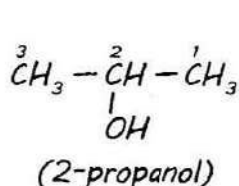
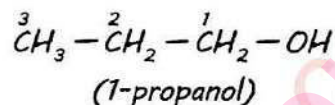
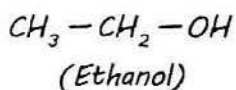
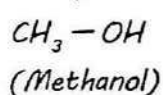
IUPAC Rules:

1. Select the longest continuous carbon chain containing maximum number of hydroxyl "-OH" groups.
2. Number the carbon chain from the side where hydroxyl functional group comes earlier.
3. The ending "e" in the basic name of alkane is replaced by "ol".
Alkane $\xrightarrow[-ol]{-e}$ alkanol
4. In case of two or more -OH groups, write down the full/basic name of alkane and then add the suffix diol for two -OH groups and triol for three.
5. Mention the position of hydroxyl group by putting its number before the parent name or before -ol.
6. Indicate the positions of the other substituents if present, using the numbers of the carbon atoms to which these are attached.
7. The substituents along with their numbers/positions are named in alphabetical order [A, B, C, D, E, F,.....Z] before the parent name.
8. If position of -OH group is same from both sides then

preference (C_2) will be given to substituent position i.e. from which side the substituent comes earlier.

9. If two -OH groups are attached to the same carbon then repeat the number of that carbon.

Examples:

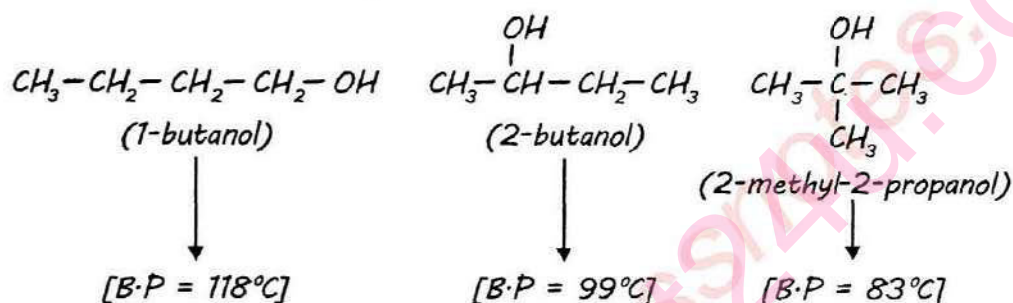


Q2: Write down the physical properties of alcohols.

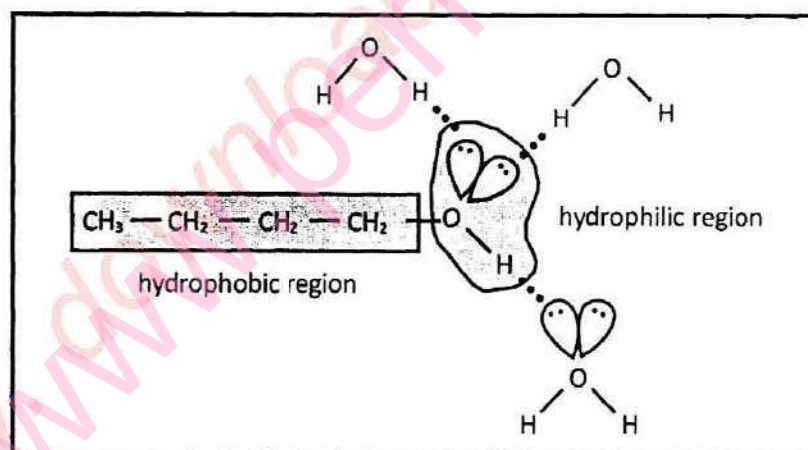
Ans: Physical Properties of Alcohols:

1. Lower alcohols are colourless and toxic (C_2) liquids.
2. These have characteristic sweet smell.
3. Their boiling point values are higher than the corresponding alkanes. It is due to the presence of hydrogen bonding.

4. Boiling point values of alcohols increases with increase in chain length.
5. Methyl alcohol is poisonous and causes blindness (اندھا پن), madness (جذبات) and even death.
6. Lower alcohols are completely water soluble in any proportion. Solubility of higher alcohols fall rapidly.
7. Among the isomeric alcohols, boiling point values decreases with increase in branching.



Methanol: 64.5°C	Ethanol: 78.3°C
1-Propanol: 97°C	1-Butanol: 118°C
1-Pentanol: 138°C	



Boiling and Melting Points of some Alcohols

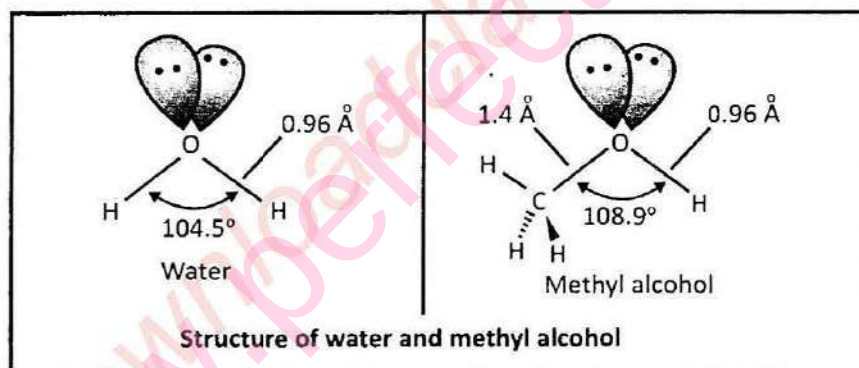
Name	Melting Point (°C)	Boiling Point (°C)
methanol	-97	64
ethanol	-115	78
n-propyl alcohol	-126	97

<i>n</i> -butyl alcohol	-90	118
isopropyl alcohol	-89	82
isobutyl alcohol	-108	108
sec-butyl alcohol	-114	99
tert-butyl alcohol	-25.5	82
ethylene	-12	197

Q3: Explain (a) structure of alcohols (b) acidity of alcohols.

Ans (a) Structure of Alcohols:

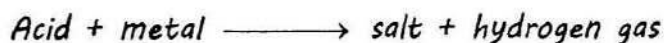
Alcohols are alkyl derivatives of water molecules. Water molecule has an angular structure with H-O-H bond angle of 104.5° , which is slightly smaller than tetrahedral angle. Alcohols molecule have a similar geometry where C-O-H angle is higher than 104.5° , and the hybridization of oxygen is sp^3 . For example the C-O-H bond angle in methyl alcohol is 108.9° . The C-O and O-H bond lengths are 142 pm ($1.42\text{\AA}$) and 96 pm ($0.96\text{\AA}$) respectively.

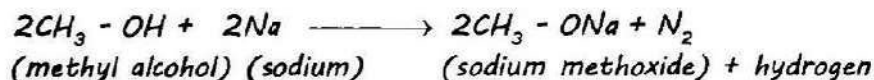
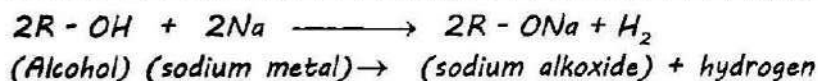


(b) Acidity of Alcohols:

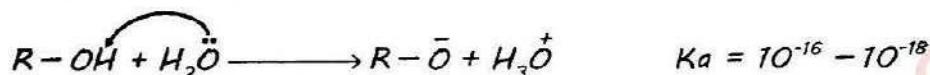
Alcohols are acidic in nature because they provide hydrogen ion $[H^+]$ in water. Hydrogen-oxygen bond in alcohols is polar. Due to greater electronegativity value of oxygen (3.5), it gets partial negative charge and hydrogen ($E.N = 2.1$) gets partial positive charge and the bond becomes polar.

Due to acidic character of alcohols, they react with sodium and potassium metals to form sodium alkoxide and potassium alkoxide and hydrogen gas is released.

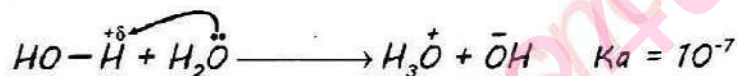




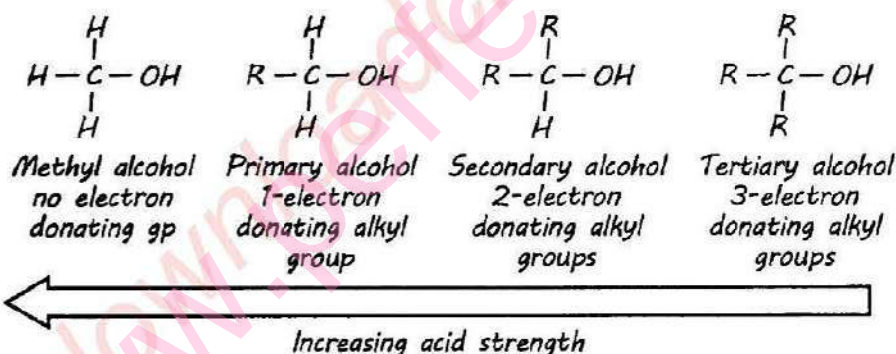
Alcohols are weakly acidic with "Ka" value $10^{-16} - 10^{-18}$.



The alkyl group in alcohols, being electron donating group, provide electrons towards oxygen atom, increases its partial negative charge and hence the release of proton $[H^+]$ becomes difficult. This presence of alkyl group makes alcohols less acidic than water where no alkyl group is present.



Tertiary alcohols are less acidic than secondary alcohols and secondary alcohols are less acidic than primary alcohols, because of the same electron donating effect of alkyl groups discussed above.



Note: Alcohols are not so much acidic to react with aqueous NaOH/ KOH.

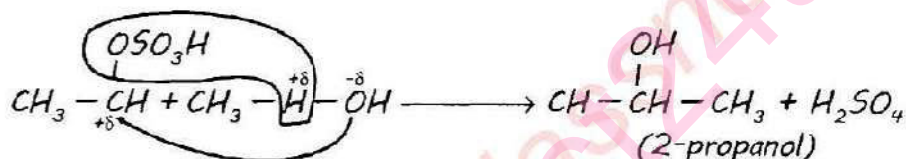
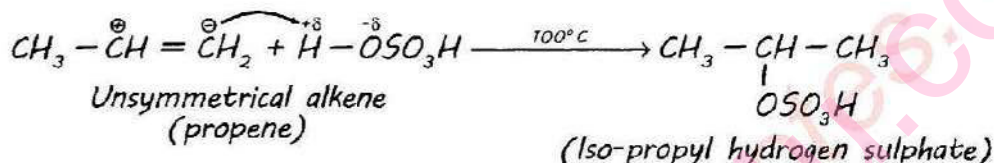
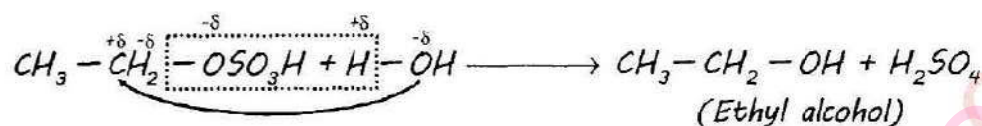
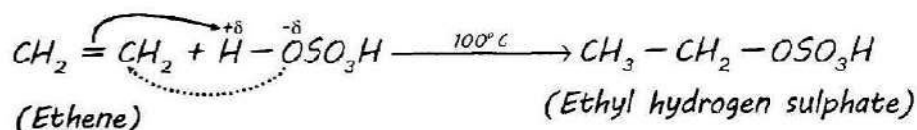


Q4: Write down various methods for the preparation of alcohols.

Ans: 1) Hydration of Alkenes:

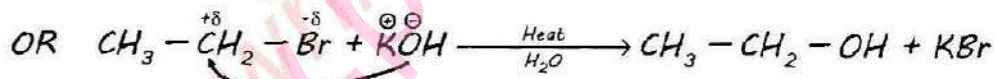
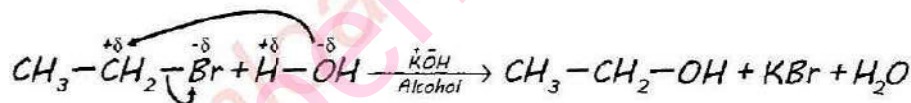
Alkene react with cold concentrated sulphuric acid to produce alkyl hydrogen sulphate, which on hydrolysis yield alcohols. Unsymmetrical

alkenes follow Markovnikov's rules-



2) Hydrolysis of Alkyl Halides: (Repetition Topic)

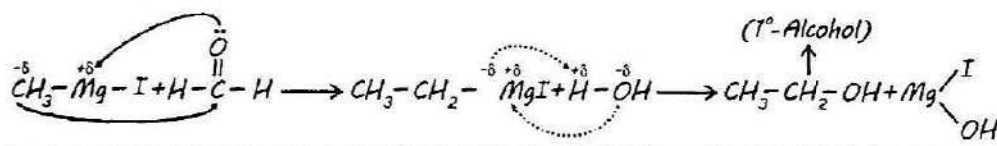
Alcohols can be prepared by the hydrolysis of alkyl halides in the presence of aqueous KOH (alkali).



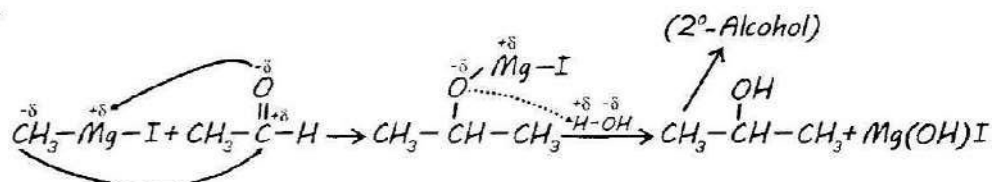
3) Grignard's Synthesis: Reaction of R-Mg-X with Aldehydes and Ketones: (Repetition Topic)

Grignard's reagent adds to the carbon-oxygen double bond [carbonyl group] of aldehydes and ketone to form an addition product, which upon acid hydrolysis produces alcohols.

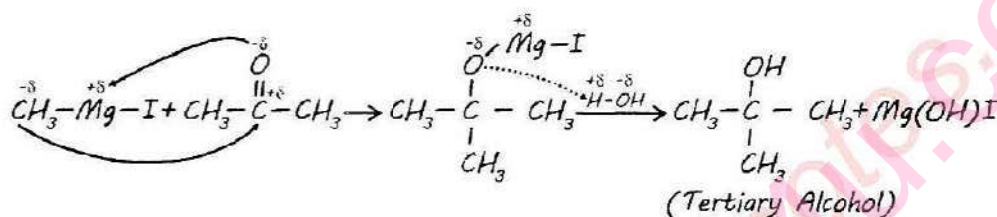
(1) Formaldehyde react with Grignard reagent and form primary alcohol.



(2) Acetaldehyde react with Grignard's reagent and form secondary alcohol.

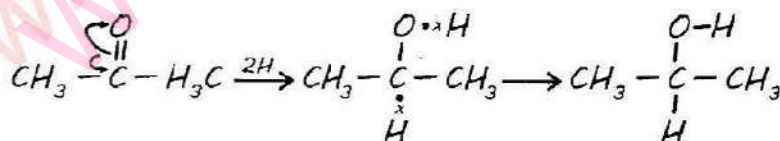
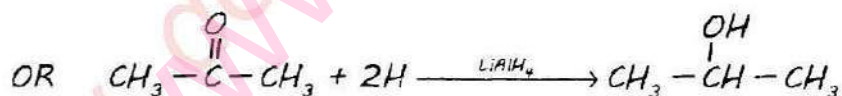
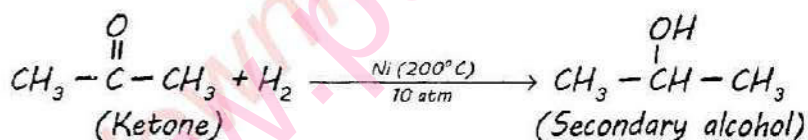
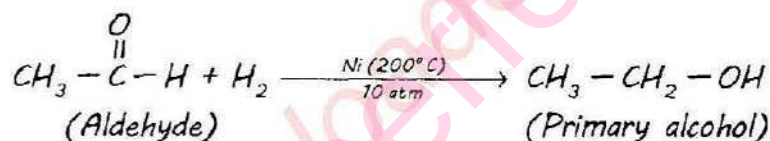


(3) Ketone react with Grignard's reagent and form tertiary alcohol.



4) Reduction of Aldehydes and Ketones:

Reduction means addition of hydrogen. Reduction of aldehydes and ketones is carried out in the presence of nickel, platinum or palladium catalyst at high temperature (200°C) and high pressure of 10 atmosphere.

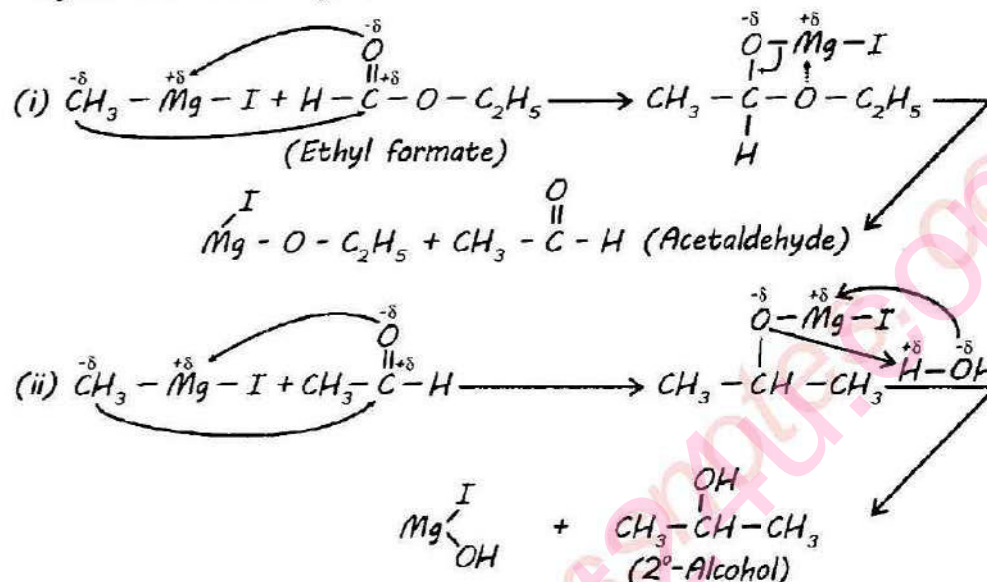


5) Reaction of Grignard Reagent with Esters: (Repetition)

(a) Reaction of Grignard Reagent with Ethyl Formate:

Grignard reagent reacts with ethyl formate, form aldehyde in the

first step. Then aldehyde react with another molecule of Grignard reagent and secondary alcohol is formed.

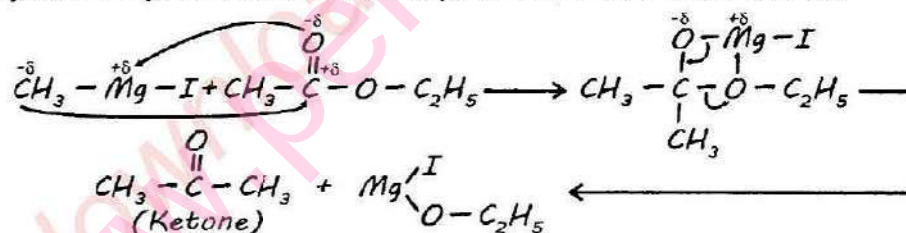


(b) Reaction of Grignard's Reagent with Ethyl Acetate: (Repetition)

Grignard reagent with ethyl acetate and form 3°-alcohol. This reaction complete in two steps.

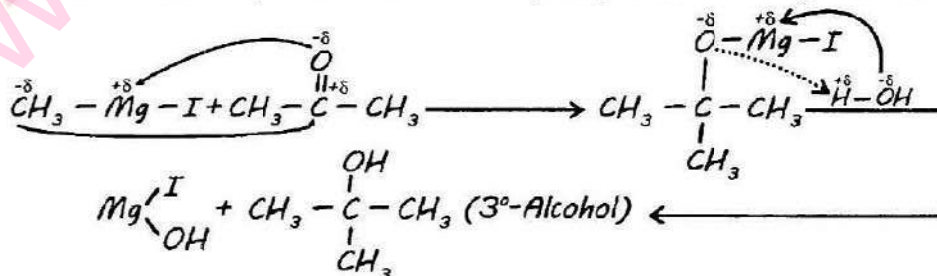
STEP-1:

Grignard reagent react with ethyl acetate and form ketone.



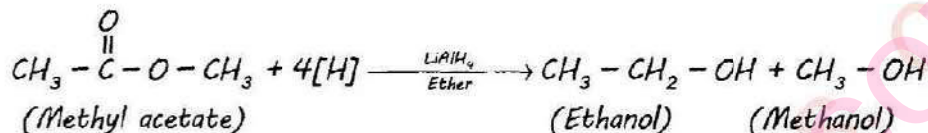
STEP-2:

Ketone [acetone] reacts with another Grignard's reagent molecule to give an unstable addition product, which on hydrolysis for tertiary alcohol.



6) Reduction of Carboxylic Acids and Esters:

Both carboxylic acids and esters can be reduced to primary alcohols with LiAlH_4 .



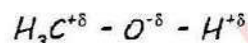
Carboxylic acids cannot be reduced with molecular hydrogen (H_2) and nickel catalyst.

Q5: Explain the reactivity of alcohol.

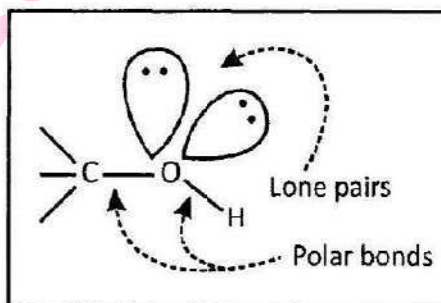
Ans: Reactivity of Alcohol:

Alcohols are reactive organic compounds. Alcohols react with polar and ionic reactants. The following two factors explain the reactivity of alcohols.

- (1) As oxygen is more electronegative than carbon and hydrogen so C-O and O-H bonds are polar.



- (2) The oxygen atom of hydroxyl group has two lone pair of electrons and thus is an electron rich center.



Generally, the reactions of alcohols involve the breaking of either the O-H bond or the breaking of C-O bond. Breaking of either of the two bonds may involve a substitution reaction or an elimination reaction.

Q6: Write down chemical reactions of alcohols.

Ans: Reactions of alcohols are as follow:

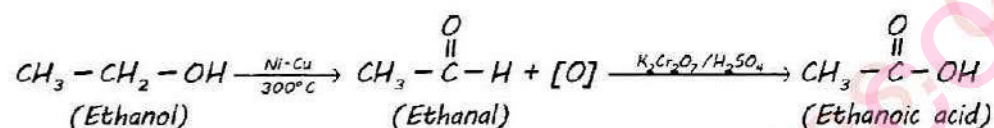
1) Reaction with Halogen Acids:

Alcohols react with halogen acids (HX) and form the corresponding (مشتق) alkyl halides.

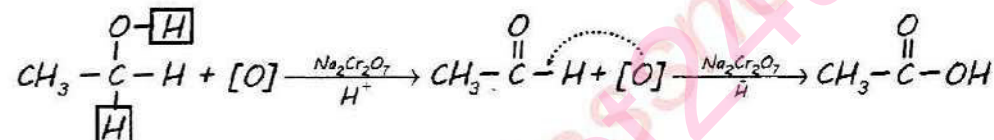
The above reaction is reversible. The equilibrium can be shifted to the forward direction by removing water as soon it is formed.

5) Oxidation:

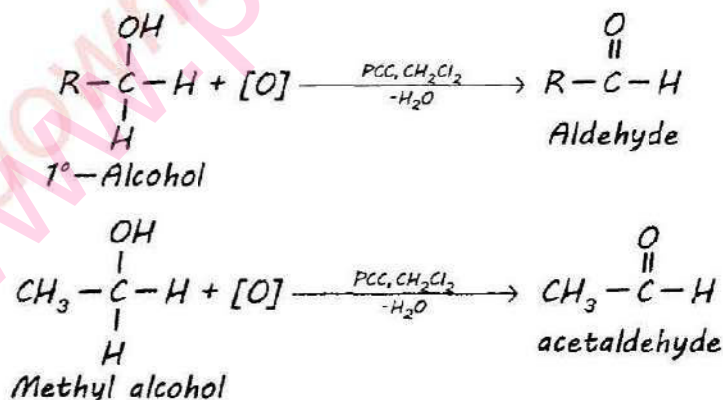
Oxidation means removal of hydrogen. It is also called dehydrogenation. When vapours of alcohols are passed over hot alloys such as nickel-Cu, dehydrogenation/oxidation takes place. Primary alcohols are converted into aldehydes and then to carboxylic acids.



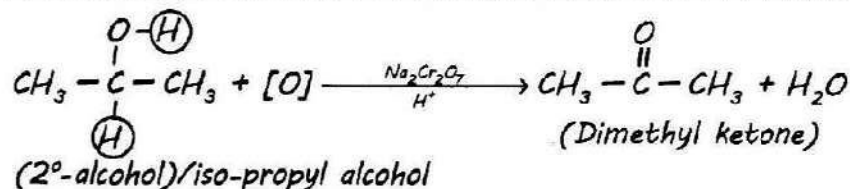
This reaction can also be carried out in the presence of strong oxidizing agent like KMnO_4 or $\text{Na}_2\text{Cr}_2\text{O}_7$.



Assume that the oxygen shown in square brackets is delivered by any of the above oxidizing agents. Oxidation of primary alcohol to aldehydes require special oxidizing agents such as pyridinium chlorochromate (PCC), $\text{C}_5\text{H}_5\text{N}^+\text{HClCrO}_3^-$. PCC is formed when chromic oxide is dissolved in HCl and then treated with pyridine in dichloromethane solvent.



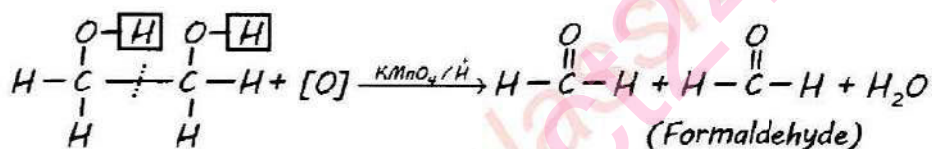
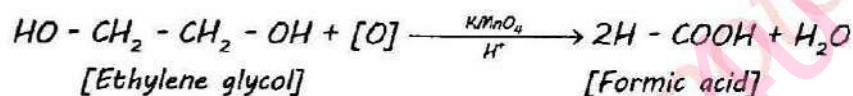
Secondary alcohols are first oxidized to ketones and further oxidation to carboxylic acids needs even more drastic conditions.



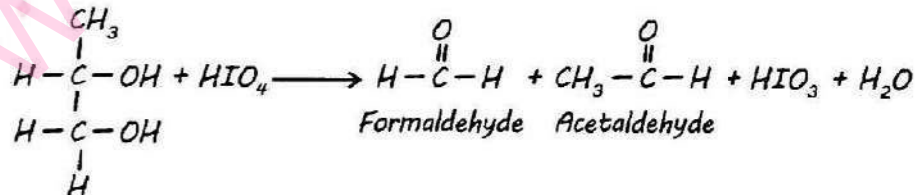
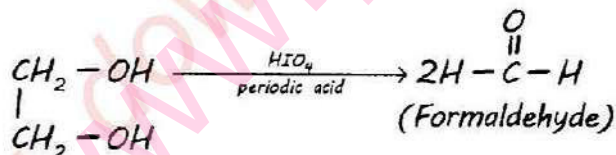
The oxidation of tertiary alcohols do not occurs due to the absence of tertiary hydrogen atom.

6) Cleavage of 1,2-diols [Glycols]:

Ethylene glycol when treated with acidic potassium permanganate [KMnO_4], results in the formation of formic acid by cleavage of C-C bond.



When glycol is treated with per iodic acid or lead tetra acetate gives two molecules of formaldehyde while propylene glycol yield mixture of formaldehyde and acetaldehyde.



Propylene glycol
(propane-1,2-diol)

Q7: What are Sulphur analogue of alcohol and ether?

Ans: Sulphur Analogues of Alcohol and Ether: (ETEA 2017)

Oxygen and Sulphur belongs to the same group (VIA) of periodic table. Thus, there are Sulphur analogues of alcohols and ethers. In these analogue compounds Sulphur atom is present in place of oxygen atom.

$R-OH$ Alcohol	$R-SH$ Thiol	$R-O-R$ Ether	$R-S-R$ Thioether
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The Sulphur analogues of alcohols are called thiols. These analogues are also called alkyl hydrogen sulphides or mercaptans.

The functional group of thiol is $-SH$. This functional group is called thiol group, mercapto or sulphydryl. As these compounds react with mercuric ions (Hg^{++}) to form insoluble salts and thus got the name mercaptan [Latin, mercurium captans = mercury catching].

Common names are formed like those of alcohols, using the name of the alkyl group with the word mercaptan. In IUPAC names, the suffix $-thiol$ is added to the name of the corresponding alkane, and number the chain in the direction that gives the lower locant to the carbon that bears the $-SH$ group.

	CH_3-SH	CH_3-CH_2-SH	$CH_3-\overset{SH}{\underset{ }{CH}}-CH_3$
IUPAC System:	Methanethiol	Ethanethiol	Propane-2-thiol
Common System:	methyl mercaptan	ethyl mercaptan	isopropyl mercaptan

1. Methane thiol [CH_3-SH] is a gas.
2. Ethane thiols and higher members are colourless volatile (evaporatable) liquids at STP.
3. Lower thiols have strong repulsive odour/smell.
4. Methane thiol and ethane thiol are added to natural gas in very small amounts to make gas leakage detectable by smell.

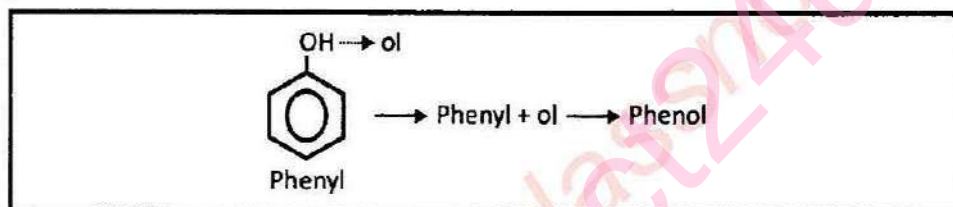
(ETEA 2017)

5. Thiols have lower boiling points than the corresponding alcohols due to the absence of hydrogen bonding.
6. These are insoluble in water and soluble in ethyl alcohol and ether.

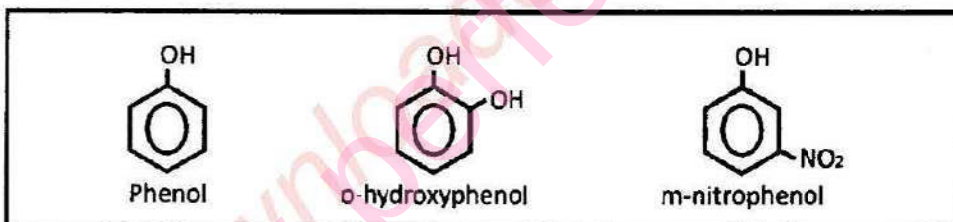
Q8: What are phenols? Write down nomenclature of phenols. Explain the structure of phenol.

Ans: Phenol [Benzenol]: "Hydroxy derivatives of benzene/aromatic hydrocarbons are called phenols." Those organic compounds in which one or more hydrogen atoms of benzene ring are substituted by hydroxyl group are called phenols. The molecular formula of its simple member is C_6H_5OH/C_6H_5O . It is also called carbolic acid. 95% phenol is called carbolic acid. (ETEA 2017)

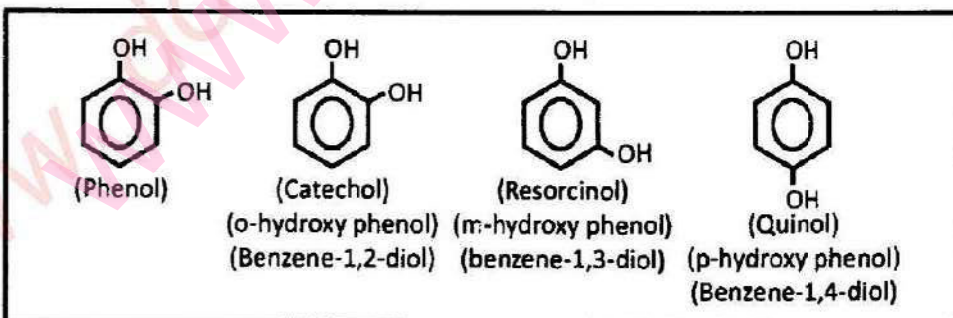
Mr. Runge in 1834 for the first time obtained phenol from coal tar. Phenols may be monohydric, dihydric and polyhydric, depending upon the number of -OH groups attached per molecule. The name "phenol" is the combination of common and IUPAC name.

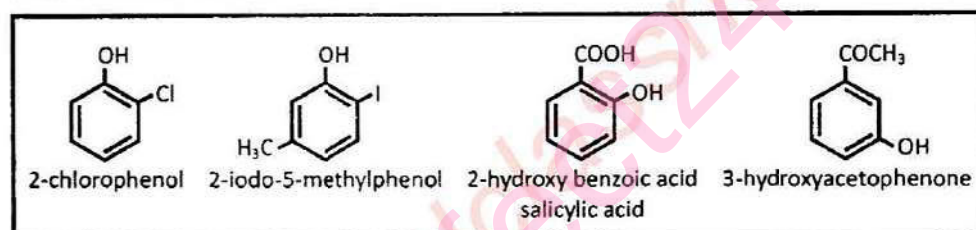
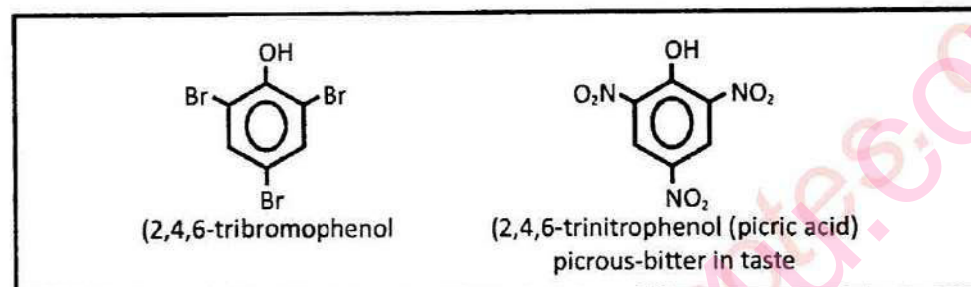
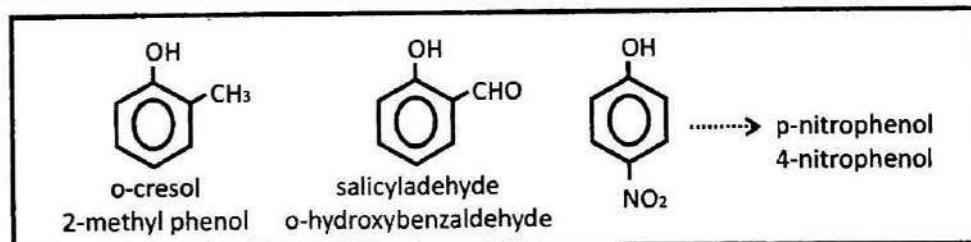


Examples:



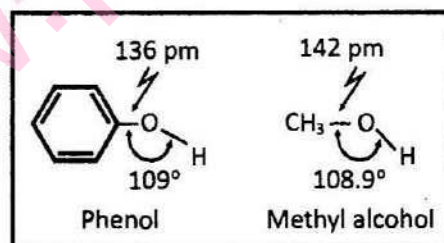
Nomenclature: [$C_6H_5-OH \rightarrow$ Benzenol]





Structure of Phenol:

In phenol hydroxyl group is attached to benzene ring. The molecule has planer structure. The $C - \hat{O} - C$ bond angle is 109° almost equal to tetrahedral angle (109.5°). This angle is not much different from 108.5° , $C - \hat{O} - H$ bond angle of methanol.



In phenol the six carbon atoms are sp^2 -hybridized forming a hexagonal ring with internal angle of 120° . Since the bonds formed by sp^2 -hybridized carbon atoms are shorter than those formed by sp^3 -hybridized carbon, therefore the C-O bond length is slightly less than the C-O bond length in methanol.

Q9: Write down physical properties of phenol.

Ans: Physical Properties of Phenol:

- (1) At room temperature and pressure, phenols are colourless liquids or low melting crystalline solids.
- (2) They have a characteristic smell.
- (3) Phenol vapours are highly toxic (زہریلا).
- (4) The boiling points of phenols are higher than aliphatic alcohols of comparable molecular weights. This is due to stronger intermolecular hydrogen bonding in phenols as compared to alcohols.
- (5) Due to stronger hydrogen bonding, phenols are more soluble in water than alcohols of comparable molecular mass.
- (6) Above 65°C phenols and water are miscible in all proportions.
- (7) The liquid phenol, containing 5% water is called carbolic acid and is used as disinfectant and germicide.
- (8) The melting point of phenol is 41°C and boiling point is 182°C.
- (9) It turns pink when exposed to air and light.
- (10) Phenol produces painful blisters (آب/آبہ) in contact with skin.

Q10: Explain the acidity of phenol.

Ans: Acidity of Phenol:

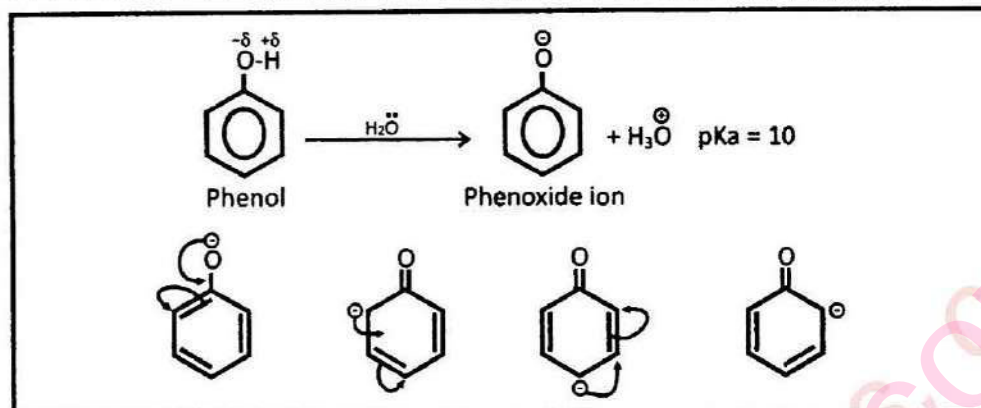
Phenols are more acidic than alcohols but less acidic than carboxylic acids and carbonic acid.

Compound	Formula	K _a (Approximately)	pK _a
Phenol	Ar - OH	10 ⁻¹⁰	10
Water	H - OH	10 ⁻⁷	7
Carboxylic acids	R - COOH	10 ⁻⁵	5
Carbonic acid	H ₂ CO ₃	10 ⁻⁷	7
Alcohol	R - OH	10 ⁻¹⁶ - 10 ⁻¹⁸	16-18

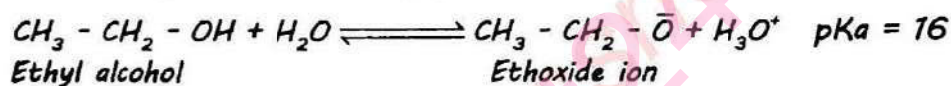
Lower the value of pK_a, stronger will be the acid.

Carboxylic acid > Water > Phenol > Alcohol

- Phenols are acidic due to the formation of stable phenoxide ions in aqueous solutions.



The negative charge spreads throughout the benzene ring and is thereby dispersed. This delocalization of the charge accounts/counts for the stability of benzene ring/phenoxide ion.

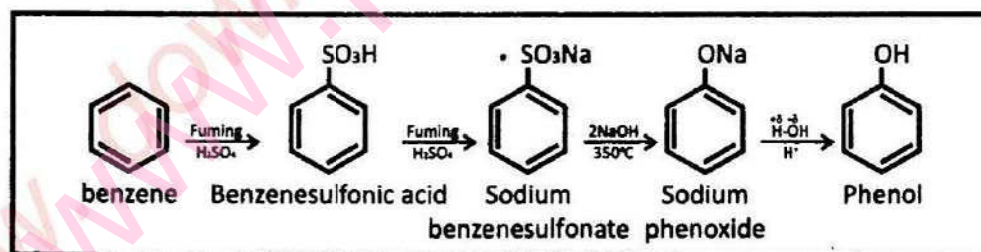


Q11: Write down various methods for the preparation of phenol.

Ans: Preparation of Phenol:

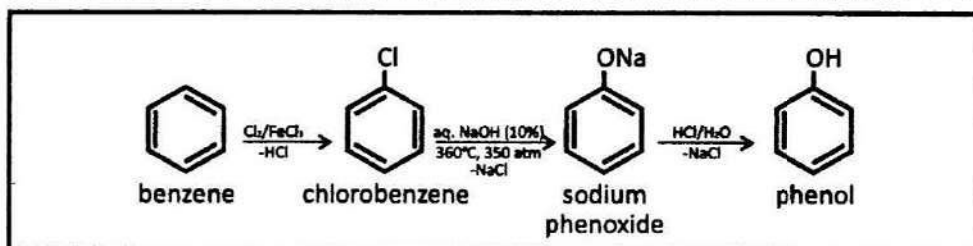
1) From Benzene Sulphonic Acid:

First benzene reacts with concentrated sulphuric acid and form benzene sulphonic acid. Then benzene sulphonic acid is neutralized by sodium hydroxide solution and form sodium phenoxide. Finally, sodium phenoxide reacts with water and form phenol.



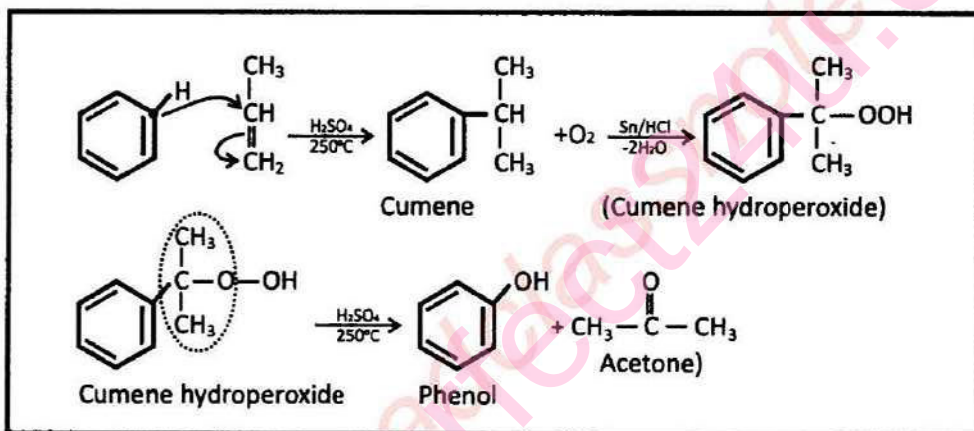
2) From Chlorobenzene [Dow Process]:

This process was developed by Dow, chemical company of USA in 1928. In this process first chlorobenzene is formed. Then it is treated with 10% aqueous solution of sodium hydroxide at 350°C and high pressure, followed by treatment with HCl.



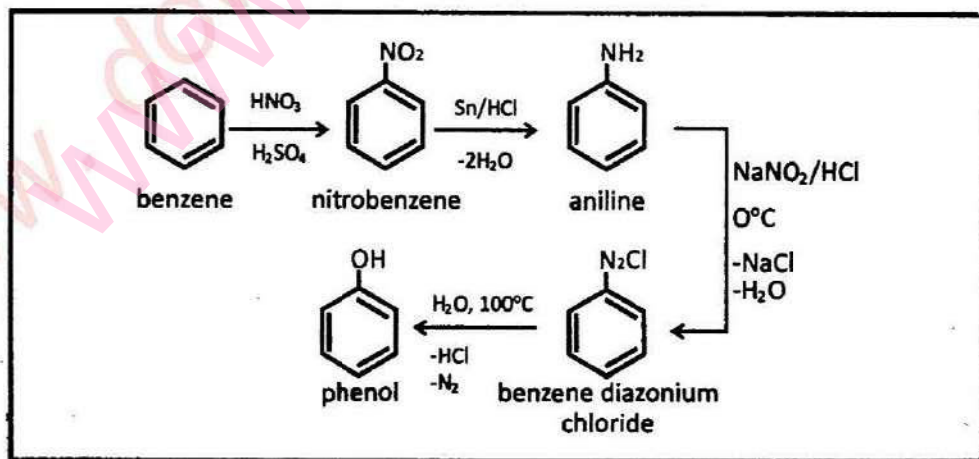
3) From Acidic Oxidation of Cumene:

This method involve air oxidation of cumene [isopropyl benzene] to cumene hydroperoxide, which on treatment with dilute HCl form phenol along with acetone/dimethyl ketone.



4) From Hydrolysis of Diazonium Salts:

It is a simple laboratory method in which a solution of benzene diazonium chloride is warmed on a water bath at 50°C . Benzene diazonium chloride is prepared from aniline.



Phenol is extracted with diethyl ether by steam distillation

Q12: (a) Explain the reactivity of phenol.
(b) Write down important reactions of phenol.

Ans: (a) Reactivity of Phenol:

Generally, phenol shows two types of reactions:

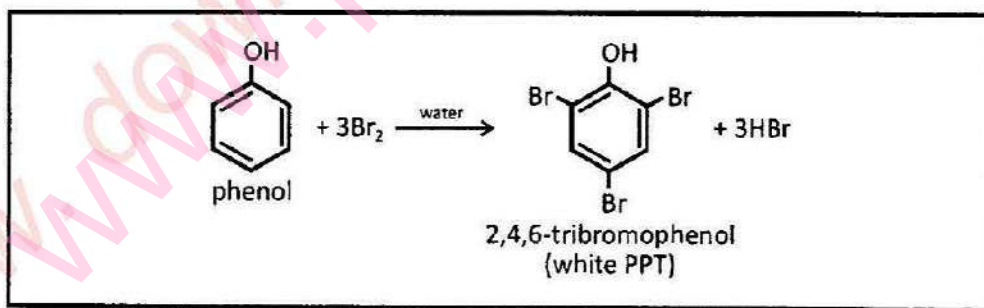
- (i) Reactions due to hydroxyl group
 - (ii) Reactions due to benzene ring
- (i) In reactions due to hydroxyl group, usually the oxygen-hydrogen bond is broken down to form salts, ethers and esters.
- (ii) In the second type of reactions, benzene ring undergoes electrophilic substitution reactions.

The -OH group is ortho/para directing group and ring activator. Hydroxyl group is electron donating group, increases electron density of the ring at ortho and para positions by giving its electron pair to the ring and thus increases the reactivity of the ring relative to benzene itself.

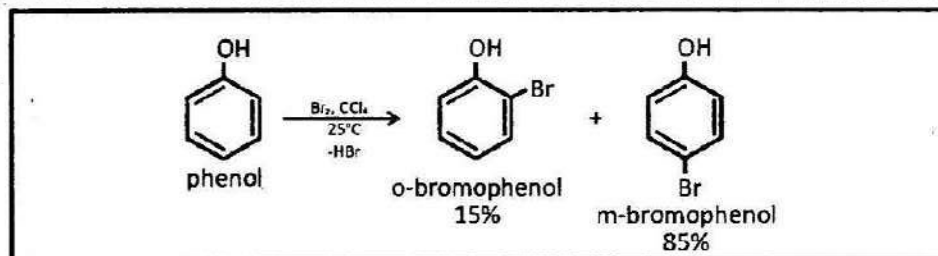
(b) Important Reactions of Phenol:

(1) Halogenation:

Phenol reacts with bromine water and give white precipitate of 2,4,6- trinitrophenol. Chlorine reacts in the presence of non-polar solvent like CCl_4 or CS_2 .



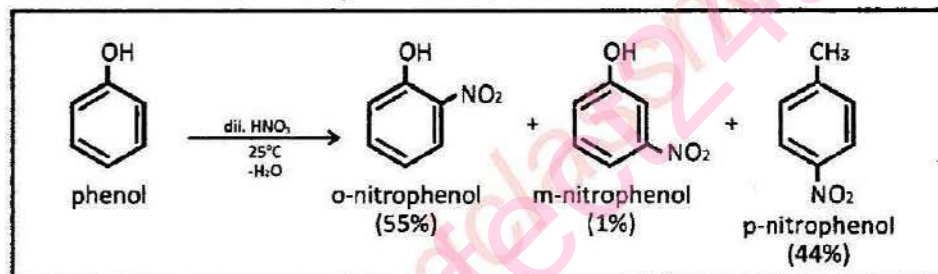
Phenol in the presence of a non-polar solvent like, carbon tetrachloride or carbon disulphide, at low temperature, yield a mixture of o- and p-bromophenol. The two isomers differ in boiling point and can be separated by distillation.

**Importance:**

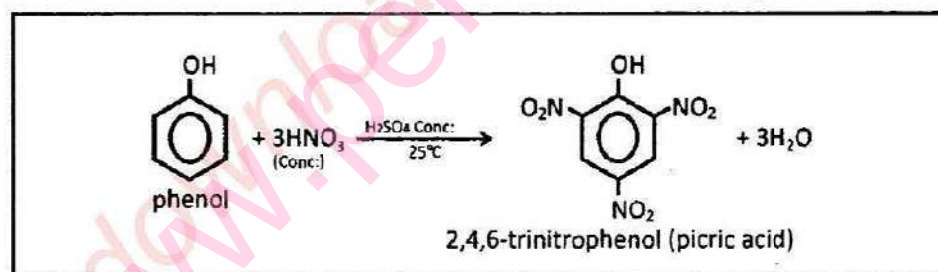
During this reaction the colour of bromine disappears, so this is one of the best test to check the presence of phenol in a mixture. For chlorination a catalyst has to be used.

(2) Nitration:

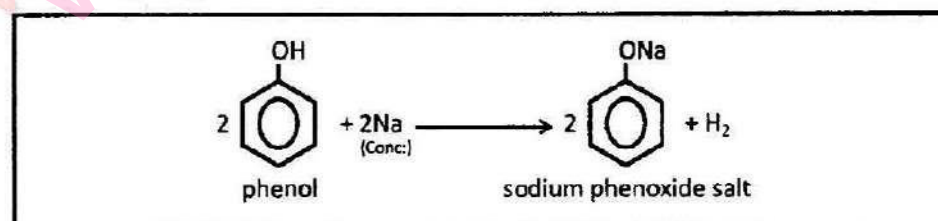
When phenol is treated with dilute HNO_3 in the presence of H_2SO_4 , a mixture of ortho and para nitrophenol is formed.



When concentrated nitric acid is used, then 2,4,6-trinitrophenol is formed.

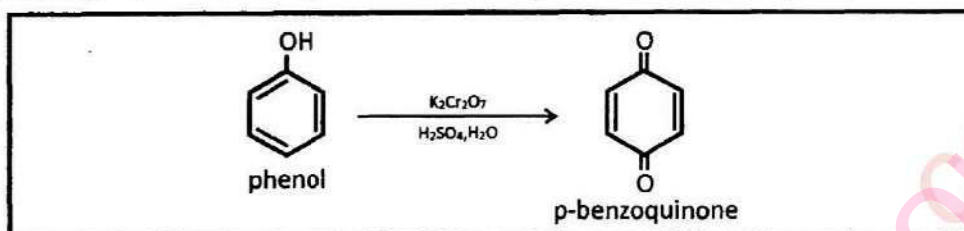
**(3) Reaction with Sodium Metal (due to -OH group reaction):**

Phenol being acidic in nature, react with sodium metal to form salt and hydrogen gas is released.

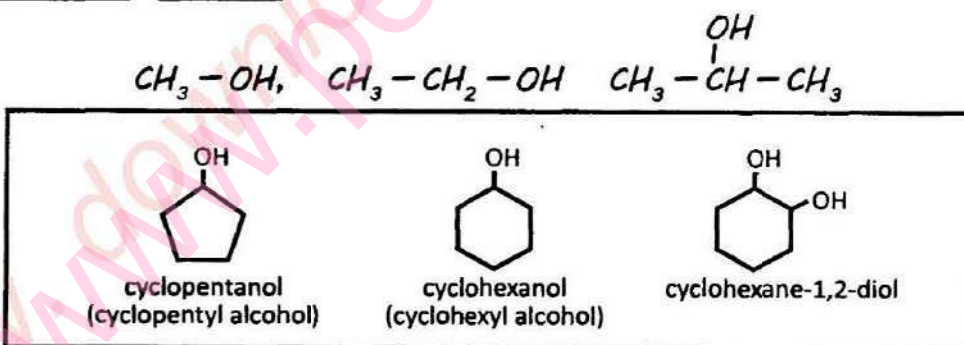
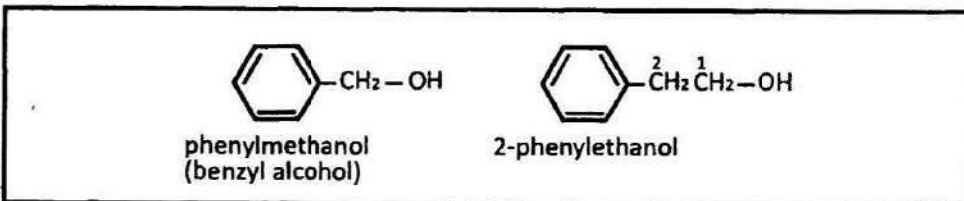


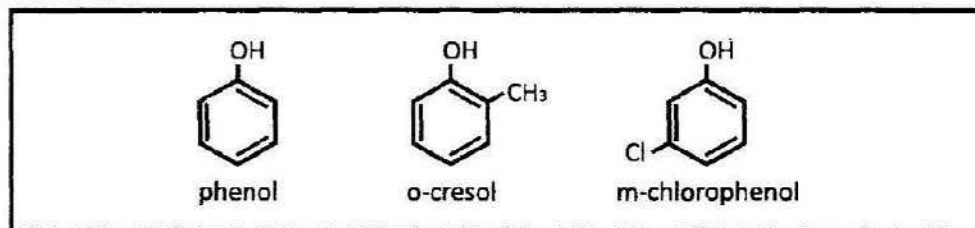
(4) Oxidation:

Phenol is observed to undergo oxidation even more readily than primary and secondary alcohols. The product is benzoquinone.

**Q13: Differentiate between alcohols and phenols.****Ans-**

1. Both alcohol and phenol contain the same functional group i.e. hydroxyl group.
2. In alcohol -OH group is attached to an alkyl group while in phenol it is attached to an aryl group.
3. Alcohols are less acidic than phenols.
4. Alkoxide ion ($\text{R} - \bar{\text{O}}$) is less stable than phenoxide ion.
5. Alcohols are more soluble in water than phenols.
6. Alcohols mainly undergo nucleophilic substitution reactions while phenol undergo electrophilic substitution reactions.
7. Alcohol reactivity is due to -OH group while the reactivity of phenol is due to both -OH group as well as benzene ring.

Examples: Alcohols:**Aromatic Alcohols:**

Phenols:

It should be noted that benzyl alcohol and cresols are also isomers. But benzyl alcohol is an aromatic alcohol, while cresols are phenols.

Q14: What are ethers? How ethers are named by common and IUPAC system?

Ans: Ethers:

Ethers are organic compounds in which an oxygen atom is directly bonded with two carbon atoms [C-O-C]. These are represented by the general formula "R-O-R".

Simple Ethers:

"When both the alkyl groups are similar then these are called simple ethers."

Mixed Ethers:

"When the alkyl groups are different then such ethers are called mixed ethers." General formula of ether is "R-O-R".

Possibilities:

R and R' both are alkyl groups:	$\text{CH}_3 - \text{O} - \text{CH}_3$
R and R' both are aryl groups:	$\text{C}_6\text{H}_5 - \text{O} - \text{C}_6\text{H}_5$
R is alkyl group and R' is aryl group:	$\text{CH}_3 - \text{O} - \text{C}_6\text{H}_5$
R and R' both are equal:	$\text{C}_2\text{H}_5 - \text{O} - \text{C}_2\text{H}_5$
R and R' both are different:	$\text{C}_2\text{H}_5 - \text{O} - \text{CH}_3$

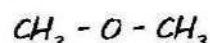
(ETBA 2017)

The most important ether is diethyl ether, commonly referred as ether. Its chemical formula is $\text{CH}_3 - \text{CH}_2 - \text{O} - \text{CH}_2 - \text{CH}_3$ OR $\text{C}_2\text{H}_5 - \text{O} - \text{C}_2\text{H}_5$.

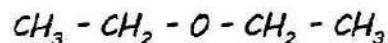
Nomenclature:**Common System:**

In common system the alkyl groups or aryl groups attached to

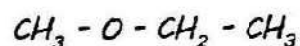
oxygen atom are named in alphabetical order, and the word "ether" is used at the end. The word "di-" is used for two similar attached groups.



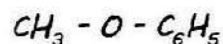
[Dimethyl ether]



[Diethyl ether] or [Ethyl ether]



[Ethyl methyl ether]

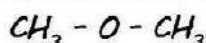


[Methyl phenyl ether] anisol

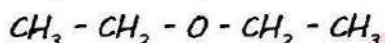


IUPAC System:

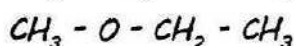
In IUPAC system, ethers are named as alkoxy alkanes. The alkyl group which is of larger size is considered to be an alkane. The name of the alkane is prefixed by the name of the alkyl group and the position number. The smaller group plus oxygen atom form the alkoxy group.



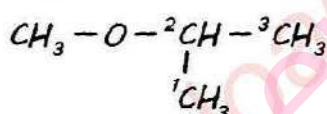
Methoxy methane



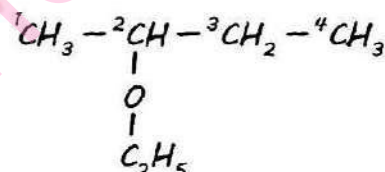
Ethoxy ethane



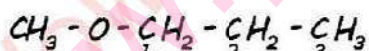
Methoxy ethane



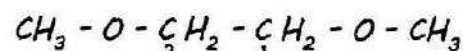
[2-methoxy propane]



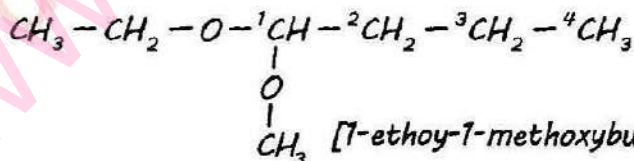
[2-ethoxy butane]



[1-Methoxy propane]



[1,2-Dimethoxy ethane]



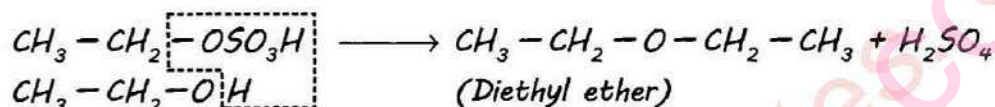
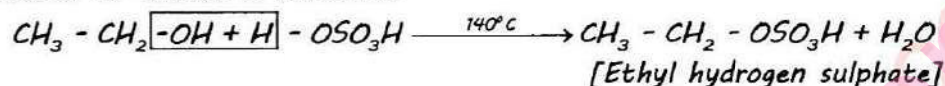
[1-ethoxy-1-methoxybutane]

Q15: Write down various methods for the preparation of ethers.

Ans: Preparation of Ether:

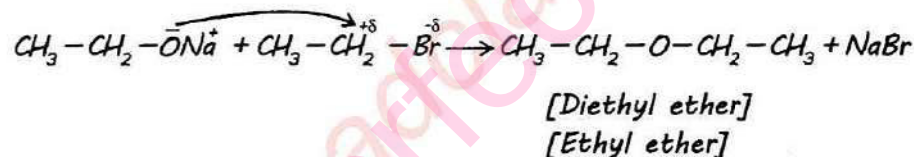
1) Dehydration of Alcohol [Intermolecular Dehydration of Alcohol]: (ETEA 2015)

This method can be used to prepare ethers with molecules having the same alkyl groups on both sides of the oxygen atom. Diethyl ether is obtained when ethanol is excess quantity is heated at 140°C with concentrated sulphuric acid. The reaction conditions must be well controlled, otherwise at temperature higher than 140°C ; the formation of alkene is favoured.



2) Williamson's Synthesis [Preparation of Mixed Ethers]:

In this method, alcohol reacts with sodium metal, to produce sodium alkoxide which produce ether when treated with an alkyl halide.



Q16: Write down physical properties of ether.

Ans: Physical Properties:

1) Physical State:

Dimethyl ether and ethyl methyl ether are gases at RTP, while others are colourless volatile liquids with pleasant odours.

2) Inflammability:

Ethers are highly inflammable.

3) Boiling Point:

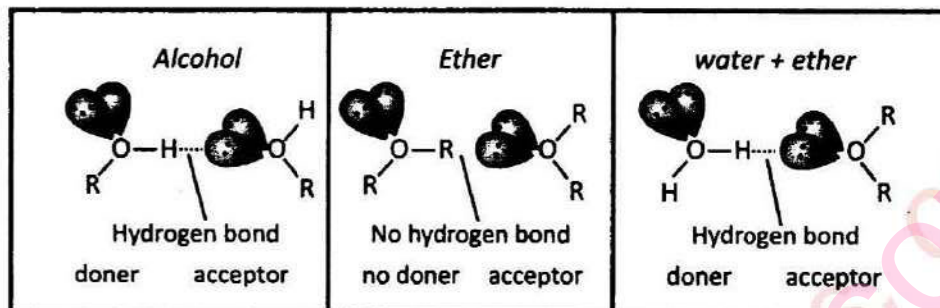
They have much lower boiling points than those of alcohols of comparable molecular weights, due to absence of hydrogen bonding.

4) Solubility:

Low molecular weight ethers show some solubility in water as they can form hydrogen bonding with water. Ethers are readily soluble in organic solvents.

5) Density:

Ethers are generally less dense than water.



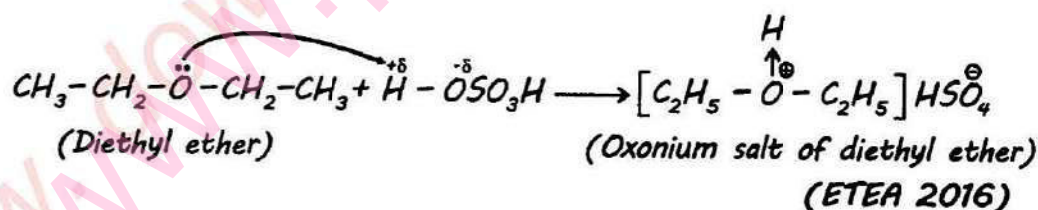
Hydrogen bonding in alcohol molecules, and between water and ethers.

Q17: Explain reactivity of ethers. Write down some important reactions of ether.

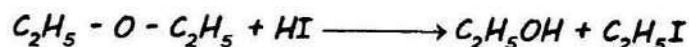
Ans: Ethers are quite stable compounds. They do not react with bases, active metals, oxidizing agents and reducing agents. These are also stable towards dilute acids. However, they form oxonium salts with strong concentrated acids.

Important Reactions of Ethers:**1) Formation of Oxonium Salt:**

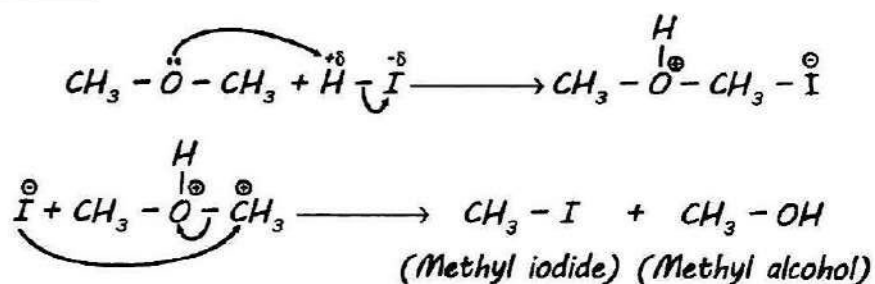
Ether react with cold and concentrated $\text{HCl}/\text{H}_2\text{SO}_4$ to form oxonium salts. Oxygen of ethers donate a pair of electrons to hydrogen ion and form these salts.

**2) Reaction with Halogen Acids:**

Ethers react with hot concentrated HI/HBr to form alcohol and alkyl halide.

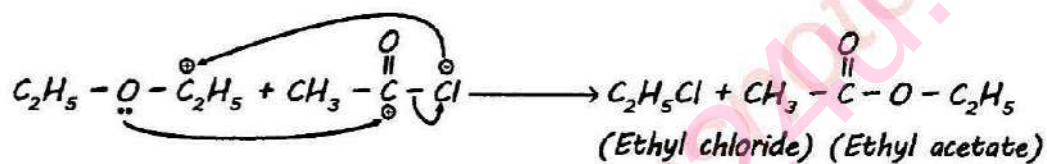


Mechanism:



3) Reaction with Acetyl Chloride: (Cleavage of Ether Linkage)

Diethyl ether react with acetyl chloride in the presence of anhydrous zinc chloride on heating, produces ethyl chloride and ethyl acetate.



Exercise**1: Choose the correct option:**

1. Isopropyl alcohol is a type of:
(a) Primary alcohol (b) Secondary alcohol✓
(c) Tertiary alcohol (d) None of these
 2. Which of the following have the highest boiling point?
(a) Dimethyl ether (b) Ethyl alcohol
(c) N-propyl alcohol✓ (d) Isopropyl alcohol
 3. Trimethylene glycol is a:
(a) Vic-diol✓ (b) Gem-diol
(c) Triol (d) None of these
 4. The final product of oxidative cleavage of ethylene glycol with periodic acid is:
(a) Formaldehyde (b) Acetaldehyde
(c) Formic acid (d) Mixture of formaldehyde and acetaldehyde✓
 5. Oxygen carrying positive charge and bonded to three other atoms is called:
(a) Oxide ion (b) Oxonium ion✓
(c) Carbocation (d) Carbanion
 6. Which of the proper reagent used for oxidation of a primary alcohol to aldehyde?
(a) Acidified dichromate (b) Acidified chromate
(c) Acidified permanganate (d) PCC✓
 7. Which one is an aromatic alcohol?
(a) Methyl alcohol (b) Ethyl alcohol
(c) Benzyl alcohol✓ (d) P-cresol
 8. Compound which is added to natural gas to make gas leakage detectable:
(a) Phenol (b) Ethanthiol✓
(c) Methanol (d) Hydrogen sulphide
 9. Which of the following is more reactive toward Lucas reagent?
(a) Methanol (b) Ethanol
-

- (c) 2-methyl-2-propanol ✓ (d) 2-butanol
10. Ethoxyethane when treated with conc. H_2SO_4 , it produces:
 (a) Carbocation (b) Oxonium ion ✓
 (c) Carbanion (d) Oxalate ion
11. Lucas reagent is:
 (a) $Zn-Hg/HCl$ (b) $ZnCl_2 + HCl$ ✓
 (c) $Zn + H_2O$ (d) $Na + liq. NH_3$
12. The reaction of an alcohol with sodium produces:
 (a) Ethane (b) Ethene
 (c) Alkoxide ✓ (d) Aldehyde
13. Benzene diazonium salt is a reactive salt and upon hydrolysis yield:
 (a) Phenol ✓ (b) Benzene
 (c) Diazobenzene (d) Benzoic acid
14. Oxidation of secondary alcohol gives:
 (a) Carboxylic acid (b) Ether
 (c) Aldehyde (d) Ketone ✓
15. The appearance of cloudiness in the Lucas test for alcohol is due to formation of:
 (a) Alkyl chloride ✓ (b) Acid chlorides
 (c) Aldehydes (d) Ketones

Short Questions

2. Briefly answer the following questions:

Q1: What is the basic difference between an alcohol and phenol, although both have the same functional group?

Ans: Please see question # 13.

Q2: How many isomeric alcohols are possible for C_4H_9OH ? Draw their structure formula and write both common and IUPAC names.

Ans: Three isomeric alcohols are possible for C_4H_9OH .

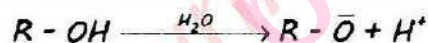
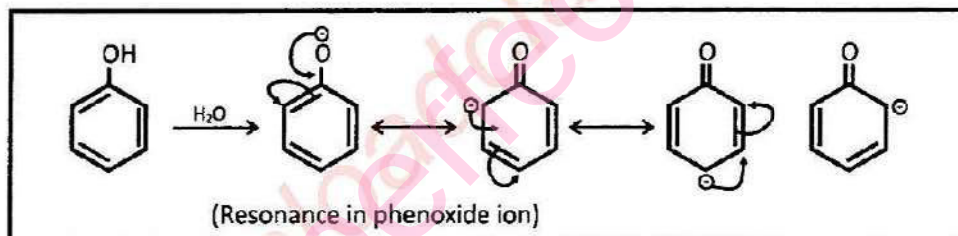
Structural Formula	Common Names	IUPAC Names
$\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{OH}$	(n-butyl alcohol)	(1-butanol)
$\begin{array}{c} \text{OH} \\ \\ \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CH}_3 \end{array}$	(sec-butyl alcohol) (iso-butyl alcohol)	(2-butanol)
$\begin{array}{c} \text{OH} \\ \\ \text{CH}_3 - \text{C} - \text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	(ter-butyl alcohol) (neo-butyl alcohol)	(2-methyl butanol)

Q3: What is Lucas test? How Lucas test is used to distinguish alcohols?

Ans: Please see question # 6.

Q4: Why phenol is more acidic than alcohol?

Ans: Phenol is more acidic than alcohol because after losing H^+ [hydrogen ion] the phenoxide ion is resonance stabilized while there is no resonance in alkoxide ion.



(No resonance in alkoxide ion)

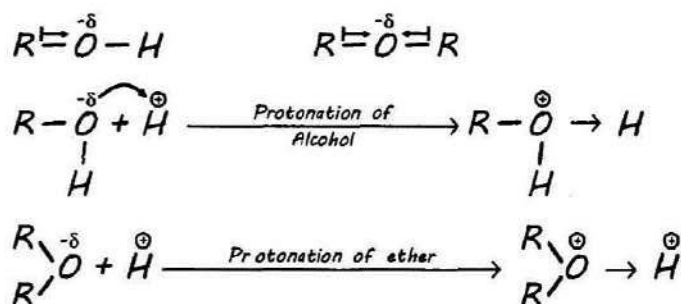
Q5: What is meant by primary, secondary and tertiary alcohols?

Ans: Please see question # 1 theory.

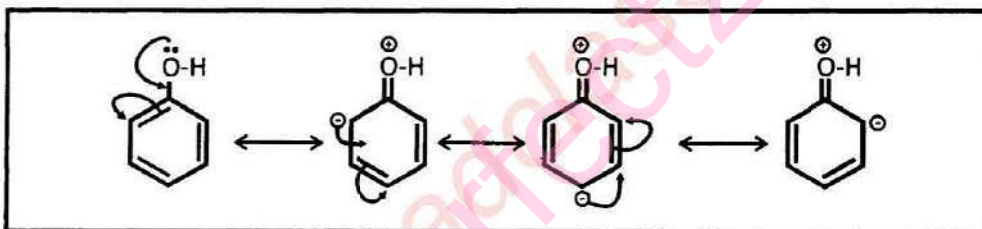
Q6: Why alcohols and ethers are easily protonated as compared to phenol?

Ans: Alcohol and ether are easily protonated. It is because in alcohol and ether electron donating groups i.e. alkyl groups are directly attached to oxygen atom of ether and oxygen atom of hydroxyl group in case of alcohol. As "R" group is electron donating group so it

increases electrons density or partial negative charge upon oxygen atom, due to which this oxygen accept proton easily and hence can be easily protonated.

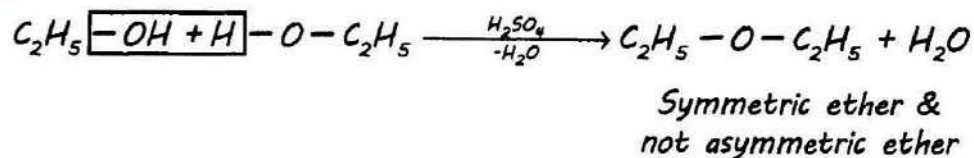


On the other hand, there is no such electron donating group (R-group) attached to oxygen of phenol so it cannot be protonated easily. Secondly the lone pair of electron of oxygen of phenol are in conjugation with the aromatic ring and are delocalized.



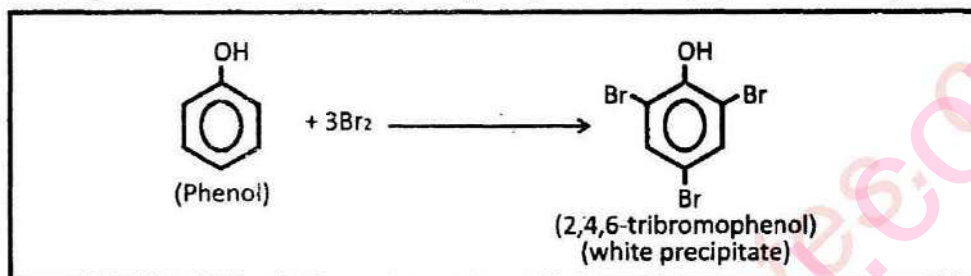
Q7: Why intermolecular dehydration of alcohol is not a suitable method for synthesis of asymmetric ethers/mixed ethers?

Ans: We know that asymmetric ethers are those in which different alkyl groups are attached to oxygen atom. Intermolecular dehydration method is not used for the preparation of asymmetric ethers because the "R" groups are similar. For example: if we want to carry out dehydration of ethyl alcohol, two ethyl groups will attach to both sides of the oxygen atom and as a result symmetric ether will be produced.

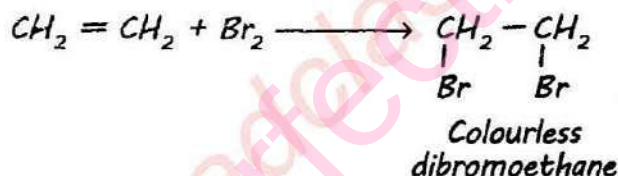


Q8: How bromine water test in alkene differ from bromine water test for phenol?

Ans: When bromine is added to phenol a white precipitate is formed. The formation of white precipitate confirms the presence of phenol in the given mixture. The white precipitate is 2,4,6-tribromophenol.



On the other hand, when bromine water is added to ethene [alkene] or when alkene is passed through bromine water, the colour of bromine rapidly discharges and a colourless dibromo-compound is formed.



Simply in case-I white precipitate is formed while in case-II only colour change takes place and no precipitate is formed.

Q9: Why benzene diazonium salt is not much stable and hydrolyze to phenol easily?

Ans: Benzene diazonium salt is unstable due to the presence of nitronium ion ($\text{N} \equiv \text{N}^+ \bar{\text{X}}$). As nitronium ion is charged body and so unstable and easily decomposes.

Q10: Why tertiary alcohol cannot be oxidized?

Ans: Tertiary alcohol cannot be oxidized by an oxidizing agent because there is no hydrogen attached to tertiary carbon atom.

Long Questions

Q1: (a) Describe the reaction for the preparation of diethyl ether, by dehydration of alcohol and Williamson's synthesis.

Ans: Please see question # 15.

(b) Write two chemical reactions of diethyl ether.

Ans: Please see question # 17.

(c) Enlist the physical properties of ethers.

Ans: Please see question # 16.

Q2: (a) What are phenols? Give methods of preparation of phenols.

Ans: Please see question # 11.

(b) Discuss the acidic behaviour of phenol.

Ans: Please see question # 12.

Q3: Give detail description of structure and chemical properties of phenols.

Ans: Please see question # 8 for structure and question # 12 for chemical properties of phenols.

Q4: (a) Discuss the structure, synthesis and chemical reactions of alcohols.

Ans: Please see question # 3 for structure of alcohol, question # 4 for synthesis of alcohol and question # 6 for chemical reactions.

(b) How alcohols are slightly acidic?

Ans: Please see question # 3 part (b).

Q5: (a) How alcohol can be prepared from Grignard's reagents?

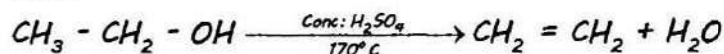
Ans: Please see question # 4 chemical reaction number 3 and 5.

(b) Mention the reactions for the formation of the following compounds from alcohol:

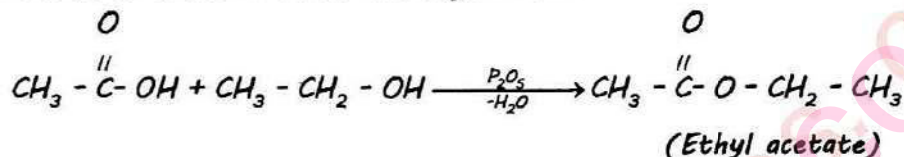
- (i) Ethene
- (ii) Ethyl acetate
- (iii) Acetone
- (iv) Formaldehyde

Ans.

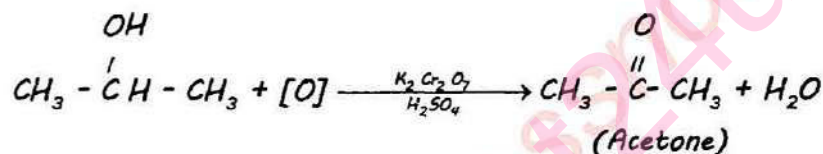
- (i) Ethene can be formed from alcohol by the dehydration of alcohol.



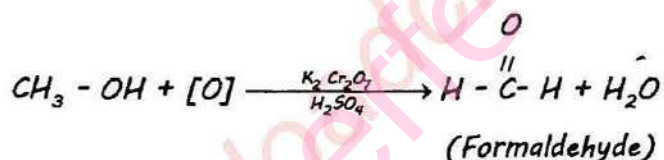
- (ii) Ethyl acetate: Ethyl acetate can be formed from alcohol when alcohol is treated with carboxylic acids.



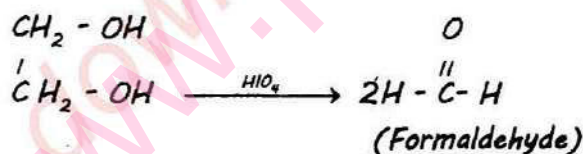
- (iii) Acetone: Acetone can be formed from alcohol, when alcohol is treated with potassium dichromate.



- (iv) Formaldehyde: Formaldehyde can be obtained when methyl alcohol is oxidized by potassium dichromate.



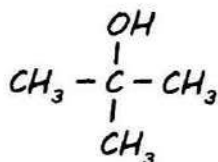
Similarly, formaldehyde can also be obtained when 1,2-ethandiol is cleaved by periodic acid.



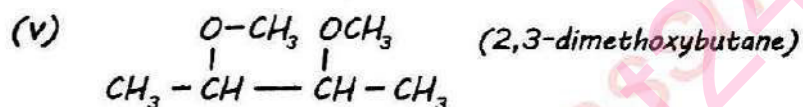
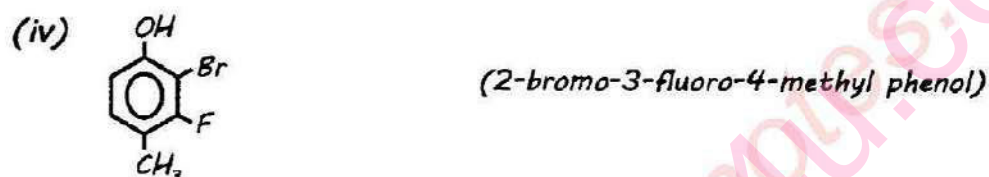
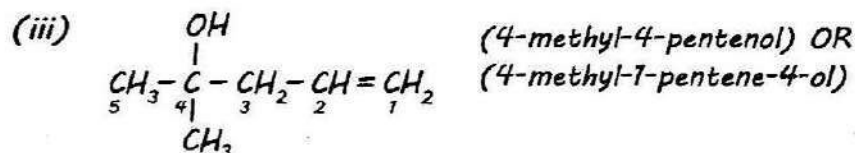
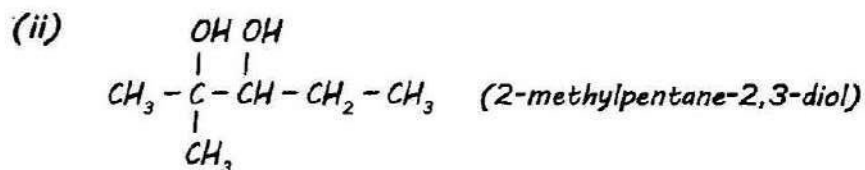
(c) Write the systematic names for the following organic compounds:

Ans.

(i)



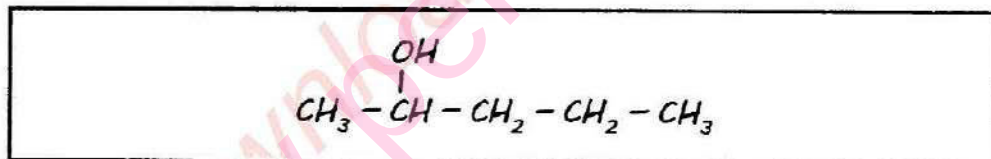
(2-methyl-2-propanol)



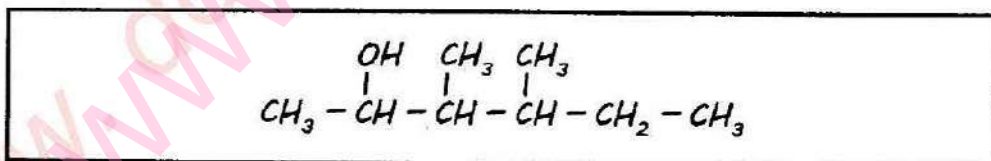
(d) Draw the structural formula of the following organic compounds:

Ans.

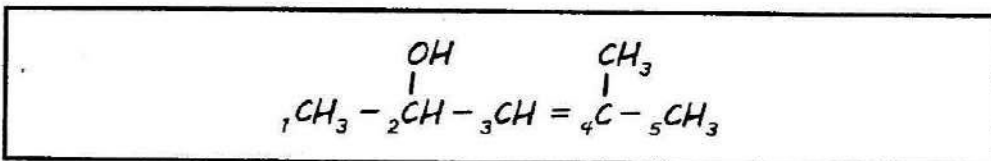
(i) Pentane-2-ol



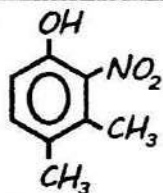
(ii) 3,4-dimethylhexane-2-ol



(iii) 4-methylpent-3-ene-2-ol



(iv) 3,4-dimethyl-2-nitrophenol



(v) 2,3-dimethoxy-4-methylpentane

