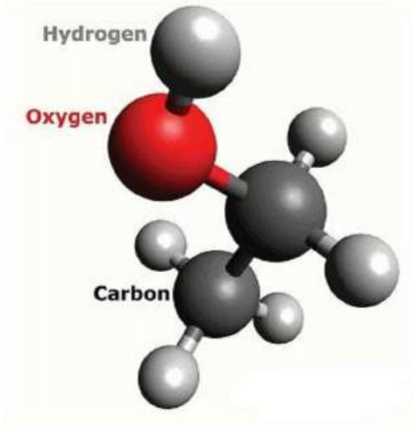
Chapter 10

Alcohols, Phenols and Ethers

Alcohols: Properties, Preparation & Reactions

What are the Properties of Alcohols?

- Alcohols are organic compounds in which a hydrogen atom of an aliphatic carbon is replaced with a hydroxyl group. Thus an alcohol molecule consists of two parts; one containing the alkyl group and the other containing functional group hydroxyl
- Group



Alcohol

- They have a sweet odour. They exhibit a unique set of physical and chemical properties.

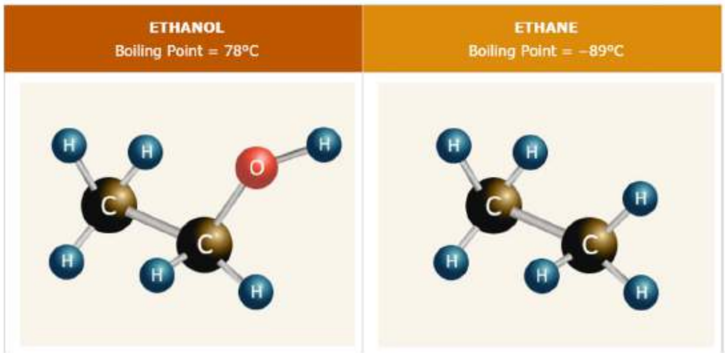
The physical and chemical properties of alcohols are mainly due to the presence of hydroxyl group.

Physical Properties

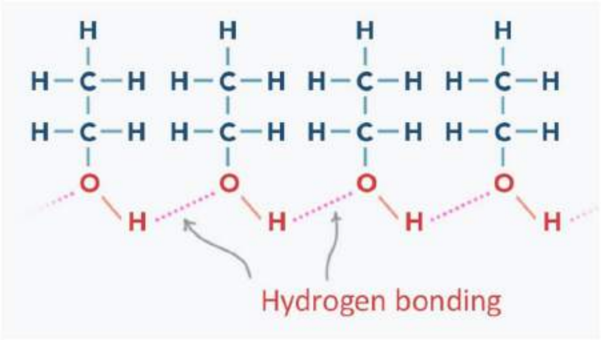
1. Boiling Point

- Alcohols show an increase in boiling point with an increase in molecular weight amongst homologues.

- Alcohols have a higher boiling point than hydrocarbons of the same molecular weight. The reason for the higher boiling point is the intermolecular H-bonding present in alcohols.



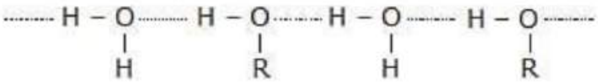
Ethanol has a higher Boiling Point than Ethane



Hydrogen Bonding in Ethanol

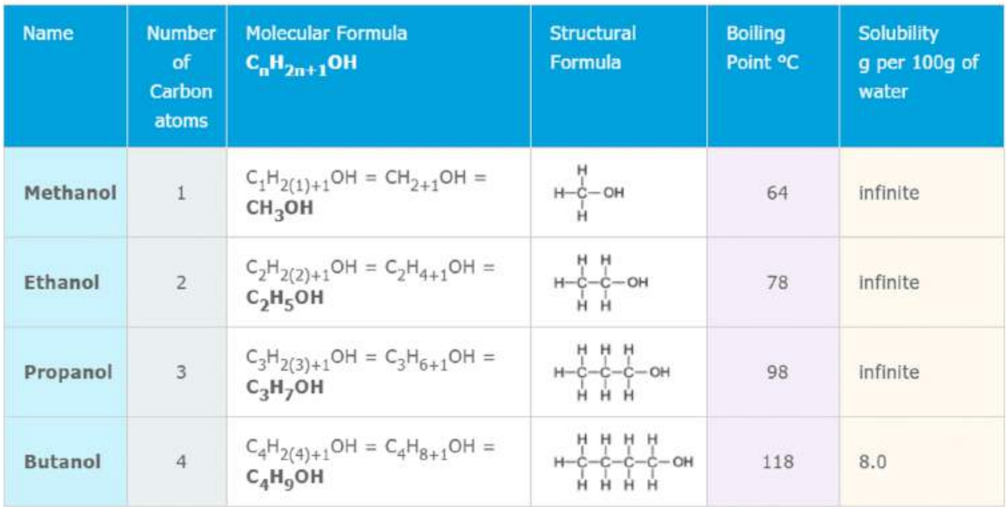
2. Solubility in Water

- As molecular weight increases solubility in water decreases.
- The lower alcohols are miscible with water. This is due to intermolecular hydrogen bonding between alcohol and water molecules.



$$\cdots H-\underset{\substack{|\\H}}{O}\cdots H-\underset{\substack{|\\R}}{O}\cdots H-\underset{\substack{|\\H}}{O}\cdots H-\underset{\substack{|\\R}}{O}\cdots$$

Intermolecular H bond between water & alcohol molecules

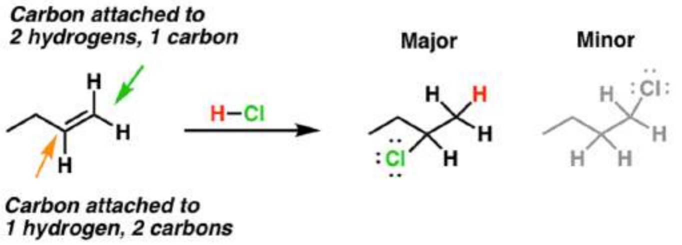


Name	Number of Carbon atoms	Molecular Formula $C_nH_{2n+1}OH$	Structural Formula	Boiling Point °C	Solubility g per 100g of water
Methanol	1	$C_1H_{2(1)+1}OH = CH_{2+1}OH =$ CH_3OH	$H-\overset{H}{\underset{H}{C}}-OH$	64	infinite
Ethanol	2	$C_2H_{2(2)+1}OH = C_2H_{4+1}OH =$ C_2H_5OH	$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-OH$	78	infinite
Propanol	3	$C_3H_{2(3)+1}OH = C_3H_{6+1}OH =$ C_3H_7OH	$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-OH$	98	infinite
Butanol	4	$C_4H_{2(4)+1}OH = C_4H_{8+1}OH =$ C_4H_9OH	$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-OH$	118	8.0

Tables showing Solubility of various Alcohols

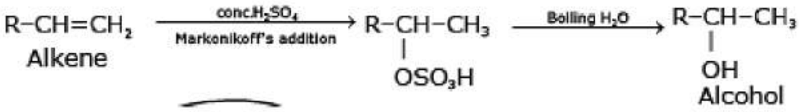
Preparation of Alcohols1. From Alkenes(a) By acid-catalyzed hydration of alkenes

- Formation of carbocation intermediate (Markovnikov addition, rearrangement possible).



The reaction of Alkenes with Acids follow Markovnikov's Rule

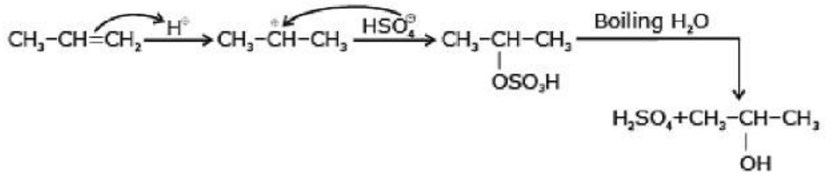
General Reaction:



$$\underset{\text{Alkene}}{R-CH=CH_2} \xrightarrow[\text{Markonikoff's addition}]{conc.H_2SO_4} R-\underset{OSO_3H}{\underset{|}{CH}}-CH_3 \xrightarrow{\text{Boiling } H_2O} R-\underset{OH}{\underset{|}{CH}}-CH_3$$

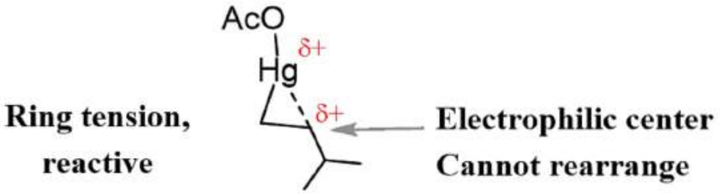
Alcohol

e.g.



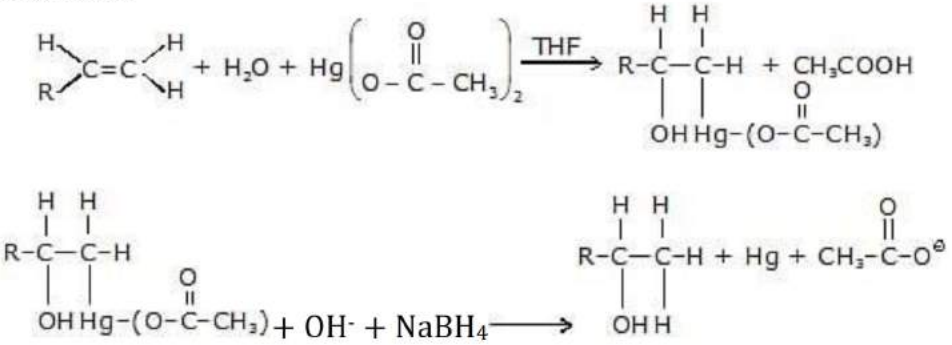
(b) By Oxymercuration - Demercuration Process

- Oxymercuration involves an electrophilic attack on the double bond by the positively charged mercury species. The product is a mercurinium ion, an organometallic cation containing a three-membered ring.

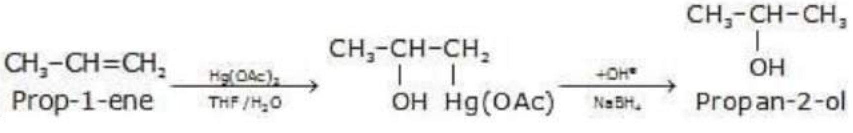


- In the second step, water from the solvent attacks the mercurinium ion to give (after deprotonation) organomercurial alcohol.
- The third step is demercuration to remove the Hg. Sodium borohydride (NaBH4, a reducing agent) replaces the mercuric acetate fragment with hydrogen.

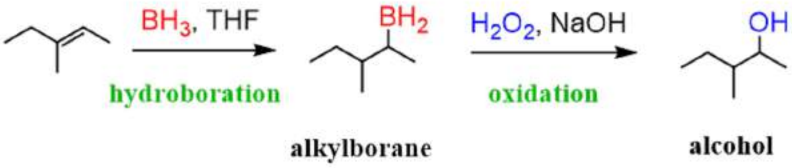
General reaction:



e.g.



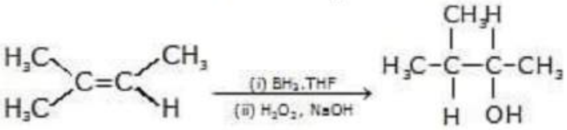
(c) By Hydroboration-oxidation process



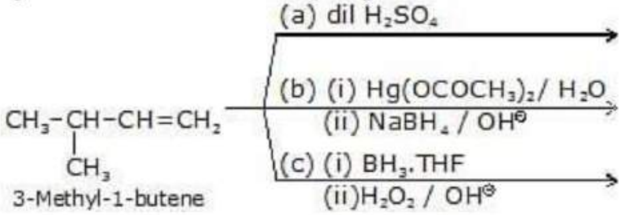
(Forms anti-Markovnikov alcohol, no rearrangement).

General reaction: $R\text{-}Ch{=}CH_2 \xrightarrow[\text{(ii) } H_2O_2,\ NaOH]{\text{(i) } BH_3.THF} R\text{-}CH_2\text{-}CH_2\text{-}OH$

e.g.

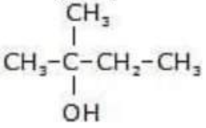


Question: Give the major product of the following reaction:



Ans. Major product is

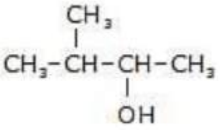
(a)



$CH_3\text{-}C(CH_3)(OH)\text{-}CH_2\text{-}CH_3$

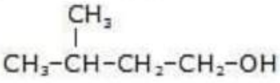
because 3° carbocation is more stable.

(b)



$CH_3\text{-}CH(CH_3)\text{-}CH(OH)\text{-}CH_3$

(c)



$CH_3\text{-}CH(CH_3)\text{-}CH_2\text{-}CH_2\text{-}OH$

2. From Alkyl Halides

By nucleophilic substitution reactions.

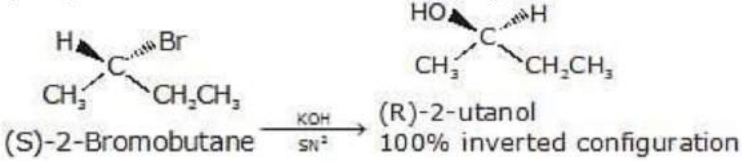
(a) By SN² Mechanism (Second-Order Substitution)

- It is given by primary (and some secondary) halides.

General reaction: $R\text{-}CH_2\text{-}Br \xrightarrow[H_2O]{KOH} R\text{-}CH_2\text{-}OH$

e.g. $(CH_3)_2CHCH_2CH_2\text{-}Br \xrightarrow[H_2O]{KOH} (CH_3)_2CHCH_2CH_2\text{-}OH$

e.g.

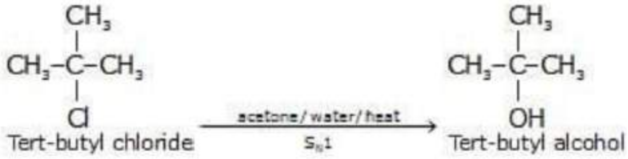


(b) By SN^1 mechanism (first-order substitution)

- It is given by tertiary and some secondary halides.

General reaction :

e.g.



3. From Grignard's Reagent

(a) From air

- A Grignard reagent may be used to synthesize an alcohol by treating it with dry oxygen and decomposing the product with acid:

General reaction:

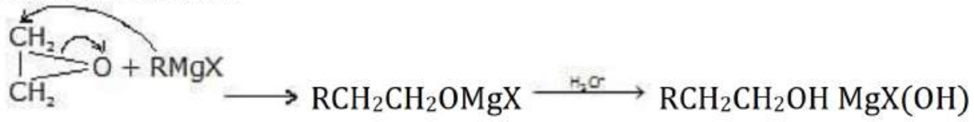
$RMgX \xrightarrow{O_2} RO_2MgX \xrightarrow{RMgX} 2ROMgX \xrightarrow{H_3O^+} 2ROH$

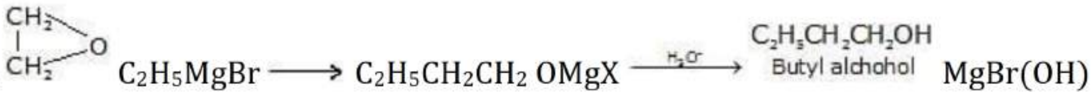
e.g. $C_2H_5MgBr \xrightarrow{O_2} C_2H_5O_2\,MgX \xrightarrow{C_2H_5MgX} 2C_2H_5OMgX \xrightarrow{H_3O^+} 2C_2H_5OH\,MgBr(OH)$

(b) From ethylene oxide

- The addition of Grignard reagent to ethylene oxide gives primary alcohol (with two carbon atoms added).

General reaction:



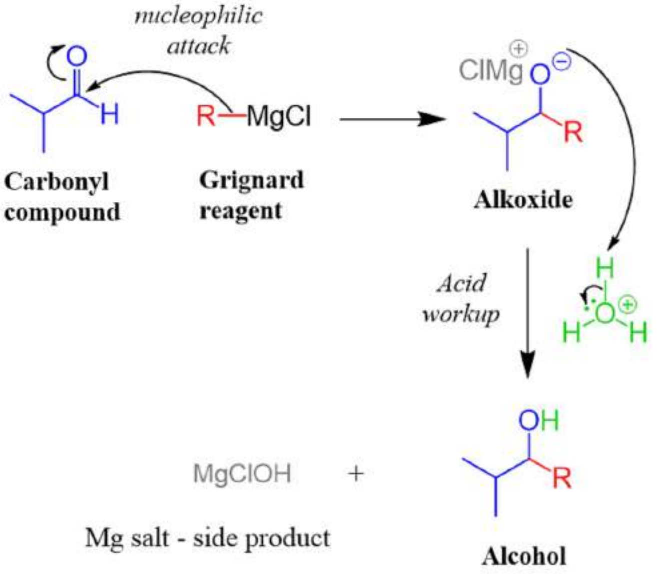
e.g. 

$$\text{CH}_2\text{CH}_2\text{O} + C_2H_5MgBr \longrightarrow C_2H_5CH_2CH_2\,OMgX \xrightarrow{H_3O^+} \underset{\text{Butyl alchohol}}{C_2H_5CH_2CH_2OH} \; MgBr(OH)$$

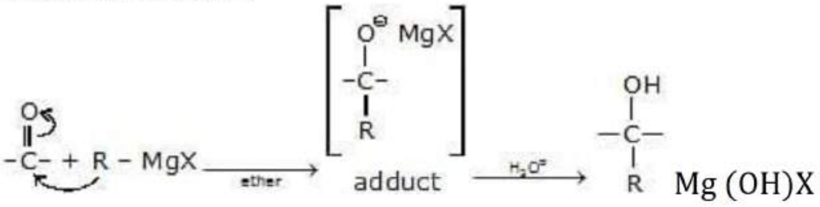
(c) From carbonyl compounds

- Nucleophilic addition to the carbonyl groups by Grignard's reagent.

The Mechanism of Grignard reaction with an Aldehyde

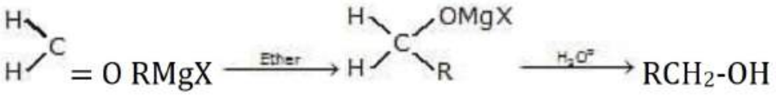


General reaction:



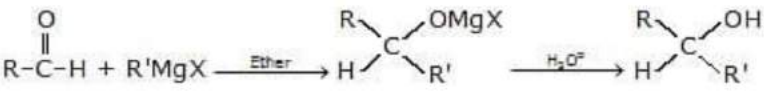
$$-\overset{\overset{\displaystyle O}{\|}}{C}- + R-MgX \xrightarrow{\text{ether}} \underset{\text{adduct}}{\left[-\overset{\overset{\displaystyle O^{\ominus}\;MgX}{|}}{\underset{\underset{\displaystyle R}{|}}{C}}-\right]} \xrightarrow{H_3O^+} -\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle R}{|}}{C}}- \; Mg\,(OH)X$$

(i) Addition of formaldehyde gives primary alcohol
General reaction:



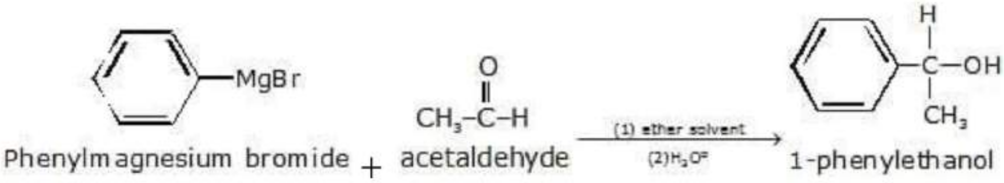
$$H_2C=O \; RMgX \xrightarrow{\text{Ether}} H_2C(OMgX)R \xrightarrow{H_3O^+} RCH_2\text{-}OH$$

(ii) Addition to an aldehyde (other than formaldehyde) gives secondary alcohol
General reaction:



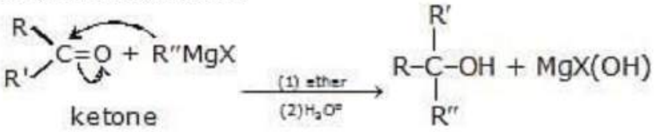
(sec-alcohol)

e.g.

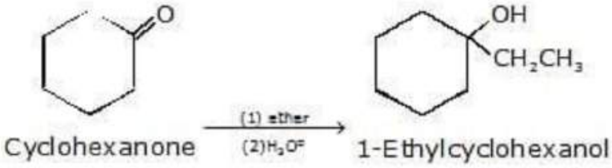


(iii) Addition to a ketone gives tertiary alcohol.

General reaction:



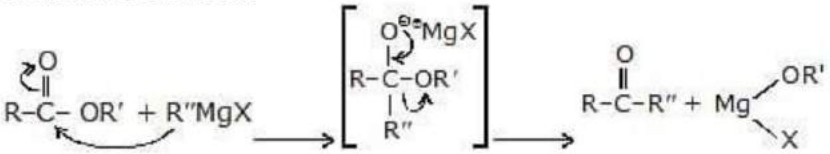
e.g. CH_3CH_2MgCl +

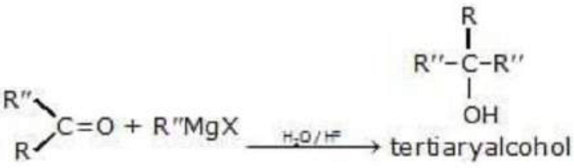


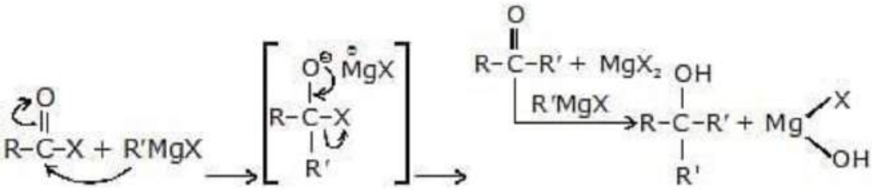
(iv) Addition to an acid halide or an ester gives tertiary alcohol.

- Esters on treatment with Grignard's reagent first form ketones which then react with the second molecule of Grignard's reagent and form tertiary alcohol.

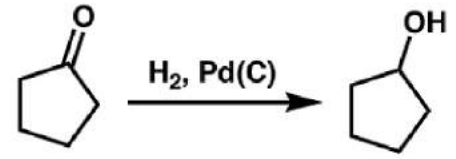
General reaction:

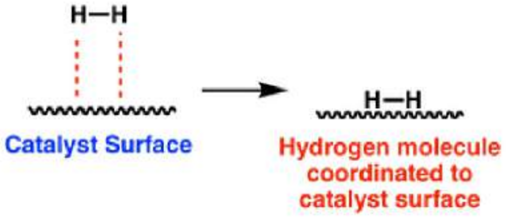






4. By Reduction of Carbonyl Compounds(a) Catalytic hydrogenation of aldehydes and ketones





General reaction:

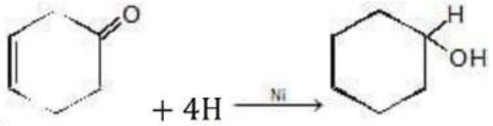
$$\underset{\text{Aldehyde}}{R\text{-}CHO} \xrightarrow{H_2/Ni} \underset{1^\circ\text{Alcohol}}{R\text{-}CH_2OH}$$

$$\underset{\text{Ketone}}{R_2C{=}O} \xrightarrow{H_2/Ni} \underset{2^\circ\text{Alcohol}}{R_2CH\text{-}OH}$$

e.g. $CH_3CHO + 2H \xrightarrow{H_2/Ni} CH_3CH_2OH$

e.g. $\underset{\text{(Acrolein)}}{CH_2{=}CHCHO + 4H} \xrightarrow[\text{Catalyst}]{\text{Ni}} CH_3CH_2CH_2OH$

e.g.



(b) Lithium aluminium hydride reduction of aldehydes and ketones

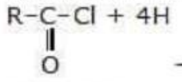
General reaction:

(i) $\underset{\text{Aldehyde}}{R\text{-}CHO} \xrightarrow{LiAlH_4} \underset{1^\circ\text{Alcohol}}{R\text{-}CH_2OH}$

(ii) $\underset{\text{Ketone}}{R_2C{=}O} \xrightarrow{LiAlH_4} \underset{2^\circ\text{Alcohol}}{R_2CH\text{-}OH}$

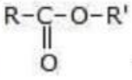
(iii) $RCOOH + 4H \xrightarrow{LiAlH_4} RCH_2OH + H_2O$

(iv)

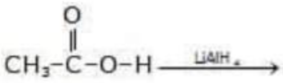


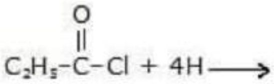
$R\text{-}\underset{\underset{O}{\|}}{C}\text{-}Cl + 4H \xrightarrow{LiAlH_4} RCH_2OH + HCl$

(v)



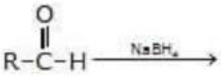
$R\text{-}\underset{\underset{O}{\|}}{C}\text{-}O\text{-}R' \xrightarrow{LiAlH_4} R\text{-}CH_2OH + R'OH$

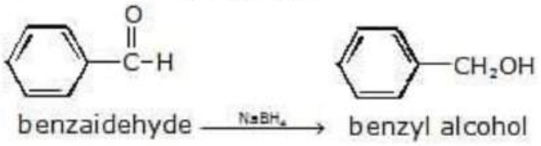
e.g. 
$CH_3-\overset{O}{\overset{\|}{C}}-O-H \xrightarrow{LiAlH_4} CH_3CH_2OH$

e.g. 
$C_2H_5-\overset{O}{\overset{\|}{C}}-Cl + 4H \longrightarrow C_2H_5CH_2OH + HCl$

(c) By NaBH4 (sodium borohydride)

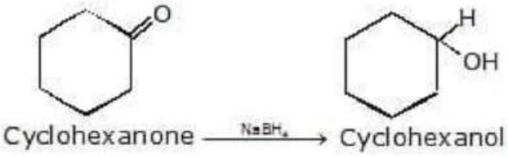
- It is insoluble in ether and is used in an aqueous ethanolic solution to reduce carbonyl compounds. It does not reduce esters and acids.


$R-\overset{O}{\overset{\|}{C}}-H \xrightarrow{NaBH_4} R-CH_2-OH$

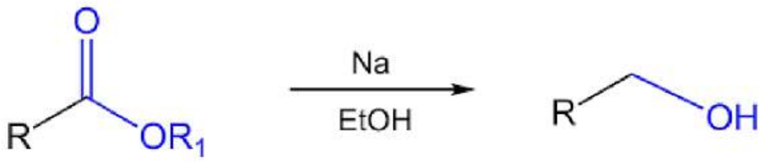
e.g. 

e.g. $CH_3CH=CHCHO + 4H \xrightarrow{NaBH_4} CH_3CH=CHCH_2OH$

(i) Reduction of a ketone gives secondary alcohol



(d) Bouveault-Blanc reduction



The reduction of aldehydes, ketones or esters by means of excess of sodium and ethanol or n-butanol as the reducing agent.

General reaction:

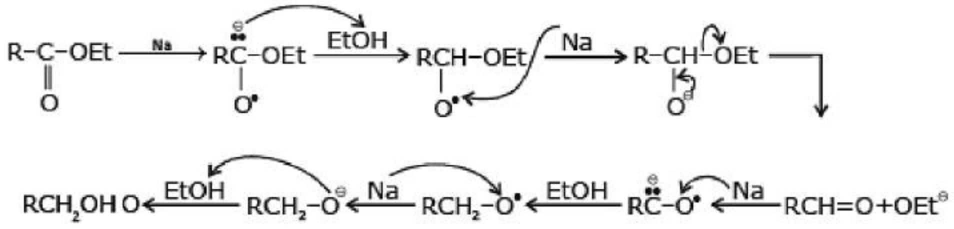
(i) Aldehyde $RCHO \xrightarrow[EtOH]{Na} RCH_2OH$

(ii) Esters $R'CO_2R'' \xrightarrow[EtOH]{Na} R'CH_2OH\ R''OH$

(iii) Ketones $R_2CO \xrightarrow[EtOH]{Na} R_2CHOH$

The Bouveault-Blanc reduction is believed to occur in steps involving transfer of one electron at a time.

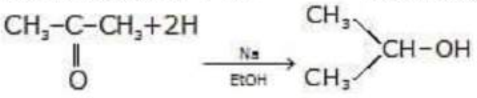
Mechanism:



e.g. $CH_3CHO + 2H \xrightarrow[EtOH]{Na} CH_3CH_2OH$

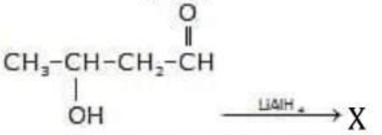
e.g. $CH_3COOC_2H_5 + 4H \xrightarrow[EtOH]{Na} 2CH_3CH_2OH$

e.g.



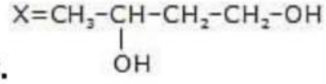
$CH_3-\underset{\underset{O}{\|}}{C}-CH_3 + 2H \xrightarrow[EtOH]{Na} \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>CH-OH$

Ex. Identify (X) in the following reaction:



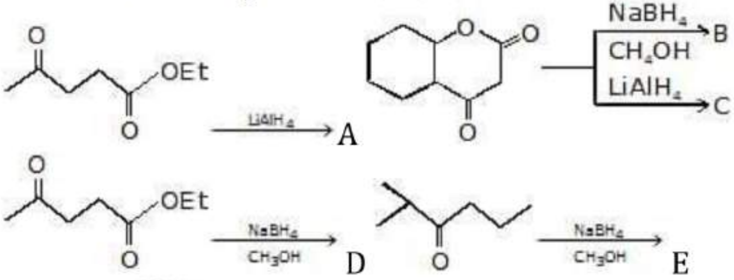
$CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-\overset{\overset{O}{\|}}{CH} \xrightarrow{LiAlH_4} X$

Ans.



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

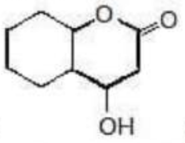
Ex. What are the product A, B, C, D and E in the following reactions?



Ans. A :

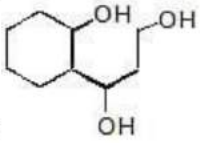
(EtOH)

B :

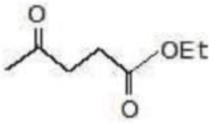


Ester part is not affected by $NaBH_4$

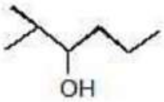
C :



Ester part and keto parts are affected by $LiAlH_4$



D:



E:

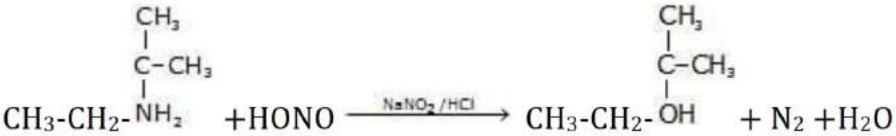
5. By Reaction of Nitrous Acid on Aliphatic Primary Amines

General reaction: R-NH_2 + HONO $\xrightarrow{NaNO_2/HCl}$ R-OH +N_2 + H_2O

Mechanism:

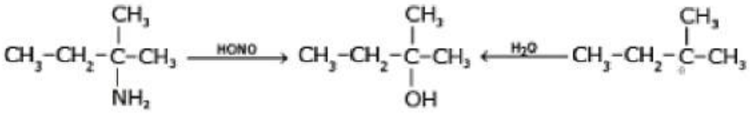
R-$NH_2 \xrightarrow{HNO_2} (RN_2^{\oplus}) \xrightarrow{H_2O}$ ROH +N_2 +$H^{\oplus}$

e.g. (i) $C_2H_5NH_2 + HNO_2 \longrightarrow C_2H_5OH + N_2 + H_2O$

(ii) 

$$CH_3\text{-}CH_2\text{-}\underset{NH_2}{\overset{\overset{CH_3}{|}}{C}}\text{-}CH_3 + HONO \xrightarrow{NaNO_2/HCl} CH_3\text{-}CH_2\text{-}\underset{OH}{\overset{\overset{CH_3}{|}}{C}}\text{-}CH_3 + N_2 + H_2O$$

Mechanism:

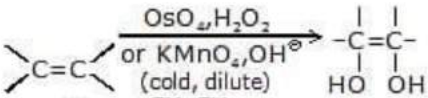


6. Hydroxylation: Forms vicinal diols (glycols)

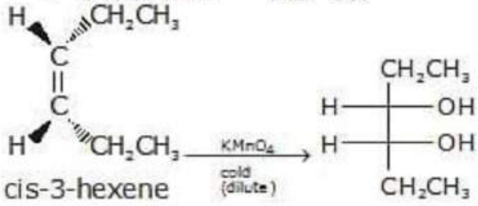
- Converting an alkene to a glycol requires adding a hydroxy group to each end of the double bond. This addition is called hydroxylation of the double bond.

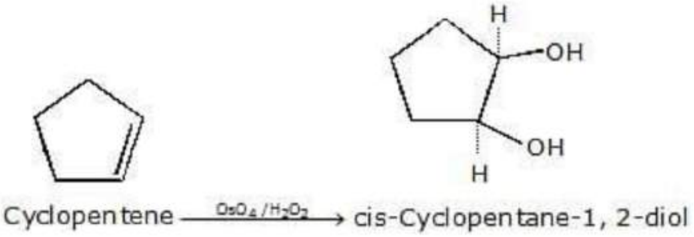
(a) Syn hydroxylation, using $KMnO_4$ / NaOH or using OsO_4/H_2O_2

General reaction:

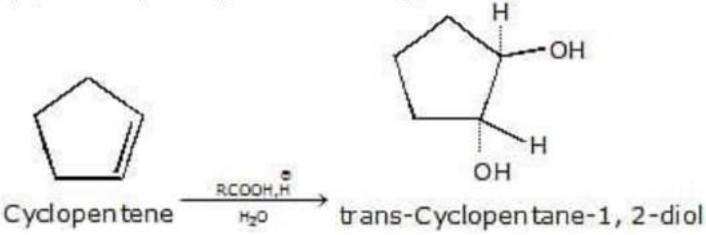


e.g.





(b) Anti hydroxylation, using peracids



Chemical Reactions of Alcohols

1. Reaction with Hydrogen Halides

General reaction:

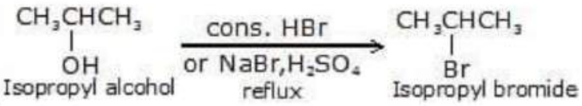
$R-OH + HX \longrightarrow R-X + H_2O$ (R may rearrange)

Reactivity of HX: HI > HBr > HCl

Reactivity of ROH: allyl > benzyl > $3^o > 2^o > 1^o$

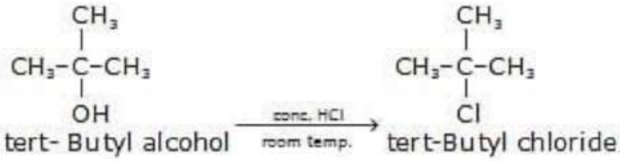
Mechanism:

$$R-OH \xrightarrow{H^{\oplus}} R-\overset{\oplus}{O}H_2 \longrightarrow \overset{\oplus}{R} \xrightarrow{X^{\ominus}} R-X$$

e.g. 

$$\underset{\text{Isopropyl alcohol}}{\underset{\displaystyle OH}{CH_3\underset{|}{C}HCH_3}} \xrightarrow[\text{or } NaBr, H_2SO_4 \text{ reflux}]{\text{cons. HBr}} \underset{\text{Isopropyl bromide}}{\underset{\displaystyle Br}{CH_3\underset{|}{C}HCH_3}}$$

e.g. $$\underset{\text{n-Pentyl alcohol}}{CH_3CH_2CH_2CH_2CH_2OH} \xrightarrow[\text{heat}]{\text{HCl, (anhydrous) } ZnCl_2 \text{ Lucas reagent}} \underset{\text{n-Pentyl chloride}}{CH_3CH_2CH_2CH_2CH_2Cl}$$

e.g. 

$$\underset{\text{tert- Butyl alcohol}}{CH_3-\underset{OH}{\overset{CH_3}{C}}-CH_3} \xrightarrow[\text{room temp.}]{\text{conc. HCl}} \underset{\text{tert-Butyl chloride}}{CH_3-\underset{Cl}{\overset{CH_3}{C}}-CH_3}$$

2. Reaction with Phosphorus Trihalides

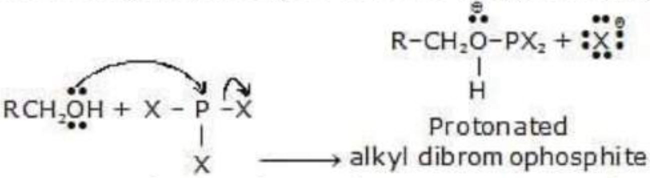
- Several phosphorus halides are useful for converting alcohols to alkyl halides. PBr_3, PCl_3, & PCl_5 work well and are commercially available.
- Phosphorus halides produce good yields of most primary and secondary alkyl halides, but none works well with ter. alcohols. The two phosphorus halides used most often are PBr_3 and the P_4 / I_2 combination.

General reaction:

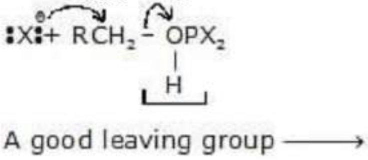
$$3R - OH + PX_3 \xrightarrow{(PX_3 = PCl_3, PBr_3, PI_3)} 3R - X + H_3PO_3$$

Mechanism:

The mechanism for the reaction involves attachment of the alcohol group on the phosphorus atom, displacing a bromide ion and forming a protonated alkyl dibromophosphite (see the following reaction).

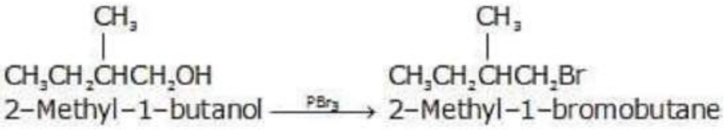


In a second step a bromide ion acts as a nucleophile to displace $HOPBr_2$, a good leaving group due to the electronegative atoms bonded to the phosphorus.



$\longrightarrow RCH_2X\ HOPX_2$

e.g.

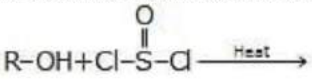


$$CH_3CH_2\underset{}{\overset{CH_3}{\overset{|}{C}}}HCH_2OH \xrightarrow{PBr_3} CH_3CH_2\overset{CH_3}{\overset{|}{C}}HCH_2Br$$

2-Methyl-1-butanol → 2-Methyl-1-bromobutane

e.g. CH_3CH_2OH Ethyl alcohol $\xrightarrow{P+I_2}$ CH_3CH_2I Ethyl iodide

3. Reaction with Thionyl Chloride



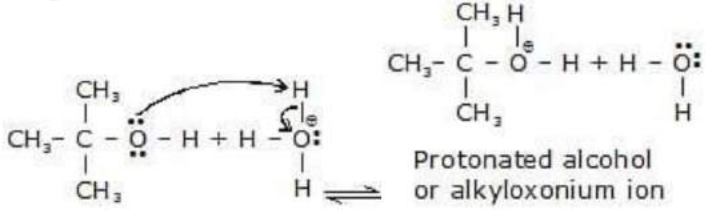
$$R{-}OH + Cl{-}\overset{\overset{O}{\|}}{S}{-}Cl \xrightarrow{Heat} R{-}Cl\ SO_2\ HCl$$

4. Dehydration of Alcohols

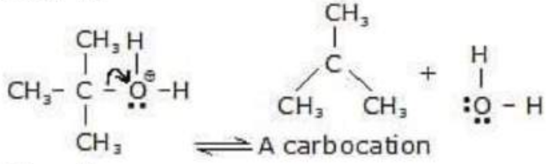
$-\underset{H}{\overset{|}{C}}-\underset{OH}{\overset{|}{C}}- \xrightarrow{acid} -\overset{|}{C}=\overset{|}{C}-$ H_2O (Rearrangement may occur)

Mechanism

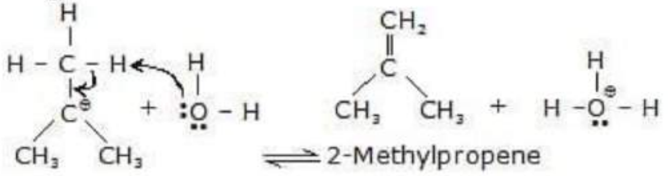
Step 1 :



Step 2:



Step 3:



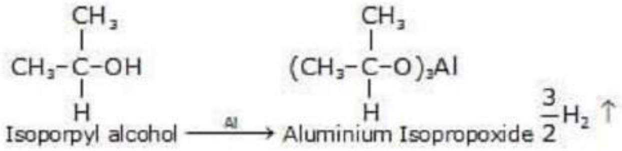
Reactivity of ROH: 3º > 2º > 1º

5. Reaction with Metals

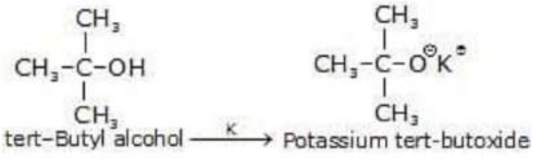
$RO{-}H + M \rightarrow RO^{\ominus}M^{\oplus} + \frac{1}{2}H_2$ M=Na, K, Mg, Al, etc

Reactivity order of ROH: $CH_3OH > 1^\circ > 2^\circ > 3^\circ$

e.g. $\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow{Na} \underset{\text{Sodium ethoxide}}{CH_3CH_2O^{\ominus}M^{\oplus} + \frac{1}{2}H_2}$

e.g. 

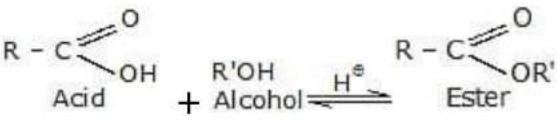
$\underset{\text{Isoporpyl alcohol}}{CH_3-\underset{H}{\overset{CH_3}{C}}-OH} \xrightarrow{Al} \underset{\text{Aluminium Isopropoxide}}{(CH_3-\underset{H}{\overset{CH_3}{C}}-O)_3Al} \frac{3}{2}H_2\uparrow$

e.g. 

$\underset{\text{tert-Butyl alcohol}}{CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH} \xrightarrow{K} \underset{\text{Potassium tert-butoxide}}{CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O^{\ominus}K^{\oplus}}$

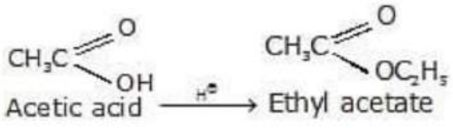
6. Ester Formation

General reaction:



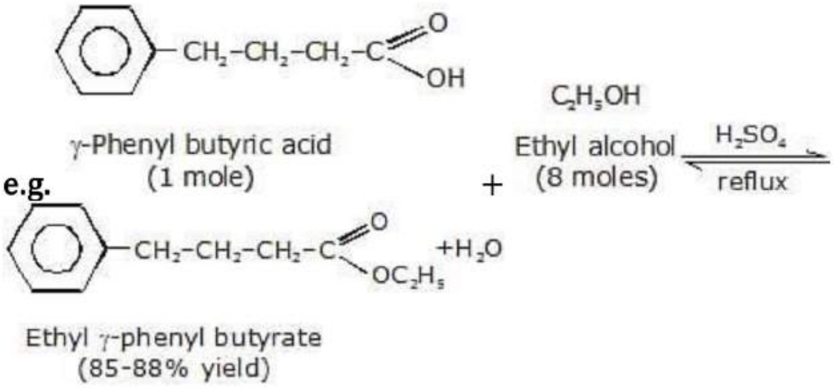
+ H_2O

e.g. CH_3CH_2O - H +



+ H_2O

e.g.



7. Oxidation Reactions

(a) Oxidation of primary alcohols

- Oxidation of primary alcohol initially forms an aldehyde. Obtaining the aldehyde is often difficult since most oxidizing agents are strong enough to oxidize the aldehydes formed. CrO_3 acid generally oxidizes primary alcohol all the way upto the carboxylic acid

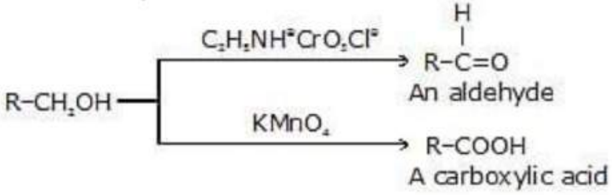
(b) Oxidation of secondary alcohols

- Sec. alcohols are easily oxidized to give excellent yields of ketones. The chromic acid reagent is often best for laboratory oxidations of secondary alcohols. The active species in the mixture is probably chromic acid, H_2CrO_4, or the acid chromate ion, $HCrO_4^{\ominus}$

(c) Resistance of tertiary alcohols to oxidation

- Oxidation of tertiary alcohol is not an important reaction in organic chemistry. Ter-alcohols have hydrogen atoms on the carbonyl carbon atom, so oxidation must take place by breaking C-C bonds. These oxidations require severe conditions and result in mixtures of products.

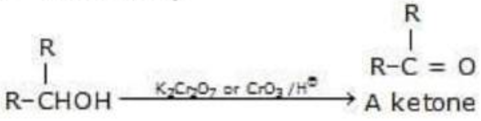
➤ **Primary**



$R{-}CH_2OH \xrightarrow{C_5H_5NH^{+}CrO_3Cl^{-}} R{-}\overset{H}{\overset{|}{C}}{=}O$ An aldehyde

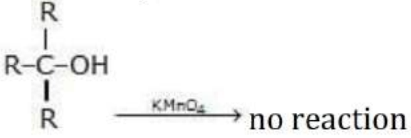
$R{-}CH_2OH \xrightarrow{KMnO_4} R{-}COOH$ A carboxylic acid

➤ **Secondary**



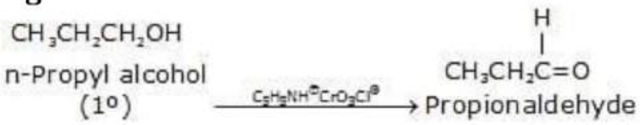
$R{-}\overset{R}{\overset{|}{C}}HOH \xrightarrow{K_2Cr_2O_7 \text{ or } CrO_3/H^{\oplus}} R{-}\overset{R}{\overset{|}{C}}=O$ A ketone

➤ **Tertiary**



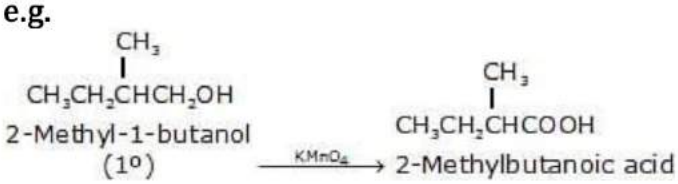
$R{-}\underset{R}{\underset{|}{\overset{R}{\overset{|}{C}}}}{-}OH \xrightarrow{KMnO_4}$ no reaction

e.g.



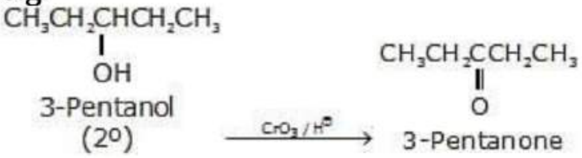
$CH_3CH_2CH_2OH$ n-Propyl alcohol (1°) $\xrightarrow{C_5H_5NH^{\oplus}CrO_3Cl^{\ominus}} CH_3CH_2\overset{H}{\overset{|}{C}}{=}O$ Propionaldehyde

e.g.

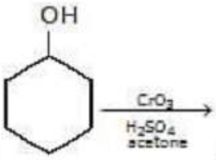


$CH_3CH_2\overset{CH_3}{\overset{|}{C}}HCH_2OH$ 2-Methyl-1-butanol (1°) $\xrightarrow{KMnO_4} CH_3CH_2\overset{CH_3}{\overset{|}{C}}HCOOH$ 2-Methylbutanoic acid

e.g.

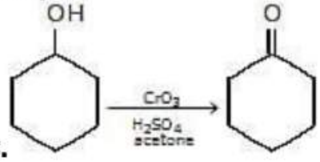


$CH_3CH_2\underset{OH}{\underset{|}{C}}HCH_2CH_3$ 3-Pentanol (2°) $\xrightarrow{CrO_3/H^{\oplus}} CH_3CH_2\underset{O}{\underset{\|}{C}}CH_2CH_3$ 3-Pentanone

Question: 

A

Identify A

Ans. 

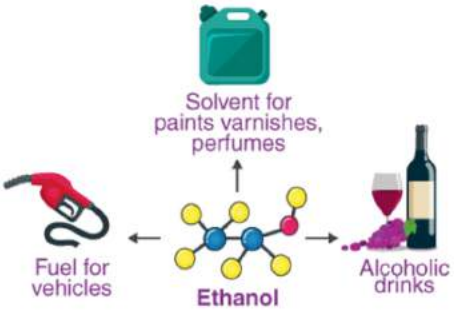
Some Commercially Important Alcohols

Methanol and Ethanol

- Methanol (CH3OH) and ethanol (C2H5OH) are the simplest members of the primary alcohol family and have a wide range of applications in the fuel industry. Some important uses of methanol and ethanol are listed in this article.

Uses of Ethanol

- Owing to its antibacterial and antifungal properties, ethanol (also known as ethyl alcohol) is used in many hand sanitizers and medical wipes.
- Ethanol is also used as an antiseptic and as a disinfectant.
- In cases of ethylene glycol poisoning or methyl alcohol poisoning, ethanol is often administered as an antidote.



- Several medications that are insoluble in water are often dissolved in ethanol. For example, ethanol (in concentrations ranging from 1% to 25%) is used as a solvent for some analgesics and mouthwashes.
- Ethanol is the primary ingredient in many alcoholic drinks that are orally consumed for recreational purposes. It acts as a psychoactive drug by

reducing anxiety and creating a feeling of euphoria in Humans. However, it also impairs cognitive and motor functions and acts as a central nervous system (CNS) depressant.

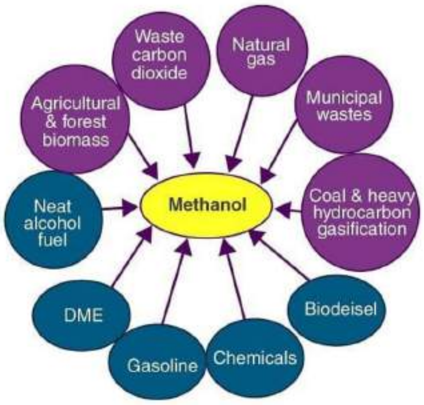
- Ethanol is used industrially in the production of ethyl esters, acetic acid, diethyl ether, and ethyl amines.
- This compound is widely used as a solvent due to its ability to dissolve both polar and nonpolar compounds.
- Since it has a melting point of -114.1°C, ethanol is used as an ingredient in cooling baths in several laboratories. It also serves as the active fluid in many spirit thermometers.

Uses of Ethanol as a Fuel

- Ethanol is widely used as a fuel additive and as an engine fuel. Some forms of gasoline are known to contain up to 25% ethanol.
- This compound has also been used as rocket fuel in some bipropellant rockets. When used in fuel, ethanol is believed to reduce carbon monoxide and nitrogen oxide emissions.
- Since it is widely available and has low toxicity and cost, ethanol is used in direct-ethanol fuel cells (or DEFCs). However, commercially used fuel cells generally use methanol, hydrogen, or natural gas.

Uses of Methanol

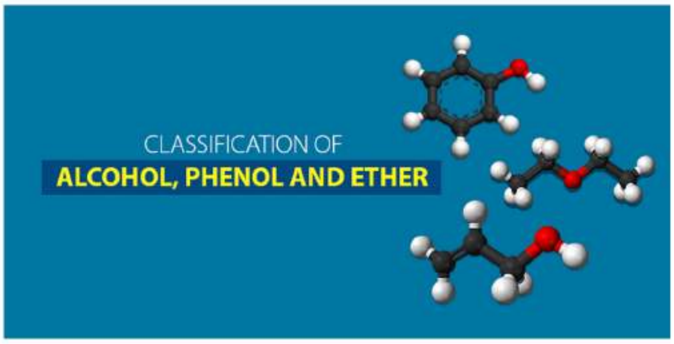
- Methanol is widely used in the production of acetic acid and formaldehyde.
- In order to discourage the recreational consumption of ethanol, methanol is often added to it as a denaturant.
- This compound is also used as an antifreeze (an additive that is used to lower the freezing point of a liquid) in many pipelines.
- It is also used in sewage treatment plants since it serves as a carbon-based food source for denitrifying bacteria.
- The polyacrylamide gel electrophoresis (PAGE) technique involves the use of methanol as a destaining agent.
- A mixture of water and methanol is used in high-performance engines in order to increase power.
- Methanol is used in the production of hydrocarbons, olefins, and some aromatic compounds.
- It is also used in the production of methyl esters and methylamines.



Uses of Methanol in Fuel

- Methanol can be used as a fuel in several internal combustion engines. The chemical equation for the burning of methanol is given by:
  - $2CH_3OH + 3O_2 \rightarrow 4H_2O + 2CO_2$
- However, the primary disadvantage of methanol as a fuel is that it has a tendency to corrode aluminum and some other metals.
- Another shortcoming of methanol as a fuel is that its energy density is approximately half of the energy density offered by gasoline. An advantage of methanol as a fuel is that it is relatively easy to store.
- The storage of liquid methanol is much easier than the storage of hydrogen gas or natural gas. Other merits of this compound include its biodegradability and its short half-life in groundwater.

Classification & Nomenclature of Alcohols, Phenols & Ethers



Classification of Alcohol, Phenol and Ether

Alcohol, phenol, ether are classes of organic compounds which find wide usage in a broad range of industries as well as for domestic purposes.

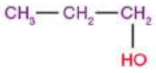
- Alcohol is formed when a saturated carbon atom is bonded to a hydroxyl (-OH) group.
- Phenol is formed when a hydrogen atom in a benzene molecule is replaced by the -OH group.
- Ether is formed when an oxygen atom is connected to two alkyl or aryl groups.

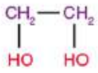
In this section, we will discuss how alcohols, phenol s and ethers are classified.

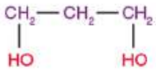
Classification of Alcohol

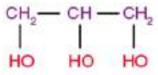
Depending on the number of hydroxyl groups attached, alcohols can be classified into three types.

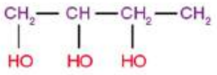
- **Monohydric alcohols**: They contain one -OH group. Example, CH_3CH_2-OH
- **Dihydric alcohols**: They contain two -OH groups. Example, 1,2-Ethandiol.
- **Trihydric alcohols**: They contain three -OH groups. Example 1,2,3-Propantriol.


Propanol


1, 2-Ethandiol

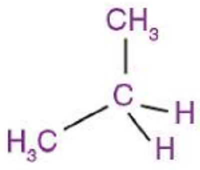

1, 3-Propandiol

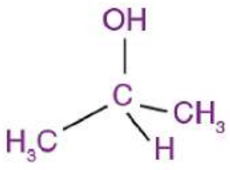

1, 2, 3-Propantriol

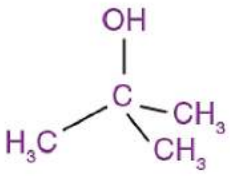

1, 2, 3-Butantriol

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

- **Primary alcohols**: One carbon atom is directly attached.
- **Secondary alcohols**: Two carbon atoms are directly attached.
- **Tertiary alcohols**: Three carbon atoms are directly attached.







Classification of Phenol

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

- **Monohydric phenols**: They contain one -OH group.
- **Dihydric phenols**: They contain two -OH groups. They may be ortho-, meta- or para- derivative.
- **Trihydric phenols**: They contain three -OH groups.

Classification of Ether

Depending on the type of the alkyl or aryl groups attached to the oxygen atom in ether, it can be classified into two types.

- **Symmetrical ether**: Also known as the simple ether, the alkyl or the aryl group attached to either side of the oxygen atoms are the same. Examples are CH_3OCH_3, $C_2H_5OC_2H_5$, etc.
- **Unsymmetrical ether**: Also known as the mixed either, the alkyl or the aryl group attached to either side of the oxygen atoms, are not the same. Examples are $CH_3OC_2H_5$, $C_2H_5OC_6H_5$, etc.

Nomenclature of Alcohols

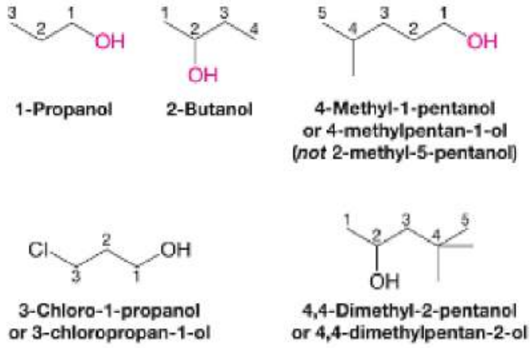
Alcohols provide the first example of how the parent alkane was the starting point for the nomenclature of all families of compounds. The -ane suffix is modified in a systematic manner to indicate the presence of a functional group. **Alcohol is named by identifying the longest straight carbon chain containing the -OH group.** The -ane suffix is replaced with -anol and the location of the -OH group on the chain is designed by a number.
The generic IUPAC name for alcohol is alkanols, and they are represented in reactions by the general formula R-H. The presence of other substituents in alcohol is indicated by their names and numerical positions, always keeping the lowest possible number for the hydroxyl group.

IUPAC Nomenclature for Alcohols

The following procedure should be followed in giving alcohol IUPAC substitutive names.

- Select the longest continuous chain to which the hydroxyl group is directly attached. Change the name of the alkane corresponding to the chain by dropping the final -e and adding the suffix -ol.
- Number the longest continuous carbon chain so as to give the carbon atom bearing the hydroxyl group the lower number. Indicate the position of the hydroxyl group by using this number as a locant.
- Indicate the position of another substituent as a prefix by using the numbers corresponding to their positions along the carbon chain as locants.

The following example shows how the rules are applied.



1-Propanol 2-Butanol 4-Methyl-1-pentanol or 4-methylpentan-1-ol (*not* 2-methyl-5-pentanol)

3-Chloro-1-propanol or 3-chloropropan-1-ol 4,4-Dimethyl-2-pentanol or 4,4-dimethylpentan-2-ol

IUPAC Nomenclature for Alcohols

Types of Nomenclature in Alcohols

There are three systems of naming alcohols

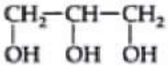
1. **Common or trivial system**
2. **Carbinol system and**
3. **IUPAC system**

Formula	**Parent Hydrocarbon**	**Common name**	**Carbinol name**	**IUPAC name**
CH_3-OH	Methane	Methyl alcohol	Carbinol	Methanol
CH_3-CH_2-OH	Ethane	Ethyl alcohol	Methyl carbinol	Ethanol
CH_3-CH(OH)-CH_3	Propane	Isopropyl alcohol	Dimethyl carbinol	2-Propanol
$(CH_3)_3$-C-OH	2-Methyl propane	Tert-butyl alcohol	Trimethyl carbinol	2-Methyl-2-propanol

Ethanol is known as ethyl alcohol, grain alcohol and the spirit of wine. The first system of nomenclature for alcohol which was based on the use of the term "carbinol" for methanol was originated by a 19th-century German chemist Harmann Kolbe. The present accepted systematic nomenclature for alcohol was adopted by the International Union of Pure and Applied Chemistry in Paris in 1957.

Solved Example

Name the following compound.



$$\underset{OH}{CH_2}-\underset{OH}{CH}-\underset{OH}{CH_2}$$

Solution: This compound has a three-carbon chain, so the parent alkane name is propane. Because the compound contains three hydroxyl groups, the suffix must be -triol. Therefore, the name is 1,2,3-propanetriol.
The common name of this compound is glycerol is also called glycerin and it is an important by-product in the manufacture of soaps.

Nomenclature of Phenols

Phenols are the organic compounds containing a benzene ring bonded to a hydroxyl group. They are also known as carbolic acids. Thus, a phenol molecule consists of two parts one aryl group part and the other hydroxyl group part. On the basis of the number of hydroxyl groups attached to the aryl group, it can be classified into mono-, di-, tri- or polyhydric phenols.

Nomenclature of Phenols

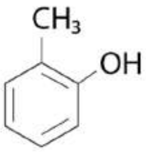
Earlier, most of the compounds with the same structural formula were known by different names depending on the regions where they were synthesized. This naming system was very trivial since it raised a lot of confusion. Finally, a common naming system enlisting standard rules was set up by IUPAC for the naming of compounds. It is both a common name and an IUPAC name for the compounds containing a benzene ring attached to a hydroxyl group. Structurally phenols are the simplest hydroxy derivative of the benzene ring. IUPAC nomenclature of phenols follows a set of rules.

Rules underlying the Nomenclature of Phenols

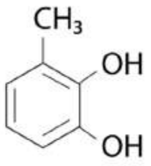
- Locate the position of a hydroxyl group attached to the benzene ring.
- Benzene rings attached to more than one hydroxyl group are labelled with the Greek numerical prefixes such as di, tri, tetra to denote the number of similar hydroxyl groups attached to the benzene ring. If two hydroxyl

groups are attached to the adjacent carbon atoms of the benzene ring, it is named as benzene1,2-diol

- In the case of substituted phenols, we start locating the positions of the other functional groups with respect to the position where the hydroxyl group is attached. For example, if a methyl group is attached at the fourth carbon atom with respect to the hydroxy group, the compound is named as, 4-Methyl phenol.



o-Cresol
2-Methylphenol



Resorcinol
Benzene-1,3 - diol

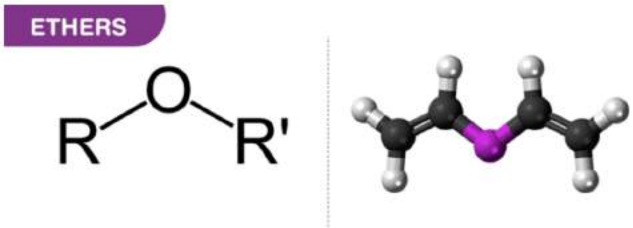
- Depending on the position of substituted functional group with respect to the hydroxyl group, words like ortho (when the functional group is attached to the adjacent carbon atom), para (when the functional group is attached to the third carbon atom from the hydroxyl group), meta (when the functional group is attached to the second carbon atom from the hydroxyl group) are also used for the nomenclature of phenols.

Nomenclature of Ethers

What are Ethers?

Ethers can be defined as a class or a group of organic compounds comprising an oxygen atom, which is bonded to two same or different alkyl or aryl groups.

The general formula for ethers is R-O-R, where R represents an alkyl group.



How are Ethers classified?

Ethers can be generally classified into two categories, based on their attached substituent groups.

- **Symmetrical ethers** – Two identical groups attached to either side of an oxygen atom.
- **Asymmetrical ethers** – Two different groups attached to either side of an oxygen atom.

Earlier, most of the compounds with the same structural formula were known by different names depending on the regions where they were synthesized. This naming system was very trivial since it raised a lot of confusion. Finally, a common naming system enlisting standard rules was set up by IUPAC (The International Union for Pure and Applied Chemistry) for the naming of compounds. This method of naming is IUPAC naming or IUPAC nomenclature. Nomenclature of ethers revolves around two standard ways of naming:

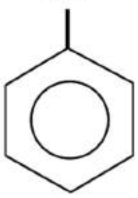
- **Common nomenclature**
- **IUPAC nomenclature**

Rules underlying the Nomenclature of Ethers

- Common nomenclature of ethers follows the rule of naming different alkyl/aryl groups attached to the oxygen atom on either side in alphabetical order and finally adding the word ether to it. For example, $CH_3OC_6H_5$ is named as Methyl phenyl ether.
- Ethers in which the oxygen atoms are attached to the same group on either side are named with the help of Greek numerical prefixes such as "di". These ethers are named by adding "di" before the alkyl/aryl groups attached to the oxygen atom. For example, CH_3OCH_3 is named as dimethyl ether.
- IUPAC's nomenclature of ethers follows different guidelines. According to IUPAC naming, a substituent group containing more carbon atoms is chosen as parent hydrocarbon. The other substituent group attached to the oxygen atom is named with a prefix "oxy". For example, $CH_3OC_2H_5$ is named as 1-methoxy ethane.

Phenols: Properties, Preparation & Reactions

Properties, Reactions and Synthesis of Phenol



An organic compound is aromatic in nature with the structural formula C_6H_5OH. It is a white crystalline rock that is volatile in nature. The molecule has of a phenyl group ($-C_6H_5$) attached to a hydroxy group ($-OH$). It is slightly acidic and needs careful handling due to its tendency for causing chemical burns. Phenol was first mined from coal tar, but today is manufactured on a large scale (around 7 billion kg/year) from petroleum. It is an important industrial product as a pioneer to various materials and useful compounds. It is principally used to manufacture plastics and related materials. Phenol and its chemical products are very important for the production of Bakelite, polycarbonates, detergents, nylon, epoxies, herbicides such as phenoxy herbicides, and many pharmaceutical drugs.

Properties

Chemical formula	C_6H_6O
Molar mass	$94.113\ g{\cdot}mol^{-1}$
Appearance	Transparent crystalline solid
Odor	Sweet and tarry
Density	$1.07\ g/cm^3$
Melting point	40.5°C (104.9°F; 313.6 K)
Boiling point	181.7°C (359.1°F; 454.8 K)
Solubility in water	8.3 g/100 mL (20°C)
log P	1.48
Vapor pressure	0.4 mmHg (20°C)
Acidity (pKa)	9.95 (in water), 29.1 (in acetonitrile)
Conjugate base	Phenoxide
UV-vis (λ_{max})	270.75 nm
Dipole moment	1.224 D

Reactions

Phenol is extremely reactive to electrophilic aromatic substitution as the oxygen atom's pi electrons give electron density into the ring. By this overall approach, several groups can be attached to the ring, through halogenation, sulfonation, acylation, and other methods. However, phenol's ring is so powerfully activated—second only to aniline—that chlorination or bromination of phenol will lead to replacement on all carbon atoms para and ortho to the hydroxy group, not only on one carbon. It reacts with dilute nitric acid at room temperature to produce a mixture of 2-nitrophenol and 4-nitrophenol while with concentrated nitric acid, many nitro groups get replaced on the ring to produce 2, 4, 6-trinitrophenol which is also known as picric acid.

The aqueous mixture of phenol is weakly acidic and changes blue litmus somewhat to red. It is easily neutralized by sodium hydroxide giving sodium phenate but is weaker than carbonic acid, it cannot be neutralized by sodium bicarbonate or sodium carbonate to release carbon dioxide.

$C_6H_5OH + NaOH \rightarrow C_6H_5ONa + H_2O$

When a mixture of phenol and benzoyl chloride is shaken in the occurrence of dilute sodium hydroxide solution, phenyl benzoate is produced. This is a case of the Schotten-Baumann reaction:

$C_6H_5OH + C_6H_5COCl \rightarrow C_6H_5OCOC_6H_5 + HCl$

Phenol is transformed to benzene when it is distilled with zinc dust, or when phenol vapor is passed over grains of zinc at 400°C:

$C_6H_5OH + Zn \rightarrow C_6H_6 + ZnO$

In the presence of boron trifluoride (BF_3) phenol is reacted with diazomethane and as a result anisole is obtained as the main product and nitrogen gas as a byproduct.

$C_6H_5OH + CH_2N_2 \rightarrow C_6H_5OCH_3 + N_2$

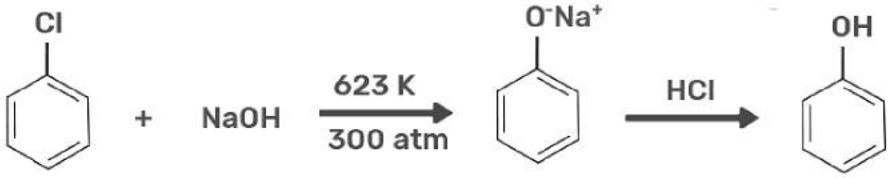
When phenol reacts with iron (III) chloride solution, a powerful violet-purple solution is produced.

Preparation of Phenols

Preparation of phenols from diazonium salts, benzene sulphonic acid, haloarenes, cumene. They are also known as carbolic acids. They are weak acids and mostly form phenoxide ions by dropping one positive hydrogen ion (H+) from the hydroxyl group., phenol was mainly manufactured from coal tar. Nowadays, with developments in technologies, some new methods have come up for the making of phenols in laboratories. In laboratories, phenol is mainly created from benzene derivatives. Some of the approaches of preparation of phenols are explained below:

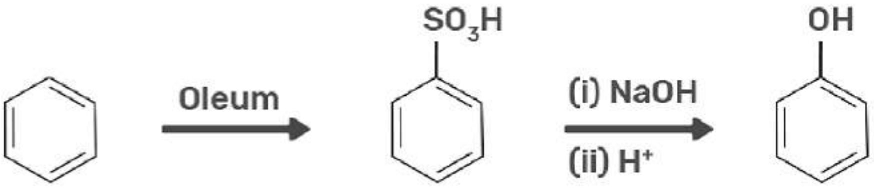
Preparation of Phenols From Haloarenes

Chlorobenzene is an example of haloarenes which is made by mono replacement of the benzene ring. When chlorobenzene is reacted with sodium hydroxide at 623K and 320 atm sodium phenoxide is formed. Finally, sodium phenoxide on acidification makes phenols.



Preparation of Phenols From Benzene Sulphonic Acid

Benzenesulphonic acid can be acquired from benzene by reacting it with oleum. Benzenesulphonic acid hence formed is fused with molten sodium hydroxide at very high temperature which leads to the development of sodium phenoxide. Lastly, sodium phenoxide on acidification gives phenols.

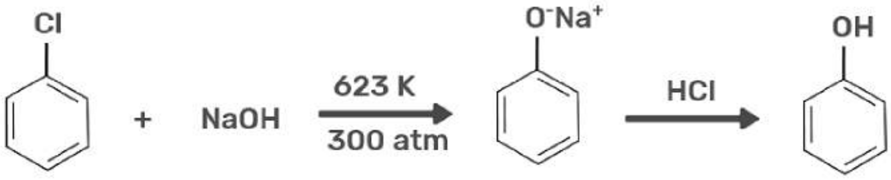


Preparation of Phenols From Diazonium Salts

When an aromatic primary amine is fused with nitrous in the presence of HCl ($NaNO_2 + HCl$) acid at 273 – 278 K, diazonium salts are gained. These diazonium salts are extremely reactive in nature. Upon warming with water, these diazonium salts, to end hydrolyze to phenols. Phenols can also be acquired from diazonium salts by treating it with dilute acids.

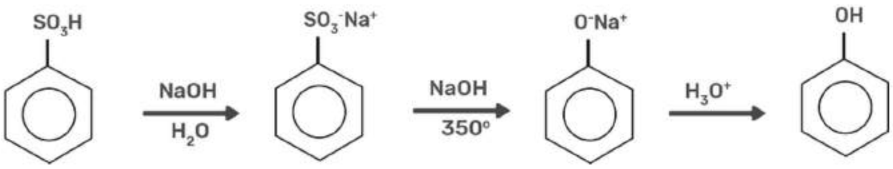
Preparation of Phenols From Cumene

Cumene is an organic compound acquired by Friedel-Crafts alkylation of benzene with propylene. On oxidation of cumene (isopropylbenzene) in the presence of air, cumene hydroperoxide is found. Upon further action of cumene hydroperoxide with dilute acid, phenols are produced. Acetone is also made as one of the by-products of this reaction in large quantities. Therefore, phenols prepared by these techniques need purifications.



Synthesis of Phenols

You can produce phenols in large amounts by the pyrolysis of the sodium salt of benzene sulfonic acid, by a process known as Dow process, and by the air oxidation of cumene. Each of these methods is described below. You can also make small amounts of phenol by the peroxide oxidation of phenylboronic acid and the hydrolysis of diazonium salts. In this method, benzene sulfonic acid is reacted with aqueous sodium hydroxide. The resulting salt is mixed with solid sodium hydroxide and reacted at a high temperature. The product of this reaction is sodium phenoxide, which is acidified with aqueous acid to make phenol.

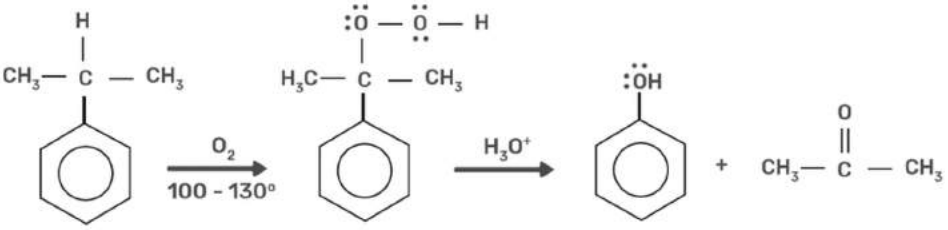


Dow Process

In this process, chlorobenzene is reacted with dilute sodium hydroxide at a temperature of about 300°C and 3000 psi pressure. The following figure exemplifies the Dow process.

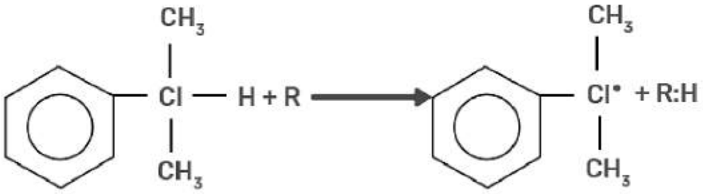
Air Oxidation of Cumene

The oxidation of cumene in the presence of air (isopropylbenzene) will lead to the making of both acetone and phenol, as shown in the following figure. The mechanisms for the development and degradation of cumene hydroperoxide need closer looks, which are delivered following the figure.

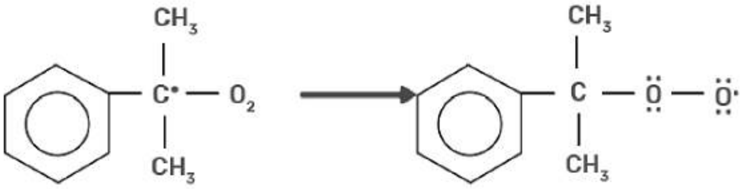


Cumene Hydroperoxide Formation

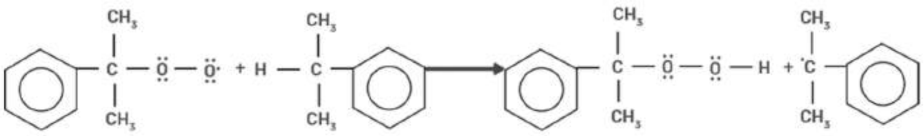
The development of the hydroperoxide continues by a free radical chain reaction. A radical initiator extracts a hydrogen-free radical from the molecule, making a tertiary free radical. The formation of the tertiary free radical is the first step in the reaction.



Further, the free radical is attracted to an oxygen molecule. This attraction yields the hydroperoxide free radical.

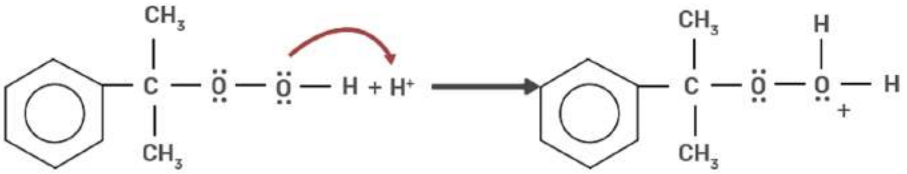


Lastly, the hydroperoxide free radical extracts a hydrogen free radical from a molecule of cumene to produce cumene hydroperoxide and a new tertiary free radical.

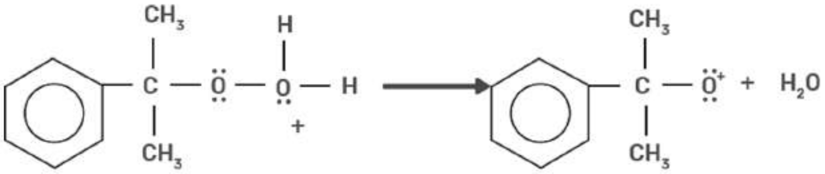


Cumene Hydroperoxide Degradation

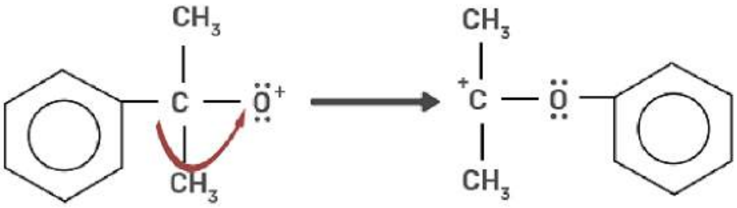
The degradation of the cumene hydroperoxide continues through a carbocation mechanism. In the 1st step, a pair of electrons on the oxygen of the hydroperoxide's "hydroxyl group" is attracted to a proton of the H_3O+ molecule, making an oxonium ion.



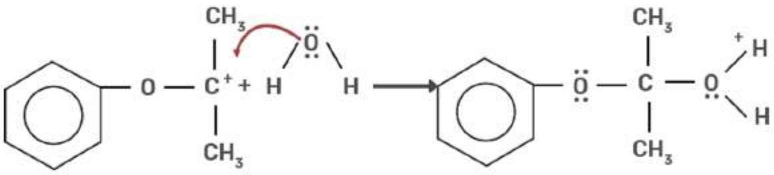
Next, the oxonium ion develops stability when the positively charged oxygen leaves in a water molecule. This loss of a water molecule yields a new oxonium ion.



A phenide ion move to the oxygen atom (which makes a tertiary carbocation) stabilizes the positively charged oxygen. (A phenide ion is a phenyl group with an electron bonding pair accessible to produce a new bond to the ring.)

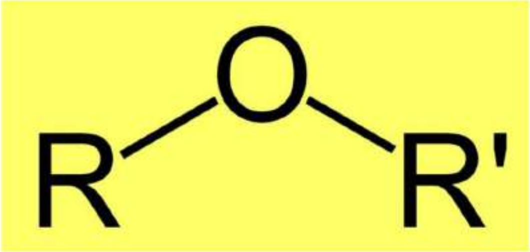


The carbocation is stabilized via acid-base reaction with a water molecule, leading to the development of an oxonium ion.

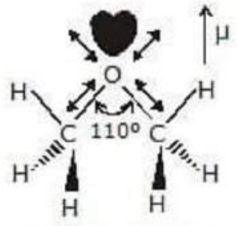


Ethers: Preparation, Properties & Reactions

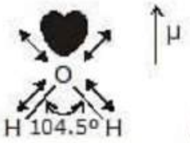
Ether



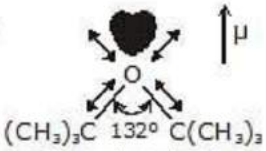
Structure of Ether



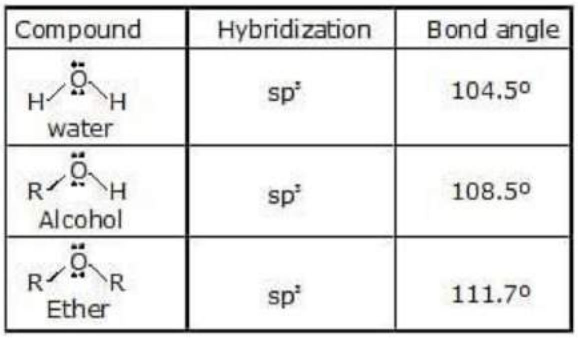
dimethyl ether



Water

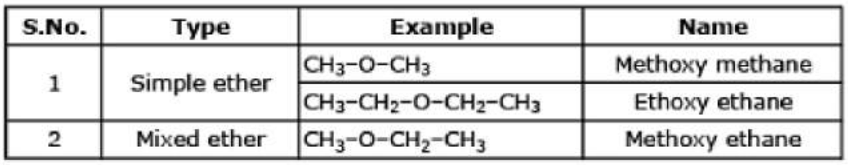


Di-ter.butyl ether



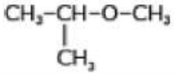
Compound	Hybridization	Bond angle
H–Ö–H water	sp^3	104.5°
R–Ö–H Alcohol	sp^3	108.5°
R–Ö–R Ether	sp^3	111.7°

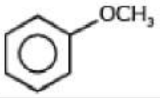
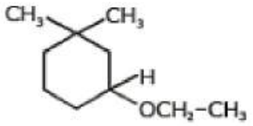
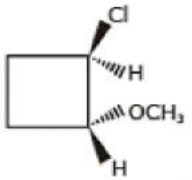
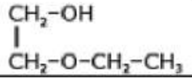
Classification of Acyclic ethers:



S.No.	Type	Example	Name
1	Simple ether	CH_3-O-CH_3	Methoxy methane
		$CH_3-CH_2-O-CH_2-CH_3$	Ethoxy ethane
2	Mixed ether	$CH_3-O-CH_2-CH_3$	Methoxy ethane

IUPAC Nomenclature of ether "Alkoxy Alkane"

S.NO.	Compound	IUPAC Name
1	 $CH_3-\underset{\underset{CH_3}{\mid}}{CH}-O-CH_3$	2-Methoxy propane
2	$Cl-CH_2-O-CH_3$	Chloromethoxy methane

3		Methoxy benzene (Anisole)
4		3-Ethoxy-1, 1-dimethyl cyclohexane
5		trans-1-Chloro-2-methoxy cyclobutane
6	 $\begin{array}{l} CH_2-OH \\ \vert \\ CH_2-O-CH_2-CH_3 \end{array}$	2-Ethoxy ethan-1-ol

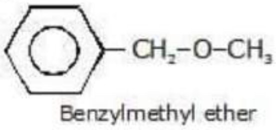
Methods of Preparation of Ethers:

(1) Williamson synthesis General reaction:

$RX + R'O^{\ominus}Na^{+} \longrightarrow R-OR'$

e.g. (i) $n\text{-}PrOH \xrightarrow{n\text{-}PrBr} \underset{\text{Di-n-propyl ether}}{CH_3CH_2CH_2O-CH_2CH_2CH_3}$

(ii) $MeOH \xrightarrow{Na} MeO^{\ominus} \xrightarrow{PhCH_2Br}$



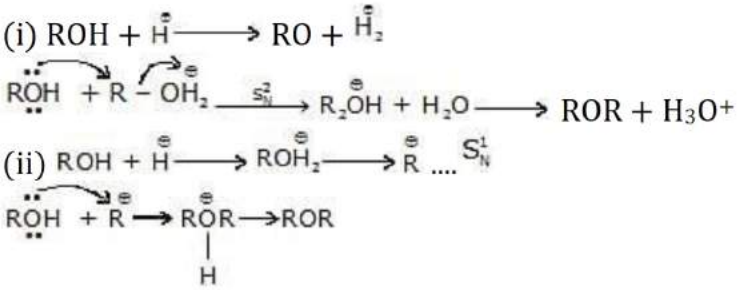
$C_6H_5-CH_2-O-CH_3$

Benzylmethyl ether

(iii) $t\text{-}BuOH \xrightarrow{Na} t\text{-}BuO^{\ominus} \xrightarrow{EtBr}$ t-Butyl ethyl ether

(This reaction produces a poor yield of ether because of the bulkiness of $t\text{-}BuO^{-}$)

(2) Williamson's Continuous Etherification process or by Dehydration of Alcohols-



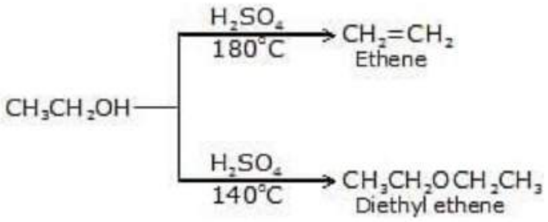
(i) $ROH + \overset{\ominus}{H} \longrightarrow RO + \overset{\ominus}{H_2}$

$R\ddot{O}H + R-\overset{\ominus}{O}H_2 \xrightarrow{S_N^2} R_2\overset{\ominus}{O}H + H_2O \longrightarrow ROR + H_3O^{+}$

(ii) $ROH + \overset{\ominus}{H} \longrightarrow R\overset{\ominus}{O}H_2 \longrightarrow \overset{\ominus}{R} \ldots S_N^1$

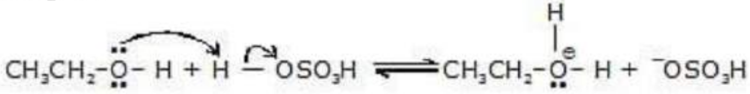
$R\ddot{O}H + \overset{\ominus}{R} \longrightarrow R\underset{\underset{H}{\vert}}{\overset{\ominus}{O}}R \longrightarrow ROR$

e.g.



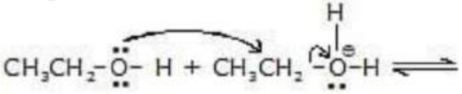
Mechanism

Step-1:



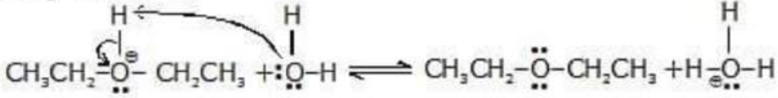
This is an acid-base reaction in which the alcohol accepts a proton from the sulfuric acid.

Step-2:



Another molecule of the alcohol acts as a nucleophile and attacks the protonated alcohol in an S_N^2 reaction.

Step-3:



Another acid-base reaction converts the protonated ether to an ether by transferring a proton to a molecule of water (or to another molecule of the alcohol). Only one combination of alkylhalide and alkoxide is appropriate for the preparation of each of the following ethers by Willianson ether synthesis. What is the correct combination in each case.

(3) From alkenes

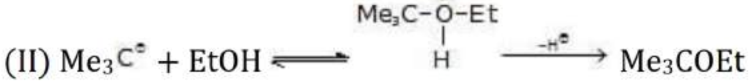
(a) By the addition of alcohols in alkenes:
When alcohol is added to alkenes in presence of an acid, we get ethers.

General reaction:

(I) $>C=C< \xrightarrow{H_2SO_4}$ carbocation

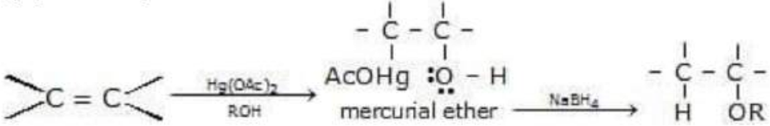
(II) Carbocation alcohol $\longrightarrow$ ether

e.g. (I) $Me_2C = CH_2 + H^{\oplus}(H_2SO_4) \longrightarrow Me_3C^{\oplus}$



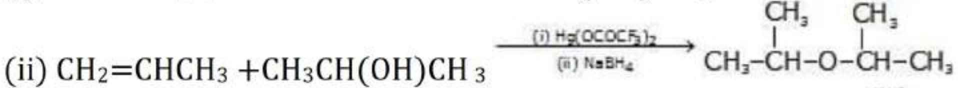
(II) $Me_3C^{\oplus} + EtOH \rightleftharpoons Me_3C-\underset{H}{\overset{\oplus}{O}}-Et \xrightarrow{-H^{\oplus}} Me_3COEt$

(b) Alkoxymercuration - demercuration:

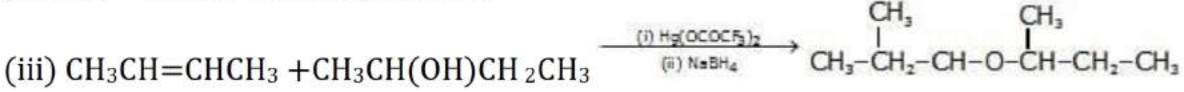


e.g.

(i) $RCH{=}CH_2 + R'OH \xrightarrow[\text{(ii) NaBH}_4]{\text{(i) Hg(OCOCF}_3)_2} RCH(OR')\,CH_3$



(ii) $CH_2{=}CHCH_3 + CH_3CH(OH)CH_3 \xrightarrow[\text{(ii) NaBH}_4]{\text{(i) Hg(OCOCF}_3)_2} CH_3-\overset{CH_3}{CH}-O-\overset{CH_3}{CH}-CH_3$



(iii) $CH_3CH{=}CHCH_3 + CH_3CH(OH)CH_2CH_3 \xrightarrow[\text{(ii) NaBH}_4]{\text{(i) Hg(OCOCF}_3)_2} CH_3-\overset{CH_3}{CH_2}-CH-O-\overset{CH_3}{CH}-CH_2-CH_3$

Physical Properties Of Ethers

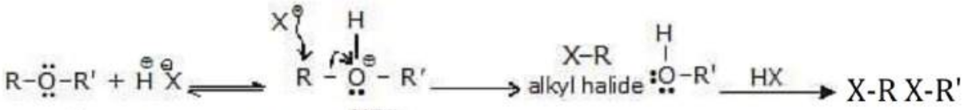
Dimethyl ether and ethyl methyl ether are both gases at room temperature. Other lower homologues are colourless, pleasant smelling, volatile liquids with a typical ether smell.

- Dipole moment: C-O-C bond angle is not 180°, dipole moments of the two C-O bonds do not cancel each other and thus ethers possess a small net dipole moment.
- Boiling point: Boiling points of ether molecules are comparable to that of alkanes but they are very low compared to that of alcohols of comparable molecular mass. This is because of the presence of hydrogen bonding in alcohol.
- Solubility: The solubility of ethers with water resembles those of alcohols of comparable molecular mass. Ether molecules are soluble in water. This is because of the fact that like alcohol, oxygen atoms of ether can also form hydrogen bonds with a water molecule. Also, solubility decreases with an increase in carbon atoms. This is because the relative increase in hydrocarbon content of the molecule decreases the tendency of H-bond formation.
- Polarity: Ether is less polar than esters, alcohols or amines because oxygen atom unable to participate in hydrogen bonding due to the presence of bulky alkyl group on both side of the oxygen atom. but ether is more polar than alkenes.

- Hybridization: In Ether oxygen atom is sp3 hybridized with a bond angle of 109.50,

Reactions of ethers1. With HX-

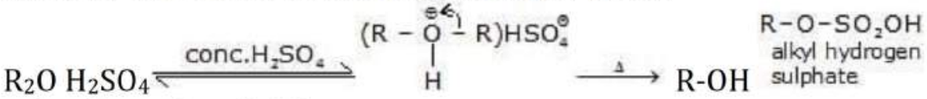
General reaction:



e.g. (i) $CH_3CH_2CH_2CH_3 \xrightarrow{HBr} 2CH_3\text{-}CH_2Br$

2. Reaction with sulphuric acid-

Ethers dissolve in concentrated solutions of strong inorganic acids to from oxonium salts, i.e. ether behave as Bronsted Lowry bases.



When heated with dilute H_2SO_4

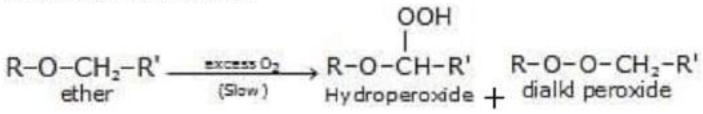
$R_2O\ H_2SO_4 \xrightarrow{\Delta} 2ROH$

e.g. $C_2H_5OC_2H_5 + H_2SO_4 \xrightarrow{\Delta} C_2H_5OH + C_2H_5OHSO_4 \xrightarrow[\Delta]{H_2O} C_2H_5OH + H_2SO_4$

3. Autoxidation of ethers:

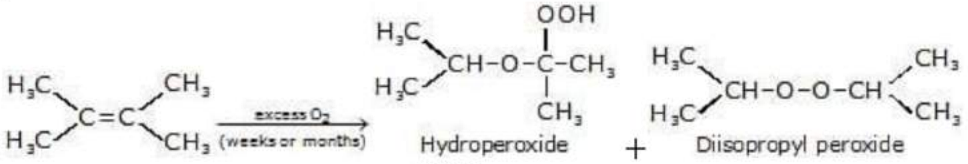
When ethers are stored in the presence of atmospheric oxygen, they slowly oxidize to produce hydroperoxides and dialkyl peroxides, both of which are explosive. Such a spontaneous oxidation by atmospheric oxygen is called an autoxidation.

General reaction:

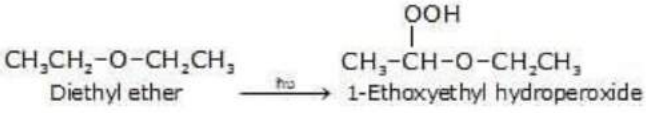


Ex.

(i)



(ii)



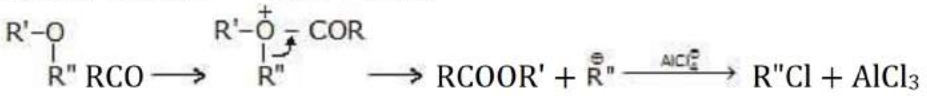
4. Reaction with acid chlorides and anhydrides:

Reagent: $ZnCl_2$, $AlCl_3$ etc.

General reaction: (i) $R\text{-}O\text{-}R + R\text{-}CO\text{-}Cl \xrightarrow{AlCl_3} R\text{-}Cl + RCOOR$

Mech.

$RCOCl + AlCl_3 \rightleftharpoons RCO + AlCl_4^-$



$$\underset{R''}{\overset{R'-O}{|}}\ RCO \longrightarrow \underset{R''}{\overset{R'-\overset{+}{O}-COR}{|}} \longrightarrow RCOOR' + \overset{\oplus}{R}'' \xrightarrow{AlCl_4^{\ominus}} R''Cl + AlCl_3$$

e.g.

$C_2H_5OC_2H_5 + CH_3COCl \xrightarrow{\text{Anhydous } ZnCl_2} C_2H_5Cl + CH_3COOC_2H_5$

(ii) $R_2O + \underset{\text{acid anhydride}}{(CH_3CO)_2O} \xrightarrow{ZnCl_2} 2CH_3COOR$

e.g. $C_2H_5OC_2H_5 + (CH_3CO)_2O \xrightarrow{\text{anhydrous } AlCl_3} 2CH_3COOC_2H_5$

5. Reaction with carbon monoxide:

Ether react with CO at 125-180°C and at a pressure of 500 atm, in the presence of BF_3 plus a little water.

$R_2O + CO \xrightarrow[125\text{-}180°C]{BF_3,\ 500\,atm} RCOOR$

6. Reaction with halogens:

When treated with chlorine or Br, ether undergoes substitution, the extent of which depends on the conditions.

$CH_3CH_2OCH_2CH_3 \xrightarrow[h\nu]{Cl_2} CH_3CHClOCH_2CH_3 \xrightarrow[h\nu]{Cl_2} CH_3CHClOCHClCH_3$

In presence of light,

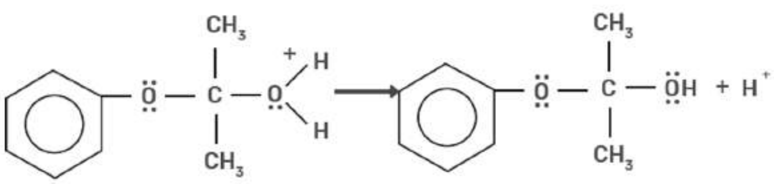
$(C_2H_5)_2O \xrightarrow[h\nu]{Cl_2} \underset{\text{Perchloro diethyl ether}}{(C_2Cl_5)_2O}$

Mech.

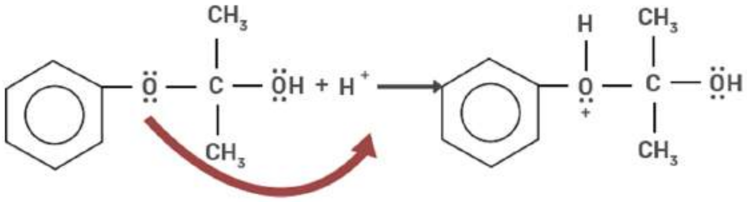
The reaction proceeds by a free-radical mechanism, and α-substitution occurs readily because of resonance stabilization of the intermediate radical.

$R'\ddot{O}-CH_2R'' \xrightarrow{Cl^{\bullet}} R'\ddot{O}-\dot{C}HR'' \longleftrightarrow R'\dot{O}=CHR \xrightarrow{Cl_2} R'\ddot{O}-\dot{C}HClR'' + Cl^{\bullet}$, etc.

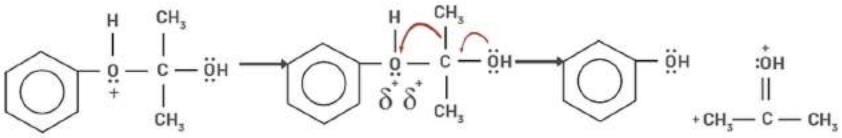
Stability of the oxonium ion is by the loss of a proton.



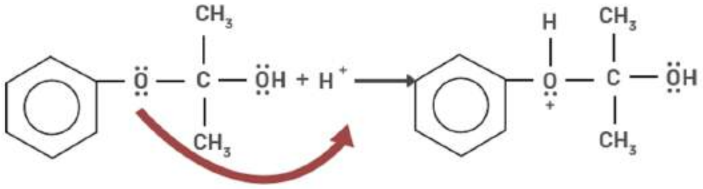
Afterward, a proton is selected by the ether oxygen in an acid-base reaction, producing a new oxonium ion.



The positively charged ether oxygen attracts the electrons in the oxygen-carbon bond toward itself, thus delocalizing the charge over both of the atoms. The fractional positive charge on the carbon attracts the nonbonding electron pair from the oxygen of the OH group, letting the electrons in the original oxygen-carbon bond to be released back to the extra electronegative oxygen atom.



Finally, a proton is lost from the protonated acetone molecule, leading to the development of acetone.



General

Use The main uses of phenol, consuming two-thirds of its making, include its transformation to precursors for plastics. Condensation with acetone develops bisphenol-A, a key precursor to epoxide resins and polycarbonates. Condensation of alkylphenols, phenol, or diphenols with formaldehyde will give phenolic resins, a well-known example of which is Bakelite. Partial hydrogenation of phenol will give cyclohexanone, a precursor to nylon. Nonionic detergents are formed by alkylation of phenol to give the alkylphenols, e.g., nonylphenol, which is then exposed to ethoxylation.

Medical

Phenol is also a useful precursor to a huge collection of drugs, most notably aspirin but also several herbicides and pharmaceutical drugs. Phenol is an element in liquid/liquid phenol–chloroform abstraction technique used in molecular biology for procurement nucleic acids from tissues or cell culture samples. Depending on the pH of the solution either DNA or RNA can be mined.

Niche

Use Phenol is so low-priced that it attracts many small-scale uses. It is a part of industrial paint strippers used in the aviation industry for the removal of polyurethane, epoxy and other chemically resistant coatings. Phenol byproducts have been used in the making of cosmetics including hair colorings, sunscreens, skin lightening preparations, as well as in skin toners or exfoliators. Still, due to safety reasons, phenol is banned from use in cosmetic merchandises in the European Union and Canada.

What is Phenol?

Phenol is an aromatic compound. The chemical formula of this organic compound is C_6H_6O.

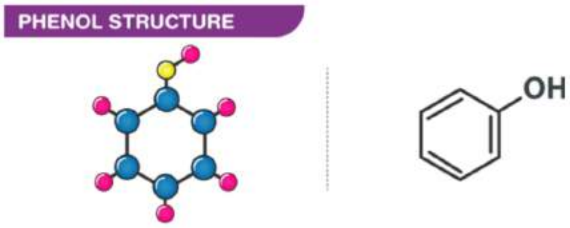
It consists of a hydroxyl group and phenyl group attached to each other. It considerably dissolves in water. Earlier it was used as carbolic soap. It is mildly acidic and is corrosive to the respiratory tract, eyes, and skin.
Phenol is a crystalline solid white in color and needs to be handled with care as it can cause chemical burns. Friedlieb Ferdinand Runge discovered Phenol in the year 1834. It was extracted from coal tar. It is also known as phenolic acid. If a compound is consisting of a six-membered aromatic ring and bonded to a hydroxyl group directly, then it can be referred to as phenol.

Natural Sources of Phenols

- Phenol is a constituent of coal tar and is formed during the decomposition of organic materials. Increased environmental levels of phenol may result from forest fires. It has been detected among the volatile components from liquid manure.

- Industrial sources of phenols and other related aromatics from a petroleum refinery, petrochemicals, basic organic chemical manufacture, coal refining, pharmaceuticals, tannery and pulp, and paper mills.

Phenol Structure – C_6H_6O



Phenol Structure – C6H5OH

Nomenclature of Phenols

Phenols are organic compounds containing at least one -OH group directly attached to the benzene ring. Depending upon the number of hydroxyl groups attached to the benzene ring, phenols can be classified as monohydric, dihydric and trihydric phenols.

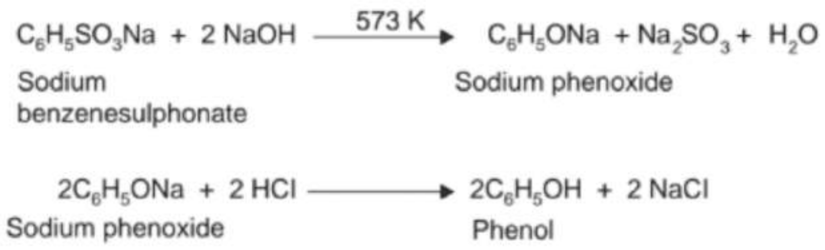
1. **Monohydric phenols** – The simplest member of the series is hydroxybenzene, commonly known as phenol, while others are named substituted phenols. The three isomeric hydroxyl toluenes are known as cresols.
2. **Dihydric phenols** – The three isomeric dihydroxy benzenes namely catechol, resorcinol, and quinol are better known by their common names.
3. **Trihydric phenols** – Trihydroxy phenols are known by the common names called pyrogallol, hydroxyquinol and phloroglucinol.

Synthesis of Phenols

Phenols can be synthesized by the following methods.

1. From sulphonic acids (by alkali fusion of sodium benzene sulphonate)

The first commercial process for the synthesis of phenol. Sodium benzene sulphonate is fused with sodium hydroxide at 573K to produce sodium phenoxide, which upon acidification yields phenol.



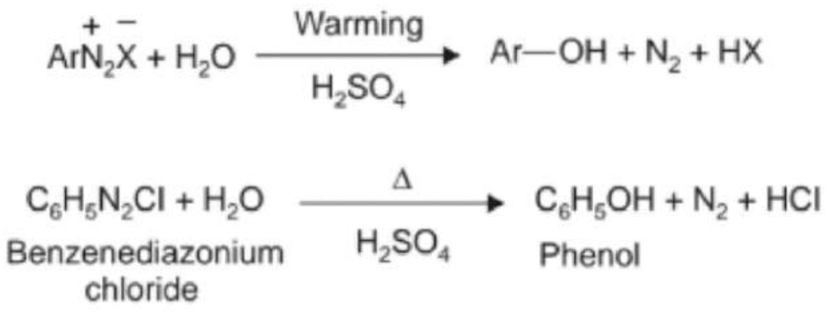
$$\underset{\text{Sodium benzenesulphonate}}{C_6H_5SO_3Na} + 2\,NaOH \xrightarrow{573\text{ K}} \underset{\text{Sodium phenoxide}}{C_6H_5ONa} + Na_2SO_3 + H_2O$$

$$\underset{\text{Sodium phenoxide}}{2C_6H_5ONa} + 2\,HCl \longrightarrow \underset{\text{Phenol}}{2C_6H_5OH} + 2\,NaCl$$

Synthesis of Phenols From Sulphonic Acids

2. From diazonium salts (by the hydrolysis of diazonium salt – laboratory method)

When a diazonium salt solution is steam distilled or is added to boiling dil.H2SO4, it forms phenol.



$$Ar\overset{+}{N_2}\overset{-}{X} + H_2O \xrightarrow[H_2SO_4]{\text{Warming}} Ar{-}OH + N_2 + HX$$

$$\underset{\text{Benzenediazonium chloride}}{C_6H_5N_2Cl} + H_2O \xrightarrow[H_2SO_4]{\Delta} \underset{\text{Phenol}}{C_6H_5OH} + N_2 + HCl$$

Synthesis of Phenols From Diazonium Salts

Properties of Phenol – C_6H_6O

C_6H_6O	**Phenol**
Molecular Weight/ Molar Mass	94.11 g/mol
Density	1.07 g/cm^3
Melting Point	40.5 °C
Boiling Point	181.7 °C

Reactions of Phenols

A hydroxyl group is attached to an aromatic ring and it is strongly activating ortho/para director, phenols possess considerable reactivity at their ortho and para carbons toward electrophilic aromatic substitution.

1. Reactions of the Aromatic Ring

The -OH group in phenol is ortho and para directing because it increases electron density at ortho and para positions due to resonance. Thus phenol undergoes electrophilic substitution reactions.

2. Halogenation

Like -NH_2 group, -OH group is so much activating that it is rather difficult to prevent poly substitution. If it is required to arrest the reaction at the mono substitution stage, the reaction should be carried out in non-polar solvents like CCl_4 and CS_2 and at lower temperatures.

C_6H_6O Uses (Phenol)

- It is used as a precursor in drugs
- It is used as an antiseptic
- It is used in the production of nylon
- It is used to preserve vaccines
- It is used in oral analgesics
- Derivatives of phenol are used in beauty products like hair colour and sunscreen
- It is used in the synthesis of plastics
- It is used to produce detergents and carbonates