

Guess Paper – 2014
Class – XII
Subject – Chemistry

1

Chapter-11

Alcohols, Phenols and Ethers

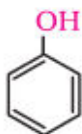
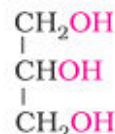
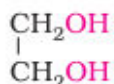
- ☞ Alcohols, phenols and ethers are the basic compounds for the formation of detergents, antiseptics and fragrances, respectively.

Alcohols and Phenols

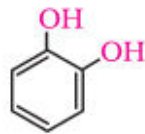
- ☞ Alcohols and phenols are formed when a hydrogen atom in a hydrocarbon, aliphatic and aromatic respectively, is replaced by –OH group.
- ☞ An alcohol contains one or more hydroxyl (-OH) group directly attached to carbon atom of an aliphatic system (CH₃OH).

❖ **Classification:-**

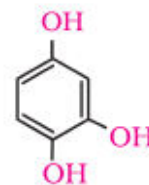
- On the basis of number of –OH group present.
 - Monohydric Alcohol.
 - Dihydric alcohol
 - Polyhydric alcohol



Monohydric

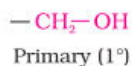


Dihydric

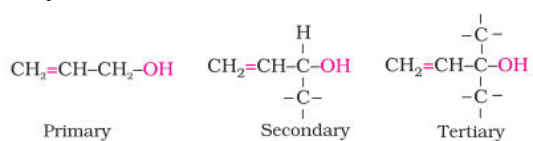


Trihydric

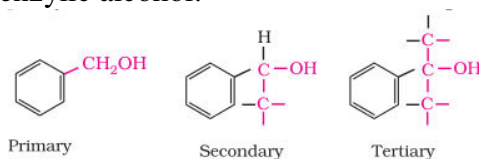
- On the basis of type of hybridization of carbon to which –OH group is attached.
 - sp³C-OH
 - Primary, Secondary and tertiary:-



II. Allylic alcohol :-

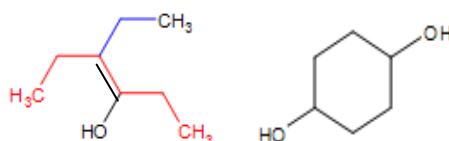


III. Benzylic alcohol:-

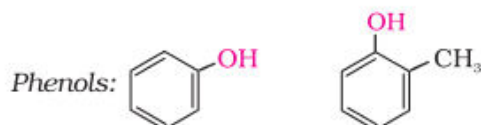


B. $\text{sp}^2\text{C}-\text{OH}$

IV. Vinylic alcohol



V. Phenols



❖ Nomenclature:

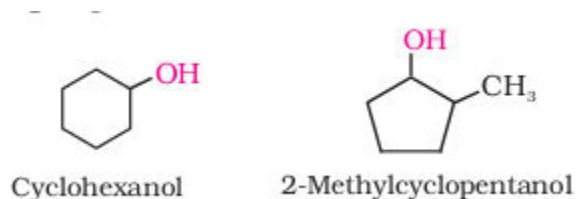
A. Alcohols:

- Common name = alkyl alcohol
- IUPAC = alkanol
- Carbinol

Structure	Common name	IUPAC Name	Carbinol name
CH_3-OH	Methyl alcohol	Methanol	Carbinol
$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{OH}$	n-Propyl alcohol	propan-1-ol	butyl carbinol
$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OH}$	n-Butyl alcohol	Butan-1-ol	Propyl carbinol

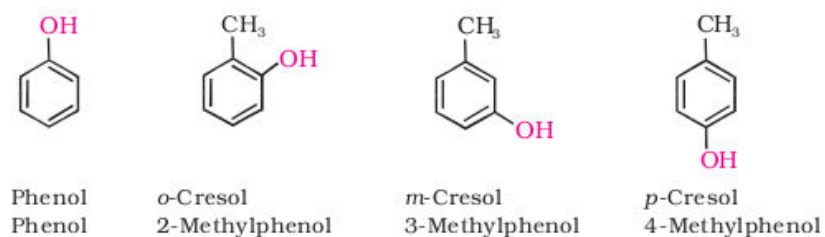
$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{OH} \\ \\ \text{CH}_3 \end{array}$	Isobutyl alcohol	2-methylpropane-1-ol	Iso propyl carbinol	3

Cyclic alcohol name as cycloalkanol and substituted name as alkylcycloalkanole.g.-

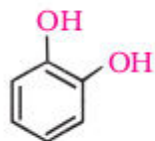


B. Phenols:

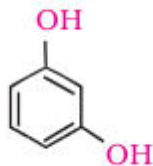
- The simplest hydroxy derivative of benzene is phenol. It is its common name as well as IUPAC name.
- As structure of phenol involves a benzene ring, in its substituted compounds the terms ortho (1,2- disubstituted), meta (1,3-disubstituted) and para (1,4-disubstituted) are often used in the common names.



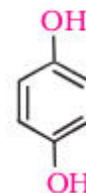
☞ Dihydroxy derivatives of benzene are known as 1, 2-, 1, 3- and 1, 4-benzenediol.



Catechol
Benzene-1,2-diol



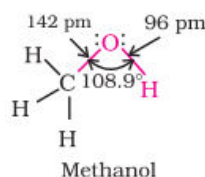
Resorcinol
Benzene-1,3-diol



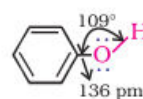
Hydroquinone or quinol
Benzene-1,4-diol

❖ Structure of Functional Groups

In alcohols, the oxygen of the –OH group is attached to carbon by a sigma (σ) bond formed by the overlap of a sp^3 hybridized orbital of carbon with a sp^3 hybridized orbital of oxygen.



Methanol



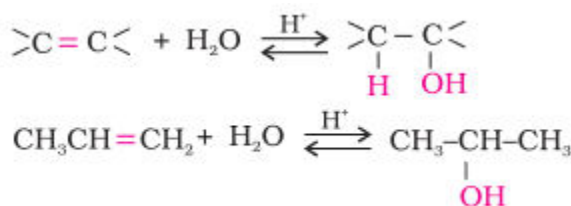
Phenol

❖ Preparation of Alcohols

Alcohols are prepared by the following methods:

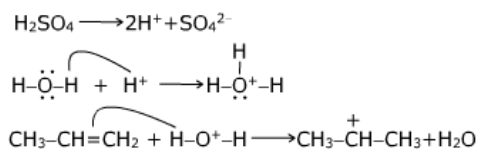
1. From alkenes

1.A: *By acid catalyzed hydration:* Alkenes react with water in the presence of acid as catalyst to form alcohols. In case of unsymmetrical alkenes, the addition reaction takes place in accordance with **Markovnikov's rule**¹.

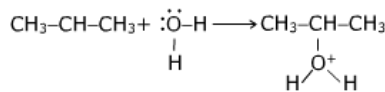


Mechanism

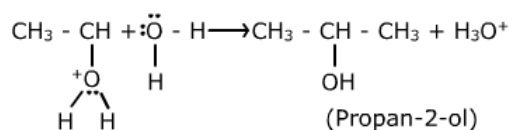
(i) *Electrophilic attack by hydroxyl union on alkenes gives a carbocation intermediate :-*



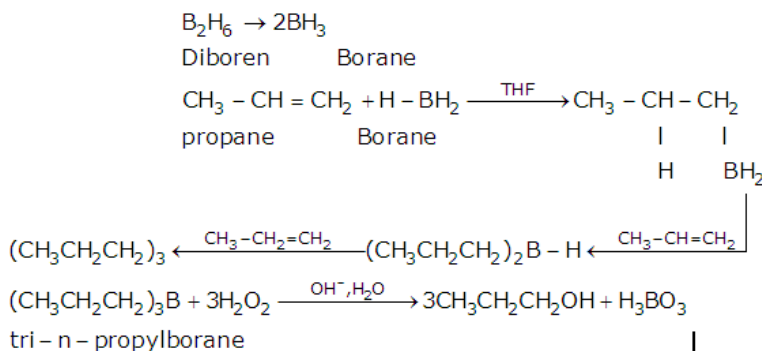
(ii) Nucleophilic attack by water on 2^o carbocation



(iii) Deprotonation

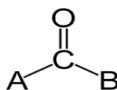


1.B: By hydroboration-oxidation: Diborane (BH₃)₂ reacts with alkenes to give trialkyl boranes as addition product. This is oxidised to alcohol by hydrogen peroxide in the presence of aqueous sodiumhydroxide.



The addition of borane to the double bond takes place in such a manner that the boron atom gets attached to the sp² carbon carrying greater number of hydrogen atoms. 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:- The carbonyl compounds are those which have carbonyl group. The structure of carbonyl group may given as-

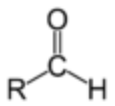
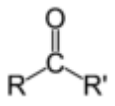
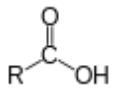
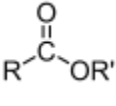
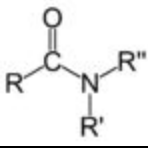


This group is present in following compounds-

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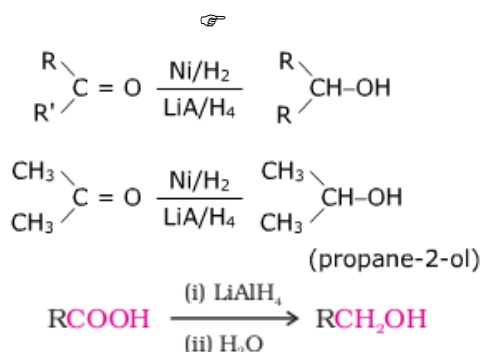
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Compound	Aldehyde	Ketone	Carboxylic acid	Ester	Acid amide
Structure					
General formula	RCHO	RCOR'	RCOOH	RCOOR'	RCO NR'R''

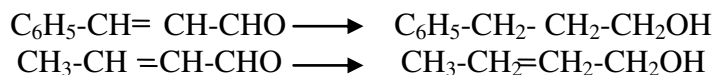
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All these can be converted to alcohols by reduction or by reaction with Grignard reagent as-
2.A: by reduction :

- The reduction is carried out with LiAlH_4 , NaBH_4 , B_2H_6 or H_2 in presence of Pt, Pd, Ni (catalytic reduction)



- LiAlH_4 can reduce all the groups except acid amide. Generally it does not reduce double bonds but reduces when an allylic group is present, e.g.-



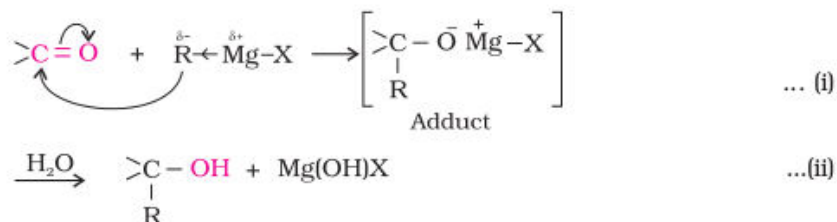
- NaBH_4 reduces all the groups except $-\text{COOH}$, $-\text{COOR}$, $-\text{CONR}'\text{R}''$. It does not reduce any type of double bond.
- Catalytic hydrogenation can convert all the carbonyl groups to alcohols and also reduce double and triple bonds irrespective of the position. Also, it prefers to reduce double bonds.

However, LiAlH_4 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.

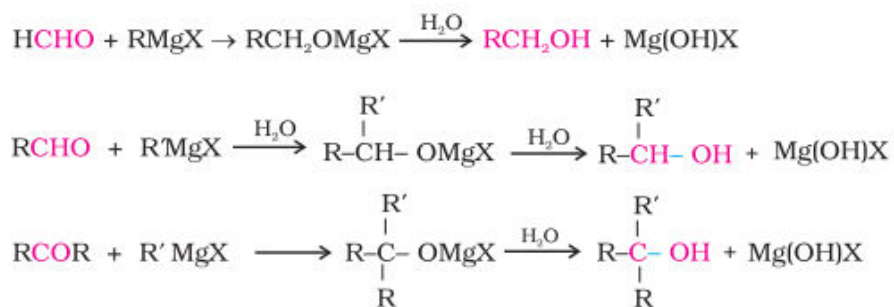


2.B From Grignard reagents

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 an alcohol.



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

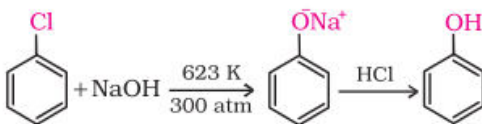


☞ Notice that the reaction produces a primary alcohol with methanal, a secondary alcohol with other aldehydes and tertiary alcohol with ketones.

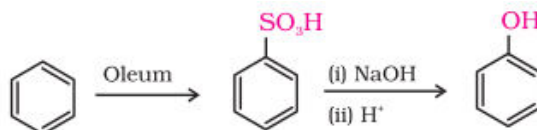
☞ Also note that the new alkyl group to carbonyl carbon comes from Grignard reagent.

❖ **Preparation of Phenols:** Phenol, also known as *carbolic acid*, was first isolated in the early nineteenth century from coal tar.

1. From haloarenes

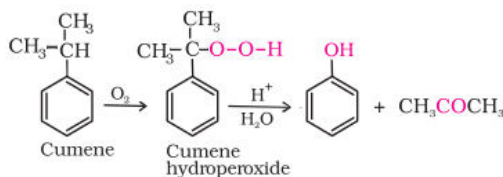


2. From benzenesulphonic acid



3. From diazonium salts.

4. From cumene: Cumene (isopropylbenzene) is oxidised in the presence of air to cumene hydroperoxide. Which on reaction with dil. Acid gives phenol and acetone.



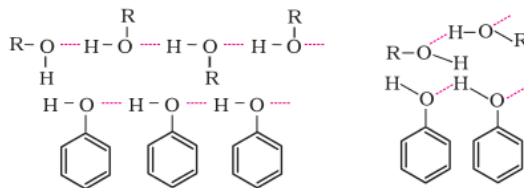
❖ **Physical Properties of alcohols and phenols:**

1. Boiling Points:

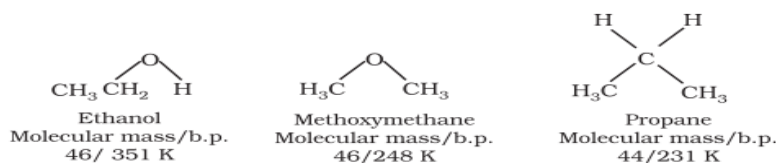
1. The boiling points of alcohols and phenols increase with increase in the number of carbon atoms due to increase in van der Waals forces.

2. In alcohol boiling points decrease with increase of branching in carbon chain because of decrease in van der Waals forces with decrease in surface area.

☞ The -OH group in alcohols and phenols is involved in intermolecular hydrogen bonding as shown below which is responsible for high boiling point of alcohol and phenol-

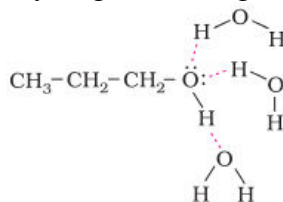


- ☞ The boiling points of alcohols and phenols are higher than hydrocarbons, ethers, haloalkanes and haloarenes of comparable molecular masses. E.g., ethanol and propane have comparable molecular masses but their boiling points differ widely.
- ☞ *The boiling point of methoxymethane is intermediate of ethanol and propane.*



2.Solubility:

The solubility decreases with increase in size of alkyl/aryl (*hydro- phobic*) groups because tendency to form hydrogen bonding decreases as molecular weight increases.

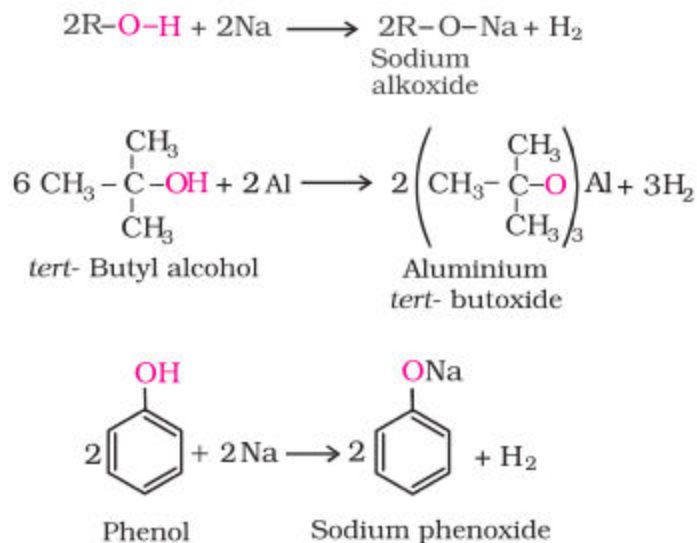


❖ Chemical Reactions of alcohol:

- ✓ All the reaction can be divided into three categories-
 - Reaction of alcohol and phenols
 - Reaction of alcohol
 - Reaction of phenols

(a) Reaction of alcohol and phenol

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

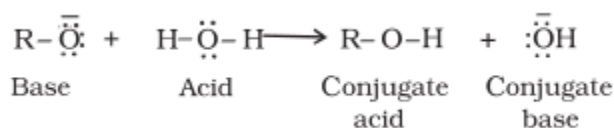


The above reactions show that alcohols and phenols are acidic in nature. In fact, **alcohols and phenols are Brönsted acids** i.e., they can donate a proton to a stronger base (B:).

(ii) Acidity of alcohols: The acidic character of alcohols is due to the polar nature of O–H bond. An electron-releasing group (–CH₃, –C₂H₅) increases electron density on oxygen tending to decrease the polarity of O–H bond. This decreases the acid strength. Hence, the acid strength of alcohols decreases in the following order:



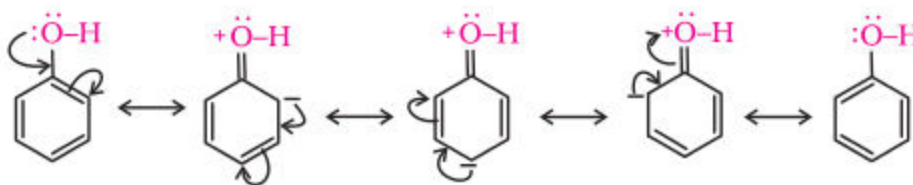
Alcohols are, however, weaker acids than water(Why). This can be illustrated by the reaction of water with an alkoxide.



This reaction shows that water is a better proton donor (so stronger acid) than alcohol. Also, 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). 11

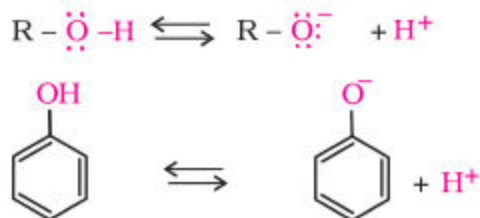
Alcohols act as Bronsted bases as well. It is due to the presence of unshared electron pairs on oxygen, which makes them proton acceptors.

(iii) Acidity of phenols: The reactions of phenol with metals (e.g., sodium, aluminium) and sodium hydroxide indicate its acidic nature. The hydroxyl group, in phenol is directly attached to the sp^2 hybridized carbon of benzene ring which acts as an electron withdrawing group. Due to this, the charge distribution in phenol molecule, 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.

The ionization of an alcohol and a phenol takes place as follows:

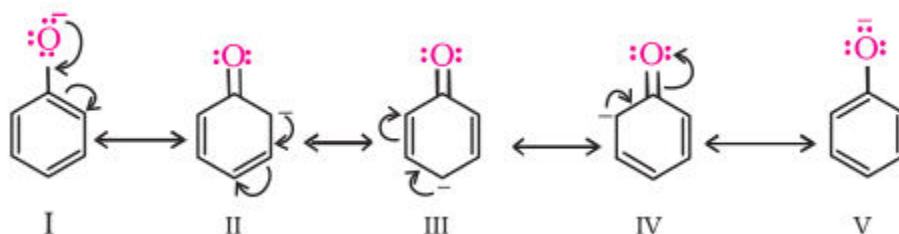


Due to the higher electronegativity of sp^2 hybridised carbon of phenol to which $-OH$ is attached, electron density decreases on oxygen.

This increases the polarity of $O-H$ bond and results in an increase in ionization of phenols than that of alcohols.

Stability of alkoxide ion and phenoxide ion: In alkoxide ion, the negative charge is localized on oxygen [no resonance] while in phenoxide ion, the charge is delocalized [resonance]. The delocalization of negative charge (structures I-V) makes phenoxide ion more stable and favors

the ionization of phenol. Although there is also charge delocalization in phenol, its resonance structures have charge separation due to which the phenol molecule is less stable than phenoxide ion. 12



In substituted phenols, the presence of electron withdrawing groups such as nitro group, enhances the acidic strength of phenol

Acidity order of substituted phenols-

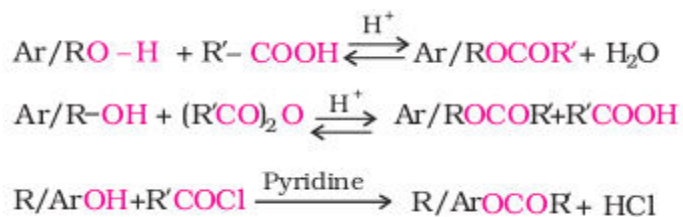
p-nitro phenol, ortho nitro phenol, meta nitro phenol

As summary the acidic order may given as

Alcohol < water < alkyl phenol < phenol < p-nitro phenol < o- nitro phenol < m- nitro phenol

2. Esterification

Alcohols and phenols react with carboxylic acids, acid chlorides and acid anhydrides to form esters. In this reaction, -OH comes out from carboxylic acids, acid chlorides or acid anhydrides and -H from alcohol to form water as shown-



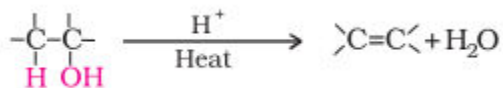
(b) Reactions involving cleavage of carbon – oxygen (C–O) bond in alcohols

The reactions involving cleavage of C–O bond take place only in alcohols. Phenols show this type of reaction only with zinc.

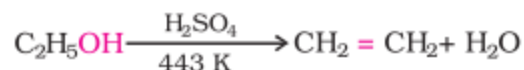
1. Formation of Alkyl Halide:



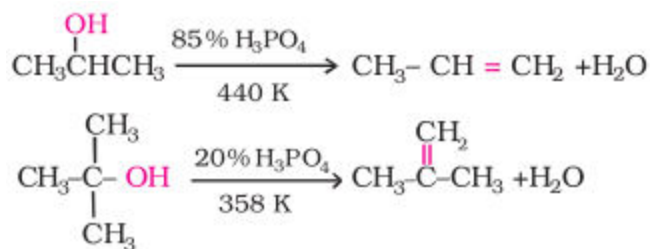
3. **Dehydration:** This is Elimination reaction .



E.g. Ethanol undergoes dehydration by heating it with concentrated H_2SO_4 at 443 K.



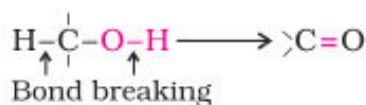
Secondary and tertiary alcohols are dehydrated under milder conditions.e.g.



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

Tertiary > Secondary > Primary

5. **Oxidation:** The product of this reaction depends up on the oxidizing agent use. The various oxidizing agents are- KMnO_4 CrO_3 PCC $\text{Na}_2\text{Cr}_2\text{O}_7$ $\text{K}_2\text{Cr}_2\text{O}_7$. Ir-respective to the agent, product always forms carbonyl group containing compounds as-

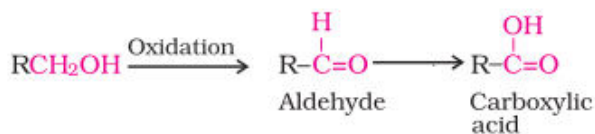


For example:-

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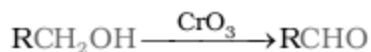
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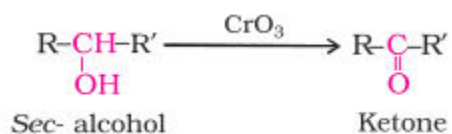
Oxidation of Primary Alcohol

Primary alcohol is on oxidation with KMnO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$ gives carboxylic acid.

Primary alcohol oxidation with CrO_3 or PCC in anhydrous medium gives aldehydes.



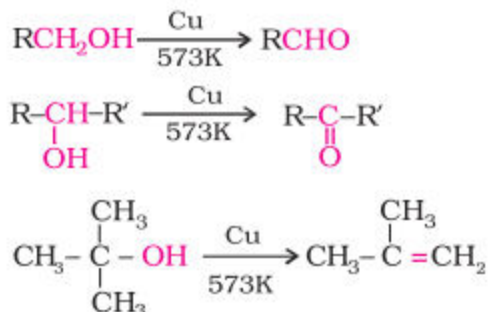
Secondary alcohols are oxidised to ketones any oxidizing agent.



Tertiary alcohols do not undergo oxidation reaction because they lack alpha hydrogen.

6. Dehydrogenation reaction:

Primary alcohols give aldehyde and secondary give ketone when treated with Cu or Ag at 573 K temp.

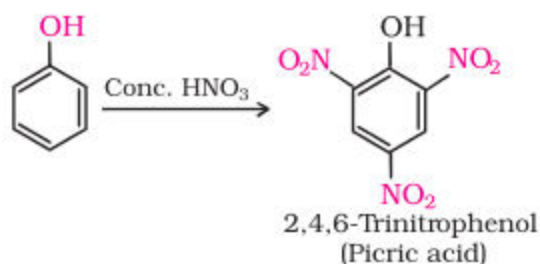


❖ **Reactions of phenols**

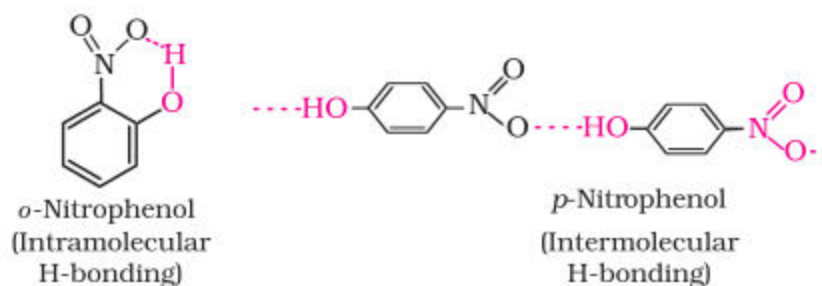
Following reactions are shown by phenols only-

1. Electrophilic aromatic substitution

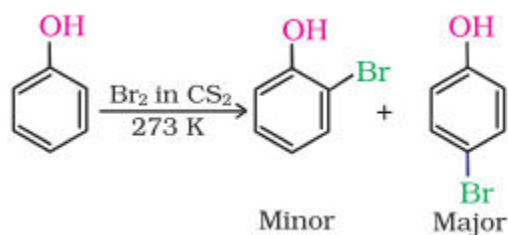
Nitration:



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.

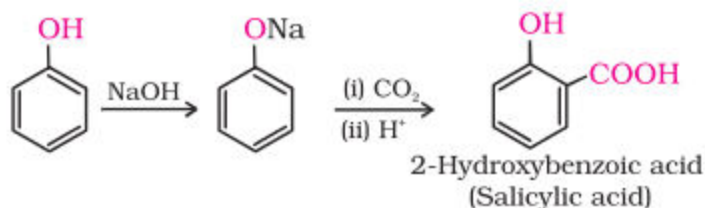


(ii) Halogenation:



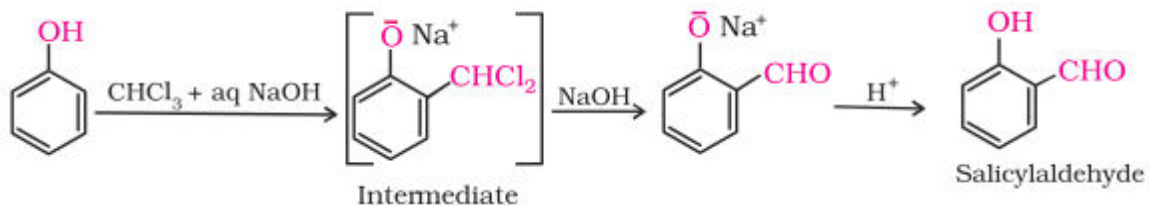
6. Kolbe's reaction

Actually this is Kolbe Schmidt Reaction. Phenoxide ion is on reaction with CO_2 followed by hydrolysis gives Salicylic Acid. In this reaction CO_2 act as electrophiles.

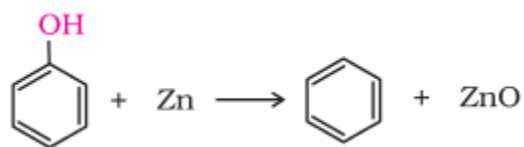


7. Reimer-Tiemann reaction

On treating phenol with chloroform in the presence of sodium hydroxide, a $-\text{CHO}$ group is introduced at ortho position of benzene ring. This reaction is known as Reimer Tiemann reaction.



8. Reaction of phenol with zinc dust



9. Oxidation



❖ Ethers

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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. 18

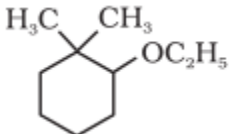
Nomenclature:-

Common Name – alkyl ether

IUPAC- alkoxy alkane

Small group is termed as alkoxy with oxygen. It may be noted that alkoxy group is always named as prefix. The alkane is counted in such a way that alkoxy group occupies lowest position and the chain must be longest.

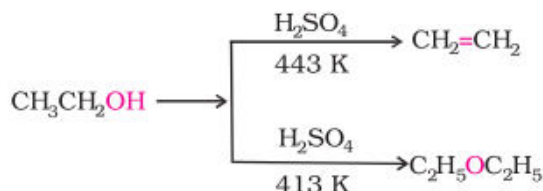
Table 11.2: Common and IUPAC Names of Some Ethers

Compound	Common name	IUPAC name
CH_3OCH_3	Dimethyl ether	Methoxymethane
$C_2H_5OC_2H_5$	Diethyl ether	Ethoxyethane
$CH_3OCH_2CH_2CH_3$	Methyl n-propyl ether	1-Methoxypropane
$C_6H_5OCH_3$	Methylphenylether (Anisole)	Methoxybenzene (Anisole)
$C_6H_5OCH_2CH_3$	Ethylphenyl ether (Phenetole)	Ethoxybenzene
$C_6H_5O(CH_2)_6-CH_3$	Heptylphenyl ether	1-phenoxyheptane
$\begin{array}{c} CH_3O-CH-CH_3 \\ \\ CH_3 \end{array}$	Methyl isopropyl ether	2-Methoxypropane
$C_6H_5-O-CH_2-CH_2-\begin{array}{c} CH-CH_3 \\ \\ CH_3 \end{array}$	Phenylisopentyl ether	3-Methylbutoxybenzene
$CH_3-O-CH_2-CH_2-OCH_3$	-	1,2-Dimethoxyethane
	-	2-Ethoxy-1,1-dimethylcyclohexane

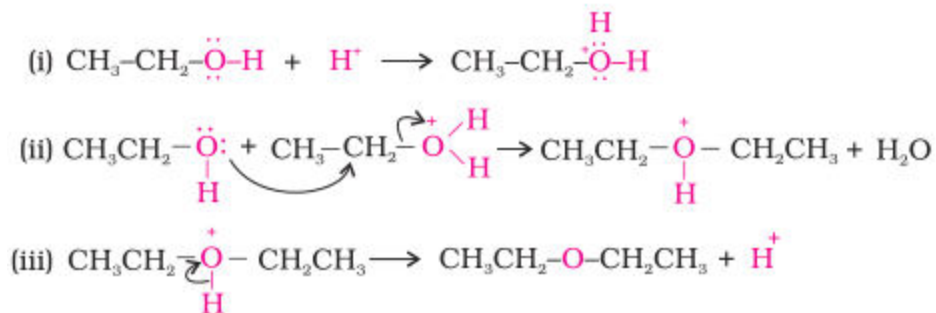
❖ Preparation of Ethers

1. By dehydration of alcohols

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 mechanism of the reaction, involves $\text{S}_\text{N}2$ mechanism, may given as-



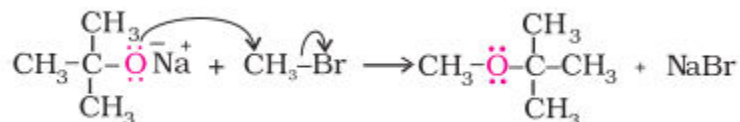
2. Williamson synthesis

☞ The reaction involves S_N2 attack of alkyl halide on an alkoxide ion on primary

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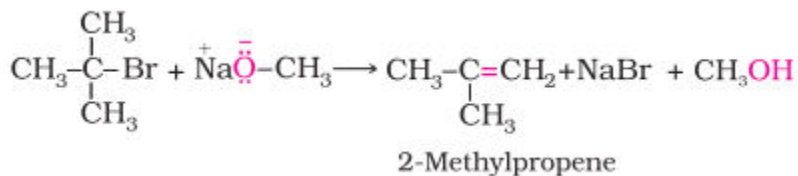


For example:

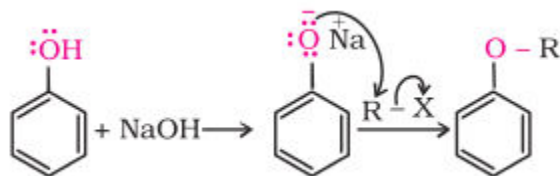


Better results are obtained if the alkyl halide is primary. In case of secondary and tertiary alkyl halides, elimination competes over substitution. If a tertiary alkyl halide is used, an alkene is the only reaction product and no ether is formed.

For example, the reaction of CH₃ONa with (CH₃)₃C-Br gives exclusively 2-methylpropene.



Phenols are also converted to ethers by this method. In this, phenol is used as the phenoxide moiety.



❖ Physical Properties

Boiling Point-

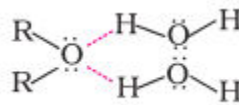
hydrocarbon < Ether < Alcohol

For example-

Formula	$\text{CH}_3(\text{CH}_2)_3\text{CH}_3$ n-Pentane	$\text{C}_2\text{H}_5\text{-O-C}_2\text{H}_5$ Ethoxyethane	$\text{CH}_3(\text{CH}_2)_3\text{-OH}$ Butan-1-ol
b.p./K	309.1	307.6	390

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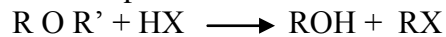
Solubility-This is due to the fact that just like alcohols, oxygen of ether can also form hydrogen bonds with water molecule as shown:



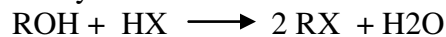
❖ Chemical Reactions

1. Cleavage of C–O bond in ethers

If ether is in excess then product is alcohol-



If halogen acid is in excess then formed alcohol, in above reaction, react further to give two molecule of alkyl halide-

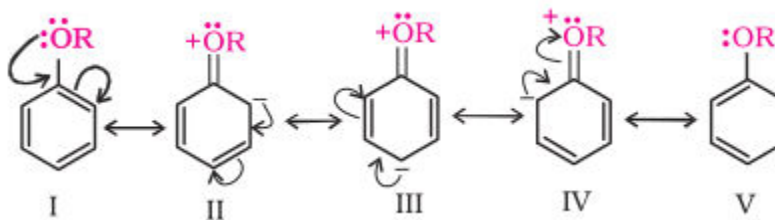


Aryl ether also react in same ways-



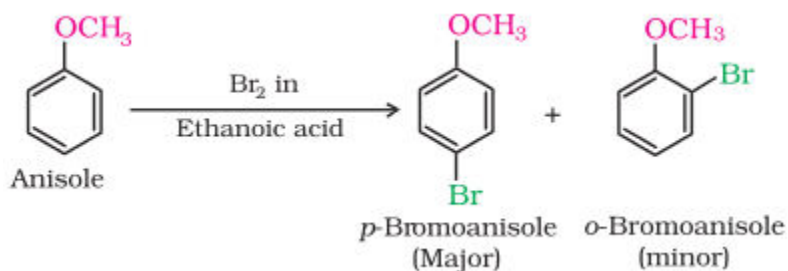
2. Electrophilic substitution

Resonance structure may given as-

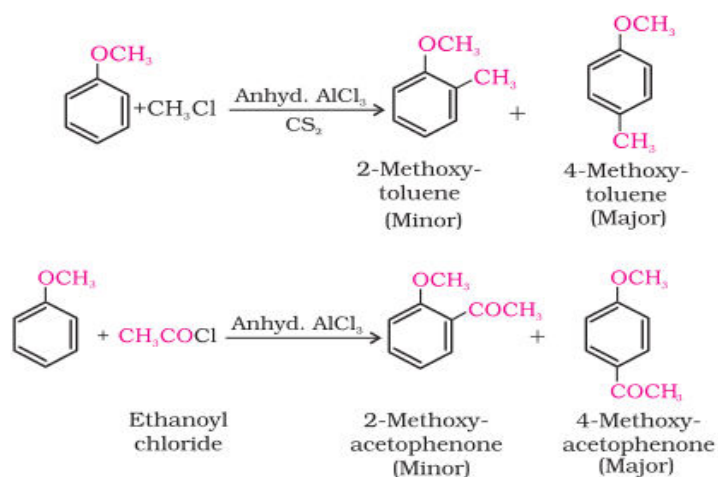


Since lone pair possessing oxygen is directly attached to ring so the product will be ortho and para.

(i) Halogenation:



(ii) Friedel-Crafts reaction:



(iii) Nitration:





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Alcohol, Phenol and Ether

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