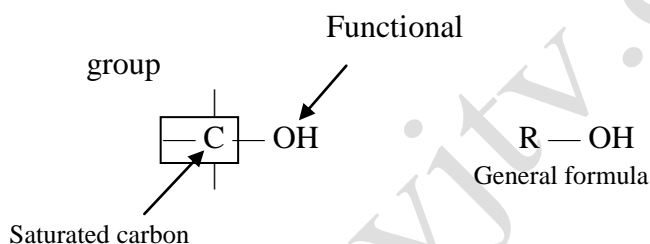


CHAPTER 6

ALCOHOLS, PHENOLS AND ETHERS

Alcohols, phenols and ethers are the derivatives of water. In alcohol one H of H_2O has been replaced by an alkyl group. In phenol one H is replaced by an aryl group while in ether both hydrogens have been replaced by alkyl/aryl groups.

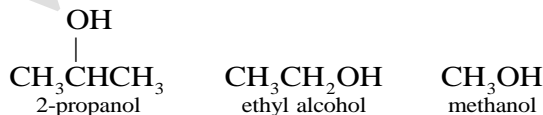
Alcohols are compounds in which a hydroxyl ($-OH$) group is attached to saturated carbon atom. These are the hydroxy derivatives of alkanes. When H atom of an alkane is replaced by hydroxyl group ($-OH$) the resulting compound is called an alcohol.



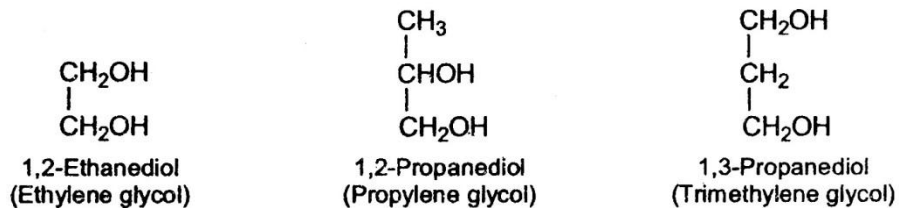
The hydroxyl group is the functional group of alcohols. $R-OH$ is the general formula of alcohol. It is represented by $C_nH_{2n+1}OH$ or $C_nH_{2n+2}O$.

Types of alcohols: On the basis of number of $-OH$ groups, alcohols may be of the following four types.

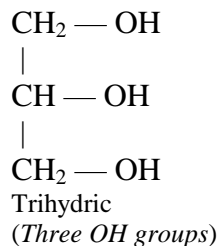
I. Monohydric Alcohols: Alcohols containing one hydroxyl group are called Monohydric Alcohols. Examples are,



II. Dihydric Alcohols: Alcohols containing two hydroxyl groups are known as Dihydric Alcohols. Dihydric alcohols or diols are usually called glycols because of their sweet taste. Glycys = Sweet. Examples are,



III. Trihydric Alcohols: Alcohols containing three hydroxyl groups are known as Trihydric Alcohols. Trihydric alcohols or triols are also called glycerols.



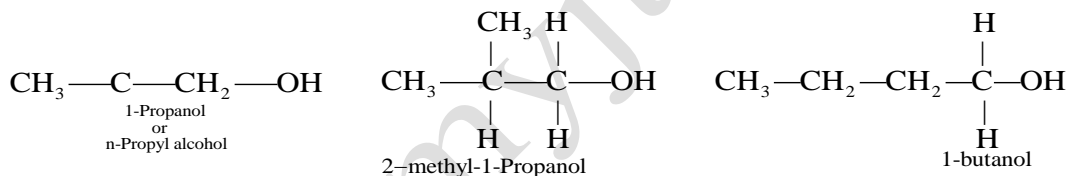
IV. Polyhydric Alcohols: Alcohols containing many hydroxyl groups are known as Polyhydric Alcohols.

The most common polyhydric alcohol is manitol which has six hydroxyl groups. It is a hexane hexaol.

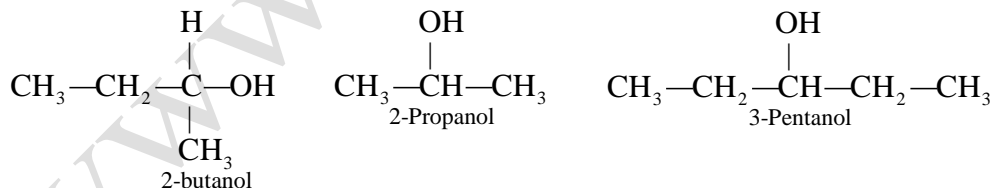
Types of monohydric alcohols

Monohydric alcohols are further of three types.

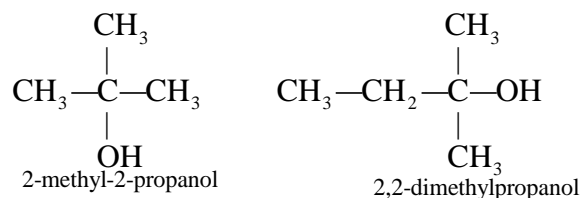
Primary or (1°) alcohols: Alcohols in which hydroxyl group (OH) is directly attached to primary carbon atom are called primary alcohols. Examples are,



Secondary or (2°) alcohols: Alcohols in which hydroxyl group is directly attached with secondary carbon atom are called secondary alcohols. Examples are,



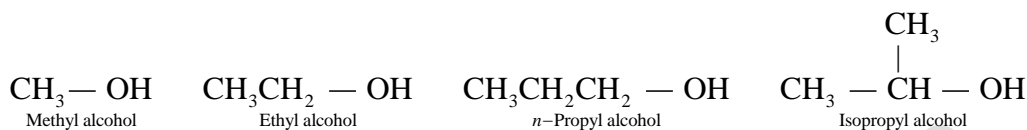
Tertiary or (3°) Alcohols: Alcohols in which the hydroxyl group is directly attached to a tertiary carbon atom are called tertiary alcohols. Examples are,



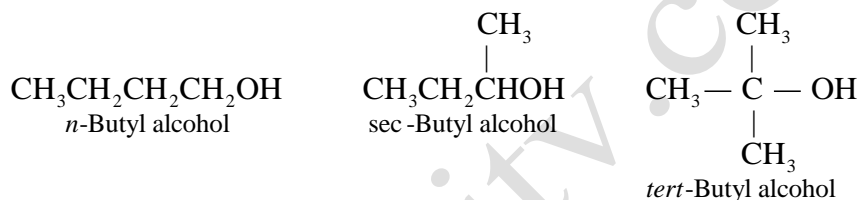
Nomenclature

Alcohols are named by three systems:

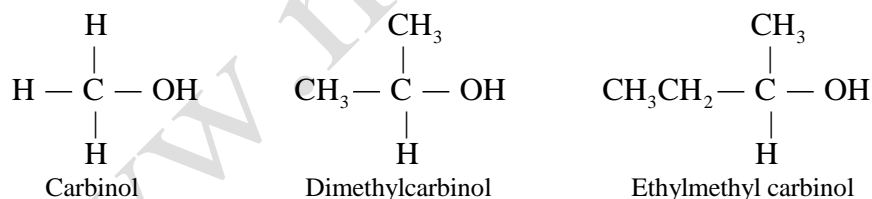
(1) **Common System:** In this system alcohols (R-OH) are named as *Alkyl Alcohols*. The alkyl group attached to the -OH group is named and 'alcohol' is added as a separate word. For example,



As we go higher in the series, it becomes necessary to indicate whether a particular alcohol is primary (1°), secondary (2°), or tertiary (3°). The prefix secondary is abbreviated as *sec-*. The prefix tertiary is abbreviated as *tert-* or *t-*. For example,



(2) **Carbinol System:** In this system alcohols are considered as derivatives of methyl alcohol which is called *Carbinol*. The alkyl group attached to the carbon carrying the -OH group are named in alphabetical order. Then the suffix *-carbinol* is added. For example,

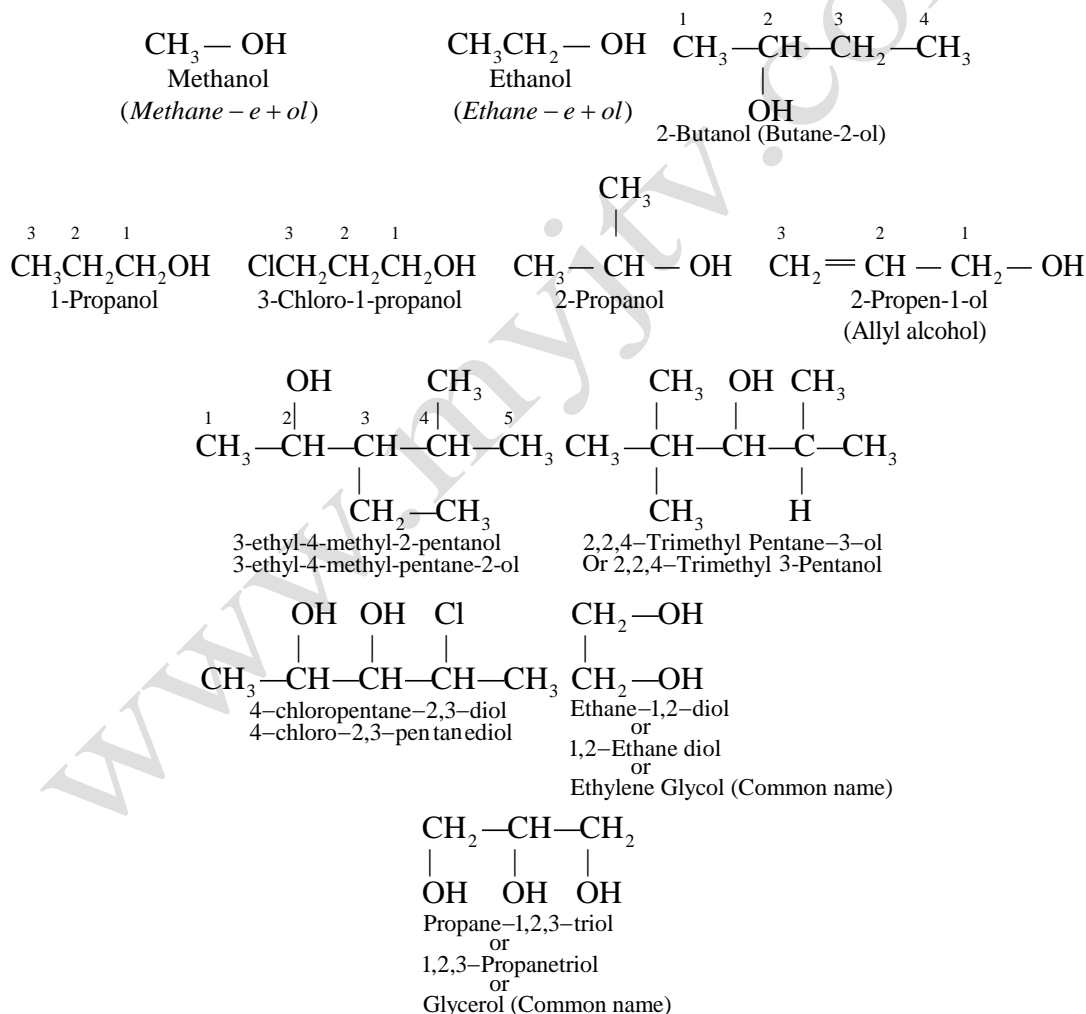


(3) **IUPAC System:** In this system alcohols are named as *Alkanols*. The IUPAC rules are:

- (1) Select the longest continuous carbon chain containing the -OH group.
- (2) Name the longest continuous carbon chain as alkane on the basis of number of carbon atoms.
- (3) Change the name of the alkane by dropping the ending *-e* and adding the suffix *-ol*. So the alkane becomes alkanol.
- (4) Number the longest chain so as to give the carbon carrying the -OH group, the lowest possible number. The position of the -OH group is indicated by this number.
- (5) Indicate the positions of other substituents or multiple bonds by numbers.

- (6) The substituents along with their positions are named in alphabetical order before the parent name.
- (7) If the number of carbon atoms carrying the hydroxyl group is the same from both sides, then number the chain from the side which is heavily substituted.
- (8) In case of dihydric, trihydric and polyhydric alcohols, the prefix di, tri, tetra etc. is used before –ol along with the number of the carbon atoms to which these hydroxyl groups are attached.
- (9) Alcohols containing two or three –OH groups are named as Alkanediols and Alkanetriols respectively. Notice that –e of the corresponding alkane name is retained.

The examples given below show how these rules are used:

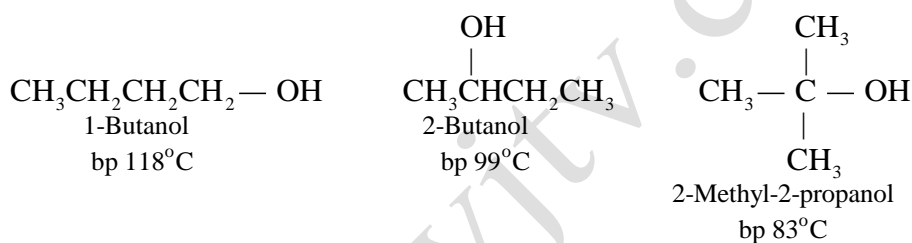


Physical Properties

- (1) Lower alcohols are colourless, toxic liquids.
- (2) They have a characteristic smell.
- (3) Boiling points of alcohols increase regularly with the increase in the number of carbon atoms.

Name	Structure	No. of Carbons	bp ^o C
Methanol	CH ₃ OH	1	64.5
Ethanol	CH ₃ CH ₂ OH	2	78.3
1-Propanol	CH ₃ CH ₂ CH ₂ OH	3	97.0
1-Butanol	CH ₃ (CH ₂) ₂ CH ₂ OH	4	118.0
1-Pentanol	CH ₃ (CH ₂) ₃ CH ₂ OH	5	138.0

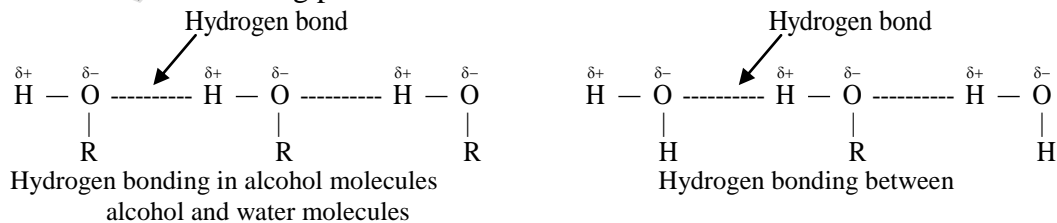
- (4) Among isomeric alcohols, as branching increases the boiling points decrease. For example,



- (5) Boiling points of alcohols are much higher than those of the corresponding alkanes.

Explanation: The O–H bond of alcohols is highly polar because oxygen is electronegative. The oxygen carries a partial negative charge (δ^-). The hydrogen carries a partial positive charge (δ^+). The polarity of the O–H bond gives rise to forces of attraction between a partially positive hydrogen in one alcohol molecule and partially negative oxygen in another alcohol molecule. These forces of attraction are referred to as Hydrogen Bonding. The reason that alcohols have higher boiling points is that a great deal of energy (in the form of heat) is required to overcome these attractive forces.

Alkanes, which have no –OH group, do not undergo hydrogen bonding. Therefore, their boiling points are low.



- (6) Lower alcohols (C₁ to C₃) are completely soluble in water. As we go higher in

the series, the water solubility falls rapidly.

A compound that forms hydrogen bonds between its own molecules can also form hydrogen bonds with water. These alcohols-water hydrogen bonds are the cause of high solubility of lower alcohols in water. In higher alcohols, the non-polar alkyl group becomes more important. They have less tendency to form hydrogen bonds with water and hence are less soluble.

Wood spirit: Methanol is called wood spirit.

Grain alcohol: Ethanol is called grain spirit or grain alcohol.

Absolute alcohol: 100% pure ethanol is called absolute alcohol.

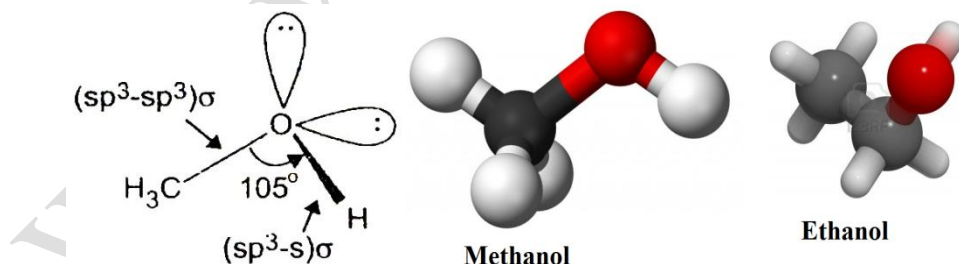
Rectified spirit: 95% ethanol + 5% water is called rectified spirit.

Methylated spirit/Denatured alcohol: 95% ethanol + 5% methanol is called methylated spirit or denatured alcohol.

Structure

Alcohols are the alkyl derivatives of water molecule. Water molecule has an angular structure with H-O-H bond angle of 104.5° . Alcohol molecules have a similar geometry where the R-O-H bond angle is 105° .

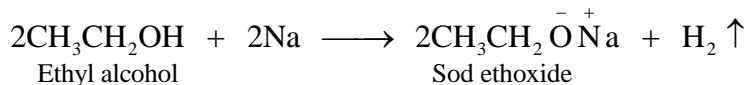
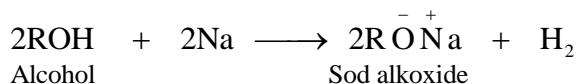
Let us consider methyl alcohol (CH_3OH) for illustrating the orbital make up of alcohols. In methyl alcohol both oxygen and carbon are sp^3 hybridized. Two of the sp^3 orbitals of oxygen are completely filled and cannot take part in bond formation. The C-O bond in methyl alcohol is formed by overlap of an sp^3 orbital of carbon and an sp^3 orbital of oxygen. The O-H bond is formed by overlap of an sp^3 orbital of oxygen and s orbital of hydrogen. The C-O-H bond angle is 105° . It is less than the normal tetrahedral angle. This is because the two completely filled sp^3 orbitals of oxygen repel each other. This results in reduction of the bond angle.



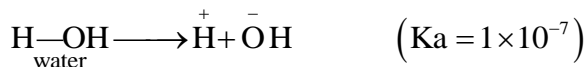
Structure of Methyl alcohol

Acidity of alcohols

Alcohols react with sodium or potassium to form alkoxides with the liberation of hydrogen gas.

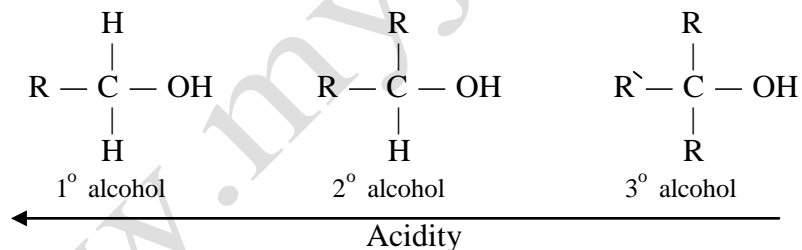


The above reaction shows that alcohols are acidic in nature. The reason for this is that the O–H bond in alcohols is polar and allows the release of the hydrogen atom as proton (H^+). However, alcohols are weaker acids ($K_a = 10^{-16}$ to 10^{-18}) than water.



This is because the alkyl groups in alcohols have a +1 effect. They release electrons towards the oxygen atom so that it becomes negatively charged. This negative charge on oxygen makes the release of the positive proton more difficult.

Tertiary alcohols are less acidic than secondary alcohols. The secondary alcohols are less acidic than primary alcohols. This is because the +1 effect would be maximum in tertiary alcohols, as they contain three alkyl groups attached to the carbon bearing the –OH group.



Alcohols are not acidic enough to react with aqueous NaOH or KOH.

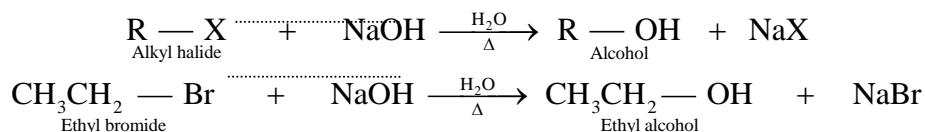


The halo derivatives of alcohols are more acidic as the halogens are more electronegative than carbon and will attract the electron density from carbon as these are electron withdrawing so electron density on oxygen will be lower in the presence of halogens and hydrogen will be easily protonated.

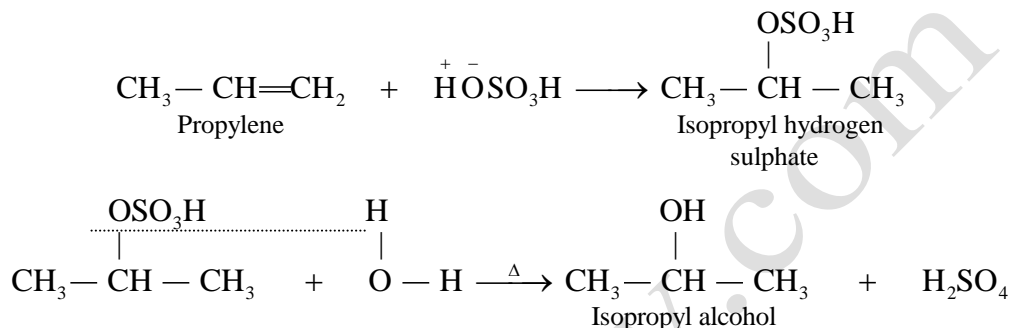
Methods of Preparation

Alcohols are prepared by the following methods:

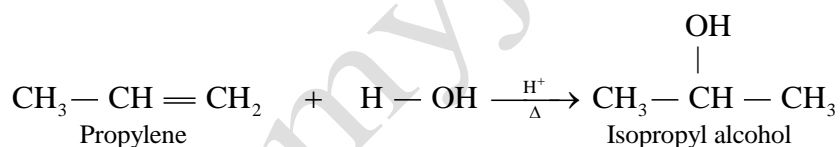
(1) Hydrolysis of Alkyl Halides: Alkyl halides react with aqueous sodium hydroxide to form alcohols.



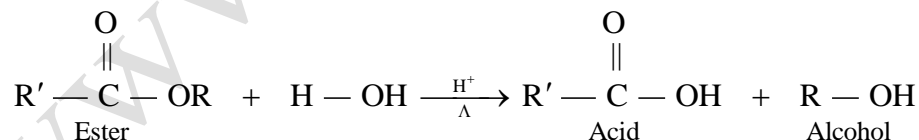
(2) Hydration of Alkenes: Alkenes react with sulphuric acid to produce alkyl hydrogen sulphates (Markovnikov rule is followed). Alkyl hydrogen sulphates on hydrolysis give alcohols. For example,



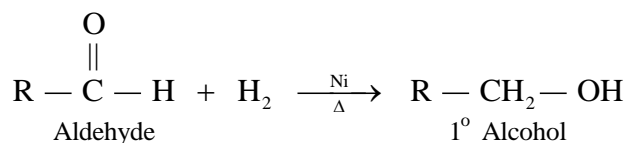
The overall result of the above reactions appears to be Markovnikov addition of H₂O (Hydration) to a double bond.

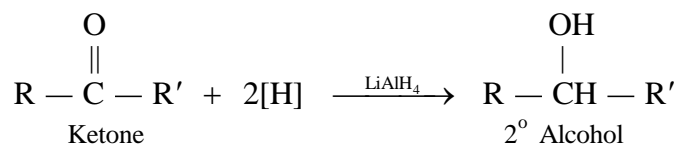


(3) Hydrolysis of Esters: Alcohols may be prepared by base or acid-catalysed hydrolysis of esters.



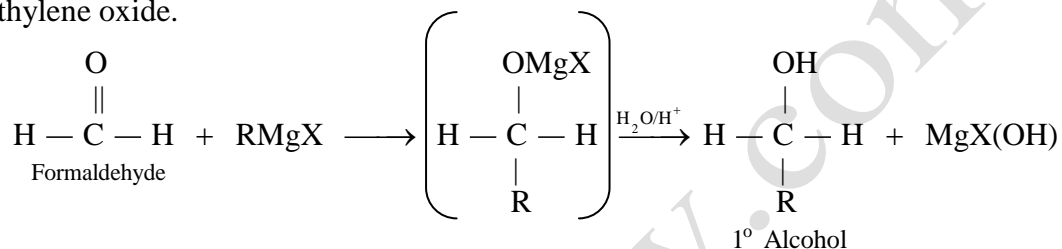
(4) Reduction of Aldehydes and Ketones: Aldehydes and ketones can be reduced with H₂/Ni or lithium aluminium hydride to form the corresponding alcohols. Aldehydes give primary alcohols. Ketones give secondary alcohols.



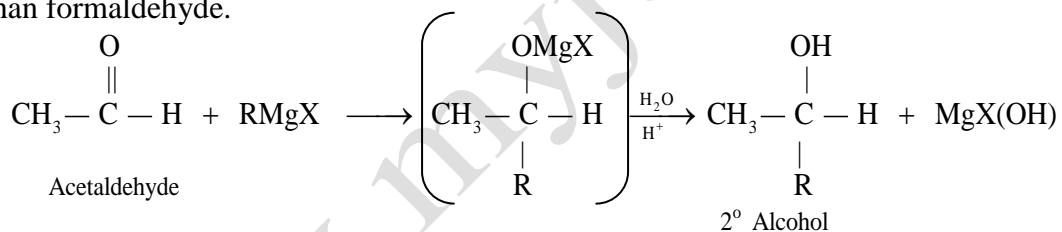


(5) Addition of Grignard Reagents to Aldehydes and Ketones: Grignard reagents react with aldehydes or ketones to form an addition compound which on hydrolysis with dilute acid gives the corresponding alcohols.

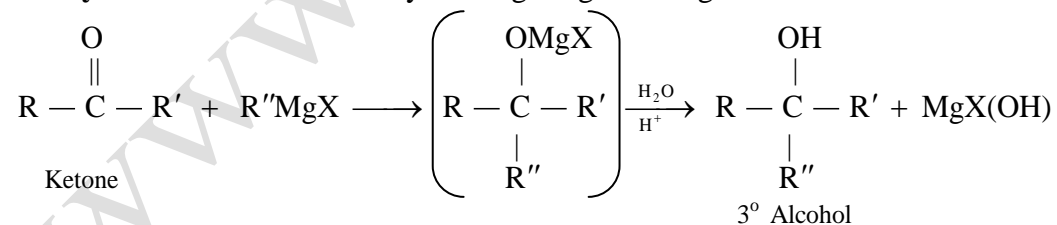
Primary alcohols are obtained by treating a Grignard reagent with formaldehyde or ethylene oxide.



Secondary alcohols are obtained by treating Grignard reagent with aldehydes other than formaldehyde.



Tertiary alcohols are obtained by treating Grignard reagents with ketones.



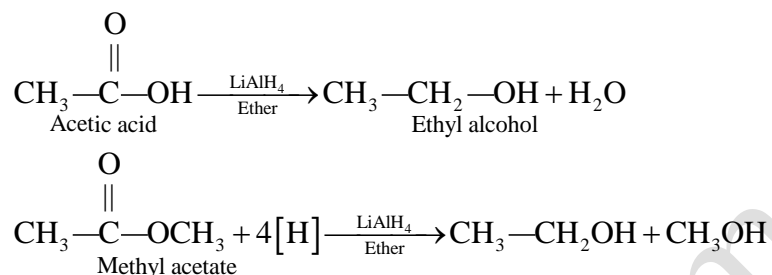
(6) Reaction of R-MgX with esters

Grignard reagent reacts with ester to yield carbonyl compound and then these carbonyl again react further with Grignard reagent to yield alcohol. Grignard reagents react with formic esters to form secondary alcohols, while other esters yield tertiary alcohols.

(a) Reaction with Ethyl Formate, Preparation of secondary alcohols:

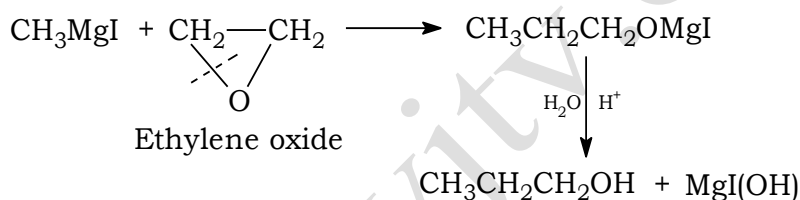
Step 1. Ethyl formate reacts with Grignard reagents to first form aldehydes.

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

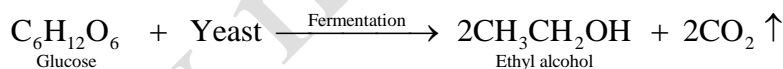


This mixture is separated by means of fractional distillation.

(8) Reaction of Grignard Reagent with Ethylene Oxide: Grignard reagents react with ethylene oxide to give an addition product which on hydrolysis forms primary alcohols.



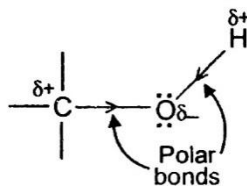
(9) Fermentation of Carbohydrates: Some alcohols can be prepared by fermentation of starches and sugars under the influence of suitable microorganisms. For example,



Reactivity of alcohols

Alcohols are reactive compounds. They are attacked by polar or ionic reagents. The reactivity of alcohols is due to the fact that:

- (1) The C-O and O-H bonds of alcohols are polar since oxygen is highly electronegative.
- (2) The oxygen atom of alcohols is an electron-rich centre because it has two unshared pairs of electrons.

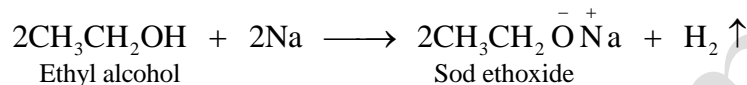
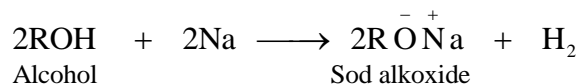


Generally the reactions of alcohols involve the fission of either the O-H bond or the C-O bond. Cleavage of either of the two bonds may involve a substitution

reaction or an elimination reaction.

Chemical properties of alcohols

(1) Reaction with Active Metals: Alcohols react with sodium or potassium to form alkoxides with the liberation of hydrogen gas.



The above reaction shows that alcohols are acidic in nature.

(2) Reaction with Hydrogen Halides: Alcohols react with hydrogen halides (HX) to form the corresponding alkyl halides.



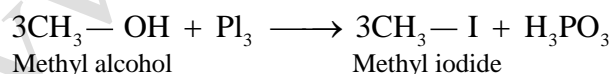
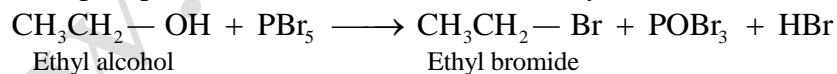
where HX = HI, HBr, HCl



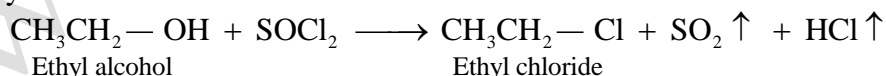
In general, tertiary alcohols react rapidly with hydrogen halides; secondary alcohols react somewhat slower; and primary alcohols, even more slowly.

The order of reactivity of hydrogen halides is HI > HBr > HCl. HCl reacts only in the presence of a catalyst (anhydrous ZnCl₂). No catalyst is required in the case of HBr and HI.

(3) Reaction with Phosphorus Halides: Alcohols react with phosphorus pentahalides (PX₅) and phosphorus trihalides (PX₃) to form alkyl halides.

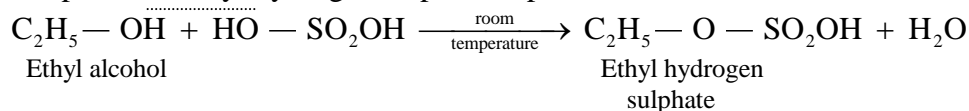


(4) Reaction with Thionyl Chloride: Alcohols react with thionyl chloride (SOCl₂) to form alkyl chlorides.

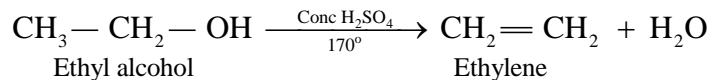


(5) Reaction with Sulphuric Acid: The reaction of alcohols with sulphuric acid is very sensitive to reaction conditions. For example,

(i) When ethyl alcohol is treated with concentrated sulphuric acid at room temperature, ethyl hydrogen sulphate is produced.

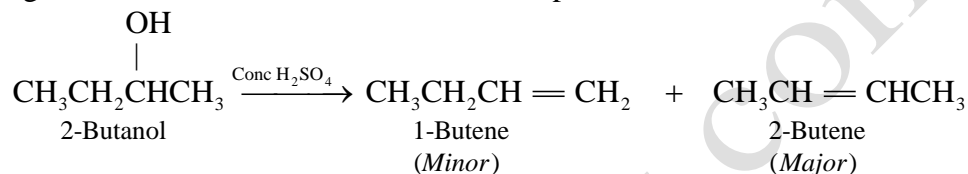


(ii) **Dehydration of Alcohols to Alkenes:** When ethyl alcohol is treated with concentrated sulphuric acid at 170°C, ethylene is formed. Notice that only one alcohol molecule is involved in the reaction.



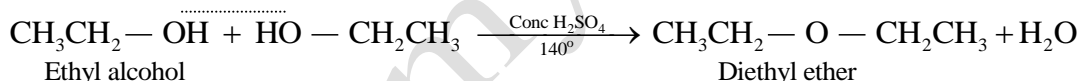
The ease of dehydration of alcohols follows the order 3° > 2° > 1° which is also the order of stability of the carbonium ions.

Dehydration of secondary and tertiary alcohols containing four or more carbon atoms gives a mixture of two alkenes. For example,

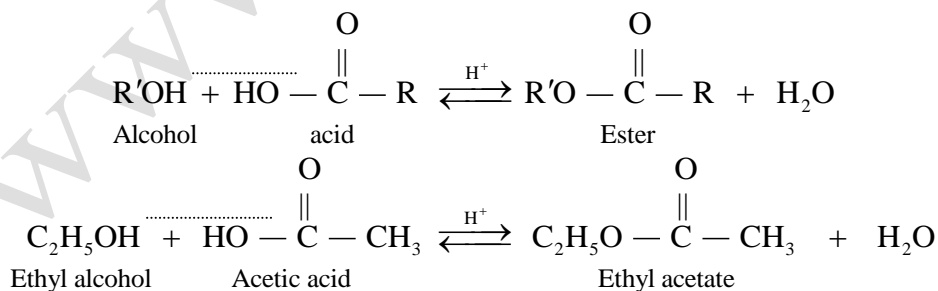


The alkene produced in greater abundance is indicated by Saytzeff Rule. It states that the alkene formed preferentially is the one containing the higher number of alkyl groups. Therefore, in the above example, 2-butene is the major product.

(iii) **Dehydration of Alcohols to Ethers:** When excess of ethyl alcohol is treated with concentrated sulphuric acid at 140°C, diethyl ether is formed. Notice that two alcohol molecules are involved in the reaction.



(6) **Reaction with Carboxylic Acids (Esterification):** Alcohols react with carboxylic acids to form esters. Concentrated sulphuric acid is used as a catalyst. The reaction is reversible and can be shifted in the forward direction by removing water as soon as it is formed.

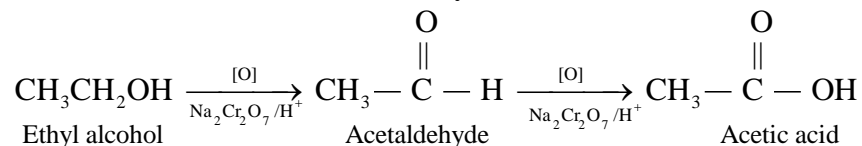


Esterification: The reaction between an alcohol and a carboxylic acid to form an ester is called esterification.

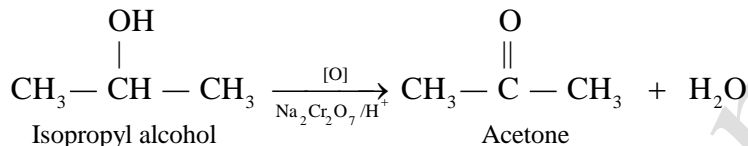
(7) **Oxidation:** Alcohols can be oxidised. The nature of the product depends on the type of alcohol and the conditions of the reaction. Most widely used oxidising agents are $\text{KMnO}_4 + \text{H}_2\text{SO}_4$ or $\text{Na}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4$. Oxidation of alcohols can be used to

distinguish between primary, secondary, and tertiary alcohols.

Primary alcohols are first oxidized to aldehydes and then to acids.

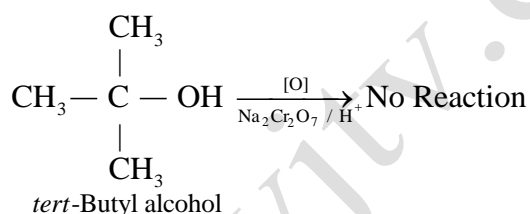


Secondary alcohols are oxidized to the corresponding ketones.



Further oxidation under very drastic conditions breaks up the ketone molecule, producing carboxylic acids containing fewer carbon atoms per molecule:

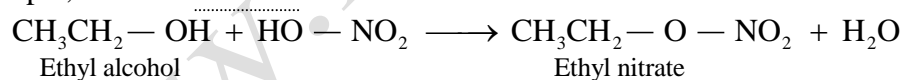
Tertiary alcohols are stable to oxidation under normal conditions.



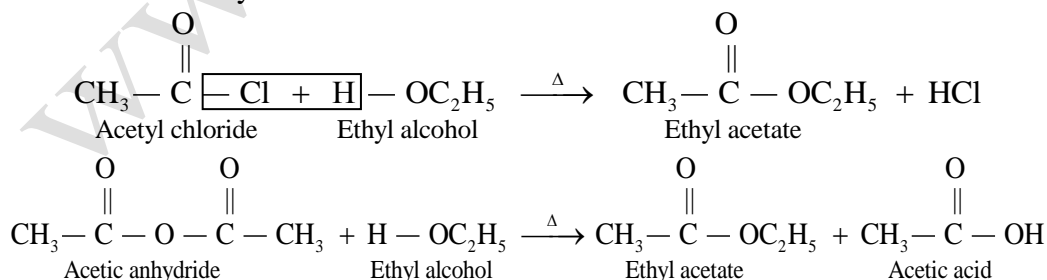
Under drastic conditions, tertiary alcohols give ketones and acids, each containing less carbons than the alcohol.

(8) Reaction with Nitric Acid: Alcohols react with nitric acid to form alkyl nitrates.

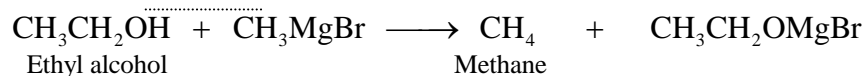
For example,



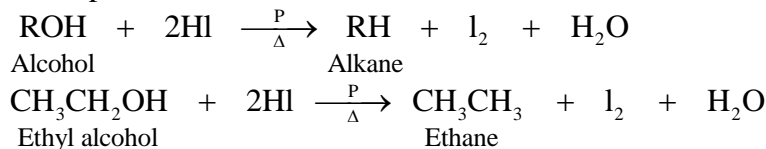
(9) Reaction with Acid Halides and Acid Anhydrides: Alcohols react with acid halides and acid anhydrides to form esters.



(10) Reaction with Grignard Reagents: Alcohols react with Grignard reagents (RMgX) to form alkanes.

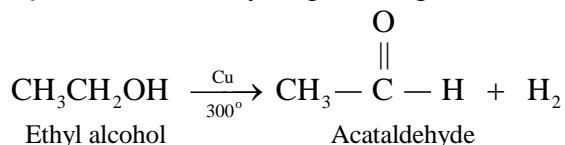


(11) **Reduction:** Alcohols undergo reduction with concentrated hydroiodic acid and red phosphorus to produce alkanes.

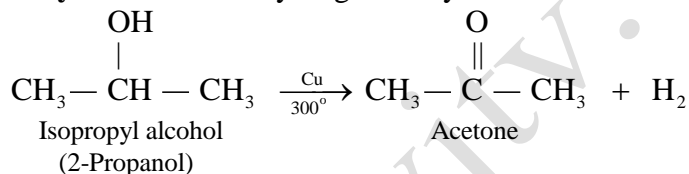


(12) **Reaction with the Hot Copper (Dehydrogenation):** Different types of alcohols give different products when their vapours are passed over copper gauze at 300°C.

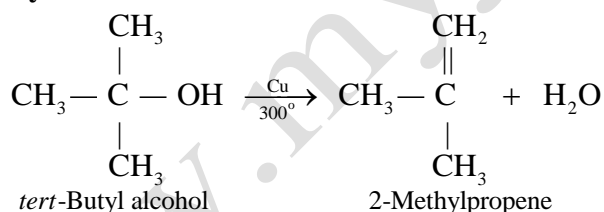
Primary alcohols lose hydrogen and give an aldehyde.



Secondary alcohols lose hydrogen and yield a ketone.



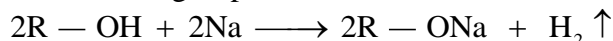
Tertiary alcohols are stable to oxidation under normal conditions.



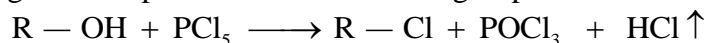
Testing of -OH Group

The following three tests may be used to detect the presence of an -OH group in organic compounds. For these tests, take the liquid compound or a solution of the solid compound in an inert solvent such as *dry*, ether or benzene.

(1) Add to it small pieces of *Sodium metal*. If bubbles of hydrogen gas are given off, the compound contains an -OH group.



(2) Add to it *Phosphorus pentachloride*. If the mixture becomes warm with evolution of HCl gas, the given compound contains an -OH group.



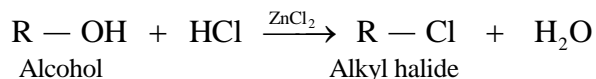
(3) Add *Acetyl chloride* or *Benzoyl chloride* to the substance. The separation of an oily layer of the ester and evolution of HCl gas indicates the presence of an -OH

group.

How to Distinguish Between 1°, 2°, and 3° Alcohols?

The following tests are used to distinguish between primary, secondary, and tertiary alcohols.

(1) **Lucas Test:** In this test, alcohols are treated with a solution of HCl and zinc chloride (*Lucas reagent*) to form alkyl halides. Zinc chloride serves as a catalyst.



The three types of alcohols undergo this reaction at different rates. Tertiary alcohols react with *Lucas reagent* very rapidly. Secondary alcohols react somewhat slower. Primary alcohols react with *Lucas reagent* even more slowly.

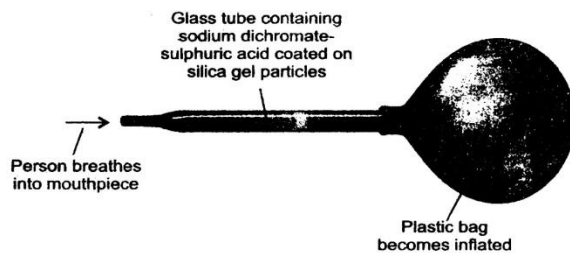
In practice, the *Lucas test* is carried out as follows: An alcohol is mixed, at room temperature, with concentrated HCl and ZnCl₂. The alkyl chloride, which is formed, is insoluble in the medium. It causes the solution to become cloudy before it separates as a distinct layer.

- With **Tertiary alcohols** cloudiness appears immediately.
- With **Secondary alcohols** cloudiness appears in 5 minutes.
- With **Primary alcohols** the solution remains clear. This is because primary alcohols do not react with *Lucas reagent* at room temperature. High temperature is needed.

(2) **Dichromate Test.** This test is based on the fact that different types of alcohols give different products on oxidation. The alcohol is treated at room temperature with sodium dichromate in sulphuric acid (orange solution). Identification of the products gives us information regarding the type of the alcohol.

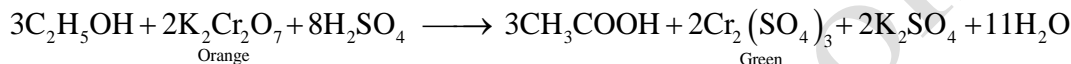
- Primary alcohols** give a carboxylic acid containing the same number of carbons. There will be a change in colour of the solution from orange to green.
- Secondary alcohols** give a ketone containing the same number of carbons. There will be a change in colour of the solution from orange to green.
- Tertiary alcohols** do not react under these conditions. Solution will remain orange.

Roadside Breath Test (Drunkometer): A novel application of the oxidation of ethyl alcohol is found in the roadside breath test, a screening device intended to give a rough measure of the quality of alcohol in the blood. It is based on the premise that the ethanol absorbed into the blood from the stomach and intestine is continuously transferred into the lungs and exhaled. A volume of exhaled breath is said to contain 1/2100 of the amount of ethanol in an identical volume of blood. It is an offense for a motor vehicle driver to have a blood alcohol level in excess of 150 mg/ 100 ml of blood (0.15%).



Apparatus for Roadside Breath Test (Drunkometer)

The operation of the **Breath analyzer/Drunkometer** used in this test is based on the potassium dichromate-sulphuric acid oxidation of ethanol:

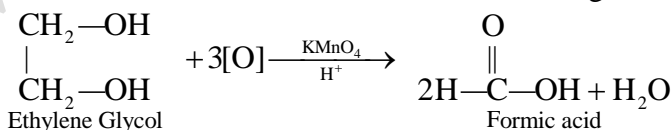


The particles of silica gel in a sealed gas ampule are impregnated with the reagents. Before the ampule is used, the ends are broken off; then one end is fitted with a plastic mouthpiece, and the other is attached to the neck of a flattened bag. When air containing ethanol is blown through the tube, a chemical reaction takes place (the temperature of the tube increases), and the chromium sulphate produced is shown by the formation of a green colour in place of the original orange reagent. If the green colour extends beyond the yellow centre mark of the tube, the motorist is considered drunk and taken to the police station for further tests.

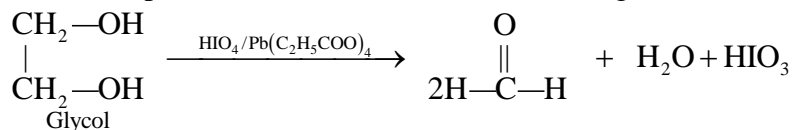
Dihydric alcohols (diols)

Compounds which contain two $-\text{OH}$ groups on different carbons are called Dihydric Alcohols or Diols. Compounds with two $-\text{OH}$ groups on one carbon are seldom encountered. This is because they are unstable and undergo spontaneous decomposition to give the corresponding carbonyl compound and water. Diols were commonly known as Glycols, since they have a sweet taste (Greek, *glycys* = sweet).

Cleavage of 1,2-diols (Glycols): 1,2 diols (Glycol) when treated with acidic KMnO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$ results in the formation of formic acid due to cleavage of $\text{C}-\text{C}$ bond.

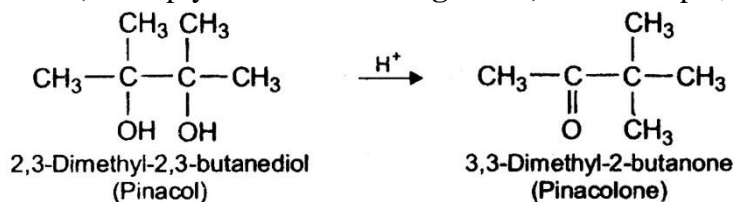


But when treated with periodic acids or lead tetra acetate it gives formaldehyde.



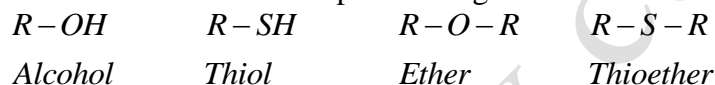
Pinacols: Completely substituted 1,2-diols, such as 2,3-dimethyl-2,3-butanediol, are called **Pinacols**. On treatment with mineral acids (HCl) they undergo dehydration and

rearrangement to form ketones. This reaction is called **Pinacol-Pinacolone Rearrangement** (or simply **Pinacol Rearrangement**). For example,



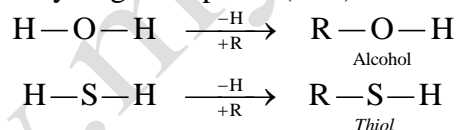
Thiols (R-SH), Thesulphur analogues of alcohols

As oxygen and sulphur both belong to the VI group of the periodic table so both are present in organic compounds and form same compounds. Oxygen form alcohols while sulphur form thioalcohols. Oxygen form ethers while sulphur form thioethers. The thioalcohols and thioethers are the sulphur analogous of alcohols and ethers.



Thiols: The sulphur analogues of alcohols are called thiols. They are also known as alkyl hydrogen sulphide or mercaptans (MercuriumCaptans = Mercury catching). Thiols are called mercaptans because they react with mercuric ions to form insoluble salts.

Just as alcohols are regarded as alkyl derivatives of water, thiols could be considered as derived from hydrogen sulphide (H₂S).



Functional group of thiols: The functional group of thiol is -SH. It is called sulphhydryl or mercapto or thiols group.

Well-known compounds of thiols are CH₃SH (methanethiol) which is a gas at ordinary conditions. While ethanethiol (C₂H₅SH) and higher members are colourless volatile liquids at STP.

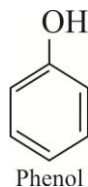
Uses: Due to their strong repulsive odor these are added to natural gas in minute amounts to give it specific smell which make the natural gas leakage detection easy.

They have lower B.P, then corresponding alcohols and insoluble in water due to lack in hydrogen bonding but soluble in methanol, ethanol and ethers.

PHENOLS

Phenols are organic compounds containing an -OH group attached directly to an aromatic ring. These are also called carbolic acids. Its general formula is R-OH where R is aryl group.

Phenol are generally represented as



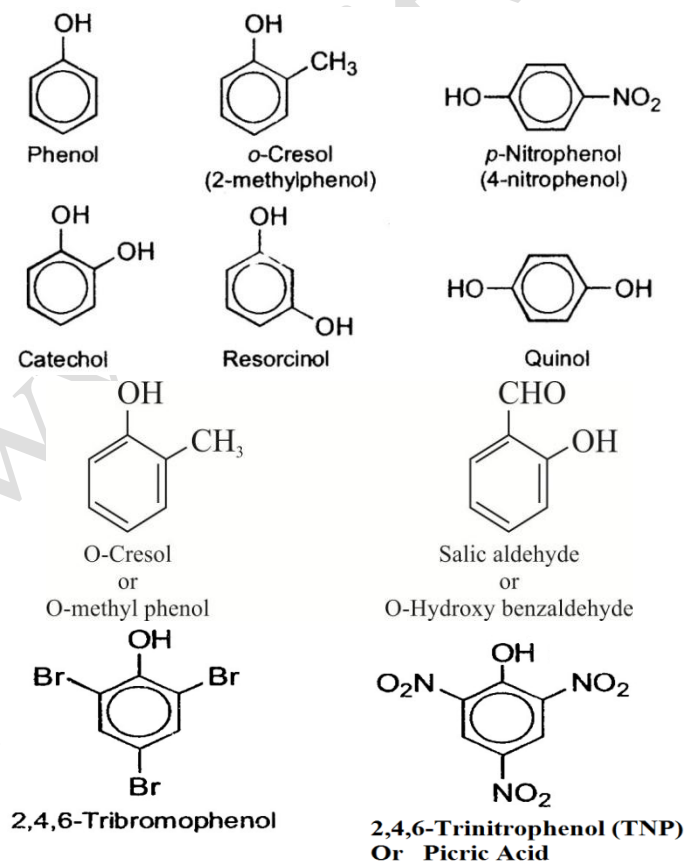
Types: Like alcohols, they may be monohydric, dihydric and polyhydric according to the number of $-OH$ groups that these contain.

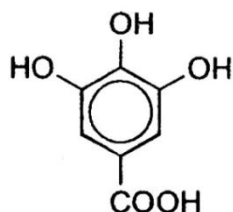
1. Monohydric phenols: Phenols that contain single $-OH$ group are called monohydric. Examples are, phenol and trinitrophenol.

2. Dihydric phenols: Phenols which contain two $-OH$ groups are called dihydric. Examples are, catechol, resorcinol and hydroquinone.

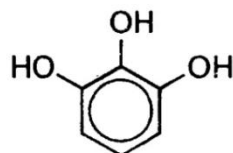
3. Polyhydric phenols: Phenols which contain three or many $-OH$ groups are called polyhydric. Examples are, Gallic acid, pyrogallol and phloroglucinol.

Nomenclature: Phenols are usually named by common system or as derivatives of the parent phenol (C_6H_5OH). Examples are:

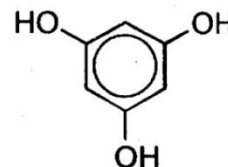




Gallic acid



Pyrogallol

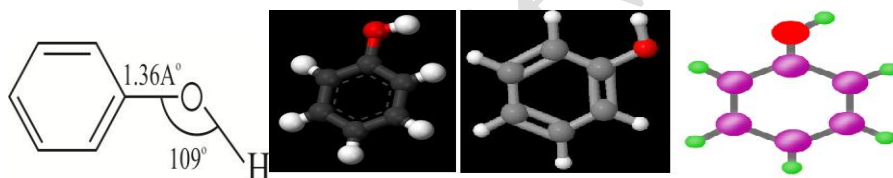


Phloroglucinol

Structure of Phenol

In phenol OH groups is attached with benzene ring. Phenol is an aromatic compound so it is a planer molecule with C—O—H bond angle is 109° almost same as in case of tetrahedral and is not different from bond angle of C—O—H in methanol i.e. 108.5° .

In case of phenol the OH group is directly attached with sp^2 hybridized carbon due to which bond length between C—O is get reduced from 1.42Å to 1.36Å . The phenol six carbon atoms are sp^2 hybridized forming hexagonal structure with internal bond angles of 120° .



Physical Properties

- (1) Most pure phenols are colourless liquids or low melting crystalline solids at room temperature and pressure (*mp* 42°C ; *bp* 182°C).
- (2) Phenols have a characteristic 'Carbolic' odour, which in case of phenol itself is highly toxic.
- (3) The boiling points of phenols are higher than aliphatic alcohols of comparable molecular weights. This is due to stronger intermolecular hydrogen bonding in phenols relative to alcohols.
- (4) The vapours of phenols are highly toxic.
- (5) Due to stronger H-bonding phenols are more soluble in water than the corresponding alcohols. Above 65°C phenols and water are miscible in all proportions.
- (6) The liquid phenol containing 5% H_2O is known as carbolic acid and is used as disinfectant and germicide.
- (7) Phenol is hygroscopic in nature.
- (8) It turns pink on exposure to air and light.
- (9) Phenol is a poison when taken orally and produces painful blisters in contact

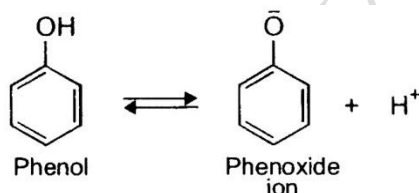
with skin.

Acidity of Phenols

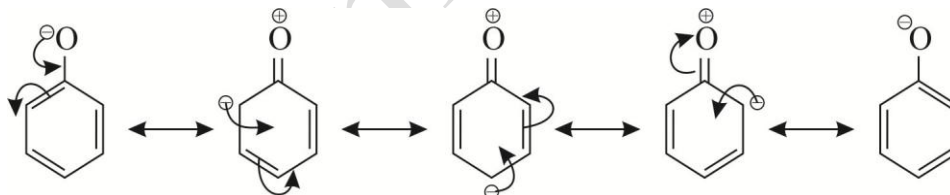
Phenols are much more acidic than alcohols but less so than carboxylic acids or even carbonic acid. This is indicated in order of acidity constants of these molecules:

Compounds	Formula	K_a (approx.)	pKa
Phenols	Ar-OH	10^{-10}	10
Alcohols	R-OH	10^{-16} – 10^{-18}	16-18
Carboxylic acids	R-COOH	10^{-5}	5
Carbonic acid	H ₂ CO ₃	10^{-7}	7
Water	H-OH	10^{-7}	7

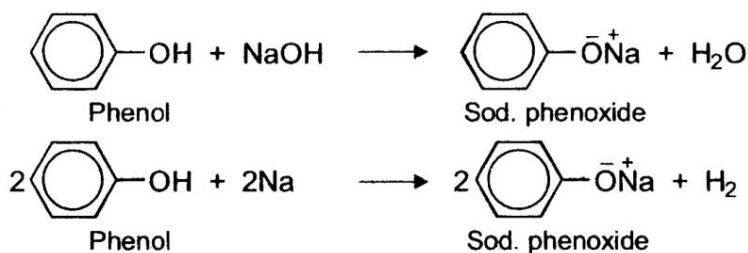
Phenols are acidic due to the formation of stable phenoxide ions in aqueous solutions. For example, phenol itself gives phenoxide ion on dissociation.



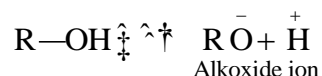
The phenoxide ion is stable due to resonance.



Notice that the negative charge is spread throughout the benzene ring, and thereby effectively dispersed. This charge delocalization is a stabilizing factor in the phenoxide ion. Phenols react with sodium metal and sodium hydroxide and form salts, which confirm its acidic nature.

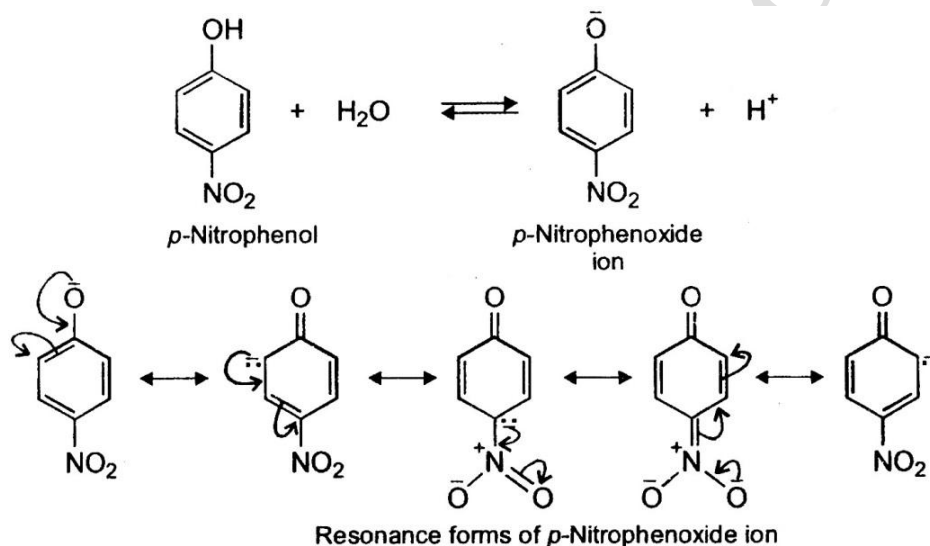


On the other hand, no resonance is possible in alkoxide ions (RO^-) derived from alcohols. The negative charge is concentrated (localized) on a single oxygen atom. Consequently, alcohols are much weaker acids than phenols.

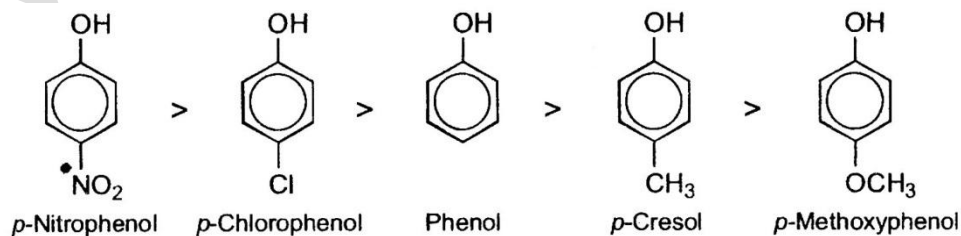


Effect of Substituents on Acidity

(1) Effect of Electron-Withdrawing Substituents: An electron-withdrawing group (e.g., $-\text{NO}_2$, $-\text{Cl}$, $-\text{CN}$, $-\text{CHO}$, $-\text{COOH}$) on the aromatic ring is acid-strengthening. It enables the ring to withdraw more electrons from the phenoxy oxygen. This stabilizes the phenoxide ion still further and results in a stronger acid. For example, *p*-nitrophenol is more acidic than phenol.

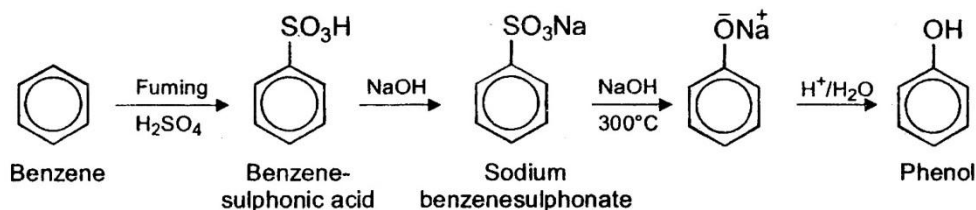


(2) Effect of Electron-Releasing Substituents: An electron-releasing group (e.g., $-\text{CH}_3$, $-\text{OCH}_3$, $-\text{NH}_2$) on the aromatic ring is acid-weakening. It strengthens the negative charge on phenoxy oxygen and inhibits the charge delocalization due to resonance. This destabilizes the phenoxide ion and results in a weaker acid. For example, *p*-cresol is less acidic than phenol.

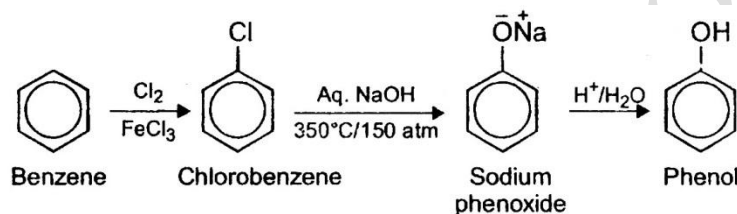


Preparation: Phenol is obtained by the following methods:

(1) **From Benzene sulphonic Acid:** This method involves the fusion of sodium benzenesulphonate with solid NaOH at 300°C followed by treatment with dilute HCl.

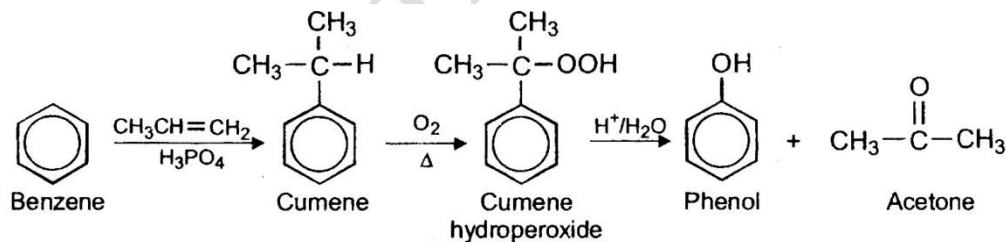


(2) **From Chlorobenzene (Dow Process):** This involves the hydrolysis of chlorobenzene with aqueous NaOH at high temperature and pressure followed by treatment with dilute HCl.



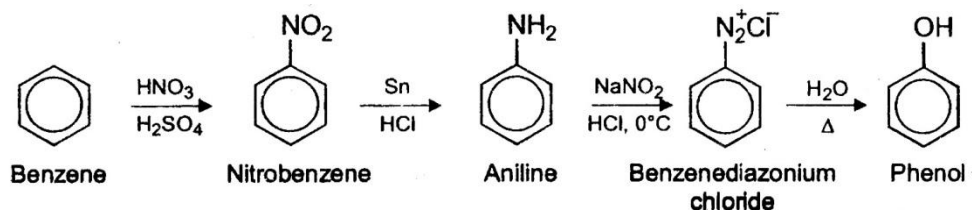
This process was first introduced in 1928 by the Dow Chemical Company of U.S.A.

(3) **From Cumene:** This process involves the air-oxidation of cumene (Isopropylbenzene) followed by treatment with dilute HCl.



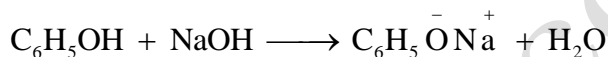
The above *Cumene Process* accounts for 80% of the total world production of phenol. The success of this method is due to the availability of benzene and propene from petroleum and to the formation of acetone, a valuable by-product.

(4) **From Benzenediazonium Salts:** This reaction can be performed easily in the laboratory and simply requires warming a solution of benzenediazonium chloride, prepared from aniline, on a water bath at 50°C.

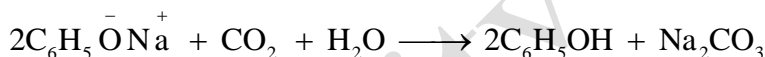


The phenol is recovered by steam distillation and extracted with diethyl ether.

(5) **From Coal Tar:** Coal tar provides a natural source of phenol and cresols, but nowadays provides less than 10% of the total supply. The *middle oil* fraction (170-240°C) of coal tar contains phenols, cresols, and naphthalene. The oil is when cooled, deposits solid naphthalene, which is removed by centrifuging the mixture. The oil left is agitated with NaOH solution when phenol and cresols dissolve as sodium salts.



The phenols are recovered from the above solution by passing carbon dioxide through it.



Phenol is finally isolated from the resulting mixture of phenols by fractional distillation.

Reactivity of Phenol

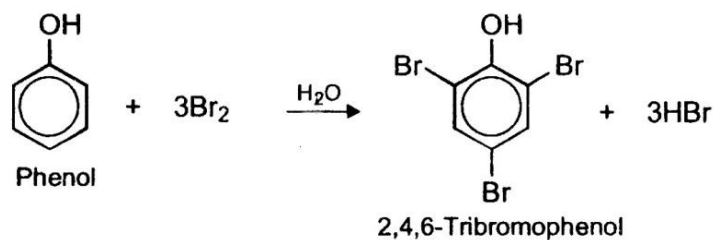
The reactivity of phenol is due to the –OH group as well as due to the aromatic benzene ring. When the hydroxyl group undergo chemical change, various salts, ethers and esters are formed. The aromatic ring undergo electrophilic aromatic substitution and addition reactions. Phenol is much more reactive as compared to benzene. The presence of an electron releasing (OH) group on benzene ring increase the electron density on the ring and increase its reactivity.

Reactions due to benzene ring

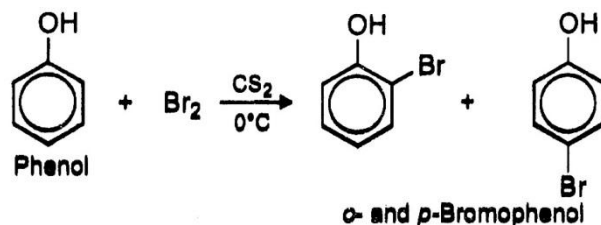
1. Electrophilic aromatic substitution reactions due to benzene ring

Phenol undergoes electrophilic substitution reactions much more readily as compared to benzene ring. The reaction conditions used for monosubstitution in benzene give trisubstitution with phenol. By moderating the reaction conditions we can obtain the monosubstitution product. Remember that the –OH group in phenol is an *o*, *p*-director and activator.

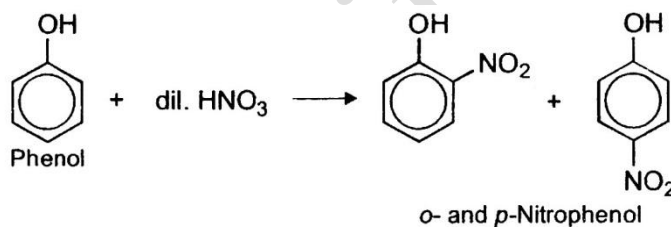
(I) **Halogenation:** Phenol reacts with bromine water (aqueous bromine) to give precipitate of 2, 4, 6-tribromophenol. Chlorine reacts in the same way.



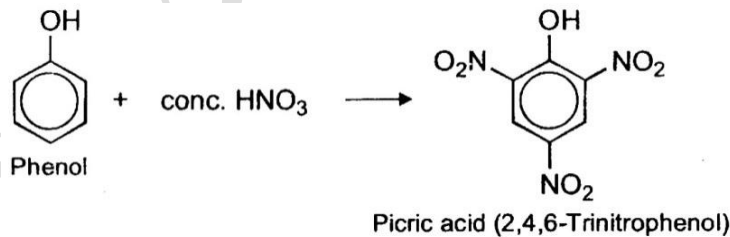
If the reaction is carried in CS₂ or CCl₄ (non-polar solvents), a mixture of *o*- and *p*-bromophenol is formed.



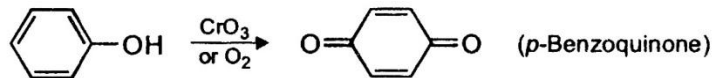
(II) Nitration: Phenol reacts with dilute nitric acid to give a mixture of *o*- and *p*-nitrophenol.



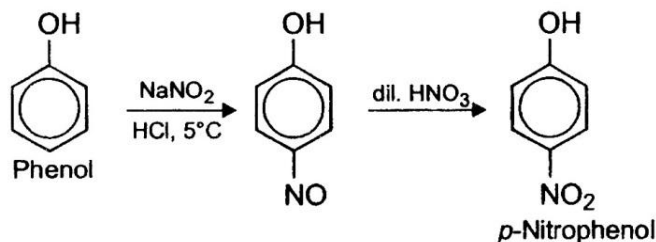
With concentrated nitric acid, picric acid is formed.



(III) Oxidation: Phenol undergoes oxidation with air or chromic acid to form *p*-benzoquinone.

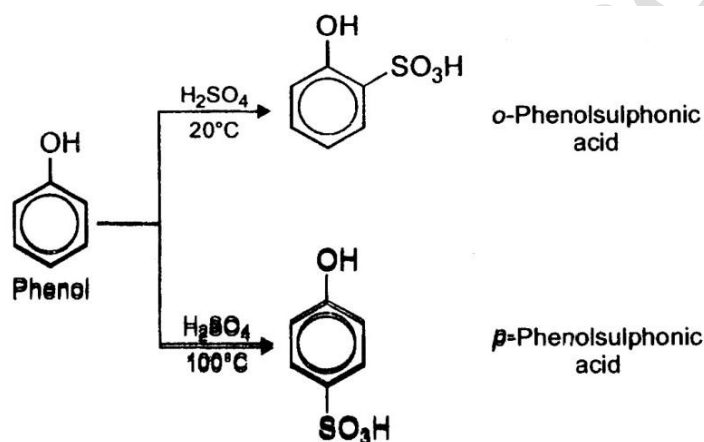


(IV) Nitrosation: Phenol reacts with nitrous acid (obtained from NaNO₂/HCl at 5°C) to form *p*-nitrosophenol exclusively.

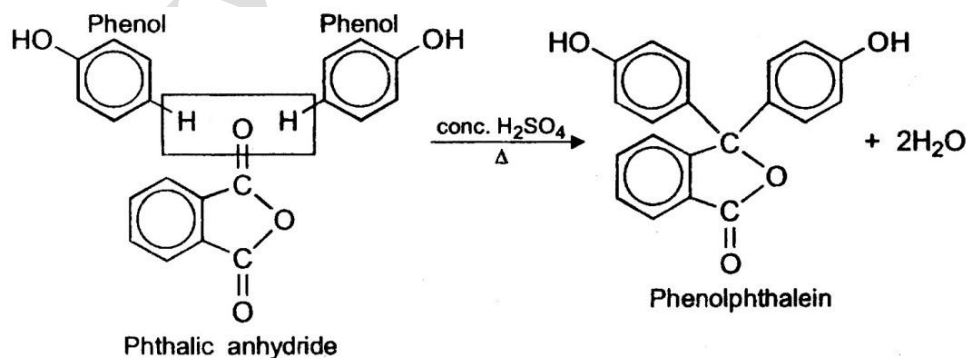


p -Nitrosophenol on oxidation with dilute nitric acid gives p -nitrophenol exclusively.

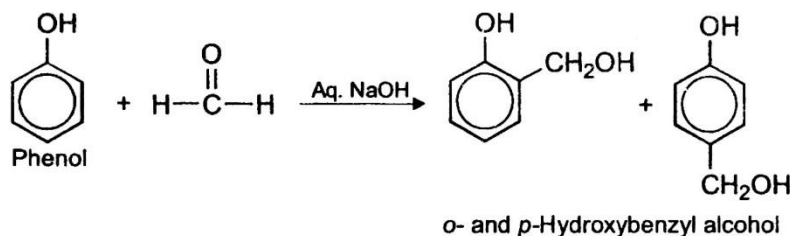
(V) Sulphonation: When phenol is treated with concentrated sulphuric acid at 20°C , o -phenolsulphonic acid is the main product. At 100°C , p -phenolsulphonic acid is the main product.



(VI) Reaction with Phthalic Anhydride: Phenol reacts with phthalic anhydride in the presence of sulphuric acid to form phenolphthalein which is used as indicator.



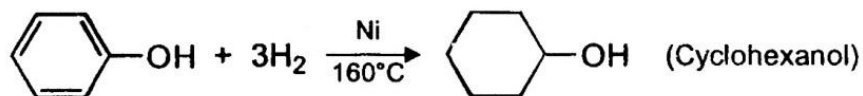
(VII) Reaction with Formaldehyde: When phenol is treated with an alkaline solution of formaldehyde, a mixture of o - and p -hydroxybenzyl alcohol is formed.



If the reaction is carried at high temperature and in excess of formaldehyde, hard thermosetting plastic *Bakelite* is formed.

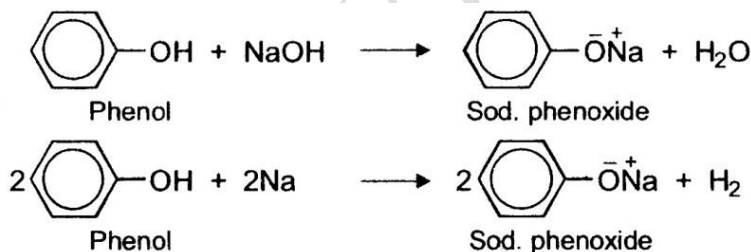
2. Addition reactions due to benzene ring

(I) Catalytic Hydrogenation: Phenol on catalytic hydrogenation gives cyclohexanol. A mixture of its vapour and hydrogen is passed over nickel catalyst at 160°C.

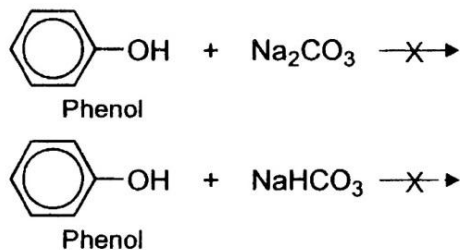


Reactions due to -OH Group

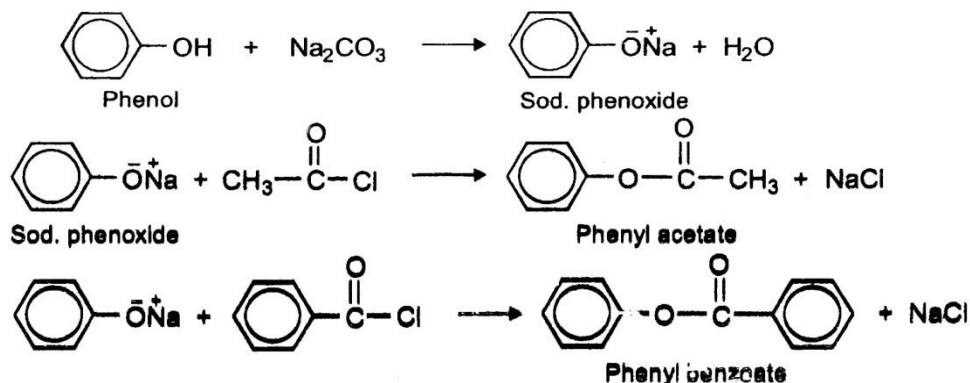
(I) Formation of Salts: Phenol is acidic. It reacts with sodium hydroxide or sodium metal to form salts.



Phenol is weaker acid than carboxylic acids. It does not react with sodium carbonate or bicarbonate.

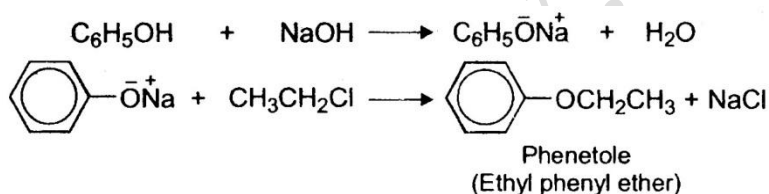


(II) Formation of Esters: Phenol reacts with acid chlorides (or acid anhydrides) in aqueous alkali solution to give phenyl esters. The alkali first forms the phenoxide ion which then reacts with the acid chloride.

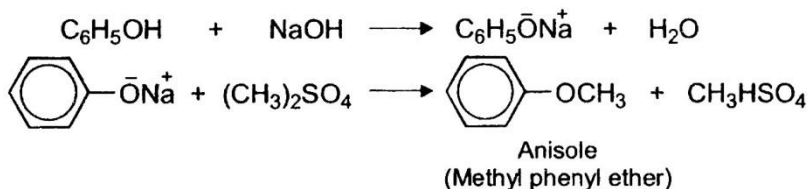


The reaction of phenol with benzoyl chloride is known as *Schotten-Baumann reaction*.

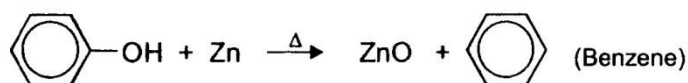
(III) Formation of Ethers: (a) Phenol reacts with alkyl halides in alkali solution to form phenyl ethers. The alkali first forms the phenoxide ion which then reacts with the alkyl halide.



(b) Phenol reacts with dimethyl sulphate in alkali solution to form anisole (Methyl phenyl ether).



(IV) Reaction with Zinc Dust: When phenol is distilled with zinc dust, low yield of benzene is obtained.



(V) Reaction with FeCl₃: Phenol gives purple colouration with one or two drops of neutral ferric chloride solution due to the formation of a complex. This reaction is given by most phenols.

Uses: (1) About half of the total world's production of phenol (two billion pounds) is used for making phenol-formaldehyde resins *e.g.*, Bakelite; (2) Phenol is used as a starting material for (i) drugs such as Salol, Aspirin; (ii) phenolphthalein and several other dyes; (iii) explosives *e.g.*, picric acid; (iv) many other valuable products of

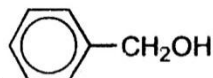
common use; wood preservatives, herbicides, nylon, antiseptics (Dettol), gasoline additives etc. Picric acid is used for making explosives Lyddite and Melinite. It is a valuable yellow dye for wool.

Difference between alcohol and phenol

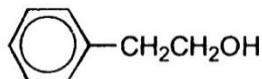
Both alcohols and phenols has hydroxyl group as their functional group.

Alcohols	Phenols
1. -OH group is attached to alkyl group.	1. -OH group is attached to aryl group.
2. Less acidic than water	2. More acidic than water.
3. K_a value is 10^{-18} .	3. K_a value is 10^{-10} .
4. pK_a value 18.	4. pK_a value is 10.
5. Alkoxide ion is less stable.	5. Phenoxide ion is more stable.
6. Undergo nucleophilic substitution reactions.	6. Undergo electrophilic substitution reactions.
7. More soluble in water.	7. Less soluble in water
8. Reactivity is due to -OH group.	8. Reactivity is due to -OH group and benzene ring both.

Aromatic Alcohols: Compounds which contain -OH group in a side-chain attached to an aromatic ring are not phenols. They are called Aromatic Alcohols. Their properties are like alcohols and not like phenols so these are alcoholic in nature and not phenolic compounds. Examples are:



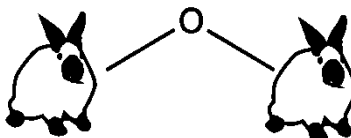
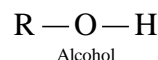
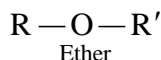
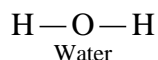
Benzyl alcohol



2-Phenylethanol

ETHERS

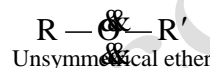
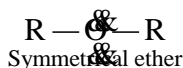
Ethers are a class of compounds which contain an oxygen atom bonded to two alkyl groups or two aryl groups or one alkyl and one aryl group. Both the alkyl or aryl groups may be the same or may be different from one another. The functional group of ethers is C-O-C and its general formula is R-O-R. Ethers are the derivatives of water molecule where both the hydrogens have been replaced by alkyl groups. The general formula of ethers is $C_nH_{2n+2}O$. These may also be considered to be derivatives of alcohols in which the hydroxyl hydrogen has been replaced by an alkyl group.



Types of ethers: Ethers are classified as symmetrical ethers or unsymmetrical ethers.

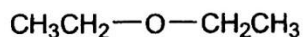
Symmetrical ethers or simple ethers: When both the alkyl or aryl groups attached to both sides of the oxygen atom are the same then the ether is called symmetrical.

Unsymmetrical ethers or mixed ethers: When both the alkyl or aryl groups attached to both sides of the oxygen atom are different then the ether is called unsymmetrical.

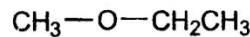


Nomenclature

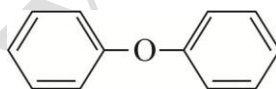
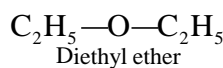
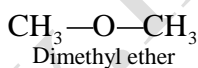
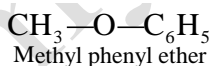
(1) **Common System:** The two alkyl groups attached to oxygen are named in alphabetic order and the word ether is added. If the two alkyl groups are same (R–O–R), the prefix *di-* is used. Although the prefix *di-* is often omitted, it is better to include it to avoid confusion.



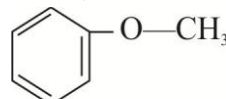
Diethyl ether
(Ethyl ether)



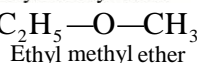
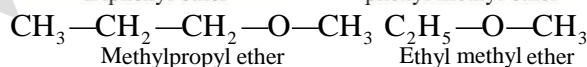
Ethyl methyl ether



Diphenyl ether



phenyl methyl ether

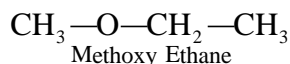
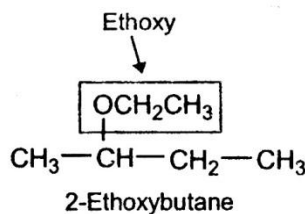
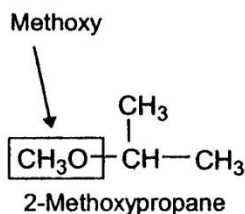


Chemistry Joke:

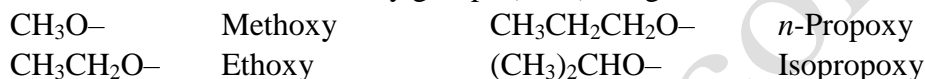
A lady named her son as alkyl. One day alkyl was out of home. His mom called him “alkyl” O ‘alkyl”. Suddenly a dimethyl ether appeared at her front and told yes mam. The lady told him that I have not called you I am calling my son. The dimethyl ether replied that you told CH₃, O, CH₃. That’s why I (CH₃-O-CH₃) came here, take care next time.

(2) **IUPAC System:** In this system, ethers are named as **Alkoxyalkanes**. The larger of the alkyl groups is considered to be the alkane and the smaller alkyl group along with the oxygen atom is named as alkoxy. The name of the alkane is prefixed by the

name of the alkoxy group.

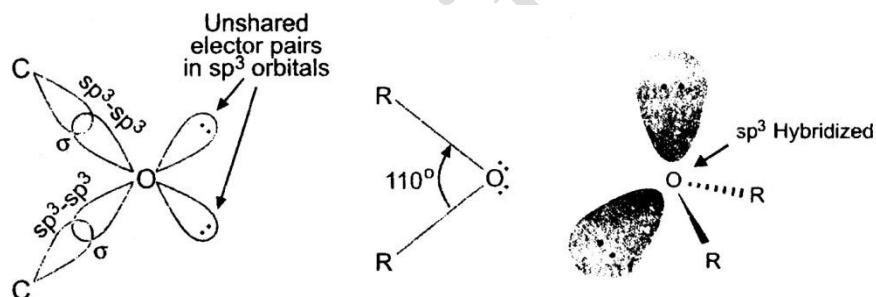


Names of some common alkoxy groups (RO-) are given below:



Structure

In ethers, the oxygen atom is sp^3 hybridized. The two C-O σ bonds are formed by sp^3-sp^3 overlap. The two unshared pairs of electrons on oxygen occupy sp^3 hybrid orbitals. The C-O-C angle is very close to 110° .

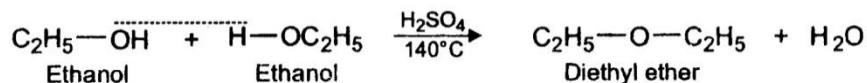
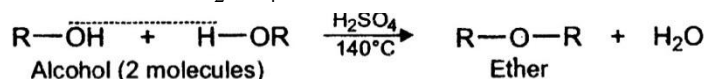


Orbital structure of an ether molecule

Methods of Preparation

Ethers are obtained by the following methods:

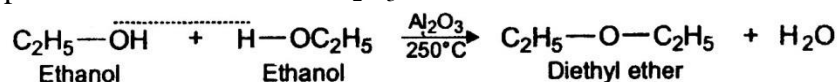
(1) **Dehydration of Alcohols:** Symmetrical ethers are prepared by heating an excess of alcohol with concentrated H_2SO_4 at 140°C .



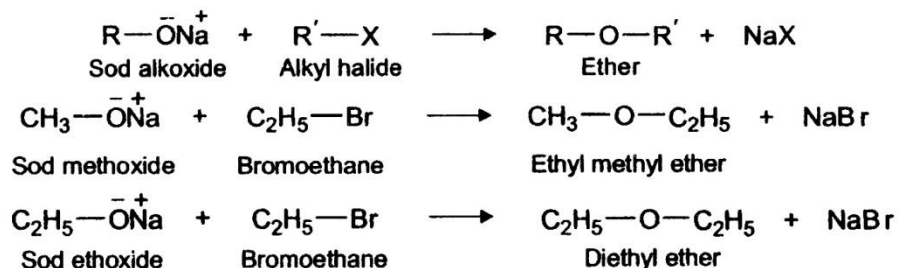
The starting alcohol in the above reaction must be primary and the reaction temperature must be kept at 140°C . This is because alkene formation is favoured at higher temperatures and with secondary or tertiary alcohols.

(2) **Passing Alcohol Vapours over Al_2O_3 :** Ethers may be obtained by passing

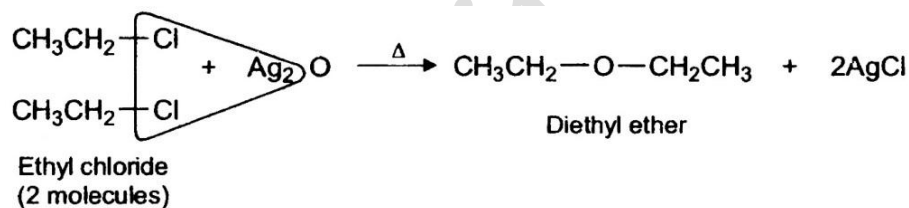
alcohol vapours over hot activated Al_2O_3 at 250°C .



(3) **Williamson Ether Synthesis:** This involves the treatment of a sodium alkoxide with an alkyl halide. Sodium alkoxides are obtained by treatment alcohols with sodium metal ($\text{ROH} + \text{Na} \rightarrow \text{RONa} + \text{H}_2$). Both symmetrical and unsymmetrical ethers can be made by this method.



(4) **Heating Alkyl Halides with Dry Silver Oxide:** This method is useful only for symmetrical ethers.



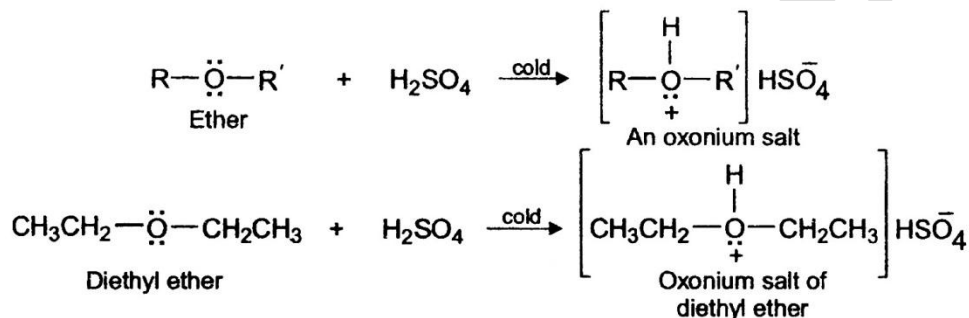
Physical Properties

- (1) Dimethyl ether and ethyl methyl ether are gases.
- (2) All ethers are colourless liquids with pleasant odours.
- (3) Lower ethers are highly volatile and very flammable.
- (4) Boiling points of ethers show a gradual increase with the increase in molecular weight.
- (5) Ethers have lower boiling points than isomeric alcohols. This is because ether molecules cannot form hydrogen bonds with each other as these have no $-\text{OH}$ groups.
- (6) The boiling points of ethers are close to the boiling points of alkanes. For example, diethyl ether (MW = 74) boils at 35°C ; *n*-pentane (MW = 72) boils at 36°C .
- (7) Ethers are slightly soluble in water. This is because they can form hydrogen bonds with water. These are readily soluble in organic solvents.

Chemical Properties

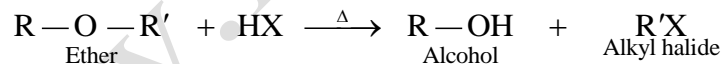
Ethers are quite stable compounds. They do not react with bases, reducing agents, oxidizing agents, and active metals. These are also stable to dilute acids, however these form oxonium salts with strong concentrated acids. In ethers the C-O bonds are polar. Also the oxygen atom has two lone pairs of electrons. The reactivity of ethers may be due to the alkyl group, due to the ethereal oxygen and due to the C-O bond.

(1) Formation of Oxonium Salts: Ethers react with cold concentrated H_2SO_4 or HCl to give oxonium salts. Ethers donate a pair of electrons to a hydrogen ion to form these salts. The oxonium salts once formed are soluble in the acid solution. The ethers can be regenerated from the oxonium salts by treatment with water.

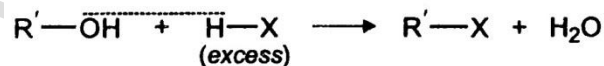


This reaction can be used to distinguish between ethers and alkanes since alkanes do not react with concentrated acids.

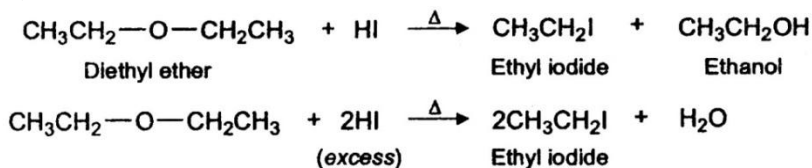
(2) Reaction with halogen Acids: Ethers react with hot concentrated HI or HBr to give an alcohol and an alkyl halide.



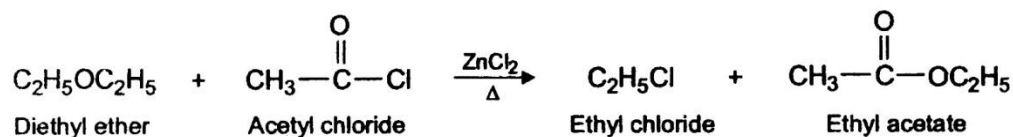
If an excess of acid is used, the alcohol initially produced is also converted to an alkyl halide by the reaction:



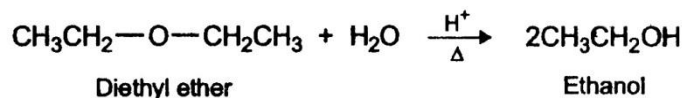
For example,



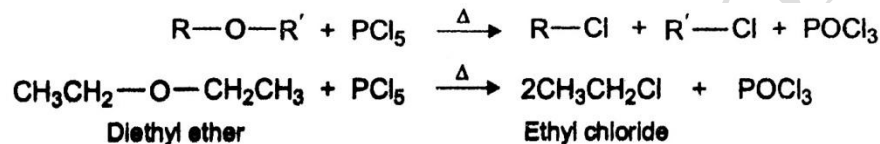
(3) Reaction with acetyl Chloride: Ethers react with acetyl chloride in the presence of anhydrous zinc chloride to form ethyl chloride and ethyl acetate.



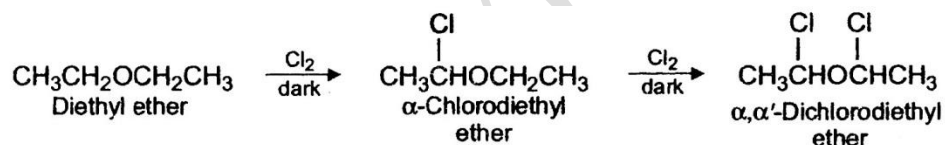
(4) **Reaction with Dilute H₂SO₄ (Hydrolysis):** When ethers are heated with dilute sulphuric acid, alcohols are formed.



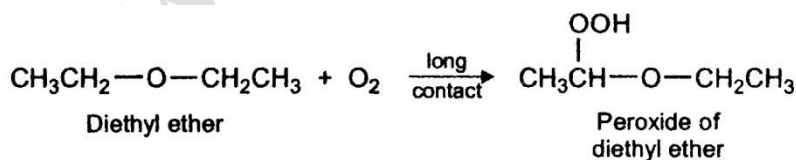
(5) **Reaction with PCl₅:** Ethers react with phosphorus pentachloride to give alkyl chlorides.



(6) **Halogenation:** When ethers are treated with Cl₂ or Br₂ in the dark, substitution products are obtained. The extent of substitution depends upon the reaction conditions. Halogenation preferentially takes place at α-carbon atoms.



(7) **Formation of Peroxides (Autoxidation):** Ethers combine with atmospheric oxygen to form peroxides.



Thioethers or Sulphides

Thioethers are sulphur analogs of ethers. Just as ethers are regarded as derivatives of water, thioethers could be considered as derived from hydrogen sulphide (H₂S).



The Sulphide Group (–S–) is the functional group in thioethers.

EXERCISE**Q.1. Choose the correct option.**

- (i) The reaction of alcohol with sodium produces.
- (a) Ethane (b) Ethene
(c)✓ Alkoxide (d) Aldehyde
- (ii) Oxidation of secondary alcohol gives
- (a) Organic acid (b) Ether
(c) Aldehyde (d)✓ **Ketone**
- (iii) The compound 'x' when heated with dry silver oxide forms an ether identify 'x'.
- (a) Alcohol (b) Phenol
(c)✓ Alkyl halide (d) Ether
- (iv) Phenol on hydrogenation with H_2 in presence of Ni catalyst gives
- (a) Benzene (b) Toluene
(c)✓ Cyclohexanol (d) Aldehyde
- (v) Diethyl ether is prepared by passing vapours of ethanol over a catalyst under high pressure and temperature. The catalyst is
- (a) SiO_2 (b) CuO
(c) Ag_2O (d)✓ Al_2O_3
- (vi) Denatured alcohol is known as
- (a) Absolute alcohol (b) Wood spirit
(c)✓ Methylated spirit (d) Rectified spirit
- (vii) A compound "x" is formed when the vapours of phenol are passed over red hot zinc dust. The compound "x" is called
- (a) Toluene (b) Xylene
(c)✓ Benzene (d) Benzoyl
- (viii) Ethoxyethane react with $Con.H_2SO_4$ to give
- (a)✓ Oxonium ion (b) Oxoanion
(c) Alkyl free radical (d) Zwitter ion
- (ix) The secondary alcohols undergo nucleophilic substitution reaction by
- (a) SN^1 (b) SN^2
(c)✓ Both SN^1 and SN^2 (d) Neither SN^1 and SN^2
- (x) 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**Q.2. Short Questions:**

(1) What is the functional group of alcohols?

Ans. Given in the theory.

(2) Indicate some physical properties of alcohols.

Ans. Given in the theory.

(3) What is Lucas test?

Ans. Given in the theory.

(4) Why phenol is more acidic than alcohols?

Ans. Given in the theory.

(5) What is meant by primary, secondary and tertiary alcohols?

Ans. Given in the theory.

(6) Why alcohol is easily protonated unlike phenol?

Ans. Alcohols are easily protonated as compared to phenol because alcohols behaves as weak Lewis bases due to lone pair of electrons on oxygen atom which are available for easily protonation, because in the alcohol to the oxygen atom an electron donating alkyl group is attached. In case of phenol the lone pair of electron on oxygen atom are not available for protonation because these are in conjugation with benzene ring due to which phenol can't be protonated easily.

(7) Differentiate between alcohol and phenol.

Ans: 1. The R group in alcohols is alkyl while the R group in phenols is aryl (aromatic).

1. Alcohols are less acidic than phenols.
2. Alkoxide ion is less stable while phenoxide ion is more stable.
3. Phenols react with NaOH and form salts but alcohols do not react.
4. Alcohols are more soluble in water compared to phenols.
5. Alcohols react with carboxylic acids and form esters while phenols do not react.
6. Alcohols react with halogen acids and form alkyl halides while phenols do not.

7. Alcohols cannot be hydrogenated while phenols can be.
8. Alcohols react with H_2SO_4 and form alkenes while phenols react and sulphonic group is attached.
9. Alcohols do not react with diazonium salts while phenol react and form azo dye.
10. Alcohols do not react with HNO_3 while phenols react.

(8) Enlist the physical properties of ether.

Ans. Given in the theory.

LONG QUESTIONS

Q.3. Long Questions:

-
- (1) (a) Describe the method for preparation of diethyl ether from alcohol and sodium methoxide.**
(b) Write two chemical reactions of diethyl ether.
-

Ans. Given in the theory.

-
- (2) (a) What are phenols? Give method of preparation of phenol.**
(b) Discuss the acidic behavior of phenol.
-

Ans. Given in the theory.

-
- (3) Give detail description of chemical properties of phenol.**
-

Ans. Given in the theory.

-
- (4) Discuss the structure of alcohol.**
-

Ans. Given in the theory.

-
- (5) (a) How alcohol can be prepared from Grignard reagents.**
(b) Mention the reaction for the formation of following compound from an alcohol.
- | | |
|--------------------|--------------------------|
| (a) Ethene | (b) Ethyl acetate |
| (c) Acetone | (d) Formaldehyde |
-

Ans. Given in the theory.