UNIT - 11

ALCOHOLS, PHENOLS and EATHERS

Alcohols and Phenols -

When a hydrogen of aliphatic or aromatic hydrocarbon is replaced by (-OH) group then the compounds which are obtained are called alcohols and phenols.

$$R-H \xrightarrow{OH} R-OH$$

Aliphatic Hydrocarbon Alcohol

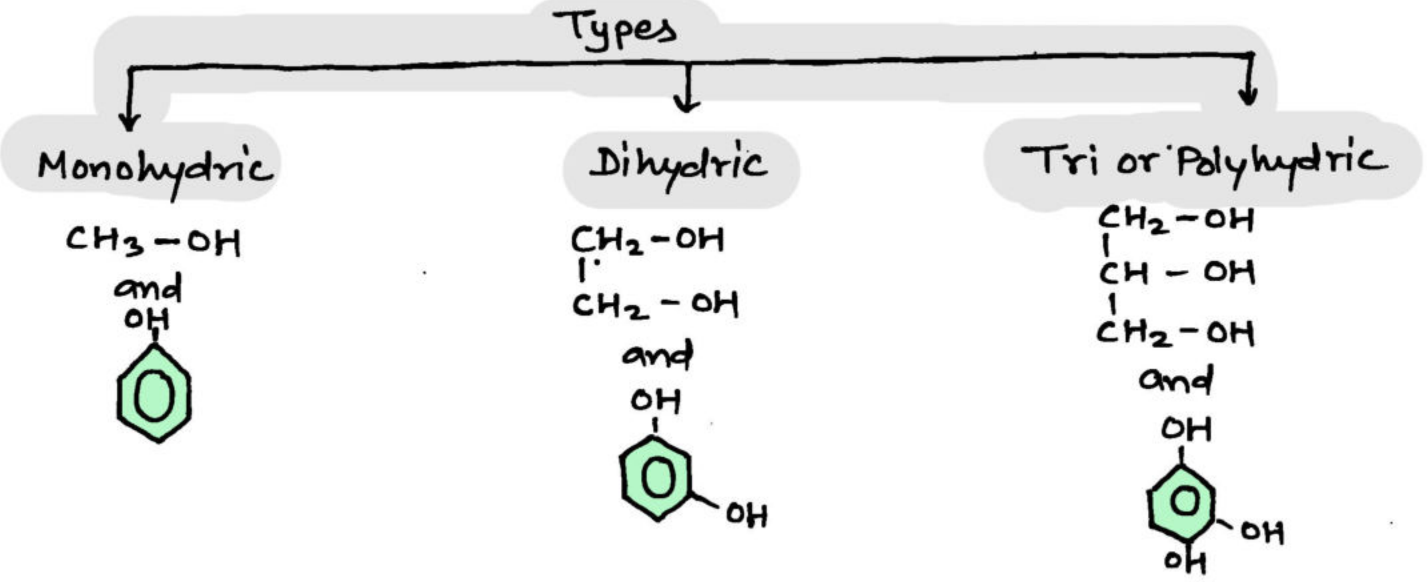
or $Ar-H \xrightarrow{OH} Ar-OH$

Aromatic hydrocarbon Phenol

- Also called Hydroxy Derivative of hydrocarbons.

Classification of Alcohols and Phenols —

[A.] On the basis of number of (-OH) group -



[B.] On the basis of hybridization state of Carbon atom to which (-OH) group is attatched

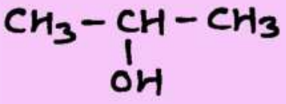
1. Compounds having $C_{sp^3}-OH$ bond.
2. Compounds having $C_{sp^2}-OH$ bond.

1.) Compounds having $C_{sp^3}-OH$ bond

(a) Primary, Secondary and tertiary Alcohols

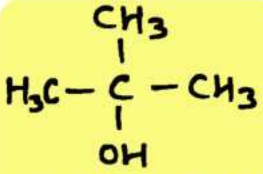
CH_3-CH_2-OH

Primary (1°)



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

secondary (2°)



$H_3C-\overset{CH_3}{\overset{|}{\underset{OH}{\underset{|}{C}}}}-CH_3$

Tertiary (3°)

(b) Allylic Alcohols

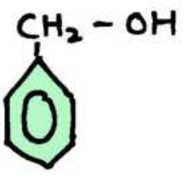
In these type of alcohols OH group is attatched to the sp^3 hybridized carbon which itself attached to a double bonded carbon atom.

$CH_2=CH-CH_2-OH$ → Prop-2-ene-1-ol

Allylic alcohol

(c) Benzylic Alcohols

In these type alcohols the OH group is attached to the sp^3 hybridized carbon which itself attached to a benzene ring.



→ Benzylic alcohol

2.1 Compounds having $C_{sp^2}-OH$ bond

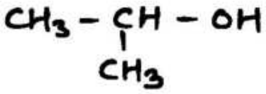
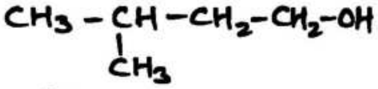
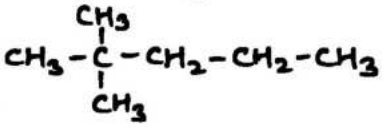
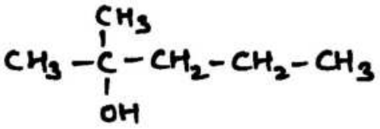
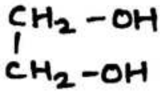
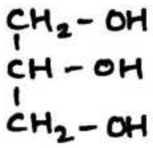
Vinylic Alcohol –

In these type of alcohols OH group is attached to a double bonded carbon atom.

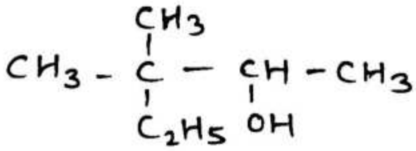
$CH_2=CH-OH$ Vinylic Alcohol

Nomenclature of Alcohols

1. In common system alcohols are named as alkyl alcohol.
2. In common system the word n, Iso, Neo, Sec., tertiary etc. are used
3. In IUPAC system the name of alcohol are derived from corresponding alkane by replacing 'e' of alkane by 'ol'.

S.N.	Compound	Common Name	IUPAC Name
1.	CH_3-OH	Methyl Alcohol	Methanol
2.	CH_3-CH_2-OH	Ethyl Alcohol	Ethanol
3.	 $CH_3-\underset{CH_3}{\underset{\vert}{CH}}-OH$	Isopropyl Alcohol	Propan-2-ol
4.	 $CH_3-\underset{CH_3}{\underset{\vert}{CH}}-CH_2-CH_2-OH$	Iso pentyl Alcohol	3-Methyl·Butan-1-ol
5.	 $CH_3-\overset{CH_3}{\overset{\vert}{\underset{CH_3}{\underset{\vert}{C}}}}-CH_2-CH_2-CH_3$	Neohexyl Alcohol	3,3-dimethyl butan-1-ol
6.	 $CH_3-\overset{CH_3}{\overset{\vert}{\underset{OH}{\underset{\vert}{C}}}}-CH_2-CH_2-CH_3$	Tert. hexyl Alcohol	2-Methyl pentan-2-ol
7.	 $\begin{array}{l}CH_2-OH\\\vert\\CH_2-OH\end{array}$	Ethylene Glycol	Ethan-1,2-diol
8.	 $\begin{array}{l}CH_2-OH\\\vert\\CH-OH\\\vert\\CH_2-OH\end{array}$	Glycerol	Propan-1,2,3-triol

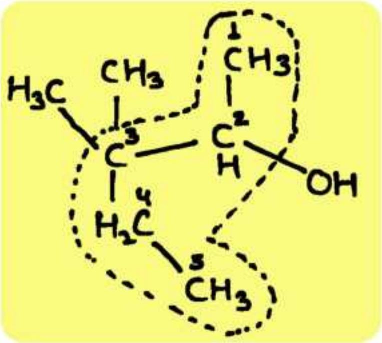
Q. Write the IUPAC Name of the following



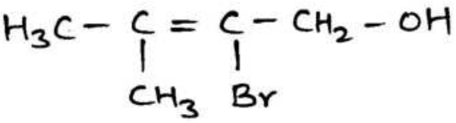
$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{C_2H_5}{|}}{C}}-\underset{\underset{OH}{|}}{CH}-CH_3$

[CBSE 2018]

Sol. The IUPAC Name of the given compound is 3,3-dimethylpentan-2-ol.



Q. Write the IUPAC Name of the following Compound



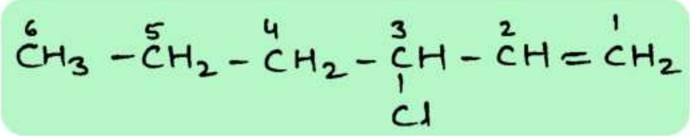
$H_3C-\underset{\underset{CH_3}{|}}{C}=\underset{\underset{Br}{|}}{C}-CH_2-OH$

[CBSE 2017]

Sol. 3-bromo-4-methylpent-3-en-1-ol

Q. Draw the structure of Hex-1-en-3-diol from ethanol?

Sol.



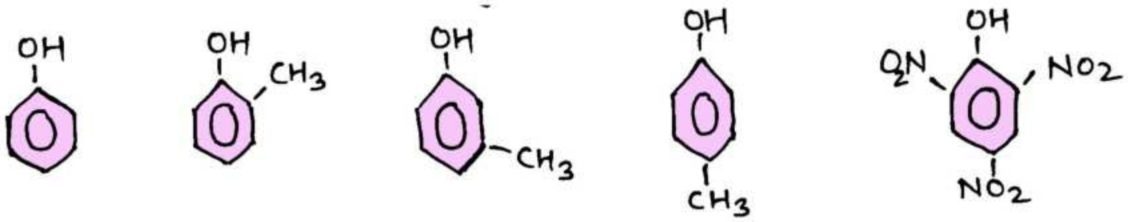
$\overset{6}{C}H_3-\overset{5}{C}H_2-\overset{4}{C}H_2-\underset{\underset{Cl}{|}}{\overset{3}{C}}H-\overset{2}{C}H=\overset{1}{C}H_2$

Nomenclature of Phenol

Phenol is a hydroxy derivative of benzene.

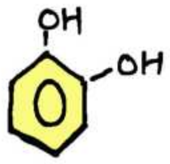
- In IUPAC and common system, it is Known as Phenol.

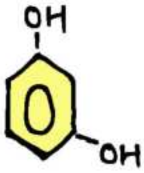
Example.



Common →	Phenol	O-Cresol	m-Cresol	P-Cresol	Picric Acid
IUPAC →	Phenol	2-Methyl Phenol	3-Methyl Phenol	4-Methyl Phenol	2,4,6-Trinitro Phenol

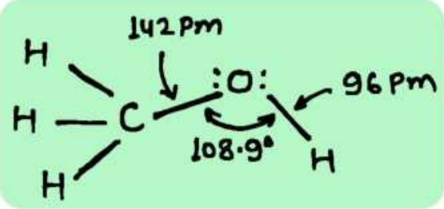
Name of Some Dihydric Phenol -

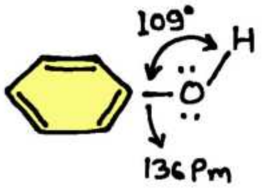




Common →	Catechol	Resorsinol	Quinol
IUPAC →	Benzen-1,2-diol	Benzene-1,3-diol	Benzene-1,4-diol

Structure of Alcohol and Phenol group -





(1.) In alcohol the oxygen atom of OH group is attached with the carbon of alkyl group by σ bond and in alcohol C-O bond length is 142 Pm and $\overset{O}{C\;\;\;H}$ bond angle is 108.9°, which is less than tetrahedral angle due to the presence of long pair of electron on oxygen atom.

In alcohol both C-O and O-H bond are polar in nature.

(2.) In phenol oxygen atom of OH group is attached with sp^2 hybridized carbon of aromatic ring.

Note CBSE 2012 The C-O bond length in phenol is 136 Pm which is less than alcohol due to following reasons-

(i) In phenol lone pair of oxygen is conjugation with π-bond of aromatic ring and acquire partial double bond character

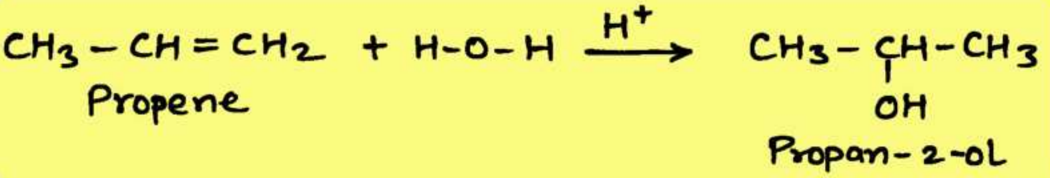
(ii) In phenol oxygen atom is attached to sp^2 hybridized carbon.

Preparation of Alcohols

1. From alkenes

(a) By hydration of alkene -

When alkene react with water in the presence of acid catalyst, then alcohol is formed. On unsymmetrical alkene, when water molecule is added, then product is formed according to Markovnikowff's Rule.



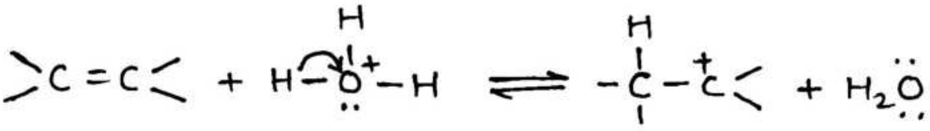
$$\underset{\text{Propene}}{CH_3-CH=CH_2} + H-O-H \xrightarrow{H^+} \underset{\text{Propan-2-ol}}{CH_3-\underset{OH}{CH}-CH_3}$$

[CBSE 2013,14 10,15]

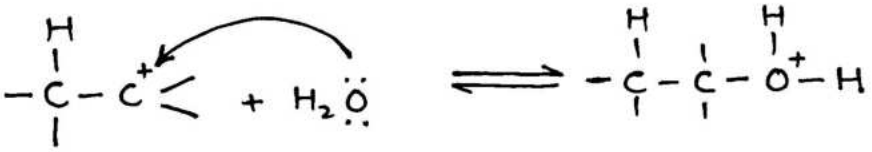
Mechanism :- [CBSE 2012]

Step 1 : $H_2O + H^+ \longrightarrow H_3O^+$

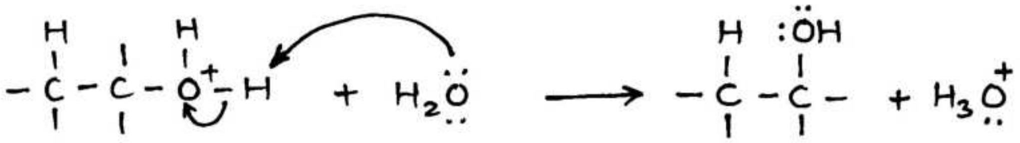
[CBSE 2017]



Step 2 :

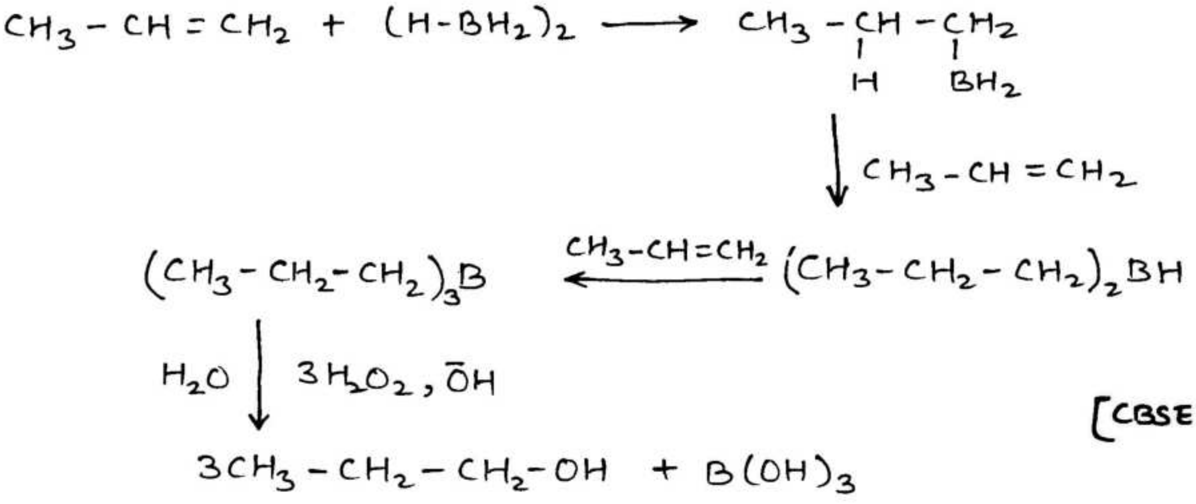


Step 3 :



(b) By hydroboration - oxidation -

When alkene react with diborane (B_2H_6), then trialkyl borane is formed which gives alcohol by the oxidation of H_2O_2 in presence of aqueous sodium hydroxide.



$$CH_3-CH=CH_2 + (H-BH_2)_2 \longrightarrow CH_3-\underset{H}{\underset{|}{C}}H-\underset{BH_2}{\underset{|}{C}}H_2 \xrightarrow{CH_3-CH=CH_2} (CH_3-CH_2-CH_2)_2BH \xrightarrow{CH_3-CH=CH_2} (CH_3-CH_2-CH_2)_3B \xrightarrow[H_2O]{3H_2O_2,\ \bar{O}H} 3CH_3-CH_2-CH_2-OH + B(OH)_3$$

Propan-1-ol

[CBSE 2013,16]

2. From Carbonil Compounds -

(a) By the reduction of aldehydes and ketones

Aldehydes and Ketones are reduced to the corresponding alcohols by addition of hydrogen in the presence of reagent like Pt, Pd, Ni, $LiAlH_4$, $NaBH_4$ etc.

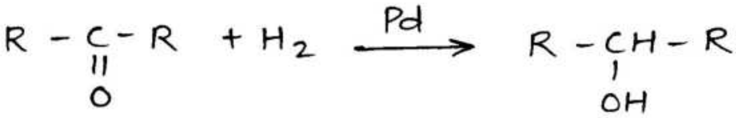
➤ **Aldehyde gives primary alcohol and ketone gives secondary alcohols by the reduction.**

{ In presence of Pt/Pd we take H_2 & rest of these take 2H }

eg.

$$R-CHO + H_2 \xrightarrow{Pd} R-CH_2-OH$$

Aldehyde Primary Alcohol



$$R-\underset{O}{\underset{||}{C}}-R + H_2 \xrightarrow{Pd} R-\underset{OH}{\underset{|}{C}}H-R$$

Ketone Secondary Alcohol

Q. Name the reagent which is used in the following conversion:
Butan-2-one to butan-2-ol

[CBSE 2008]

Sol. NiN_2 or $LiAlH_4$

(b) From the reduction of carboxylic acid and ester -

Carboxylic acid and ester gives alcohol by reduction.

$$R-\underset{\underset{O}{\|}}{C}-OH + 4H \xrightarrow{LiAlH_4} R-CH_2-OH + H_2O$$

Carboxylic Acid Alcohol

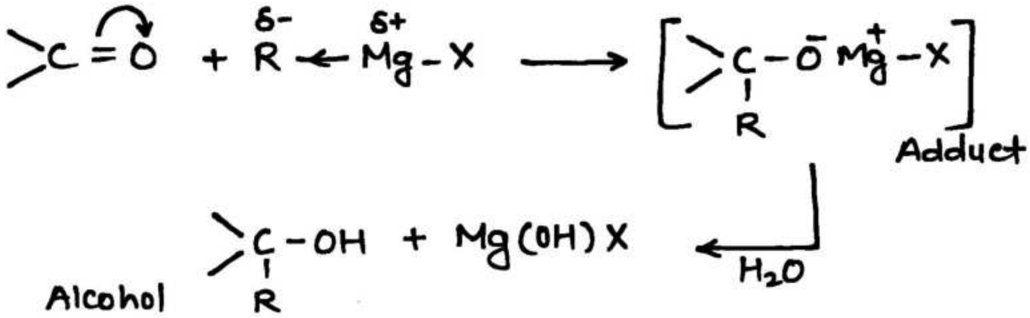
$$R-\underset{\underset{O}{\|}}{C}-O-R + 4H \xrightarrow{LiAlH_4} R-CH_2-OH + R-OH$$

Ester Alcohol

3. From Grignard Reagent -

[CBSE 2009]

When grignard reagent react with aldehyde and Ketone, then alcohol is formed

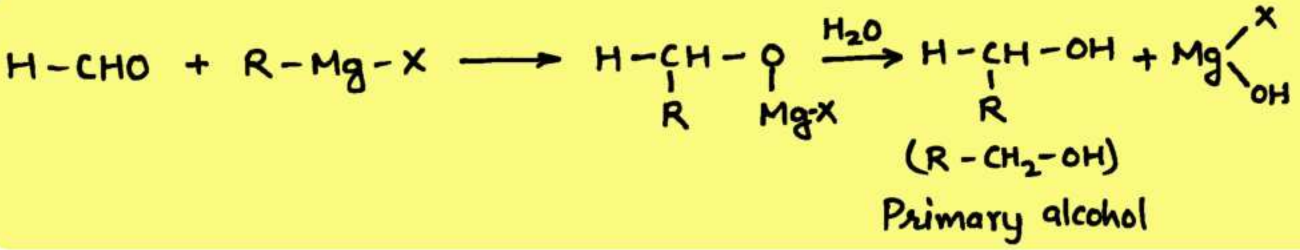


$$>C=O + \overset{\delta-}{R} \leftarrow \overset{\delta+}{Mg}-X \longrightarrow \left[>\underset{R}{\underset{|}{C}}-\bar{O}\overset{+}{Mg}-X\right] \xrightarrow{H_2O} >\underset{R}{\underset{|}{C}}-OH + Mg(OH)X$$

Adduct

Alcohol

(a) When formaldehyde (HCHO) react with Grignard reagent then primary alcohol is formed



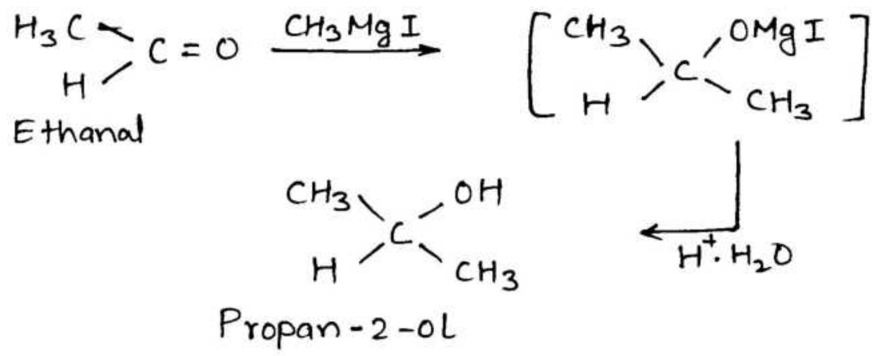
$$H-CHO + R-Mg-X \longrightarrow H-\underset{R}{\underset{|}{C}}H-\underset{MgX}{\underset{|}{O}} \xrightarrow{H_2O} H-\underset{R}{\underset{|}{C}}H-OH + Mg\begin{matrix}X\\OH\end{matrix}$$

$(R-CH_2-OH)$
Primary alcohol

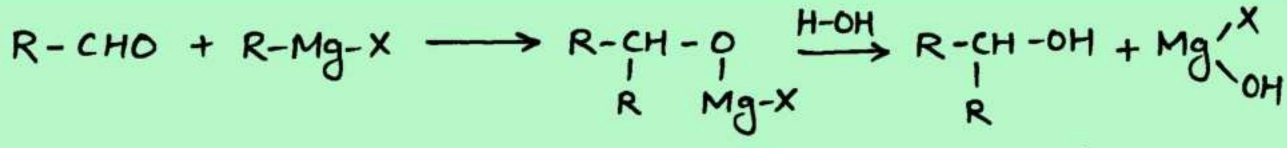
Q. How will you convert ethanal to propan-2-ol ?

[CBSE 2013]

Sol.



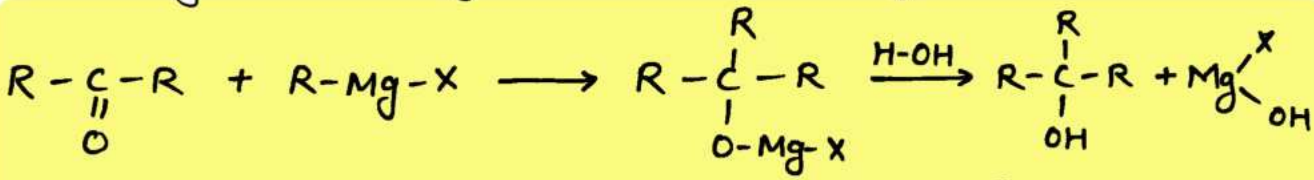
(b) Other aldehyde gives secondary alcohols with R-Mg-X



$$R-CHO + R-Mg-X \longrightarrow \underset{R}{\underset{|}{R-CH}}-\underset{Mg-X}{\underset{|}{O}} \xrightarrow{H-OH} \underset{R}{\underset{|}{R-CH}}-OH + Mg\begin{smallmatrix}X\\OH\end{smallmatrix}$$

Sec. Alcohol

(c) Ketone gives tertiary alcohol with R-Mg-X



$$R-\underset{O}{\underset{\|}{C}}-R + R-Mg-X \longrightarrow R-\overset{R}{\overset{|}{\underset{O-Mg-X}{\underset{|}{C}}}}-R \xrightarrow{H-OH} R-\overset{R}{\overset{|}{\underset{OH}{\underset{|}{C}}}}-R + Mg\begin{smallmatrix}X\\OH\end{smallmatrix}$$

Ter. Alcohol

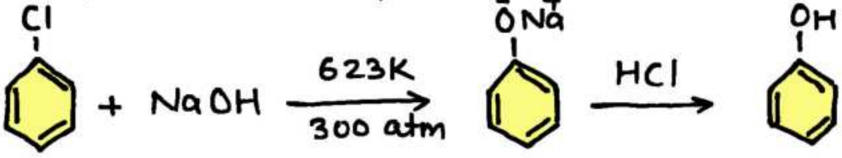
Preparation Method of Phenol

[CBSE 2019]

In laboratory phenol is prepared by **benzene** derivative by anyone of the following method -

1. From haloarenes

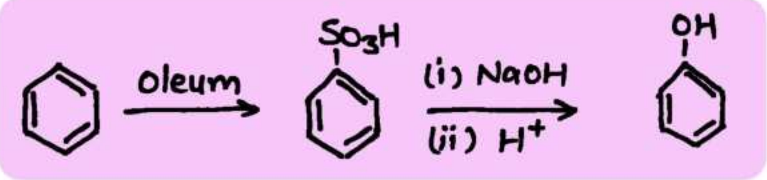
Chlorobenzene is fused with NaOH at 623K and 320 atmospheric pressure. Phenol is obtained by acidification of sodium phenoxide so produced.



2. From benzenesulphonic acid -

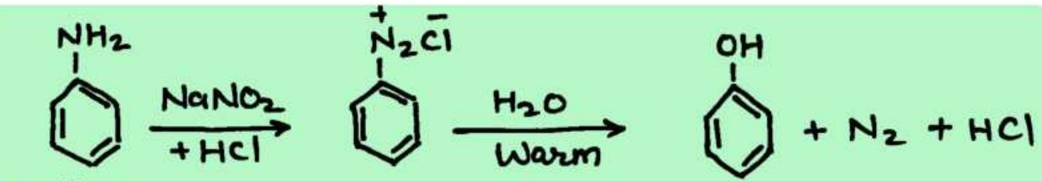
Benzene is sulphonated with oleum and benzene sulphonic acid so formed is converted to sodium phenoxide on heating with molten sodium hydroxide.

Acidification of the sodium salt gives phenol.



3. From diazonium salts -

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

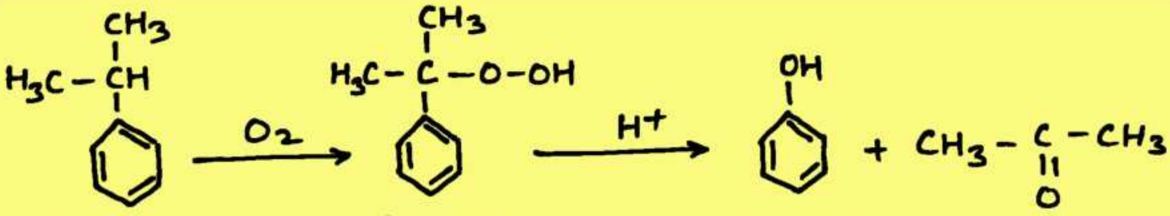


Aniline Benzene diazonium Chloride

Imp.

4. From Cumene -

Most of the phenol is manufactured from cumene. In this method cumene is oxidised in the presence of air then cumene Hydroperoxide is obtained. Now it react with dilute acid and gives phenol and acetone.



Cumene Cumene Hydroperoxide Phenol Acetone

Physical Properties

Boiling point -

→ The boiling point of alcohols and phenols increase with increase in the number of carbon atoms (increase in van der walls forces).

Eg. Boiling point of Butanol is more than ethanol because in butanol alkyl group is large and its molecular weight is also more than ethanol.

[CBSE 2009, 11]

→ In isomeric alcohol, the boiling point of unbranched alcohol will be more than branched alcohol.

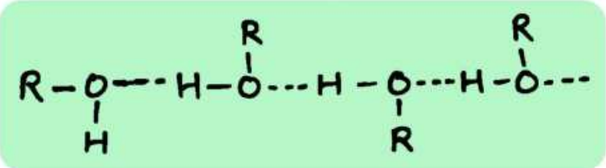
Therefore the boiling point of different alcohol will be as -

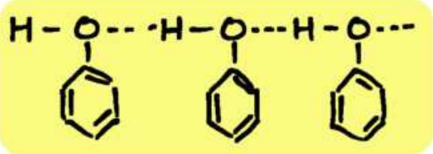
Primary Alcohol > Sec. Alcohol > Tertiary Alcohol

[because of decrease in Van der walls forces with decrease in surface area]

[CBSE 2008, 11]

→ The OH group in Alcohols and phenols is involved in intermolecular hydrogen bonding

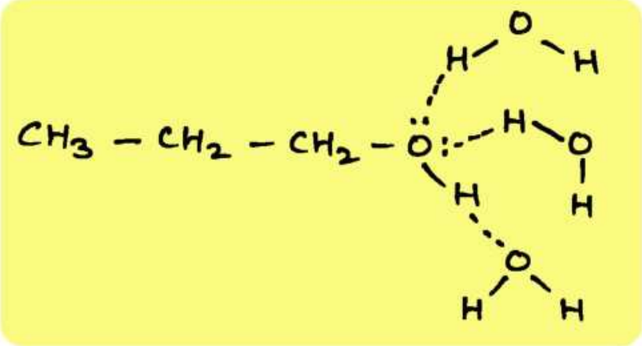




Solubility

→ Solubility of alcohols and phenols in water is due to their ability to form hydrogen bonds with water molecules.

→ The solubility decreases with increase in size of alkyl / aryl (hydrophobic) groups.



Chemical Properties of Alcohols

Alcohol represent the following two types of chemical reaction -

1. Reaction in which cleavage of $-O-H$ bond takes place
2. Reaction in which cleavage of $-C-OH$ bond takes place

(1.) Reaction in which cleavage of $-O-H$ bond takes place

In this type reaction alcohol react as nucleophile and the order of reactivity of different alcohol is as -

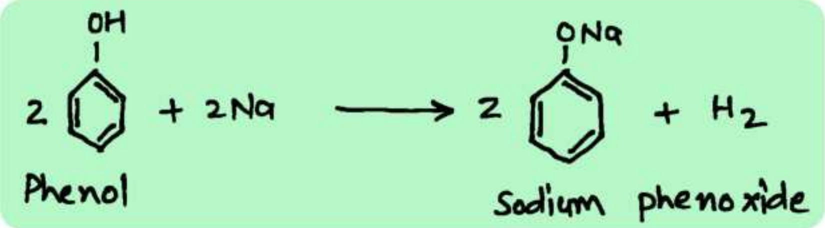
Primary Alcohol > Sec. Alcohol > Tertiary Alcohol

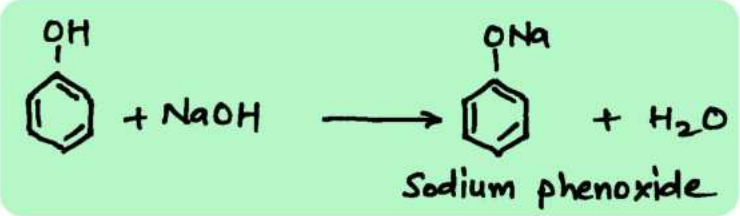
(i) Acidic Nature of Alcohol and Phenol

(a) Reaction with metal :

Alcohols and Phenols react with active metals such as sodium, potassium and aluminium to yield corresponding alkoxides / phenoxides and hydrogen.

$$2R-O-H + 2Na \longrightarrow \underset{\text{Sodium Alkoxide}}{2R-O-Na} + H_2$$



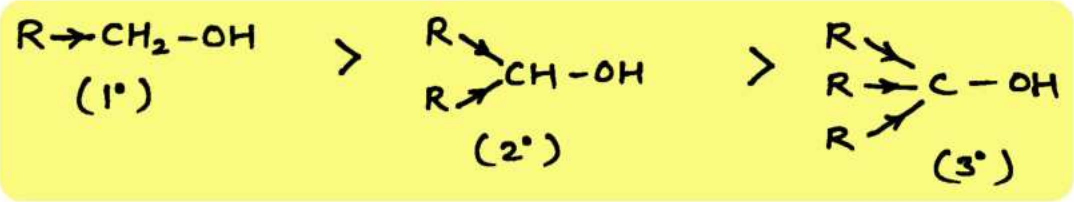


(b) Acidity of Alcohol –

The acidic nature of alcohol is due to the polar nature of -O-H bond.

- In alcohol an electron releasing group $(-CH_3, -C_2H_5)$ increase the electron density on oxygen atom and decrease the polarity of -O-H bond. Due to this the acidic strength of alcohol also decrease.

Therefore the order of acidity of different alcohol is as



Q. Why alcohols are weak acid than compare to water? Explain.

Sol. In alcohol, alkoxide ion is formed after removing H^+ ion and in water hydroxide ion is formed after removing H^+ ion.

But alkoxide ion is less stable than compare to OH^- ion due to the presence of more electron density on oxygen atom. Therefore, alcohol act as weak acid than compare to water.

$$R-O\,\vert\,H \longrightarrow \underset{\text{Alkoxide ion (Less Stable)}}{R-\bar{O}} + \overset{+}{H}$$

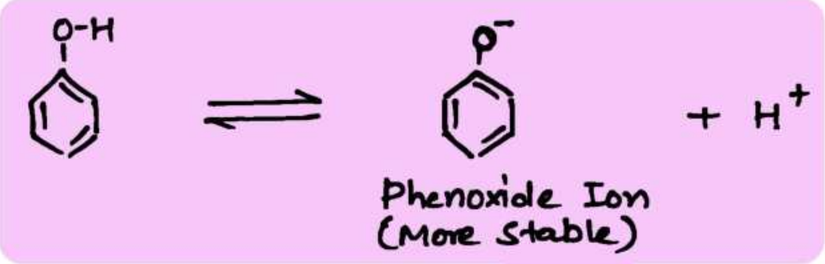
(c) Acidity of Phenol –

[CBSE 2009, 11, 15]

Phenol is more acidic in nature than compare to alcohol.

- **Reason –** The ionisation of alcohol and phenol takes place as

$$R-OH \rightleftharpoons \underset{\text{Alkoxide Ion}}{R-\bar{O}} + H^+$$

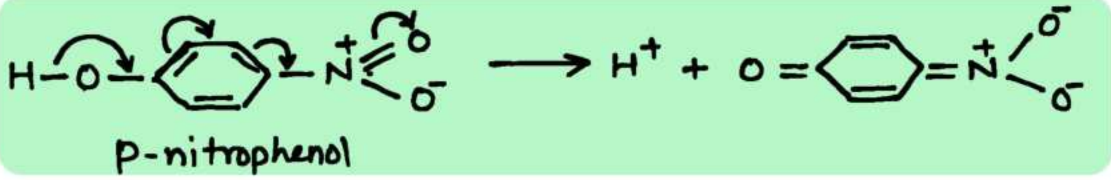


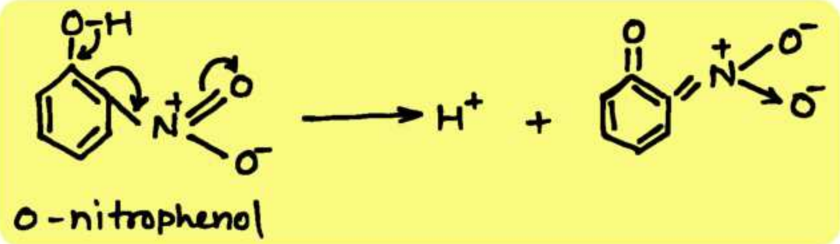
Due to the higher electronegativity of sp^2 hybridised carbon of phenol to which –OH is attached, electron density decreases on oxygen. This increase the polarity of O-H bond and result in an increase in ionisation of phenols than that of alcohols.

In alcohol, alkoxide ion is formed and in phenol, phenoxide ion after removing H^+ ion. Phenoxide ion is more stable due to resonance than compare to alkoxide ion. Therefore phenol is more acidic than alcohol.

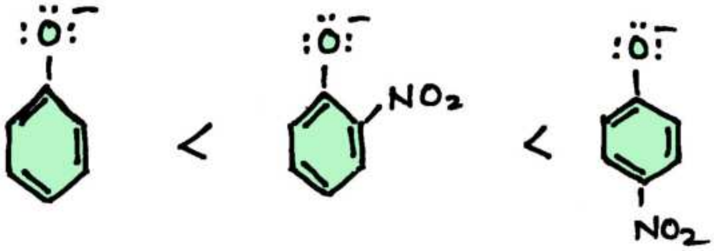
Q. Explain the following observation - [CBSE 2009,11]
o and p nitrophenols are more acidic than phenol.

Sol. NO_2 being an electron withdrawing group when present at ortho and para-positions withdraws electron density from benzene ring thereby decreasing the electron density of O-H bond and thus, make the release of proton easier.





Also, the $-NO_2$ group intensifies the negative charge of phenoxide ion and thus, stablises it and hence increases its acidic strength as



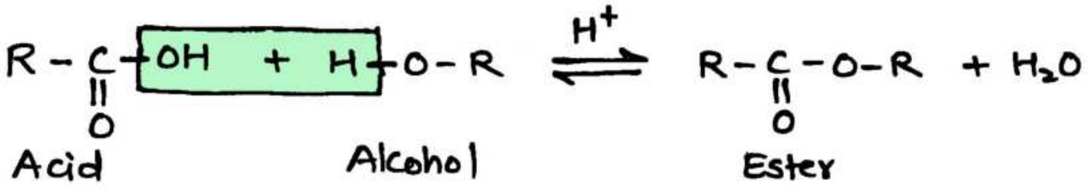
Hence ortho and Para nitrophenol are more acidic than phenol.

(ii) Esterification of Alcohol –

When alcohol react with carboxylic acid, acid chloride and acid anhydride, then ester is formed and the clevage of OH bond of alcohol takes place. This is called esterification.

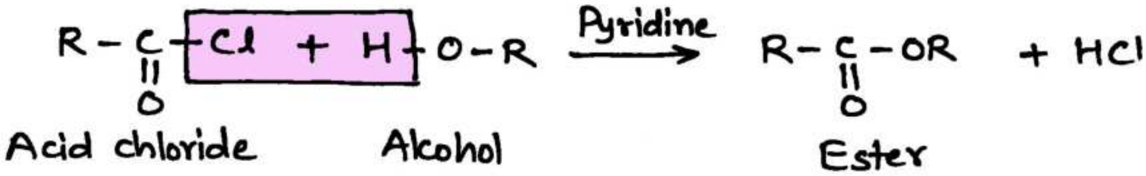
(a) Reaction with carboxylic acid –

The reaction takes place in the presence of Concentrate H_2SO_4.



$$R-\underset{\underset{O}{\|}}{C}\boxed{-OH + H-}O-R \xrightleftharpoons{H^+} R-\underset{\underset{O}{\|}}{C}-O-R + H_2O$$

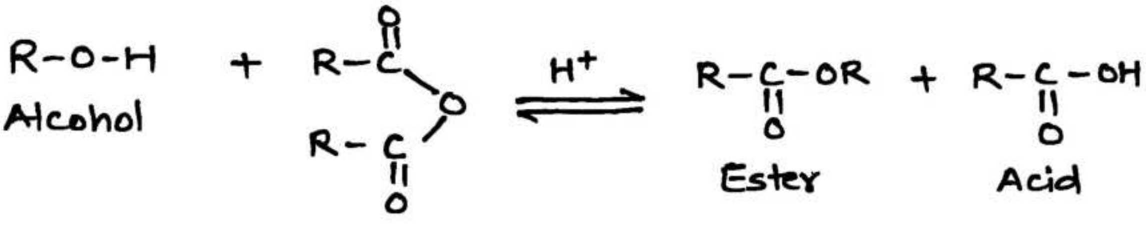
(b) Reaction with Acid chloride –



$$R-\underset{\underset{O}{\|}}{C}\boxed{-Cl + H-}O-R \xrightarrow{Pyridine} R-\underset{\underset{O}{\|}}{C}-OR + HCl$$

(C) Reaction with Acid Anhydride

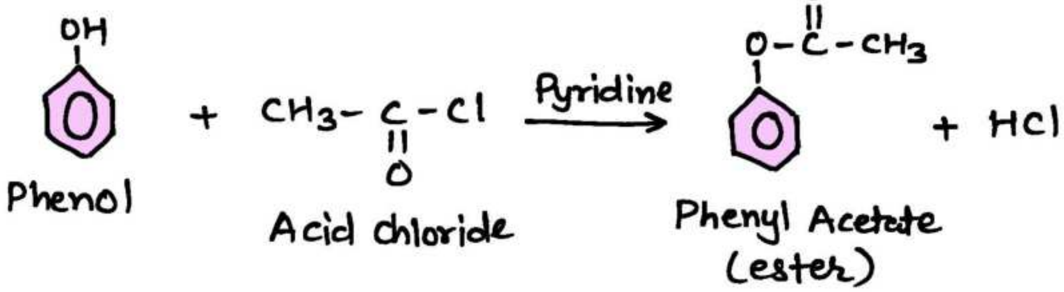
This reaction takes place in the presence of acid.



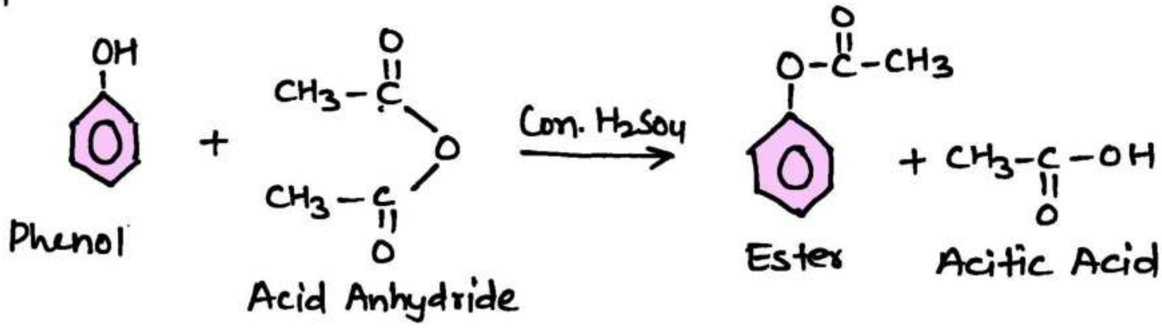
$$R-O-H + \begin{array}{l} R-\overset{\overset{O}{\|}}{C}\diagdown \\ \qquad\quad O \\ R-\underset{\underset{O}{\|}}{C}\diagup \end{array} \xrightleftharpoons{H^+} R-\underset{\underset{O}{\|}}{C}-OR + R-\underset{\underset{O}{\|}}{C}-OH$$

(iii) Esterification of Phenol -

When phenol react with acid chloride or with acid anhydride, then ester is formed.



and



(2.) Reaction in which cleavage $\geq C - OH$ bond takes place -

In these type of reaction, alcohol behaves as a electrophile.

(i) Reaction with hydrogen halides -

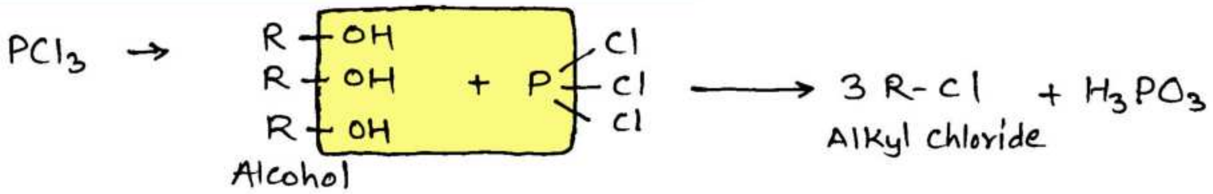
$$\underset{\text{Alcohol}}{R-}\boxed{OH + H}\underset{\text{Hydrogen Halide}}{-X} \xrightarrow{\text{Conc. HCl + ZnCl}_2} \underset{\text{Alkyl Halide}}{R-X} + H_2O$$

- Conc. HCl + $ZnCl_2$ → Lucas Reagent

Eg.

$$\underset{\text{Ethanol}}{CH_3-CH_2-}\boxed{OH + H}-Cl \xrightarrow{\text{Conc. HCl+ZnCl}_2} \underset{\text{Ethyl Chloride}}{CH_3-CH_2-Cl} + H_2O$$

(ii) Reaction with phosphorous halide -

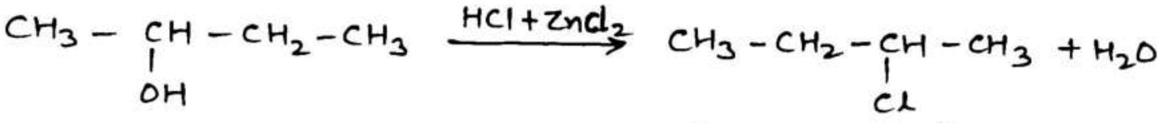


$$PCl_3 \rightarrow \underset{\text{Alcohol}}{\begin{matrix} R-OH \\ R-OH \\ R-OH \end{matrix}} + P\begin{matrix} -Cl \\ -Cl \\ -Cl \end{matrix} \longrightarrow \underset{\text{Alkyl chloride}}{3\,R-Cl} + H_3PO_3$$

Q. How will you distinguish between butan-1-ol and butan-2-ol ?

Sol. by Lucas reagent [Conc. HCl + $ZnCl_2$] [CBSE 2019]

$$CH_3-CH_2-CH_2-CH_2-OH \xrightarrow{HCl+ZnCl_2} \text{No reaction}$$

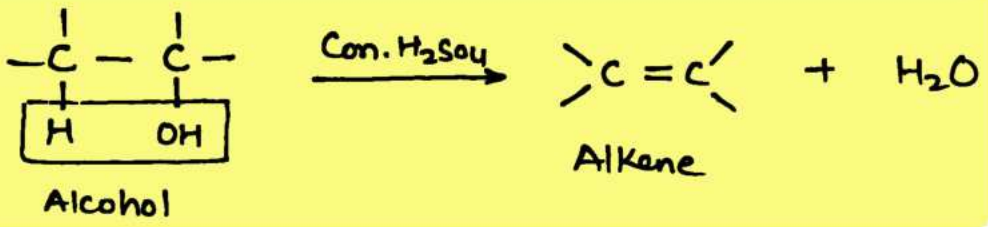


$$\underset{\displaystyle OH}{CH_3-\overset{}{CH}-CH_2-CH_3} \xrightarrow{HCl+ZnCl_2} CH_3-CH_2-\underset{\displaystyle Cl}{CH}-CH_3 + H_2O$$

(white ppt.)

(3.) Dehydration -

Removing of water molecule from alcohol is called dehydration of alcohol. It is an elimination reaction in which Concentrate H_2So_4, Phosphorus Pentaoxide (P_2O_5), Alumina (Al_2O_3) is used for dehydration and alkene is formed as product.



➤ The order of reactivity of different alcohols towards dehydration is as follows -

Tertiary Alcohol > Secondary Alcohol > Primary Alcohol

• Dehydration of Ethanol -

[CBSE 2011, 13]

Ethanol undergoes dehydration by heating it with Con. H_2So_4 at 443K temperature.

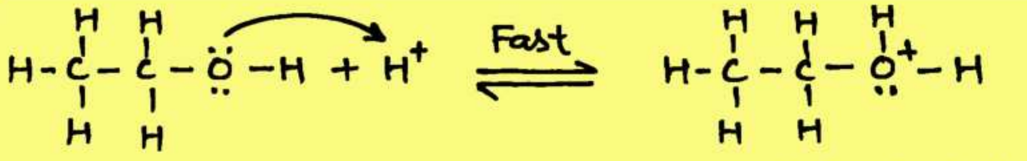
$$\underset{H}{CH_2}-\underset{OH}{CH_2} \xrightarrow[443K]{Con.\ H_2So_4} CH_2=CH_2 + H_2O$$

Ethanol   Ethene

• Mechanism of dehydration of Ethanol – [CBSE 2015]

The mechanism of dehydration of ethanol in the presence of Con. H_2SO_4 involve the following steps-

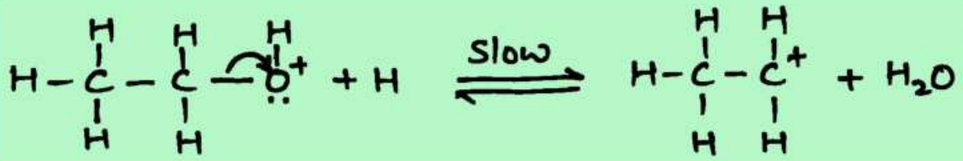
Step 1: In this step ethanol accept proton and form the protonated alcohol or oxonium Ion.



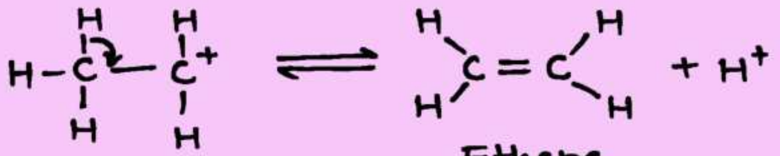
Ethanol

Protonated alcohol [Ethyl oxonium ion]

Step 2: In this step carbocation is formed. It is slow and rate determining step.



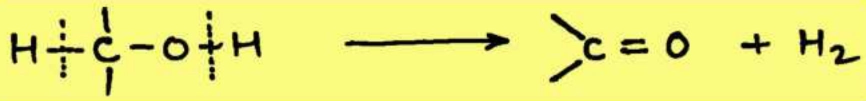
Step 3: In this step ethene is formed by the elimination of a proton.



Ethene

(4.) Oxidation –

Oxidation of alcohol involve the formation of carbon-oxygen bond with cleavage of an 'O-H' bond and 'C-H' bond.



- This process is also known as **dehydrogenation**.

Primary, Secondary and Tertiary Alcohol give different product when oxidised by acidic $K_2Cr_2O_7$ or basic $KMnO_4$.

(i) Primary Alcohol –

[CBSE 2008]

It is oxidised into aldehyde which is further oxidised into an acid.

$$CH_3-CH_2-OH \xrightarrow[-H_2O]{[O]} \underset{\text{Aldehyde}}{CH_3-CHO} \xrightarrow{[O]} \underset{\text{Acid}}{CH_3-COOH}$$

$$CH_3-CH=CH-CH_2-OH \xrightarrow{PCC} CH_3-CH=CH-CHO$$

[CBSE 2017]

Q. How is the following conversion carried out?

Ethyl chloride to ethanal? [CBSE 2014]

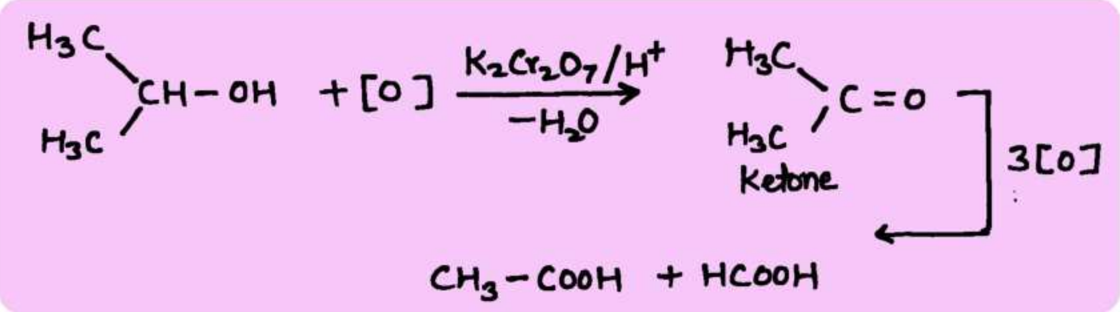
Sol.

$$\underset{\text{Ethyl chloride}}{CH_3-CH_2-Cl} \xrightarrow[\substack{S_N2\\ \text{reaction}}]{aq.\ NaOH} \underset{\text{Ethanol}}{CH_3-CH_2-OH}$$

$$\underset{\text{Ethanol}}{CH_3-CH_2-OH} \xrightarrow[\substack{CrO_3/PCC\\ \text{oxidation}}]{[O]} \underset{\text{Ethanal}}{CH_3-CHO}$$

(ii) Secondary Alcohol –

It is oxidised into Ketone which is further oxidised into acids.



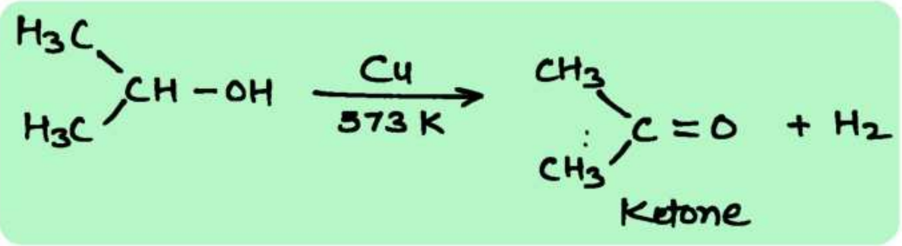
(iii) Tertiary Alcohol -

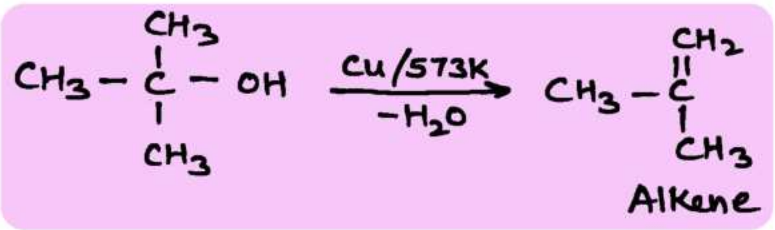
It is not oxidised in ordinary condition but in the presence of strong oxidising agent, a mixture of carboxylic acid is formed.

(5.) Dehydrogenation -

When the vapour of primary and secondary alcohol is passed over heated copper at 573 K (300°C), then dehydrogenation takes place and aldehyde & Ketone is formed while tertiary alcohol give alkane by dehydration

$$\underset{\text{Primary Alcohol}}{CH_3-CH_2-OH} \xrightarrow[573K]{Cu} \underset{\text{Aldehyde}}{CH_3-CHO} + H_2$$





$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-OH \xrightarrow[-H_2O]{Cu/573K} CH_3-\underset{CH_3}{\overset{CH_2}{\underset{|}{\overset{\|}{C}}}}$$

Alkane

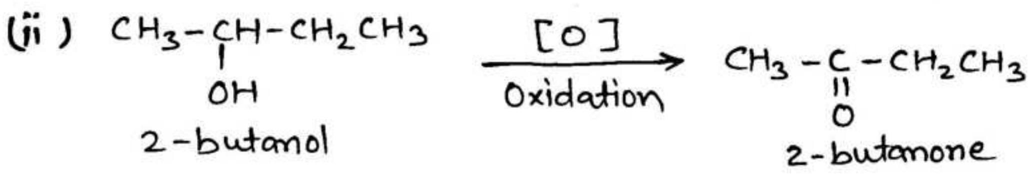
Q. Draw the structure and name the product formed if the following alcohols are oxidised. Assume that an excess of oxidising agent is used.

(i) $CH_3CH_2CH_2CH_2OH$ (ii) 2 - butanol

(iii) 2 - methyl - 1 - propanol [CBSE 2012]

Sol. (i) $CH_3-CH_2-CH_2-CH_2-OH \xrightarrow[\text{Oxidation}]{[O]} CH_3-CH_2CH_2COOH$

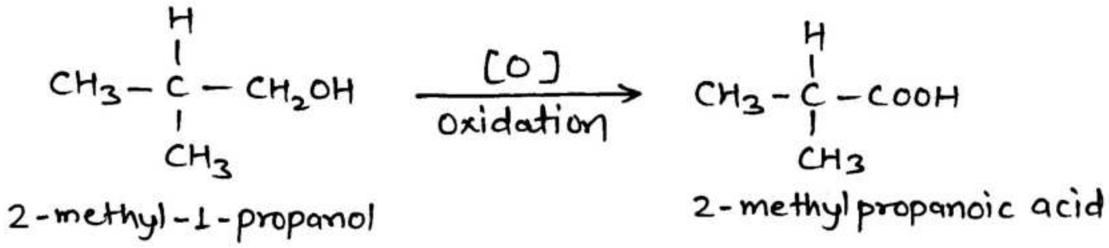
Butanoic Acid



(ii) $$CH_3-\underset{OH}{\underset{|}{C}H}-CH_2CH_3 \xrightarrow[\text{Oxidation}]{[O]} CH_3-\underset{O}{\underset{\|}{C}}-CH_2CH_3$$

2-butanol 2-butanone

(iii)

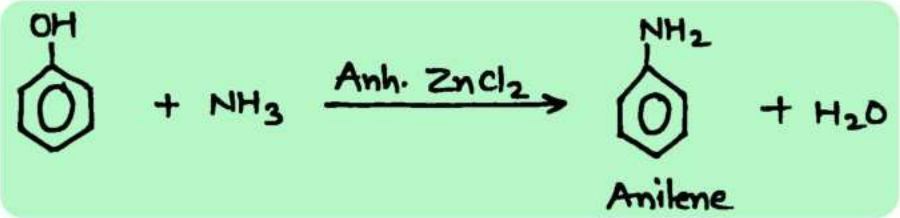


$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}}-CH_2OH \xrightarrow[\text{Oxidation}]{[O]} CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}}-COOH$$

Reaction due to -OH group of phenol-

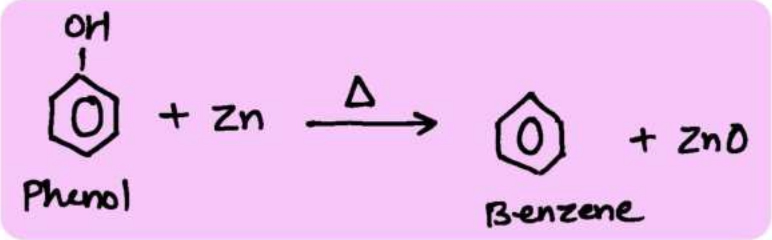
(i) Reaction with Ammonia (NH_3)-

When phenol react with ammonia in the presence of anhydrous $ZnCl_2$, then anilene is formed as a product.



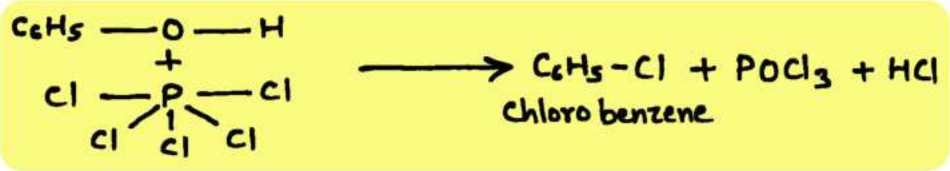
(ii) Reaction with Zinc-Powder -

When phenol is heated with zinc powder, then benzene is formed as a product.



(iii) Reaction with phosphorous Pentachloride (PCl_5)-

When phenol react with PCl_5, then chlorobenzene is formed as a product



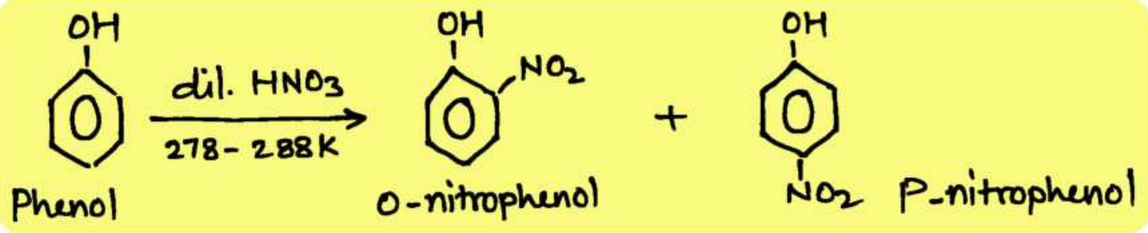
Reaction due to Benzene ring of Phenol

In phenol electrophilic substitution reaction takes place due to benzene ring. The -OH group in phenol is ortho and para directing group.

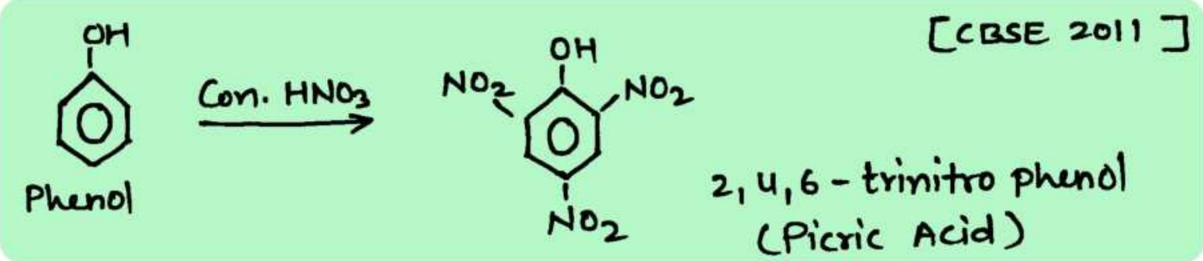
Therefore electrophilic substitution takes place at ortho and para position in benzene ring.

(i) Nitration -

At low temperature (278 K to 288 K), in the presence of dilute HNO_3 (Nitric Acid), phenol gives ortho and para nitro-phenol.

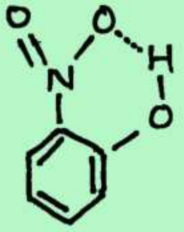


In nitration takes place in the presence of concentrate HNO_3, then 2-4-6 - trinitrophenol (Picric Acid) is formed as a product.

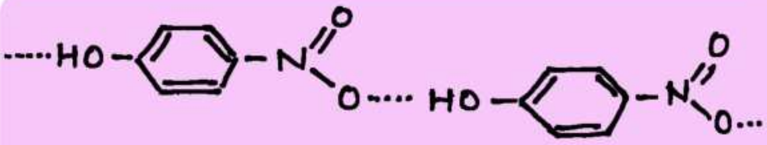


Note- [CBSE 2014]

The ortho and para isomers can be separated by steam distillation. O-Nitrophenol is steam volatile due to intra-molecular hydrogen bonding, while p-nitrophenol is less volatile due to intramolecular hydrogen bonding which causes the association of molecules.



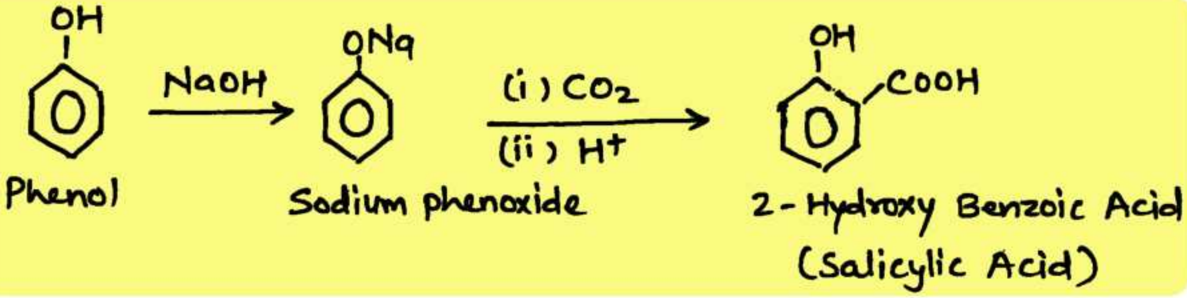
o-Nitrophenol
(Intramolecular H-bonding)



p-nitrophenol
(Intermolecular H-bonding)

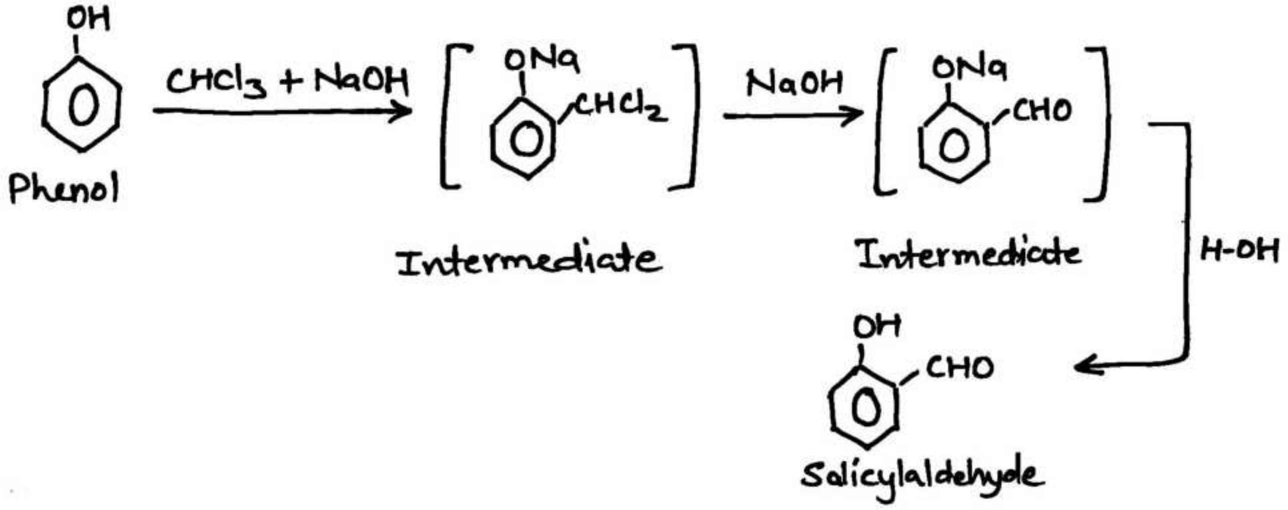
(ii) Kolbe's Reaction – [CBSE 2011,12,14,16]

Phenoxide ion is more reactive than phenol towards electrophilic substitution reaction. Therefore when phenoxide ion react with CO_2, then salicylic acid is formed as a product. This reaction is called Kolbe's reaction.



(iii) Reimer – Tiemann Reaction – [CBSE 2014]

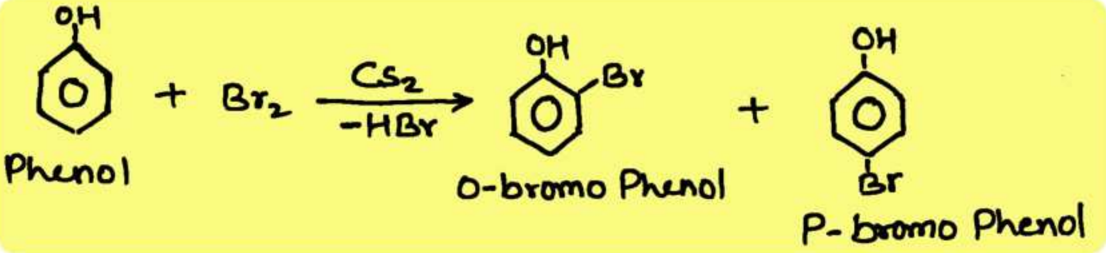
When phenol react with chloroform in the presence of sodium hydroxide then salicylaldehyde is formed as a product. This is called Reimer-Tiemann reaction.



(iv) Halogenation -

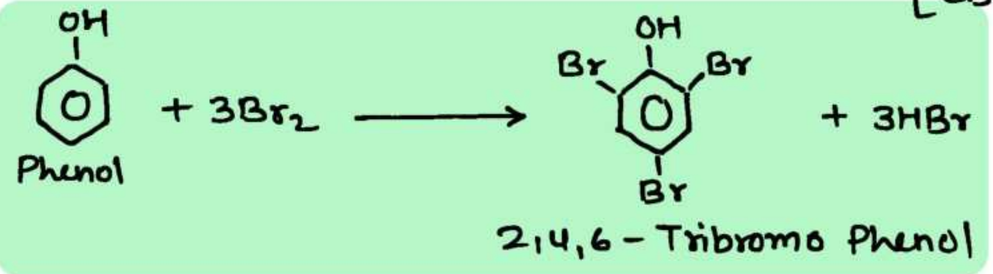
[CBSE 2017]

When phenol react with bromine in the presence of CS_2, $CHCl_3$ or CCl_4 at low temperature, then ortho and para bromophenol is formed.



When phenol react with excess of bromine (bromine water) then 2,4,6 - tribromo phenol is formed.

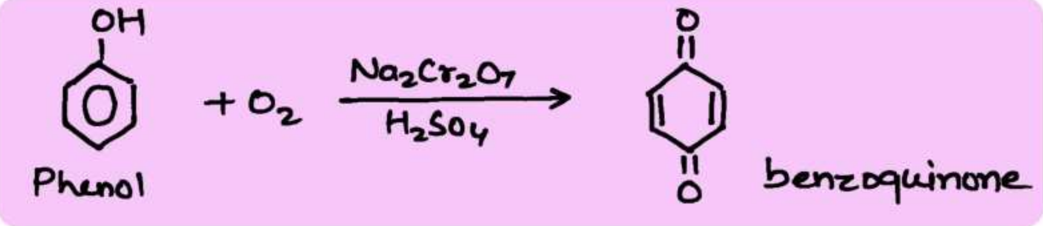
[CBSE 2008,13]



(V) Oxidation -

[CBSE 2011]

Oxidation of Phenol in the presence of air with Chromic Acid ($Na_2Cr_2O_7 + H_2SO_4$) form benzoquinone.



Some Commercially Important Alcohols

(1.) Methanol (CH_3OH) -

[its also Known as wood sprit]

Preparation method -

Methanol is produced by catalytic hydrogenation of carbon monoxide at high temperature and pressure.

$$CO + 2H_2 \xrightarrow[200 - 300\ atm.\ 573 - 673\ K]{ZnO - Cr_2O_3} \underset{Methanol}{CH_3OH}$$

➤ Properties of Methanol -

(1) Methanol is colourless liquid and its boiling point is 337K.

(2) It is highly poisonous in nature.

(3) It is used as solvant in paints, varnishes and for making formaldehyde (HCHO)

(4) It is used for denaturation of ethanol

When 1% methanol is added in ethanol, then it becomes toxic and cannot be used for drinking purpose.

(5) Ingestion of even small quantities of methanol can cause blindness and large quantities causes even death.

(2) Ethanol (CH_3CH_2OH)

➤ Preparation method - Ethanol is obtained commercially by formation of sugar.

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

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

➤ Properties of Ethanol -

(i) Ethanol is Colourless liquid whose boiling point is 351 K.

(ii) Ethanol is used as a solvant in paint industory and it is used for the preparation of large number of carbon compounds.

➤ Denaturation of Alcohol (Ethanol) - The commercial alcohol is made unfit for drinking purpose by adding copper sulphate (to give colour → blue) and pyridine (for smell → foul)

This is known as denaturation of alcohol (ethanol).

(iii) Ethanol is used as a motor fuel in the form of power alcohol.

- Power Alcohol → Ethanol + Benzene + Petrol

Ethers (R−O−R)

The general formula of ether is $C_nH_{2n+2}O$.

➤ In ether two alkyl group are attached with the both side of oxygen atom. R−O−R

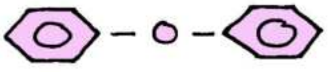
➤ Ether is also known as anhydride of alcohol.

$$\underset{\text{Alcohol}}{R-O\boxed{H + OH}-R} \longrightarrow \underset{\substack{\text{Ether} \\ \text{(Anhydride of alcohol)}}}{R-O-R} + H_2O$$

Types of Ether−

(1) Simple Ether− In both the alkyl groups attached with oxygen atom are same, then it is called simple ether.

Eg. CH_3-O-CH_3 Dimethyl ether , $C_6H_5-O-C_6H_5$ or



Diphenyl ether

(2) Mixed Ether− In both the alkyl group attached to oxygen atom are different then it is known as mixed ether.

Eg. $CH_3-O-C_2H_5$ Ethyl Methyl Ether , $C_6H_5-O-CH_3$

➤ Nomenclature of Ether−

(1) Common System− In common system ethers are named by 'Alkyl ether'.

- If both the alkyl group are same then 'di' is used as a prefix before the name of alkyl group.

- In mixed ether name of alkyl group are written in alphabetical order.

Eg.
(i) CH_3-O-CH_3 → Dimethyl Ether
(ii) $CH_3-O-C_2H_5$ → Ethyl Methyl Ether
(iii) $C_2H_5-O-C_2H_5$ → Diethyl Ether
(iv) $C_6H_5-O-C_2H_5$ → Ethyl Phenyl Ether
(v) $C_6H_5-O-C_6H_5$ → Diphenyl Ether

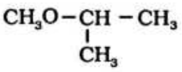
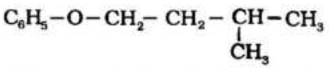
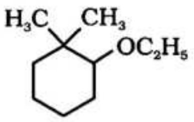
(2) IUPAC System-

(i) In IUPAC system ether is named as 'alkoxy alkane'.

(ii) In ether, oxygen atom is kept with smaller alkyl group and it is named as Alkoxy.

(iii) And remaining alkyl group is named as alkane.

Common and IUPAC Names of Some Ethers

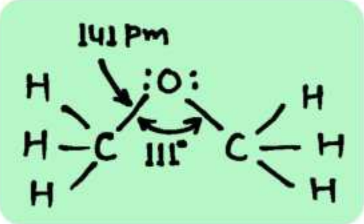
Compound	Common name	IUPAC name
CH_3OCH_3	Dimethyl ether	Methoxymethane
$C_2H_5OC_2H_5$	Diethyl ether	Ethoxyethane
$CH_3OCH_2CH_2CH_3$	Methyl n-propyl ether	1-Methoxypropane
$C_6H_5OCH_3$	Methyl phenyl ether (Anisole)	Methoxybenzene (Anisole)
$C_6H_5OCH_2CH_3$	Ethyl phenyl ether (Phenetole)	Ethoxybenzene
$C_6H_5O(CH_2)_6-CH_3$	Heptyl phenyl ether	1-Phenoxyheptane
 $CH_3O-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_3$	Methyl isopropyl ether	2-Methoxypropane
 $C_6H_5-O-CH_2-CH_2-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_3$	Phenyl isopentyl ether	3- Methylbutoxybenzene
$CH_3-O-CH_2-CH_2-OCH_3$	—	1,2-Dimethoxyethane
	—	2-Ethoxy- -1,1-dimethylcyclohexane

Structure of Ethere -

In the structure of ether oxygen atom is in Sp^3 hybridization state with tetrahaderal geometry.

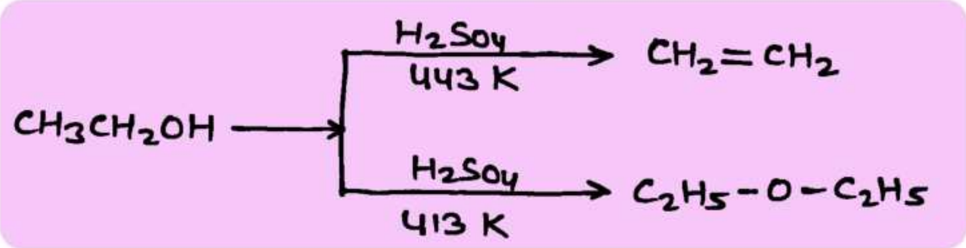
Oxygen atom has four sp^3 hybrid orbitals in which two hybrid orbitals overlap with carbon atom of alkyl group and remaining to hybrid orbitals are present as a lone pair of electron on oxygen.

- The bond angle between $\left(\overset{O}{C \quad C}\right)$ is 111° due to the repulsion between alkyl groups which are attached to the oxygen atom.



Preparation of Ether -

(1) By dehydration of Alcohol -



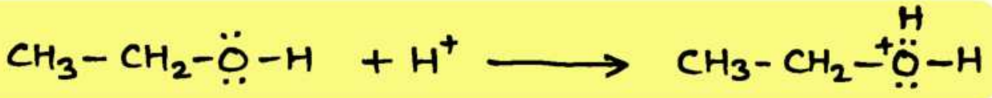
$$CH_3CH_2OH \xrightarrow[443\,K]{H_2SO_4} CH_2{=}CH_2$$

$$CH_3CH_2OH \xrightarrow[413\,K]{H_2SO_4} C_2H_5-O-C_2H_5$$

- **Mechanism -** [CBSE 2016]

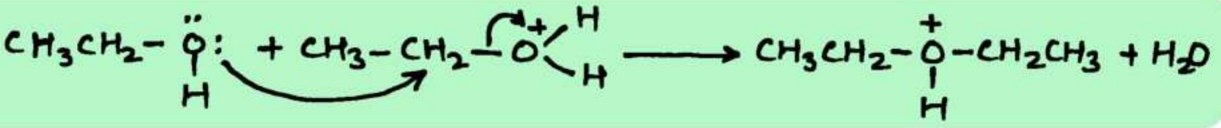
The formation of ether is nucleophilic biomolecular reaction (S_N2) involving the attack of alcohol molecule on a protonated alcohol.

(i)



$$CH_3-CH_2-\ddot{O}-H + H^+ \longrightarrow CH_3-CH_2-\overset{H}{\overset{+}{\ddot{O}}}-H$$

(ii)



$$CH_3CH_2-\underset{H}{\ddot{O}}: + CH_3-CH_2-\overset{+}{O}\begin{smallmatrix}H\\H\end{smallmatrix} \longrightarrow CH_3CH_2-\underset{H}{\overset{+}{O}}-CH_2CH_3 + H_2O$$

(iii) $CH_3CH_2-\overset{+}{\underset{H}{O}}-CH_2CH_3 \longrightarrow CH_3CH_2-O-CH_2CH_3 + H^+$

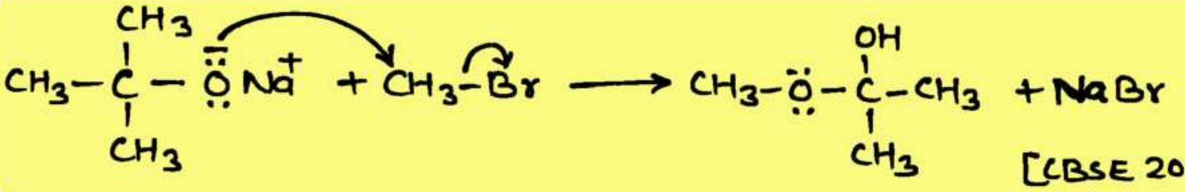
(2) Williamson synthesis -

[CBSE 2013,14]

When sodium or pottasium alkoxide are heated with alkyl halide, then ether is formed.

It is a nucleophilic substitution reaction which takes place by S_N2 mechanism.

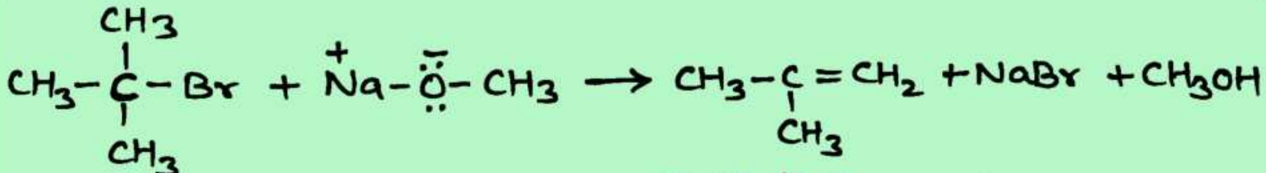
$$R-X + R'-\ddot{\underset{..}{O}}^{-}-\overset{+}{Na} \longrightarrow R-\ddot{\underset{..}{O}}-R' + NaX$$



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\ddot{\underset{..}{O}}^{-}\overset{+}{Na} + CH_3-Br \longrightarrow CH_3-\ddot{\underset{..}{O}}-\underset{CH_3}{\overset{OH}{C}}-CH_3 + NaBr$$

[CBSE 2009,10,18]

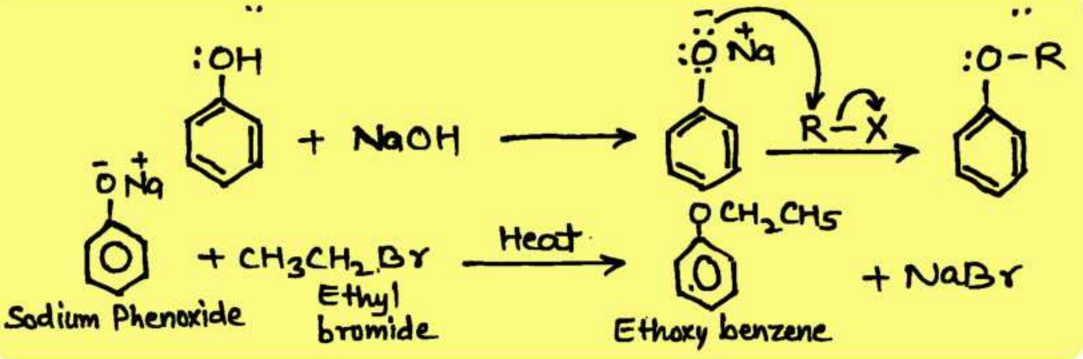
In case of 2° and 3° alkyl halides, elimination competes over substitution. If a 3° alkyl halide is used an alkene is the only reaction product and no ether is formed.



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Br + \overset{+}{Na}-\ddot{\underset{..}{O}}^{-}-CH_3 \longrightarrow CH_3-\underset{CH_3}{C}=CH_2 + NaBr + CH_3OH$$

2-Methylpropene

Phenols are also converted to ethers by this method.



> Physical Properties -

(i) Dimethyl ether, Diethyl ether are gaseous and other ethers are liquid in nature.

(ii) Ethers are lighter than water. Hence it flows over water (i.e. density is less than water).

(iii) Ethers are highly volatile in nature.

(iv) Solubility - ethers are partially soluble in water and are highly soluble in Chloroform and Benzene.

Q. Ethers are less soluble in water than compare to Alcohol. Explain why?

Sol. In ether C-O bond is less polar. Therefore it does not form intermolecular H-bond with water and are less soluble than compare to alcohol.

(v) Boiling Point - The boiling point of ether is very less than compare to isomeric alcohol because in ether intermolecular H-bond is not present.

The boiling point of ether is similar to the same molecular weight alkane.

> Chemical Properties -

Ether is a less reactive compound because in ether oxygen atom behave as a inert atom. Therefore ether is inert towards base, oxidising and reducing agent.

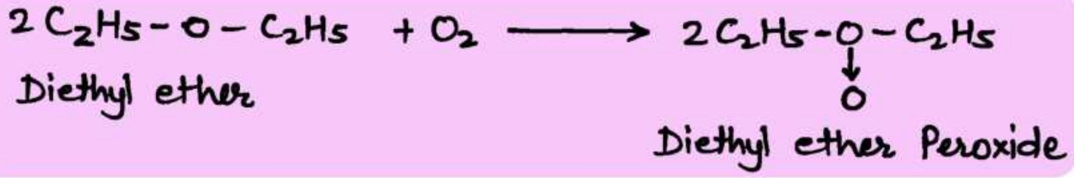
Ether represents the following types of chemical reactions -

1. Reaction due to oxygen of ether (Ethernal oxygen) -

(i) Reaction with atmospheric oxygen -

Ether when exposed in atmosphere, then it absorb oxygen and form peroxide.

It is a very slow process and peroxide is a explosive substance.



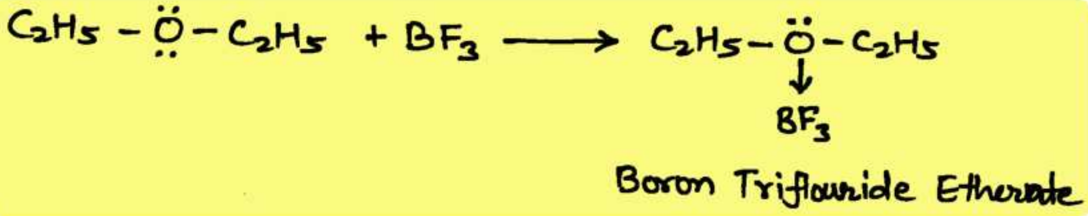
$$2C_2H_5-O-C_2H_5 + O_2 \longrightarrow 2C_2H_5-\underset{\substack{\downarrow\\ O}}{O}-C_2H_5$$

Diethyl ether

Diethyl ether Peroxide

(ii) Formation of coordination Compound-

Ether form coordination compound when react with Lewis Acid (BF_3, $AlCl_3$ etc.)



$$C_2H_5-\ddot{\underset{\cdot\cdot}{O}}-C_2H_5 + BF_3 \longrightarrow C_2H_5-\underset{\substack{\downarrow\\ BF_3}}{\ddot{O}}-C_2H_5$$

Boron Triflouride Etherate

(2) Reaction due to Cleavage of C-O bond -

(i) Hydrolysis-

When ether is boiled with water, then it is hydrolised into alcohol.

$$C_2H_5-O \vdots C_2H_5 + H-OH \xrightarrow[\Delta]{Con.\ H_2SO_4} 2C_2H_5OH$$

Diethyl ether Ethanol

(ii) Reaction with halogen acid (Hydrogen Halide)-

The order of reactivity of halogen acid towards ether is as follows

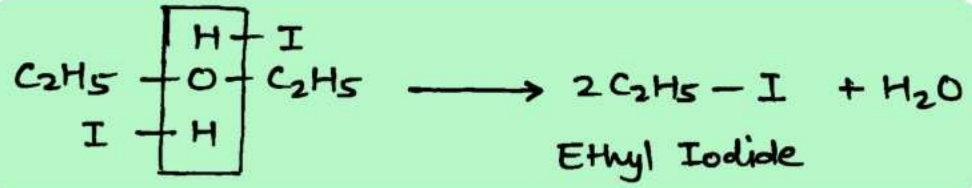
$$\boxed{HI > HBr > HCl > HF}$$

(a) Reaction with HI -

When ether react with HI in hot and cold medium, then different product is formed.

(I) Reaction in Hot medium-

When ether is heated with HI then two mole of HI is used and alkyl halide is formed.

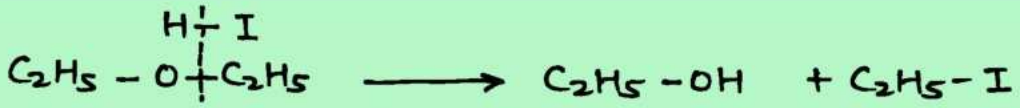


$$C_2H_5-O-C_2H_5 + 2HI \longrightarrow 2C_2H_5-I + H_2O$$

Ethyl Iodide

(II) Reaction in Cold medium-

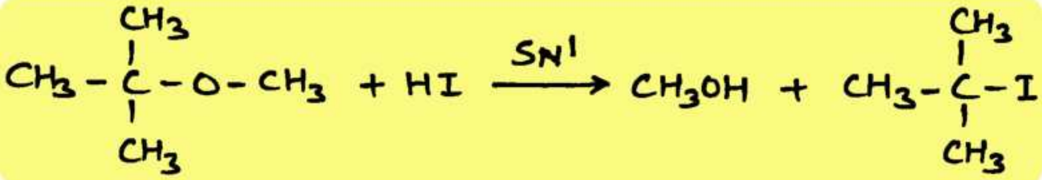
In cold medium one mole of HI is used and alkyl halide and alcohol is formed as a product.



$$C_2H_5-O-C_2H_5 \overset{H-I}{} \longrightarrow C_2H_5-OH + C_2H_5-I$$

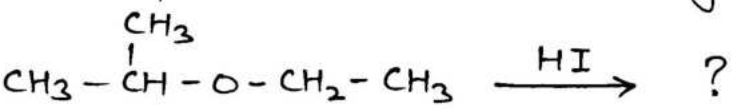
Diethyl ether Ethyl Alcohol Ethyl Iodide

- When one of the alkyl group is a tertiary group, the halide formed is a tertiary halide. [CBSE 2015,16]



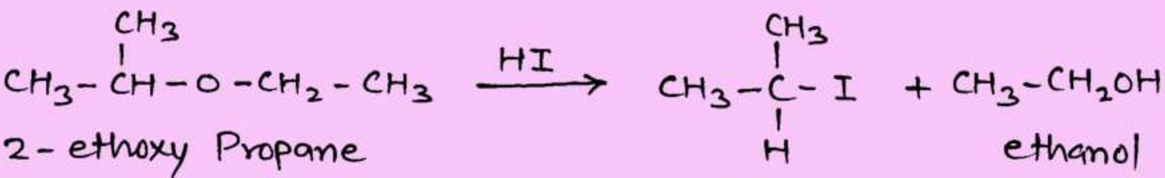
$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O-CH_3 + HI \xrightarrow{S_N1} CH_3OH + CH_3-\underset{CH_3}{\overset{CH_3}{C}}-I$$

Q. Write the products in the following reaction- [CBSE 2017]



$$CH_3-\overset{CH_3}{CH}-O-CH_2-CH_3 \xrightarrow{HI} ?$$

Sol.

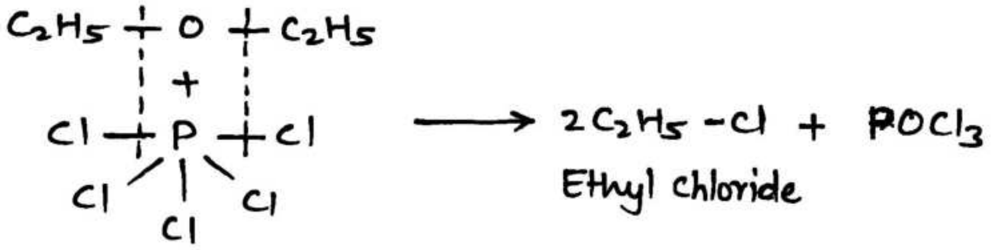


$$CH_3-\overset{CH_3}{CH}-O-CH_2-CH_3 \xrightarrow{HI} CH_3-\underset{H}{\overset{CH_3}{C}}-I + CH_3-CH_2OH$$

2-ethoxy Propane ethanol

2-iodopropane

(iii) Reaction with phosphorus Pentachloride (PCl_5) -

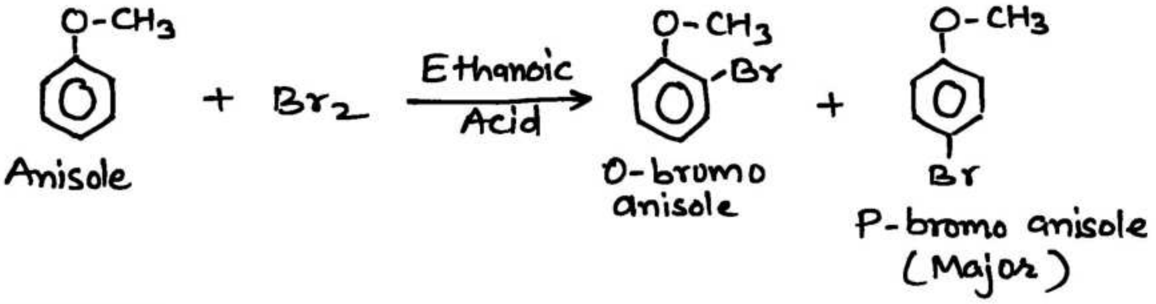


(3) Electrophilic Substitution Reaction -

In phenyl ethyl ether (aromatic ether), –OR group is ortho and para directing group. Therefore electrophilic substitution takes place on ortho and para position of benzene ring.

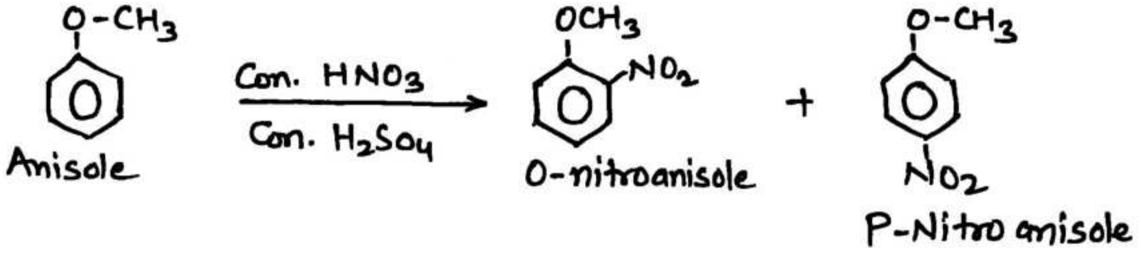
(i) Halogenation -

When anisol react with bromine in the presence of Ethanoic acid (CH_3COOH) then ortho and para bromo anisole is formed as a product.



(ii) Nitration -

When anisol react with the mixture of Con. HNO_3 and Con. H_2SO_4 than ortho and para-nitro anisole formed as product.



(iii) Alkylation (Friedel Crafts Reaction) – [CBSE 2010,11,15]

When anisole react with alkyl halide or acyl halide in the presence of anh. $AlCl_3$ (a Lewis acid) the substitution takes place on ortho and para position. This is called Friedel crafts reaction.