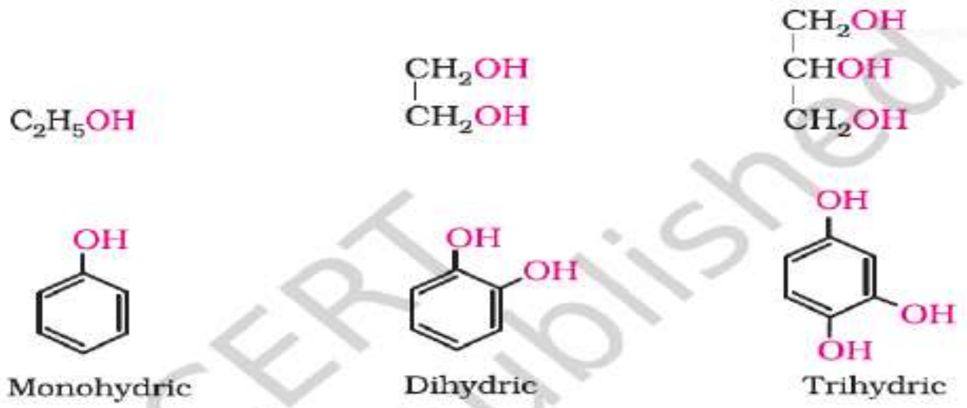
Chapter-11

Alcohols, Phenols, And Ethers

LECTURE 01

Alcohols, phenols, and ethers are the basic compounds for the formation of detergents, antiseptics, and fragrances. Alcohols and phenols are formed when a hydrogen atom in a hydrocarbon, aliphatic and aromatic respectively, is replaced by –OH group. These compounds find wide applications in industry as well as in day-to-day life. The sugar we eat, the cotton used for fabrics, the paper we use for writing, are all made up of compounds containing –OH groups.

Classification: (Mono, Di, Tri or Polyhydric Compounds:)



Monohydric alcohols may be further classified according to the hybridization of the carbon atom to which the hydroxyl group is attached.

(i) Compounds containing sp^3 C-OH

In this class of alcohols, the –OH group is attached to an sp^3 hybridized carbon atom of an alkyl group. They are further classified as follows:

Primary, secondary and tertiary alcohols:

In these three types of alcohol, the –OH group is attached to a primary, secondary, and tertiary carbon atom, respectively.

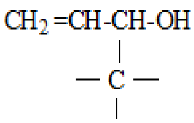
$R-CH_2-OH$	$R-CH(OH)-R$	$(R)_3C-OH$
1°-Alcohol	2°-Alcohol	3°-Alcohol

Allylic alcohols:

In these alcohols, the —OH group is attached to an sp3 hybridized carbon next to the carbon-carbon double bond, which is to an allylic carbon. For example

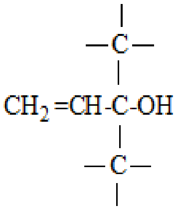
$CH_2=CH-CH_2-OH$

Primary



$CH_2=CH-CH(-C-)-OH$

Secondary

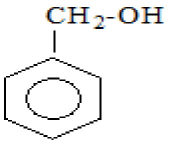


$CH_2=CH-C(-C-)(-C-)-OH$

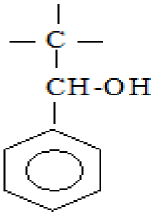
Tertiary

Benzylic alcohols:

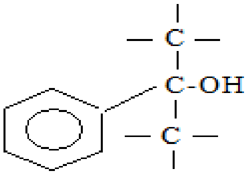
In these alcohols, the —OH group is attached to an sp3—hybridized carbon atom next to an aromatic ring. For example



Primary



Secondary



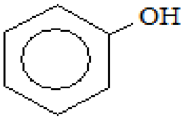
Tertiary

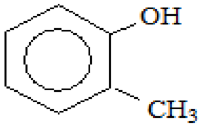
(ii) Compounds containing sp^{2}C-OH bond:

_These alcohols contain —OH group bonded to a carbon-carbon double bond i.e., to a vinylic carbon or an aryl carbon. These alcohols are also known as vinylic alcohols.

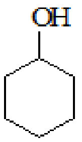
Vinylic alcohol: $CH_2 = CH - OH$

Phenols:

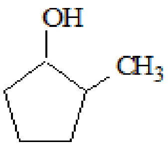




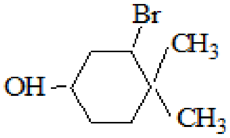
IUPAC Name of Some Compounds:



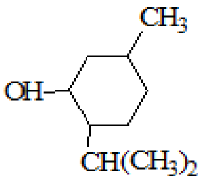
Cyclohexanol



2-Methylcyclopentanol



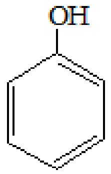
3-Bromo-4,4-dimethyl cyclohexanol



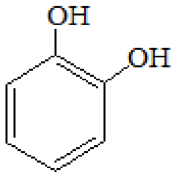
2-Isopropyl-5-methylhexanol

$CH_2=CH-CH_2-CH(OH)-CH(CH_3)_2$: 2-Methylhex-5-en-3-ol

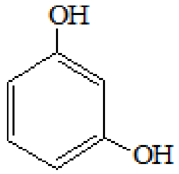
$CH_2=CH-CH_2-CH(OH)-CH(CH_3)_2$: 2-Methylhex-5-en-3-ol



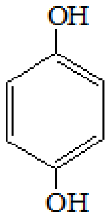
Phenol



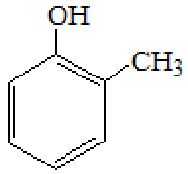
Benzene-1,2-diol
C.N : Catechol



Benzene-1,3-diol
C.N : Resrcinol

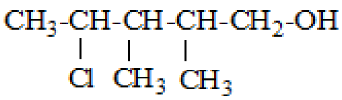


Benzene-1,4-diol
C.N : Hydroquinone / quinol

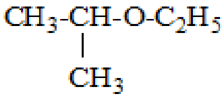


2-Methylphenol
C.N : o-Cresol

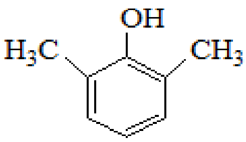
1. Give IUPAC name of following Compounds:

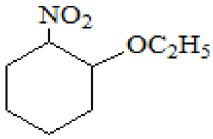
i) 

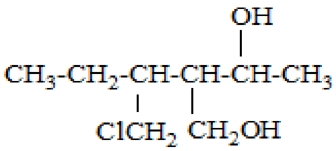
$CH_3-\underset{Cl}{\underset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-CH_2-OH$

ii) 

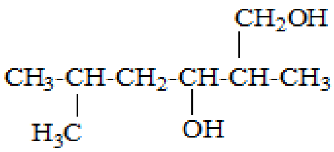
$CH_3-\underset{CH_3}{\underset{|}{CH}}-O-C_2H_5$

iii) 

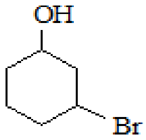
iv) 

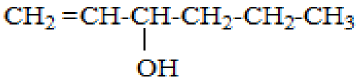
v) 

$CH_3-CH_2-\underset{ClCH_2}{\underset{|}{CH}}-\underset{CH_2OH}{\underset{|}{CH}}-\overset{OH}{\overset{|}{CH}}-CH_3$

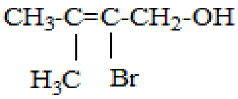
vi) 

$CH_3-\underset{H_3C}{\underset{|}{CH}}-CH_2-\underset{OH}{\underset{|}{CH}}-\overset{CH_2OH}{\overset{|}{CH}}-CH_3$

vii) 

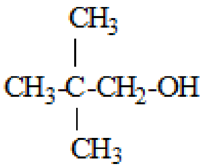
viii) 

$CH_2=CH-\underset{OH}{\underset{|}{CH}}-CH_2-CH_2-CH_3$

ix) 

$CH_3-\underset{H_3C}{\underset{|}{C}}=\underset{Br}{\underset{|}{C}}-CH_2-OH$

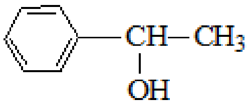
Classify the following as primary, secondary and tertiary alcohols

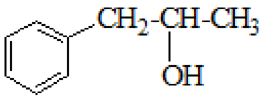
viii) 

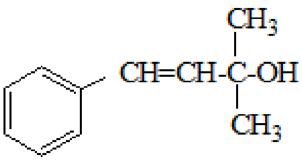
$CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_2-OH$

ix) $CH_2-CH=CH_2-OH$

x) $CH_2-CH-CH_2-OH$

xi) 

xii) 

xiii) 

Identify allylic alcohols in the above examples.

2. Write IUPAC name of the following:

i) $CH_3-CH(CH_3)-CH(OH)-C(CH_3)_3$ ii) $CH_3-CH(OH)-CH_2-CH(OH)-CH(C_2H_5)_2$
iii) $CH_3CH(OH)-CH(OH)CH_3$ iv) $HOCH_2CH(OH)CH_2OH$ v) $CH_3-O-CH_2-CH(CH_3)_2$
vi) $C_6H_5-O-C_2H_5$ vii) $C_6H_5-O-C_7H_{15}(n-)$ viii) $CH_3-CH_2-O-CH(CH_3)(C_2H_5)$

Write structures of the compounds whose IUPAC names are as follows:

(i) 2-Methylbutan-2-ol (ii) 1-Phenylpropan-2-ol
(iii) 3,5-Dimethylhexane –1, 3, 5-triol
(iv) 2,3 – Diethylphenol (v) 1 – Ethoxypropane (vi) 2-Ethoxy-3-methylpentane
(vii) Cyclohexylmethanol
(viii) 3-Cyclohexylpentan-3-ol (ix) Cyclopent-3-en-1-ol (x) 4-Chloro-3-ethylbutan-1-ol.

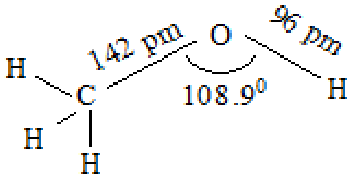
4. (i) Draw the structures of all isomeric alcohols of molecular formula C5H12O and give their IUPAC names.
(ii) Classify the isomers of alcohols in question
(i) as primary, secondary, and tertiary alcohols.

5. Give the structures and IUPAC names of monohydric phenols of molecular formula, C_7H_8O.

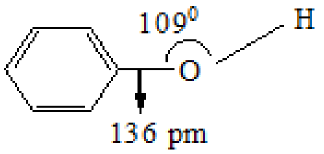
LECTURE 02

Structures of Functional Functional Groups:

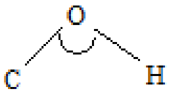
In alkanols and dialkyl ethers, the O- atom is attached to sp3 hybridized orbital of a carbon atom by a sigma bond. Whereas in phenol the O-atom is attached to sp^2 hybridized orbital of the carbon atom of an aromatic ring.



Methanol



Phenol

The bond angle  in alcohols is slightly less than the tetrahedral angle (109°-28'). It is due to the repulsion between the unshared electron pairs of oxygen.

In phenols, the –OH group is attached to sp^2 hybridised carbon of an aromatic ring. The carbon - oxygen bond length (136 pm) in phenol is slightly less than that in methanol. This is due to the following reson.

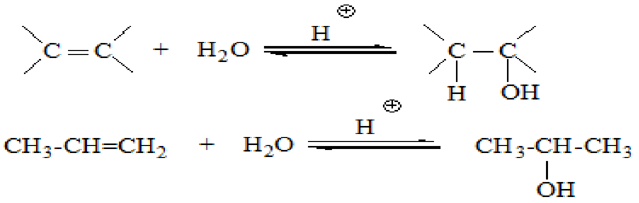
(i) The partial double bond character on account of the conjugation of unshared electron pair of oxygen with the aromatic ring.

(ii) SP^2 hybridized carbon to which oxygen is attached.

Preparation of Alcohols:

1. From alkenes

(i) By acid-catalyzed hydration: Alkenes react with water in the presence of acid as a catalyst to form alcohols. In the case of unsymmetrical alkenes, the addition reaction takes place according to Markovnikov's rule.



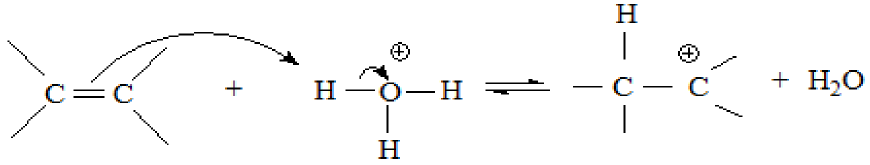
$$CH_3\text{-}CH{=}CH_2 + H_2O \xrightleftharpoons{\overset{\oplus}{H}} CH_3\text{-}\underset{OH}{\underset{|}{CH}}\text{-}CH_3$$

Mechanism:

The mechanism of the reaction involves the following three steps:

Step 1: Protonation of alkene to form carbocation.

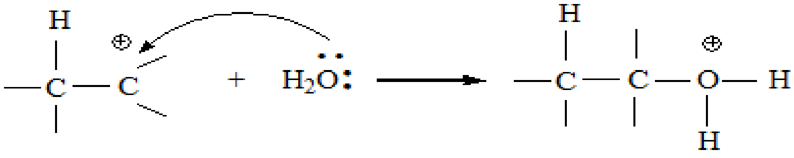
$H_2O + \overset{\oplus}{H} \longrightarrow H_3\overset{\oplus}{O}$ (Hydronium ion)



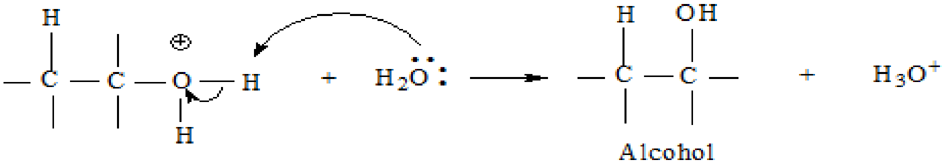
(Carbocation)

Step 2: Nucleophilic attack of water on carbocation:

Step-2 :



Step 3: Deprotonation to form an alcohol:



Alcohol

(ii) By hydroboration–oxidation: Diborane $(BH_3)_2$ reacts with alkenes to give trialkyl boranes as addition product. This is oxidised to alcohol by H_2O_2 in the presence of aqueous NaOH.

$$CH_3-CH=CH_2+(H-BH_2)_2 \rightarrow CH_3-CH_2-CH_2-BH_2$$

$$CH_3-CH_2-CH_2-BH_2 \xrightarrow{CH_3-CH=CH_2} (CH_3-CH_2-CH_2)_2BH$$

$$(CH_3-CH_2-CH_2)_2BH \xrightarrow{CH_3-CH=CH_2} (CH_3-CH_2-CH_2)_3B$$

$$(CH_3-CH_2-CH_2)_3B \xrightarrow{H_2O_2/OH^-/H_2O} \underset{\text{Propan}-1-\text{ol}}{3CH_3-CH_2-CH_2-OH}+B(OH)_3$$

The alcohol so formed looks as if it has been formed by the addition of water to the alkene in a way opposite to the Markovnikov’s rule. In this reaction, alcohol is obtained in excellent yield

2. From carbonyl compounds:

(i) By reduction of aldehydes and ketones:

Aldehydes and ketones are reduced to the corresponding alcohols by the addition of hydrogen in the presence of catalysts (catalytic hydrogenation) like finely divided metal such as platinum, palladium, or nickel. It is also prepared by treating aldehydes and ketones with sodium borohydride ($NaBH_4$)or lithium aluminum hydride ($LiAlH_4$). Aldehydes yield primary alcohols whereas ketones give secondary alcohols.

$$RCHO+H_2 \xrightarrow{Pd} RCH_2OH$$

$$RCOR' \xrightarrow{NaBH_4} R-CH(OH)-R'$$

(ii) By reduction of carboxylic acids and esters:

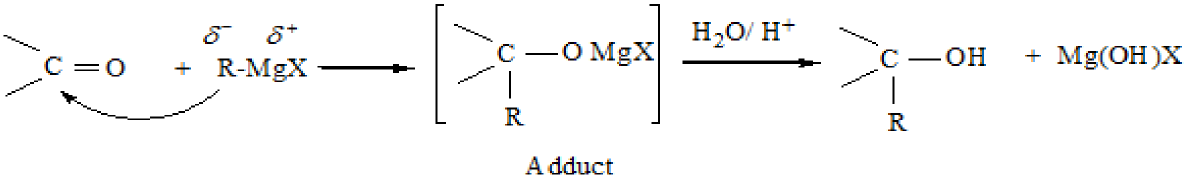
Carboxylic acids are reduced to primary alcohols in excellent yields by lithium aluminum hydride, a strong reducing agent.

$$RCOOH \xrightarrow{LiAlH_4/H_2O} RCH_2OH$$

However, LiAlH4 is an expensive reagent, and therefore, used for preparing special chemicals only. Commercially, acids are reduced to alcohols by converting them to the esters followed by their reduction using hydrogen in the presence of a catalyst (catalytic hydrogenation).

$$RCOOH \xrightarrow{R'OH/H^+} RCOOR' \xrightarrow{H_2/Catalyst} RCH_2OH+R'OH$$

3. From Grignard reagents: Alcohols are produced by the reaction of Grignard reagents with aldehydes and ketones. The first step of the reaction is the nucleophilic addition of Grignard reagent to the carbonyl group to form an adduct. Hydrolysis of the adduct yields alcohol.

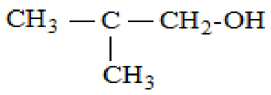


The overall reactions using different aldehydes and ketones are as follows:

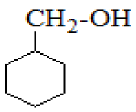
$$HCHO + RMgX \rightarrow RCH_2OMgX \xrightarrow{H_2O/H^+} RCH_2OH + Mg(OH)X$$
$$RCHO + R'MgX \rightarrow RCHR'OMgX \xrightarrow{H_2O/H^+} RCHR'OH + Mg(OH)X$$
$$RCOR + R'MgX \rightarrow (R)_2CR'OMgX \xrightarrow{H_2O/H^+} (R)_2CR'OH + Mg(OH)X$$

Methanol produces primary alcohol, other aldehydes produce secondary alcohol and ketones produce tertiary alcohol with G.R

1.. **Give the structures and IUPAC names of the products expected from the following reactions:**
   (a) Catalytic reduction of butanal.
   (b) Hydration of propene in the presence of dilute sulphuric acid.
   (c) The reaction of propanone with methylmagnesium bromide followed by hydrolysis.
2. What is meant by the hydroboration-oxidation reaction? Illustrate it with an example.
3. Write the mechanism of hydration of ethene to yield ethanol
4. **Show how will you synthesize:**
   (i) 1-phenyl ethanol from a suitable alkene.
   (ii) cyclohexyl methanol using an alkyl halide by an SN2 reaction.
   (iii) pentan-1-of using a suitable alkyl halide?
5. Write the mechanism of acid dehydration of ethanol to yield ethene.
6. Show how would you synthesize the following alcohols from appropriate alkenes?
7. Show how are the following alcohols prepared by the reaction of a suitable Grignard reagent on methanol?

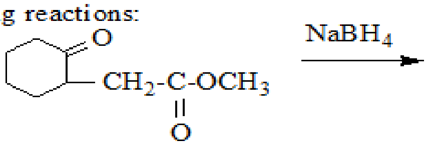
i)


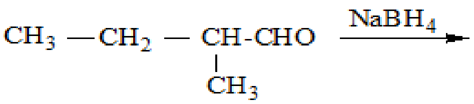
$CH_3-C(CH_3)-CH_2-OH$

ii)


Write structures of the products of the following reactions:

i) $CH_3-CH=CH_2 \xrightarrow{H^+/H_2O}$

ii)


iii)


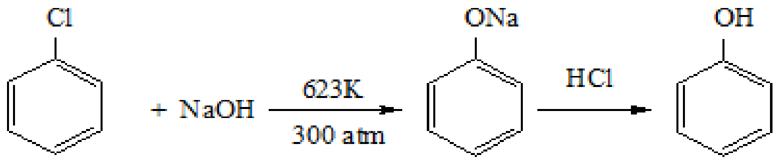
$CH_3-CH_2-CH(CH_3)-CHO \xrightarrow{NaBH_4}$

LECTURE-3

Preparation of Phenols:

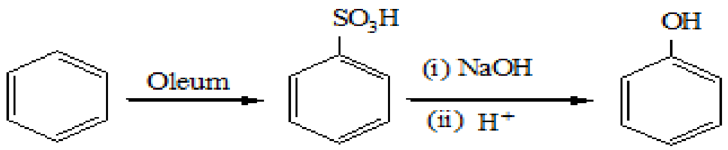
1. From haloarenes:

Chlorobenzene is fused with NaOH at 623K and 320 atmospheric pressure. Phenol is obtained by acidification of sodium phenoxide so produced.



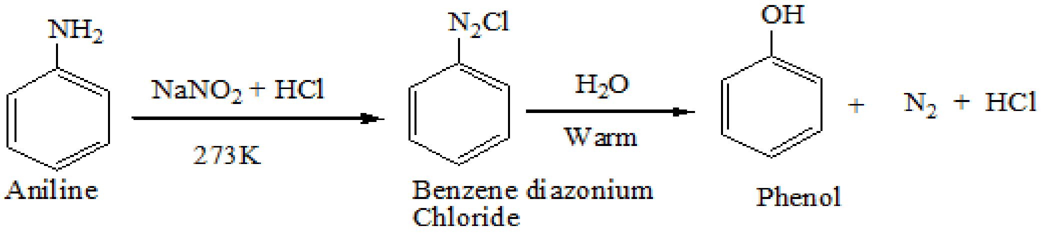
2. From benzene sulphonic acid:

Benzene is sulphonated with oleum and benzene sulphonic acid so formed is converted to sodium phenoxide on heating with molten sodium hydroxide. Acidification of the sodium phenoxide gives phenol.



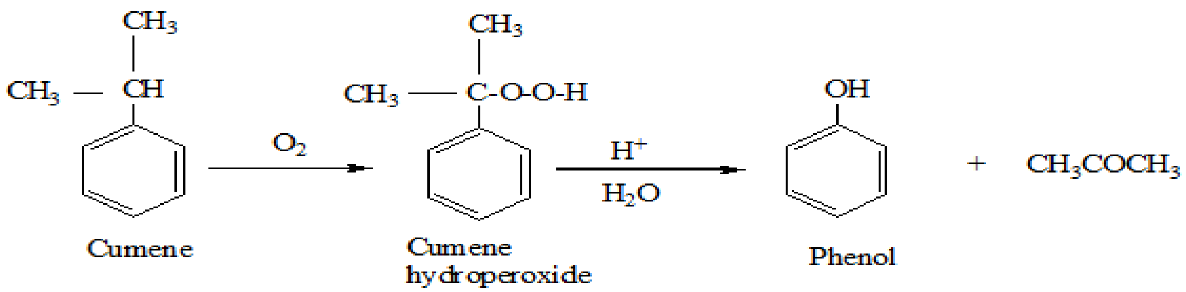
3. From diazonium salts:

A diazonium salt is formed by treating an aromatic primary amine with nitrous acid ($NaNO_2$ + HCl) at 273-278 K. Diazonium salts are hydrolyzed to phenols by warming with water or by treating with dilute acids



4. From cumene:

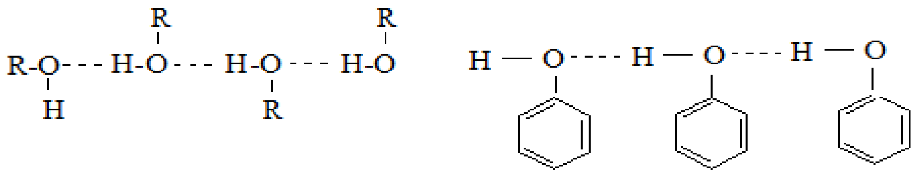
Phenol is manufactured from cumene. Cumene (isopropylbenzene) is oxidized in the presence of air to cumene hydroperoxide. It is converted to phenol and acetone as a by-product treating it with dilute acid.



Physical Properties:

Boiling Points:

The boiling points of alcohols and phenols increase with an increase in the number of carbon atoms (increase in van der Waals forces). In alcohols, the boiling points decrease with the increase of branching in the carbon chain (because of a decrease in van der Waals forces with a decrease in surface area). The –OH group in alcohols and phenols is involved in intermolecular hydrogen bonding as shown below:



It is interesting to note that boiling points of alcohols and phenols are higher in comparison to other classes of compounds, namely hydrocarbons, ethers, haloalkanes and haloarenes of comparable molecular masses. For example, ethanol and propane have comparable molecular masses but their boiling points differ widely. The boiling point of methoxymethane is intermediate of the two boiling points.

CH_3-CH_2-OH	CH_3-O-CH_3	CH_3-CH_2-CH_3
Ethanol (B.P : 351K)	Dimethyl ether(B.P :248K)	Propane (B.P : 231K)

The high boiling points of alcohols are mainly due to the presence of intermolecular hydrogen bonding in them which is lacking in ethers and hydrocarbons.

Solubility: Solubility of alcohols and phenols in water is due to their ability to form hydrogen bonds with water molecules. The solubility decreases with an increase in the size of alkyl/aryl (hydrophobic) groups. Several of the lower molecular mass, alcohols are miscible with water in all proportions.

Answer the following questions:

1. Arrange the following sets of compounds in order of their increasing boiling points:
   (a) Pentan-1-ol, butan-1-ol, butan-2-ol, ethanol, propan- 1-ol, methanol.
   (b) Pentan-1-ol, n-butane, pentanal, ethoxyethane.
2. Give the equations of reactions for the preparation of phenol from cumene.

3. Write a chemical reaction for the preparation of phenol from chlorobenzene.
4. You are given benzene, conc. H_2SO_4 and NaOH. Write the equations for the preparation of phenol using these reagents.
5. How will you get phenol starting from benzene?
6. How is phenol obtained from aniline?
7. Discuss the reactivity of mono, di, and tri nitro chlorobenzenes with aq.NaOH.
8. Complete the following reaction.

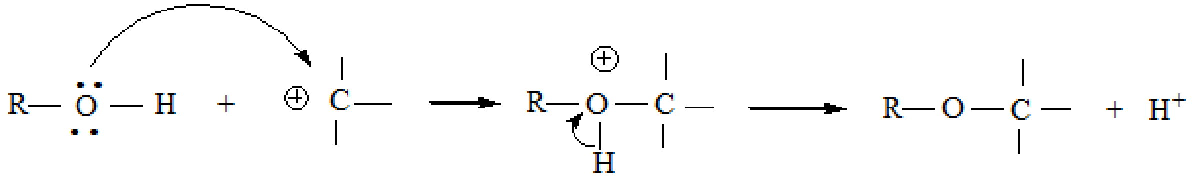
$$C_2H_4Cl_2 \xrightarrow{\text{Alc.KOH}} A \xrightarrow{\text{Red hot iron tube}} B \xrightarrow{Cl_2/AlCl_3} C \xrightarrow[\text{623K, 300atm}]{\text{aq.NaOH}} D$$

9. Explain why propanol has a higher boiling point than that of the hydrocarbon, butane?
10. Alcohols are comparatively more soluble in water than hydrocarbons of comparable molecular masses. Explain this fact.
11. Give a reason for the higher boiling point of ethanol in comparison to methoxymethane.

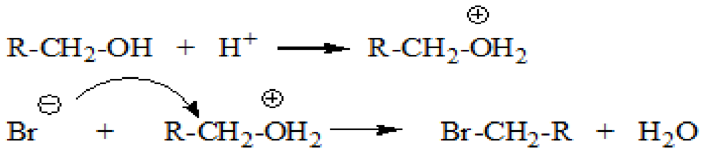
LECTURE-4

Chemical Reactions: Alcohols are versatile compounds. They react both as nucleophiles and electrophiles. The bond between O–H is broken when alcohols react as nucleophiles.

Alcohols as nucleophiles:



Protonated alcohols as electrophiles: The bond between C–O is broken when they react as electrophiles. Protonated alcohols react in this manner.



$$R\text{-}CH_2\text{-}OH + H^+ \longrightarrow R\text{-}CH_2\text{-}\overset{\oplus}{O}H_2$$

$$\overset{\ominus}{Br} + R\text{-}CH_2\text{-}\overset{\oplus}{O}H_2 \longrightarrow Br\text{-}CH_2\text{-}R + H_2O$$

Based on the cleavage of O–H and C–O bonds, the reactions of alcohols and phenols may be divided into two groups:

(a) Reactions involving cleavage of the O–H bond:

1. The acidity of alcohols and phenols:

(i) Reaction with metals: Alcohols and phenols react with active metals such as sodium, potassium, and aluminum to yield corresponding alkoxides/phenoxides and hydrogen.

$$2R-O-H+2Na \rightarrow \underset{\text{Sodium alkoxide}}{2R-O-Na} + H_2$$

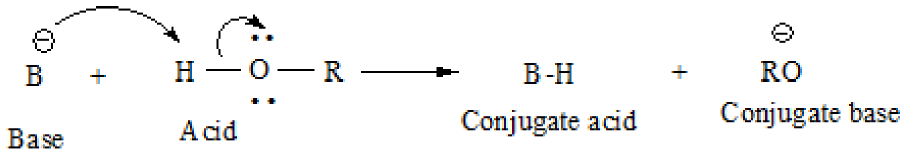
$$\underset{\text{Tertiarybutyl alcohol}}{6(CH_3)_3C-OH} + 2Al \rightarrow \underset{\text{Aluminium tert.butoxide}}{2Al[(CH_3)_3C-O]_3} + 3H_2$$

$$\underset{\text{Phenol}}{2C_6H_5-OH} + 2Na \rightarrow \underset{\text{Sod.phenoxide}}{2C_6H_5-ONa} + H_2$$

In addition to this, phenols react with aqueous sodium hydroxide to form sodium phenoxides.

$$C_6H_5-OH + NaOH \rightarrow C_6H_5-ONa + H_2O$$

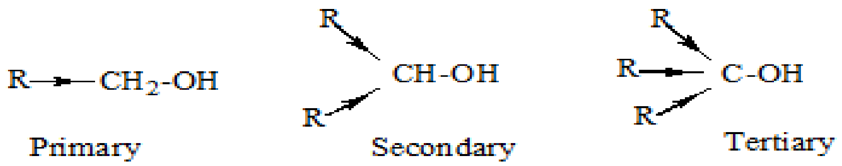
The above reactions show that alcohols and phenols are acidic. Alcohols and phenols are Brönsted acids i.e., they can donate a proton to a stronger base (B:).



(ii) The acidity of alcohols:

* The acidic character of alcohol is due to the polar nature of the O–H bond.

* An electron-releasing group (–CH_3, –C_2H_5) increases electron density on oxygen tending to decrease the polarity of the O-H bond. This decreases the acid strength. For this reason, the acid strength of alcohols decreases in the following order:



* Alcohols are, however, weaker acids than water. This can be illustrated by the reaction of water with an alkoxide.

$$\underset{\text{Base}}{R-O^{\ominus}} + \underset{\text{Acid}}{H_2O} \longrightarrow \underset{\text{Conjugate acid}}{R-O-H} + \underset{\text{Conjugate base}}{O-H^{\ominus}}$$

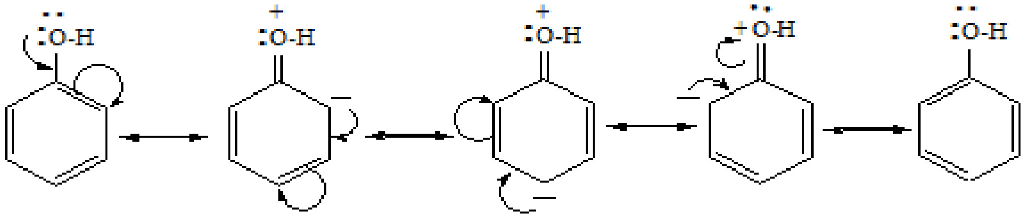
* This reaction shows that water is a better proton donor (i.e. stronger acid) than alcohol.

* In the above reaction, we note that an alkoxide ion is a better proton acceptor than hydroxide ion, which suggests that alkoxides are stronger bases (sodium ethoxide is a stronger base than sodium hydroxide).

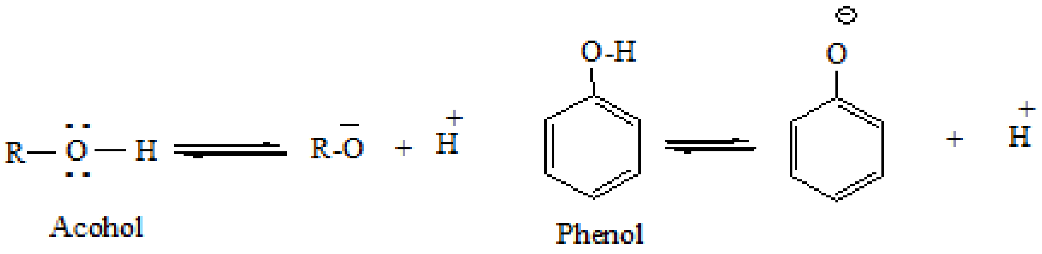
* Alcohols act as Bronsted bases as well. It is due to the presence of unshared electron pairs on oxygen, which makes them proton acceptors.

(iii) The acidity of phenols:

The reactions of phenol with metals (e.g., sodium, aluminum) and sodium hydroxide indicate its acidic nature. The hydroxyl group, in phenol, is directly attached to the sp^2 *hybridized carbon of the benzene ring which acts as an electron-withdrawing group. Due to this, the charge distribution in the phenol molecule, as depicted in its resonance structures, causes the oxygen of –OH group to be positive.*

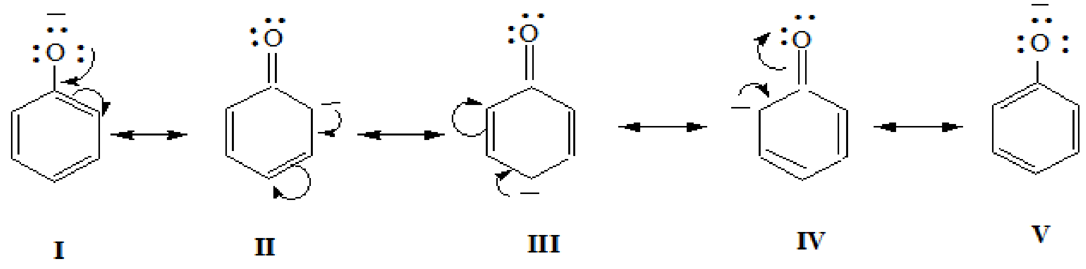


The reaction of phenol with aqueous sodium hydroxide indicates that phenols are stronger acids than alcohols and water. A compound in which the hydroxyl group attached to an aromatic ring is more acidic than the one in which the hydroxyl group is attached to an alkyl group. The ionization of alcohol and a phenol takes place as follows:



Due to the higher electronegativity of sp^2 hybridized carbon of phenol to which –OH is attached, electron density decreases on oxygen. This increases the polarity of the O–H bond and results in an increase in ionization of phenols than that of alcohol. Now let us examine the stabilities of

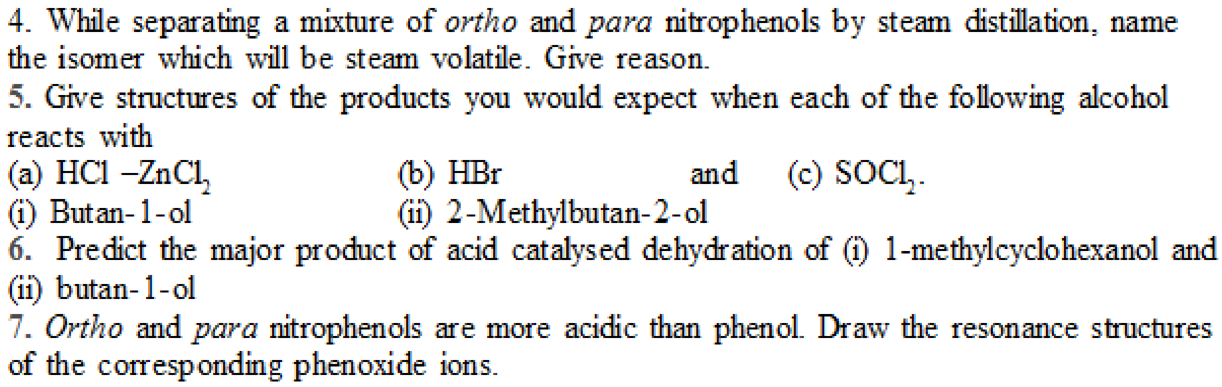
alkoxide and phenoxide ions. In alkoxide ion, the negative charge is localized on oxygen while in phenoxide ion, the charge is delocalized. The delocalization of negative charge makes phenoxide ion more stable and favors the ionization of phenol. The resonance structures of phenol have charge separation due to which the phenol molecule is less stable than phenoxide ion. The alkoxide ion formed from alcohol is not stabilized due to the absence of resonance. Phenoxide ion is more stable than alkoxide ion. This explains why phenol is more acidic than aliphatic alcohol.



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

Answer the following questions:

1. Arrange the following compounds in increasing order of their acid strength: Propan-1-ol, 2,4,6-trinitrophenol, 3-nitrophenol, 3,5-dinitrophenol, phenol, 4-methyl phenol.
2. Give two reactions that show the acidic nature of phenol. Compare acidity of phenol with that of ethanol.
3. **Explain why is *ortho nitrophenol more acidic than ortho methoxy phenol?***



4. While separating a mixture of *ortho* and *para* nitrophenols by steam distillation, name the isomer which will be steam volatile. Give reason.

5. Give structures of the products you would expect when each of the following alcohol reacts with

(a) HCl –$ZnCl_2$ (b) HBr and (c) $SOCl_2$.

(i) Butan-1-ol (ii) 2-Methylbutan-2-ol

6. Predict the major product of acid catalysed dehydration of (i) 1-methylcyclohexanol and (ii) butan-1-ol

7. *Ortho* and *para* nitrophenols are more acidic than phenol. Draw the resonance structures of the corresponding phenoxide ions.

LECTURE 05

2. Esterification:

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

$$\text{Ar / R-OH} + \text{R'-COOH} \xrightleftharpoons{H^+} \text{Ar / ROCOR'} + H_2O$$

$$\text{Ar / R-OH} + (\text{R'CO})_2\text{O} \xrightleftharpoons{H^+} \text{Ar / ROCOR'} + \text{R'COOH}$$

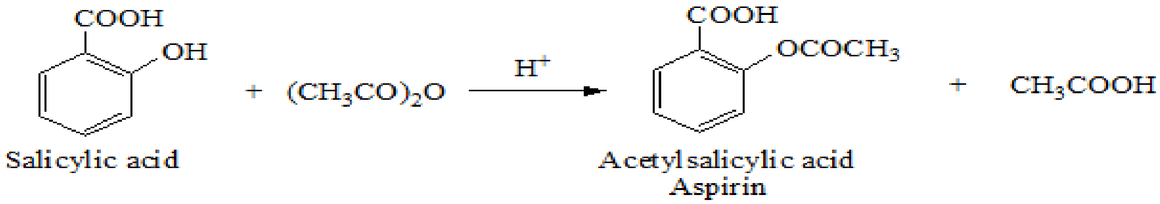
$$\text{R/ Ar-OH} + \text{R'COCl} \xrightarrow{\text{Pyridine}} \text{R / ArOCOR'} + \text{HCl}$$

Aspirin possesses analgesic, anti-inflammatory, and antipyretic properties:

The reaction with carboxylic acid and acid anhydride is carried out in the presence of a small amount of concentrated sulphuric acid. The reaction is reversible, and therefore, water is removed as soon as it is formed.

The reaction with acid chloride is carried out in the presence of a base (pyridine) to neutralize HCl which is formed during the reaction. It shifts the equilibrium to the right-hand side.

The introduction of acetyl (CH_3CO) group in alcohols or phenols is known as acetylation. Acetylating of salicylic acid produces aspirin.



(b) Reactions involving cleavage of carbon-oxygen (C–O) bond in alcohols.

The reactions involving cleavage of the C–O bond take place only in alcohol.

1. Reaction with hydrogen halides:

Alcohols react with hydrogen halides to form alkyl halides

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

The difference in reactivity of three classes of alcohols with HCl distinguishes them from one another (**Lucas test). Alcohols are soluble in Lucas reagent (conc. HCl and $ZnCl_2$) while their halides are immiscible and produce turbidity in solution. Tertiary alcohol forms turbidity immediately. Primary alcohol doesn't form turbidity at room temperature.**

Phenols can show a reaction involving the cleavage of the C-O bond, only with zinc.

$$C_6H_5OH\xrightarrow{Zn/\Delta}C_6H_6$$

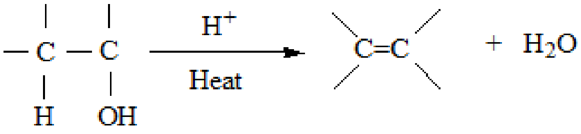
2. Reaction with phosphorus trihalides:

Alcohols are converted to alkyl bromides by reaction with phosphorus tribromide.

$$3R-OH+PBr_3\rightarrow 3R-Br+H_3PO_3$$

3. Dehydration:

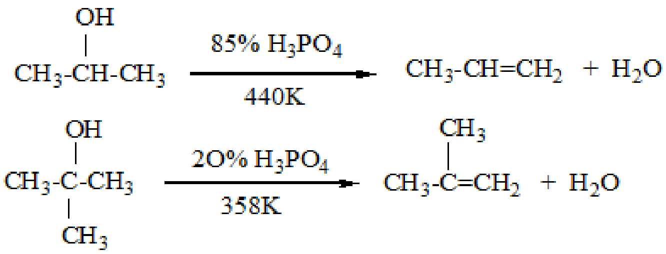
Alcohols undergo dehydration (removal of a molecule of water) to form alkenes on treating with a protic acid-like concentrated H_2SO_4 or H_3PO_4 or catalysts such as anhydrous zinc chloride or alumina.



Ethanol undergoes dehydration by heating it with concentrated H2SO4 at 443 K.

$$C_2H_5OH\xrightarrow{H_2SO_4/443K}CH_2=CH_2+H_2O$$

Secondary and tertiary alcohols are dehydrated under milder conditions. For example



$$CH_3\text{-}\underset{}{\overset{OH}{\overset{|}{C}H}}\text{-}CH_3 \xrightarrow[440K]{85\%\ H_3PO_4} CH_3\text{-}CH{=}CH_2 + H_2O$$

$$CH_3\text{-}\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}\text{-}CH_3 \xrightarrow[358K]{20\%\ H_3PO_4} CH_3\text{-}\overset{\overset{CH_3}{|}}{C}{=}CH_2 + H_2O$$

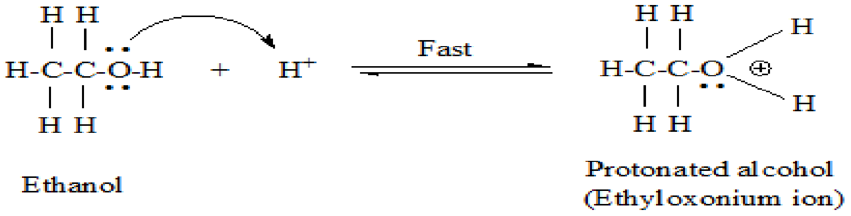
Thus, the relative ease of dehydration of alcohols follows the following order:

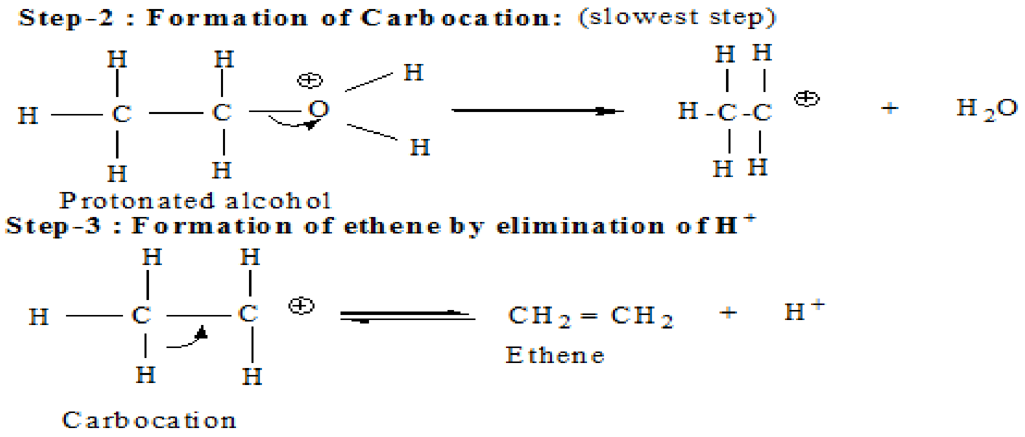
Tertiary > Secondary > Primary

The mechanism of dehydration of ethanol involves the following steps:

Mechanism

Step 1: Formation of protonated alcohol.

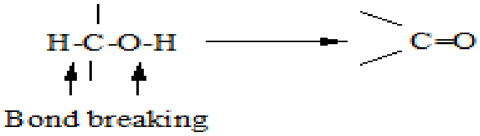




The acid used in step 1 is released in step 3. To drive the equilibrium to the right, ethene is removed as it is formed.

4. Oxidation:

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



Such a cleavage and formation of bonds occur in oxidation reactions. These are also known as **dehydrogenation reactions as these involve loss of dihydrogen from an alcohol molecule.**

Depending on the oxidizing agent used, a primary alcohol is oxidized to an aldehyde which in turn is oxidized to a carboxylic acid.

$$\underset{Alcohol}{R-CH_2OH} \xrightarrow{Oxidation} \underset{Aldehyde}{R-CHO} \rightarrow \underset{Carboxylic\ acid}{R-COOH}$$

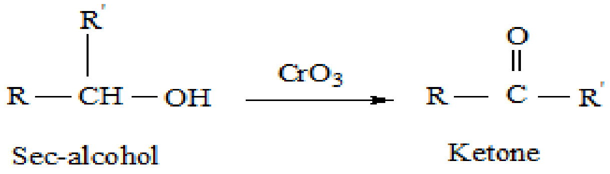
Strong oxidizing agents such as acidified potassium permanganate are used for getting carboxylic acids from alcohols directly. Anhydrous CrO_3 is used as the oxidizing agent for the isolation of aldehydes.

$$R-CH_2OH \xrightarrow{CrO_3} R-CHO$$

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

$$CH_3-CH=CH-CH_2OH \xrightarrow{PCC} CH_3-CH=CH-CHO$$

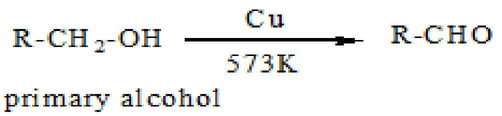
Secondary alcohols are oxidized to ketones by chromic anhydride (CrO_3).



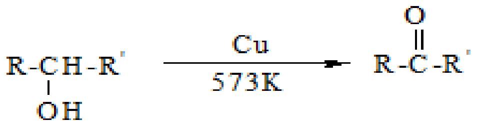
$$R-\overset{R'}{\overset{|}{CH}}-OH \xrightarrow{CrO_3} R-\overset{O}{\overset{\|}{C}}-R'$$

Tertiary alcohols do not undergo an oxidation reaction. Under strong reaction conditions such as strong oxidizing agents ($KMnO_4$) and elevated temperatures, cleavage of various C-C bonds takes place and a mixture of carboxylic acids containing a lesser number of carbon atoms is formed.

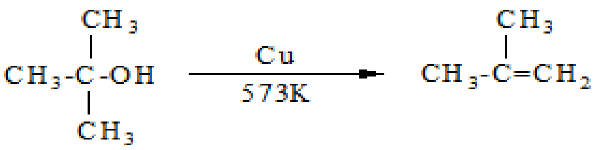
When the vapors of primary or secondary alcohol are passed over heated copper at 573 K, dehydrogenation takes place and an aldehyde or a ketone is formed while tertiary alcohols undergo dehydration.



$$R-CH_2-OH \xrightarrow[573K]{Cu} R-CHO$$



$$R-\underset{OH}{\underset{|}{CH}}-R' \xrightarrow[573K]{Cu} R-\overset{O}{\overset{\|}{C}}-R'$$

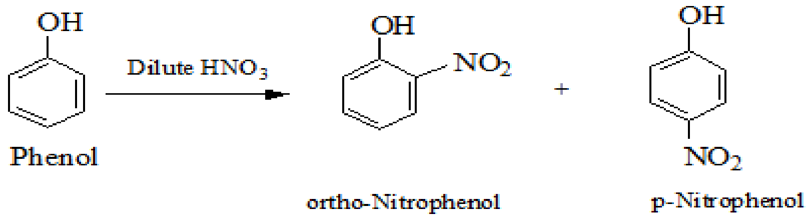


$$CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-OH \xrightarrow[573K]{Cu} CH_3-\overset{CH_3}{\overset{|}{C}}=CH_2$$

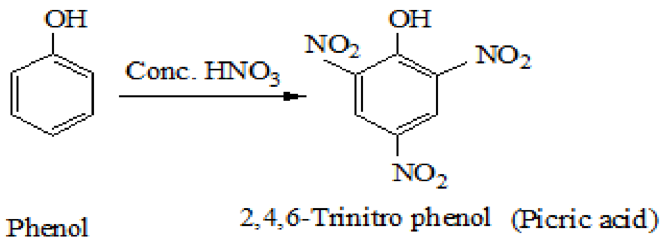
c) <u>Reactions of phenols:</u>

1. <u>Electrophilic aromatic substitution:</u>

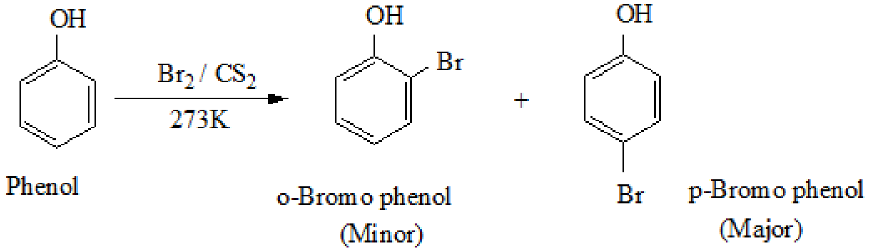
(i) Nitration: With dilute nitric acid at low temperature (298 K), phenol yields a mixture of ortho and para nitrophenols.



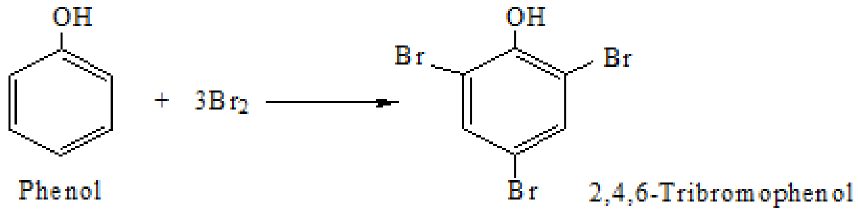
The ortho and para isomers can be separated by steam distillation. o-Nitrophenol is steam volatile due to intramolecular hydrogen bonding while p-nitrophenol is less volatile due to intermolecular hydrogen bonding which causes the association of molecules.
With concentrated nitric acid, phenol is converted to 2,4,6-trinitrophenol. The product is commonly known as picric acid. The yield of the reaction product is poor.



Nowadays picric acid is prepared by treating phenol first with concentrated sulphuric acid which converts it to phenol-2,4-disulphonic acid, and then with concentrated nitric acid to get 2,4,6-trinitrophenol. Can you write the equations of the reactions involved?
(ii) <u>Halogenation</u>*:* On treating phenol with bromine, different reaction products are formed under different experimental conditions.
(a) When the reaction is carried out in solvents of low polarity such as $CHCl_3$ or CS_2 and at low temperature, monobromophenols are formed.

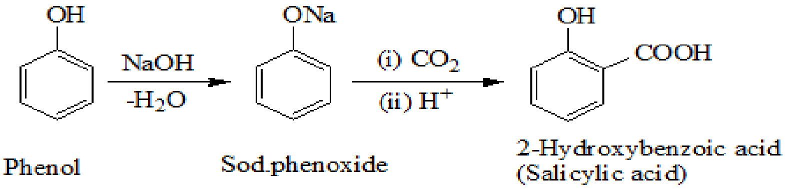


The usual halogenation of benzene takes place in the presence of a Lewis acid, such as $FeBr_3$ which polarises the halogen molecule. In the case of phenol, the polarisation of the bromine molecule takes place even in the absence of Lewis acid. It is due to the highly activating effect of –OH group attached to the benzene ring.
(b) When phenol is treated with bromine water, 2,4,6-tribromophenol is formed as a white precipitate.



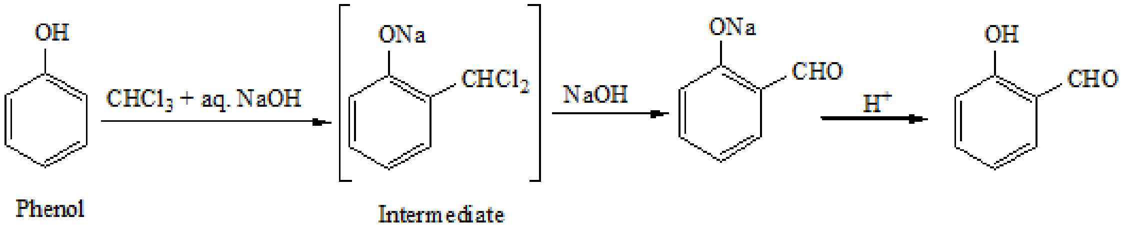
2. Kolbe’s reaction:

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



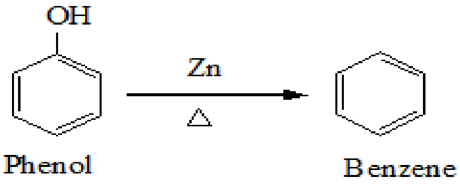
3. Reimer-Tiemann reaction:

On treating phenol with chloroform in the presence of sodium hydroxide, a –CHO group is introduced at the ortho position of the benzene ring. This reaction is known as Reimer - Tiemann reaction. The intermediate substituted benzal chloride is hydrolyzed in the presence of alkali to produce salicylaldehyde.



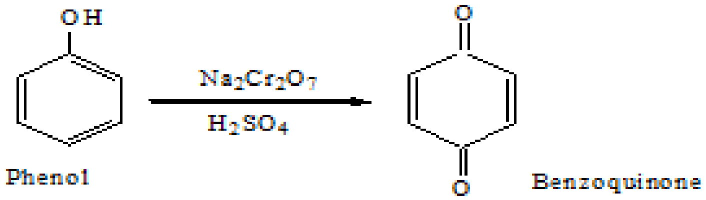
4. The reaction of phenol with zinc dust:

Phenol is converted to benzene on heating with zinc dust.



5. Oxidation:

Oxidation of phenol with chromic acid produces a conjugated diketone known as benzoquinone. In the presence of air, phenols are slowly oxidized to dark-colored mixtures containing quinones.



Some Commercially Important Alcohols:

Methanol and ethanol are among the two commercially important alcohols.

1. **Methanol**:

Methanol, CH_3OH, also known as ‘wood spirit’, was produced by destructive distillation of wood. Today, most of the methanol is produced by catalytic hydrogenation of carbon monoxide at high pressure and temperature and in the presence of ZnO – Cr2O3 catalyst.

$$CO + 2H_2 \xrightarrow[\substack{200\text{-}300\,atm \\ 573\text{-}673\,K}]{ZnO\text{-}Cr_2O_3} CH_3\text{-}OH$$

Methanol is a colorless liquid and boils at 337 K. It is highly poisonous. Ingestion of even small quantities of methanol can cause blindness and large quantities cause even death. Methanol is used as a solvent in paints, varnishes, and chiefly for making formaldehyde.

2. **Ethanol:**

Ethanol, C_2H_5OH, is obtained commercially by fermentation; the oldest method is from sugars. The sugar in molasses, sugarcane, or fruits such as grapes is converted to glucose and fructose, (both of which have the formula $C_6H_{12}O_6$), in the presence of an enzyme, invertase. Glucose and fructose undergo fermentation in the presence of another enzyme, zymase, which is found in yeast.

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

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

Ethanol is a colorless liquid with boiling point 351 K. It is used as a solvent in the paint industry and the preparation of several carbon compounds. The commercial alcohol is made unfit for drinking by mixing in it some copper sulphate (to give it a color) and pyridine (a foul-smelling liquid). It is known as the **denaturation of alcohol.**

Nowadays, large quantities of ethanol are obtained by hydration of ethene.

Answer the following questions:

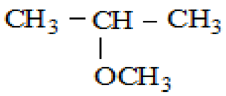
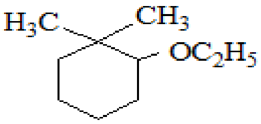
1. What happens when phenol reacts with dil.HNO_3?
2. How will you prepare picric acid from phenol?
3. What happens when phenol reacts with bromine?

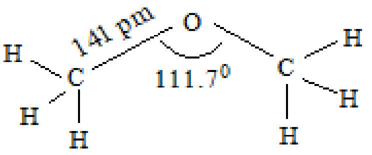
4. How will you convert phenol to salicylic acid?
5. How will you convert phenol to salicylaldehyde?
6. What happens when phenol is heated with zinc dust?
7. How phenol can be converted to benzoquinone?
8. Suggest how methanol is prepared from wood spirit?
9. Describe the manufacture of ethanol from sugar.
10. Write the sources of ethanol.

LECTURE 06

Classification, Nomenclature, the structure of Functional group of ethers:

Ethers: Ethers are classified as simple or symmetrical, if the alkyl or aryl groups attached to the oxygen atom are the same, and mixed or unsymmetrical if the two groups are different. Diethyl ether, $C_2H_5OC_2H_5$, is a symmetrical ether whereas $C_2H_5OCH_3$ and $C_2H_5OC_6H_5$ are unsymmetrical ethers.

Compound	**IUPAC name**	**Common name**
CH_3-O-CH_3	Methoxymethane	Dimethyl ether
C_2H_5-O-C_2H_5	Ethoxyethane	Diethy ether
CH_3-O-CH_2-CH_2-CH_3	1-Methoxypropane	Methyl n-propyl ether
C_6H_5-O-CH_3	Methoxybenzene(Anisole)	Methyl phenyl ether(Anisole)
C_6H_5-O-CH_2-CH_3	Ethoxybenzene	Ethyl phenyl ether(Phenetole)
C_6H_5-O-$(CH_2)_6$-CH_3	1-Phenoxyheptane	Heptyl phenyl ether
 $CH_3-\underset{\displaystyle OCH_3}{\underset{\vert}{CH}}-CH_3$	2-Methoxypropane	Methyl isopropyl ether
C_6H_5-O-CH_2-CH_2-$CH(CH_3)_2$	3-Methylbutoxybenzene	Methyl isopentyl ether
CH_3-O-CH_2-CH_2-O-CH_3	1,2-Dimethoxyethane	
	2-Ethoxy-1,1-dimethylcyclohexane	

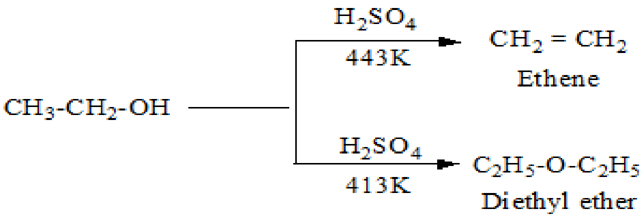


Methoxymethane

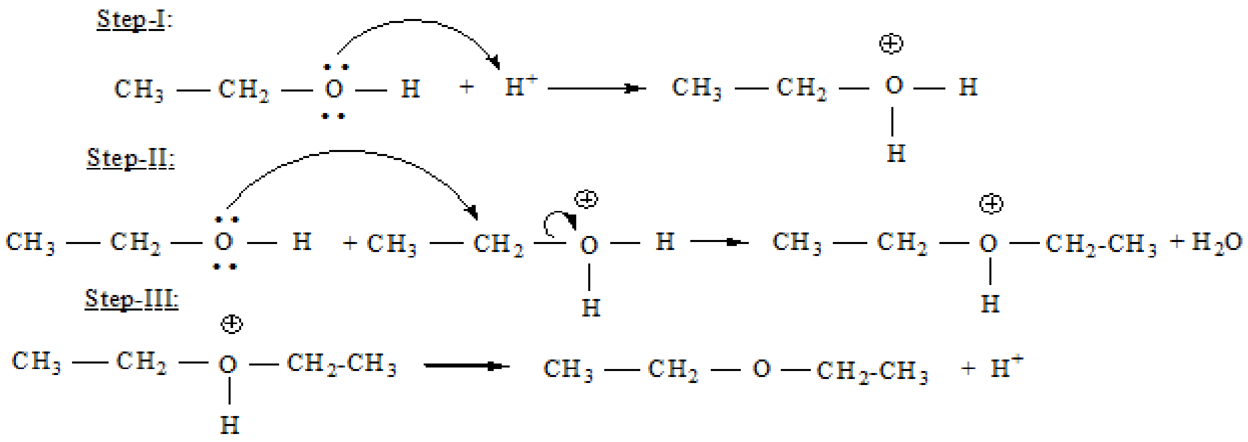
In ethers, the four-electron pairs, i.e., the two bond pairs and two lone pairs of electrons on oxygen are arranged approximately in a tetrahedral arrangement. The bond angle is slightly greater than the tetrahedral angle due to the repulsive interaction between the two bulky (–R) groups. The C–O bond length (141 pm) is almost the same as in alcohol.

Preparation of Ethers:

1. By dehydration of alcohol: Alcohols undergo dehydration in the presence of protic acids (H_2SO_4, H_3PO_4). The formation of the reaction product, alkene, or ether depends on the reaction conditions. For example, ethanol is dehydrated to ethene in the presence of sulphuric acid at 443 K. At 413 K, ethoxyethane is the main product.



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



Acidic dehydration of an alcohol, to give an alkene is also associated with substitution reaction to give an ether.

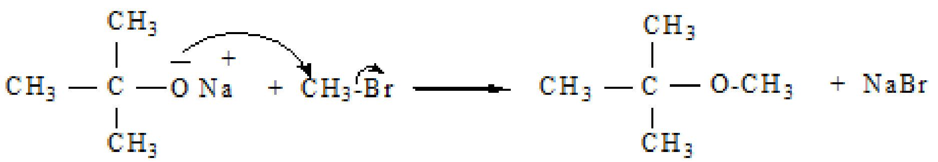
The method is suitable for the preparation of ethers having primary alkyl groups only. The alkyl group should be unhindered and the temperature is kept low. Otherwise, the reaction favors the formation of an alkene. However, the dehydration of secondary and tertiary alcohols to give corresponding ethers is unsuccessful as elimination competes over substitution, and as a consequence, alkenes are easily formed.

2. **Williamson synthesis:**

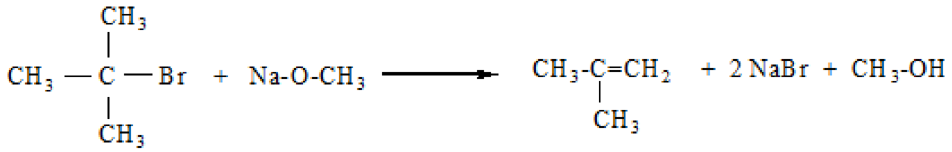
It is an important laboratory method for the preparation of symmetrical and unsymmetrical ethers. In this method, an alkyl halide is allowed to react with sodium alkoxide.

$$R - X + R'\!-\!\overset{-}{O}Na \rightarrow R - O - R + NaX$$

Ethers containing substituted alkyl groups (secondary or tertiary) may also be prepared by this method. The reaction involves the SN2 attack of an alkoxide ion on primary alkyl halide.



Better results are obtained if the alkyl halide is primary. In the case of secondary and tertiary alkyl halides, elimination competes over substitution. If a tertiary alkyl halide is used, an alkene is the only reaction product and no ether is formed. For example, the reaction of CH_3ONa with $(CH_3)_3C–Br$ gives exclusively 2-methylpropene.

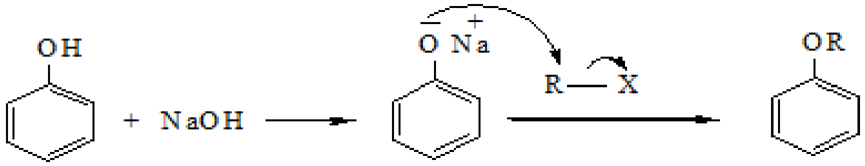


tert-Butyl bromide

2-Methylpropene

It is because alkoxides are not only nucleophiles but strong bases as well. They react with alkyl halides leading to elimination reactions.

Phenols are also converted to ethers by this method.



3. **By the reaction of an alkyl halide with dry Ag_2O:**

When alkyl halide is heated with dry silver oxide then ether is formed.

$$2R-X + Ag_2O \rightarrow R-O-R + 2AgX$$

Answer the following questions:

1. Write the equations involved in the following reactions:
   (i) Reimer - Tiemann reaction (ii) Kolbe's reaction

2. The following is not an appropriate reaction for the preparation of t-butyl ethyl ether.

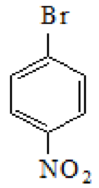
$$\underset{\text{Sod.ethoxide}}{C_2H_5-ONa+}\quad\underset{\text{tert}-\text{Butyl chloride}}{(CH_3)_3C-Cl}\quad\underset{\text{Ethyl tertiary butyl ether}}{\rightarrow(CH_3)_3C-OC_2H_5}$$

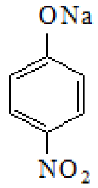
(i) What would be the major product of this reaction?

(ii) Write a suitable reaction for the preparation of t-butyl ethyl ether.

3. Write the reactions of Williamson synthesis of 2-ethoxy-3-methyl pentane starting from ethanol and 3-methyl pentane-2-ol.

4. Which of the following is an appropriate set of reactants for the preparation of 1-methoxy-4-nitrobenzene and why?

i)  + CH_3ONa

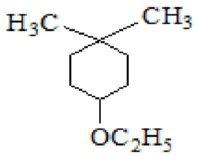
ii)  + CH_3Br

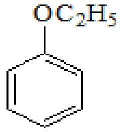
5. Explain the following with an example.

(i) Williamson ether synthesis. (ii) Unsymmetrical ether.

6. Give IUPAC names of the following ethers:

i) $C_2H_5OCH_2CH(CH_3)_2$ ii) $CH_3OCH_2CH_2Cl$ iii) $O_2N-C_6H_4-OCH_3(p)$ iv) $CH_3CH_2CH_2OCH_3$

v) 

vi) 

7. Write the names of reagents and equations for the preparation of the following ethers by Williamson's synthesis:

(i) 1-Propoxypropane (ii) Ethoxybenzene

(iii) 2-Methoxy-2-methylpropane (iv) 1-Methoxyethane

8. Illustrate with examples of the limitations of Williamson synthesis for the preparation of certain types of ethers.

9. How is 1-propoxypropane synthesized from propan-1-ol? Write the mechanism of this reaction.

10. The preparation of ethers by acid dehydration of secondary or tertiary alcohols is not a suitable method. Give reason.

LECTURE 07

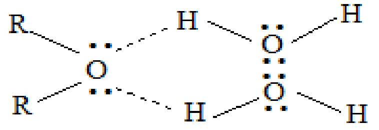
Physical Properties:

The C-O bonds in ethers are polar and thus, ethers have a net dipole moment. The weak polarity of ethers do not appreciably affect their boiling points which are comparable to those of the alkanes of comparable molecular masses but are much lower than the boiling points of alcohols as shown in the following cases:

Formula	$CH_3(CH_2)_3CH_3$ n-Pentane	C_2H_5-O-C_2H_5 Ethoxyethane	$CH_3(CH_2)_3$-OH Butan-1-ol
b.p./K	309.1	307.6	390

The large difference in boiling points of alcohols and ethers is due to the presence of hydrogen bonding in alcohols.

The miscibility of ethers with water resembles those of alcohols of the same molecular mass. Both ethoxyethane and butan-1-ol are miscible to almost the same extent i.e., 7.5 and 9 g per 100 mL water, respectively while pentane is essentially immiscible with water. Can you explain this observation? This is because just like alcohols, oxygen of ether can also form hydrogen bonds with water molecule as shown:



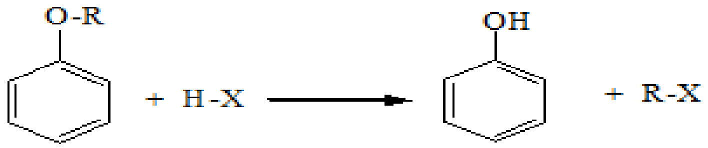
Chemical Reactions:

1. Cleavage of C–O bond in ethers:

Ethers are the least reactive of the functional groups. The cleavage of the C-O bond in ethers takes place under drastic conditions with an excess of hydrogen halides. The reaction of dialkyl ether gives two alkyl halide molecules.

$$R-O-R+HX \rightarrow R-X+R-OH$$
$$R-OH+HX \rightarrow R-X+H_2O$$

Alkyl aryl ethers are cleaved at the alkyl-oxygen bond due to the more stable aryl-oxygen bond. The reaction yields phenol and alkyl halide.



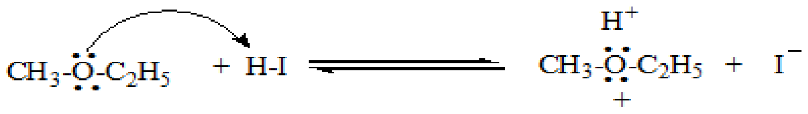
Ethers with two different alkyl groups are also cleaved in the same manner.

$$R-O-R'+HX \rightarrow R-X+R'-OH$$

The order of reactivity of hydrogen halides is as follows: HI > HBr > HCl. The cleavage of ethers takes place with concentrated HI or HBr at high temperatures.

Mechanism:

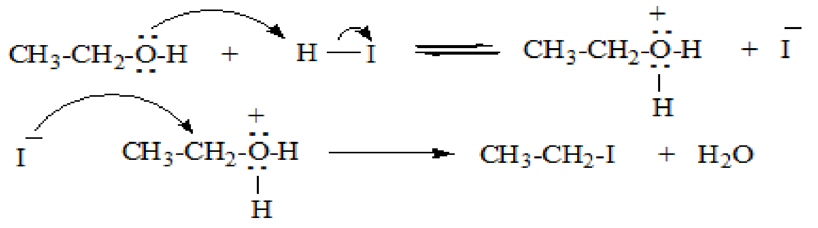
Step 1: The reaction of the ether with concentrated HI starts with protonation of ether molecule. The reaction takes place with HBr or HI because these reagents are sufficiently acidic.



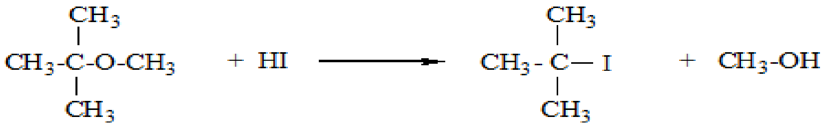
Step 2: Iodide is a good nucleophile. It attacks the least substituted carbon of the oxonium ion formed in step 1 and displaces an alcohol molecule by an SN2 mechanism.
Thus, in the cleavage of mixed ethers with two different alkyl groups, the alcohol and alkyl iodide formed, depending on the nature of alkyl groups. When primary or secondary alkyl groups are present, it is the lower alkyl group that forms alkyl iodide (SN2 reaction).

Step 3:

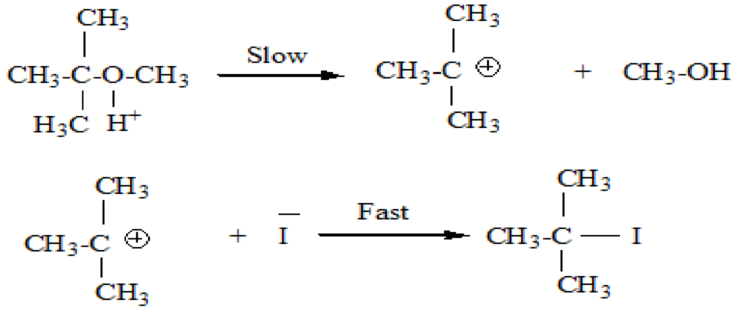
When HI is in excess and the reaction is carried out at a high temperature, ethanol reacts with another molecule of HI and is converted to ethyl iodide.



However, when one of the alkyl group is a tertiary group, the halide formed is a tertiary halide.



It is because, in step 2 of the reaction, the departure of the leaving group (HO–CH3) creates a more stable carbocation [$(CH_3)_3C^+$], and the reaction follows the SN1 mechanism.

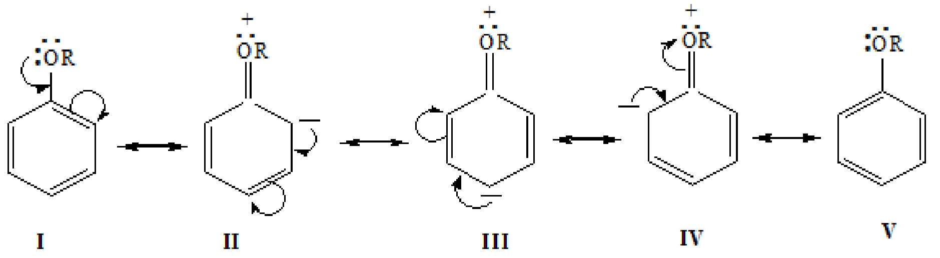


In the case of anisole, methyl phenyl oxonium ion, formed by protonation of ether. The bond between O–CH_3 is weaker than the bond between O–C6H5 because the carbon of the phenyl group is sp2 hybridized and there is a partial double bond character.

Therefore the attack by I⁻ ion breaks O–CH3 bond to form CH3I. Phenols do not react further to give halides because thesp2 hybridized carbon of phenol cannot undergo nucleophilic substitution reaction needed for conversion to the halide.

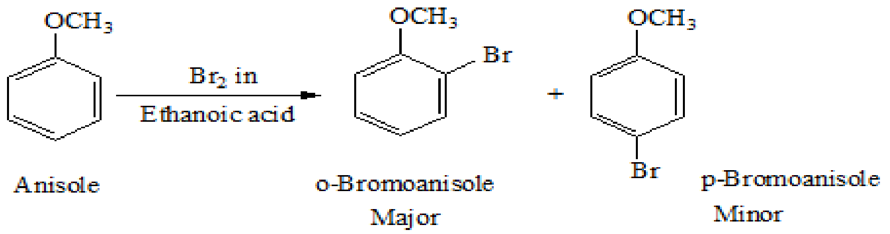
2. Electrophilic substitution:

The alkoxy group (-OR) is ortho, para directing, and activates the aromatic ring towards electrophilic substitution in the same way as in phenol.



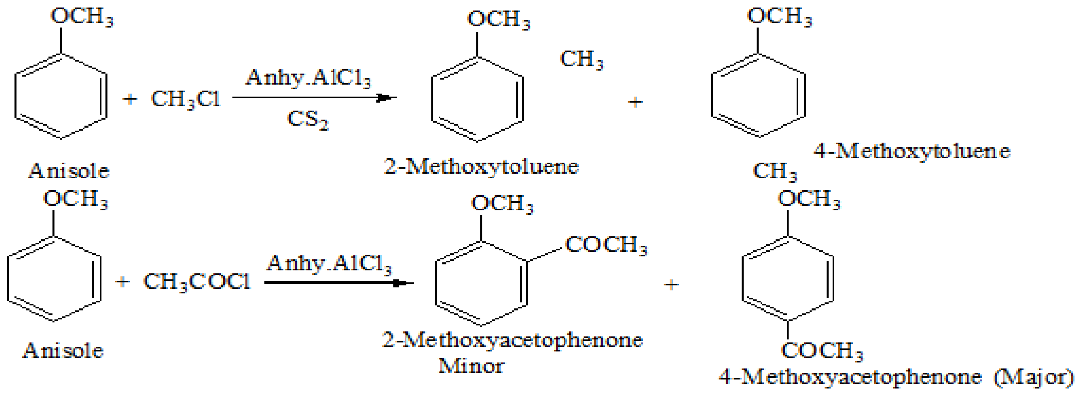
(I) Halogenation:

Phenylalkyl ethers undergo usual halogenation in the benzene ring, ex: anisole undergoes bromination with bromine in ethanoic acid even in the absence of iron (III) bromide catalyst. It is due to the activation of the benzene ring by the methoxy group. Para isomer is obtained in 90% yield.

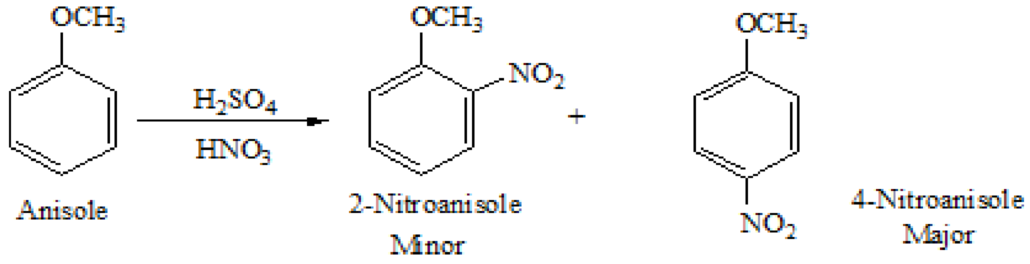


(ii) Friedel-Crafts reaction:

Anisole undergoes Friedel-Crafts reaction, i.e., the alkyl and acyl groups are introduced at ortho and para positions by reaction with an alkyl halide and acyl halide in the presence of anhydrous aluminum chloride (a Lewis acid) as a catalyst.



(iii) **Nitration:** Anisole reacts with a mixture of concentrated sulphuric and nitric acids to yield a mixture of *ortho and para nitro anisole*

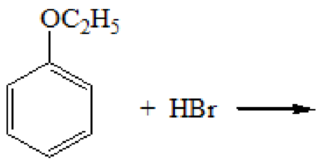
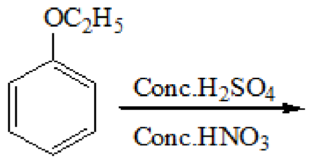


Answer the following questions:

1. Predict the products of the following reactions:

$i)\ CH_3-CH_2-CH_2-O-CH_3+HBr\rightarrow$

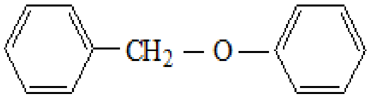
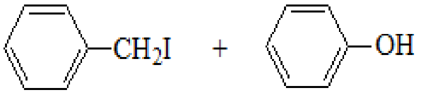
$ii)\ (CH_3)_3C-OC_2H_5\xrightarrow{HI}$

iii  iv) 

2. Give the major products that are formed by heating each of the following ethers with HI.

$i)\ CH_3-CH_2-CH(CH_3)-CH_2-O-CH_2-CH_3$

$ii)\ CH_3-CH_2-CH_2-O-C(CH_3)_2-CH_2-CH_3$

iii)  iv) 

$v)\ CH_3-CH_2-CH(CH_3)-CH_2OH+CH_3CH_2I$

$vi)\ CH_3CH_2CH_2OH+CH_3CH_2C(CH_3)_2I$

3. Write the equation of the reaction of hydrogen iodide with
   (i) 1-propoxypropane (ii) methoxybenzene and (iii) benzyl ethyl ether.
4. Explain the fact that in aryl alkyl ethers (i) the alkoxy group activates the benzene ring towards electrophilic substitution and (ii) it directs the incoming substituent to ortho and para positions in the benzene ring.
5. Write the mechanism of the reaction of HI with methoxymethane.
6. Write equations of the following reactions:
   (i) Friedel-Crafts reaction – alkylation of anisole. (ii) Nitration of anisole.
   (iii) Bromination of anisole in ethanoic acid medium. (iv) Friedel-Craft's acetylation of anisole.