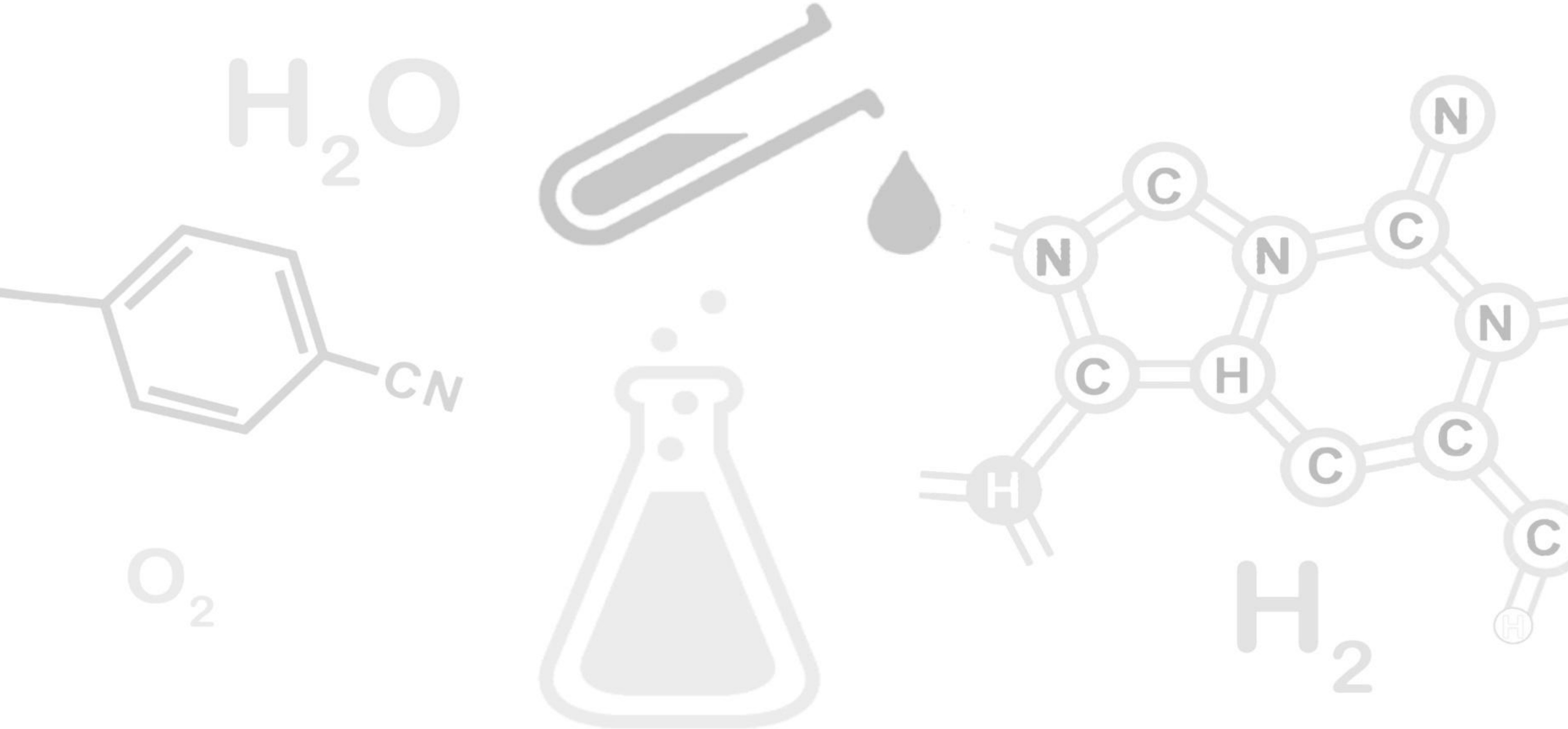
CHEMISTRY



Alcohols, Phenols and Ethers

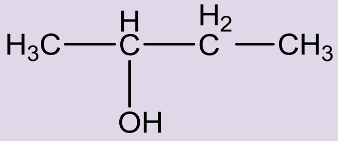
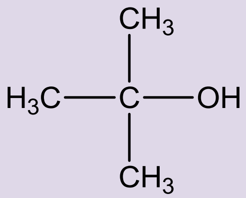
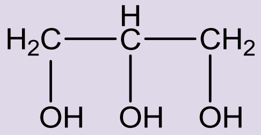
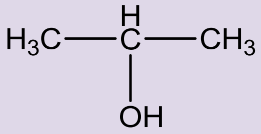
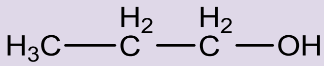
Introduction

- Alcohols and phenols are compounds formed when a hydrogen atom in a hydrocarbon is replaced by –OH group.
- An alcohol contains one or more hydroxyl (OH) group(s) directly attached to carbon atom(s) of an aliphatic system.
- A phenol contains –OH group(s) directly attached to carbon atom(s) of an aromatic system (C_6H_5OH).
- The substitution of a hydrogen atom in a hydrocarbon by an alkoxy or aryloxy group (R-O/Ar-O) gives another class of compounds known as ethers.

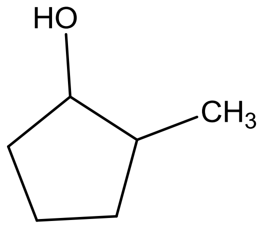
  For example:
  C_2H_5-O-C_2H_5
  Dimethyl ether

Nomenclature

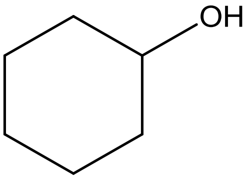
Alcohols

Compound	Common name	IUPAC name
 $H_3C-\underset{OH}{\overset{H}{C}}-\overset{H_2}{C}-CH_3$	*sec*-Butyl alcohol	Butan-2-ol
 $H_3C-\underset{CH_3}{\overset{CH_3}{C}}-OH$	*tert*-Butyl alcohol	2-Methylpropan-2-ol
 $\underset{OH}{H_2C}-\underset{OH}{\overset{H}{C}}-\underset{OH}{CH_2}$	Glycerol	Propane -1, 2, 3-triol
 $H_3C-\underset{OH}{\overset{H}{C}}-CH_3$	Isopropyl alcohol	Propan-2-ol
 $H_3C-\overset{H_2}{C}-\overset{H_2}{C}-OH$	*n*-Propyl alcohol	Propan-1-ol

In case of cyclic compounds, we use the prefix cyclo if the –OH group is attached to C-1.

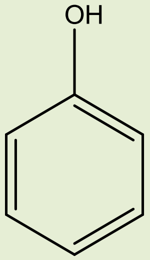
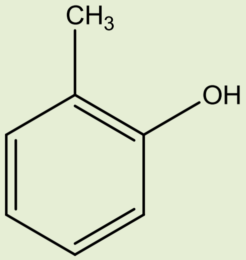
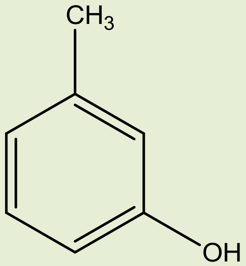
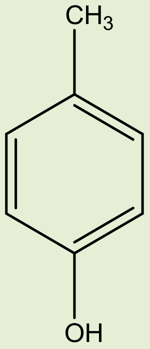


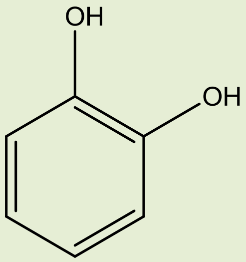
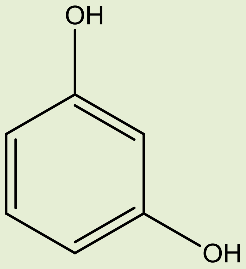
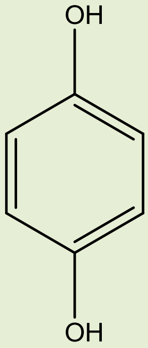
2-Methylcyclopentanol



Cyclohexanol

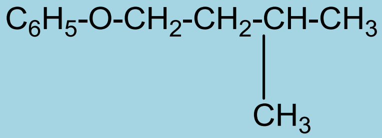
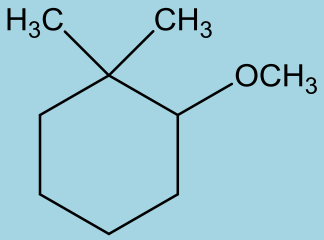
Phenols

Compound	**Common name**	**IUPAC name**
	Phenol	Phenol
	*o*-Cresol	2-Methylphenol
	*m*-Cresol	3-Methylphenol
	*p*-Cresol	4-Methylphenol

	Catechol	Benzene-1,2-diol
	Resorcinol	Benzene-1,3-diol
	Hydroquinone or quinol	Benzene-1,4-diol

Ethers

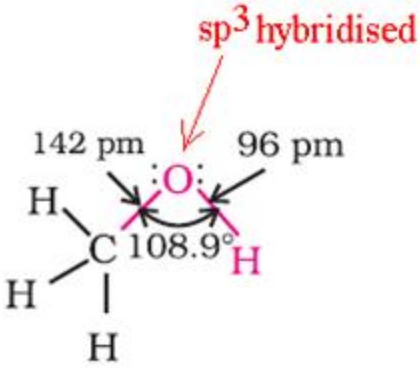
Compound	Common name	IUPAC name
CH_3OCH_3	Dimethyl ether	Methoxymethane
$C_2H_5OC_2H_5$	Diethyl ether	Ethoxyethane
$C_6H_5O(CH_2)_6\text{-}CH_3$	Heptyl phenyl ether	1-Phenoxyheptane
	Phenyl isopentyl ether	3- Methylbutoxybenzene

 $C_6H_5\text{-}O\text{-}CH_2\text{-}CH_2\text{-}\underset{\displaystyle CH_3}{\underset{\mid}{CH}}\text{-}CH_3$	----	1,2-Dimethoxyethane
$CH_3\text{-}O\text{-}CH_2\text{-}CH_2\text{-}OCH_3$	---	
		2-Ethoxy- -1,1-dimethylcyclohexane

Structures of Functional Groups

Alcohols

- For alcohols, the –OH group is linked to carbon by a sigma bond.
- The bond is formed by the overlap of sp^3 hybridised orbital of carbon with a sp^3 hybridised orbital of oxygen.



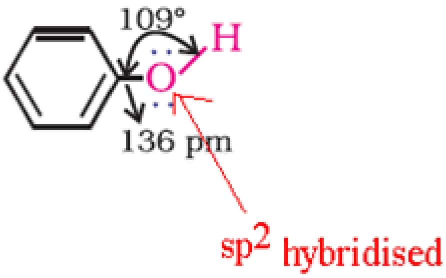
Methanol

(Alcohol)

- In alcohols, the bond angle is slightly less than the tetrahedral angle (109°-28’) due to the repulsion between the unshared electron pairs of oxygen.

Phenols

- In phenols, the –OH group is linked to carbon by sp^2 hybridisation.
- The C-O bond length (136 pm) in phenol is slightly less than that in methanol.
- This arises due to:
  - Partial double bond character on account of the conjugation of unshared electron pair of oxygen with the aromatic ring.
  - sp^2 hybridised carbon to which oxygen is linked.

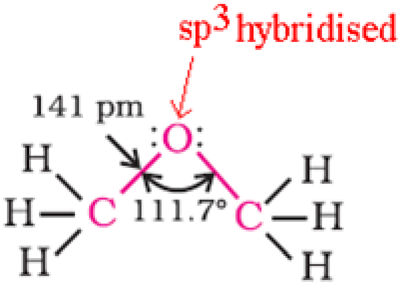


Phenol

(Phenol)

Ethers

- In ethers the two bond pairs and two lone pairs of electrons on oxygen form a tetrahedral arrangement.
- Due to the repulsive interaction between the two bulky (-R) groups the bond angle is slightly greater than the tetrahedral angle.
- The C-O bond length is almost the same like alcohols.



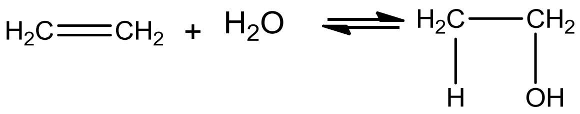
Methoxymethane

(Ether)

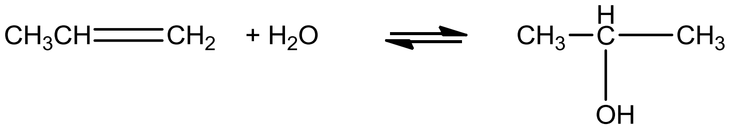
Preparation of Alcohols

From Alkenes

- **Acid catalysed hydration:**
  Alcohols are prepared by treating alkenes with water in the presence of acid as catalyst.

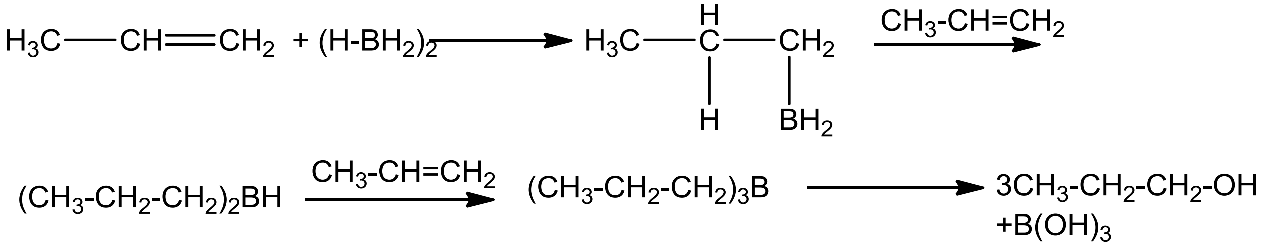


$$H_2C{=}CH_2 + H_2O \rightleftharpoons \underset{H}{H_2C}-\underset{OH}{CH_2}$$



$$CH_3CH{=}CH_2 + H_2O \rightleftharpoons CH_3-\overset{H}{\underset{OH}{C}}-CH_3$$

- **Hydroboration-oxidation:**
  Alkenes on treatment with diborane give trialkyl boranes as addition product which is then oxidised to alcohol by hydrogen peroxide in the presence of aqueous sodium hydroxide.



$$H_3C-CH{=}CH_2 + (H\text{-}BH_2)_2 \longrightarrow H_3C-\overset{H}{\underset{H}{C}}-\underset{BH_2}{CH_2} \xrightarrow{CH_3\text{-}CH{=}CH_2}$$

$$(CH_3\text{-}CH_2\text{-}CH_2)_2BH \xrightarrow{CH_3\text{-}CH{=}CH_2} (CH_3\text{-}CH_2\text{-}CH_2)_3B \longrightarrow 3CH_3\text{-}CH_2\text{-}CH_2\text{-}OH + B(OH)_3$$

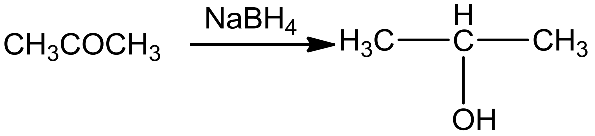
Propan-1-ol

The addition of borane to the double bond takes place in such a way that the boron gets added to the sp^2 carbon with more number of hydrogen atoms.

From Carbonyl Compounds

- **Reduction of Aldehydes & Ketones**
  - Aldehydes yield primary alcohols whereas ketones give secondary alcohols.

$$CH_3CHO + H_2 \xrightarrow{Pd} CH_3CH_2OH$$



$$CH_3COCH_3 \xrightarrow{NaBH_4} H_3C-\overset{H}{\underset{OH}{C}}-CH_3$$

- **Reduction of Carboxylic acids and Esters**
  - $LiAlH_4$ is a strong reducing agent and reduces carboxylic acids to primary alcohols in excellent yields.

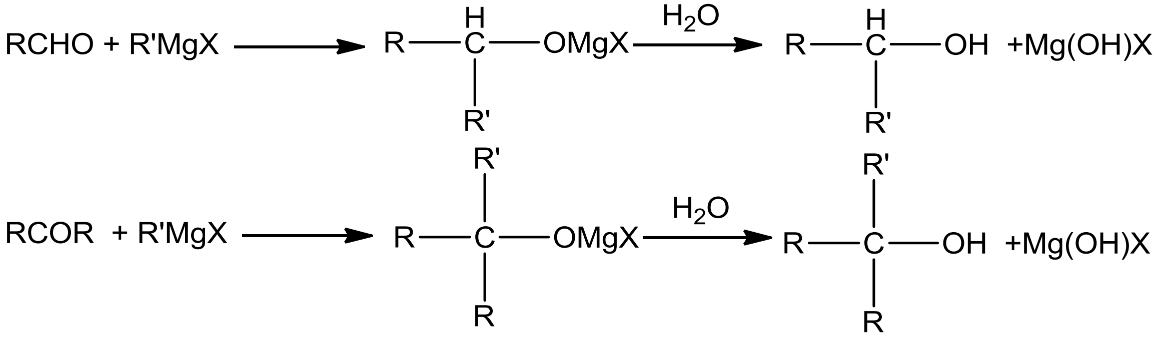
$$CH_3COOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } LiAlH_4} CH_3CH_2OH$$

- Alcohols are prepared on a commercial scale by converting acids to esters followed by reduction with hydrogen in the presence of catalyst.

$$CH_3COOH \xrightarrow{CH_3OH} CH_3COOCH_3 \xrightarrow[\text{Catalyst}]{H_2} CH_3CH_2OH + CH_3OH$$

From Grignard reagents

Grignard reagents on reacting with aldehydes and ketones yield alcohols.

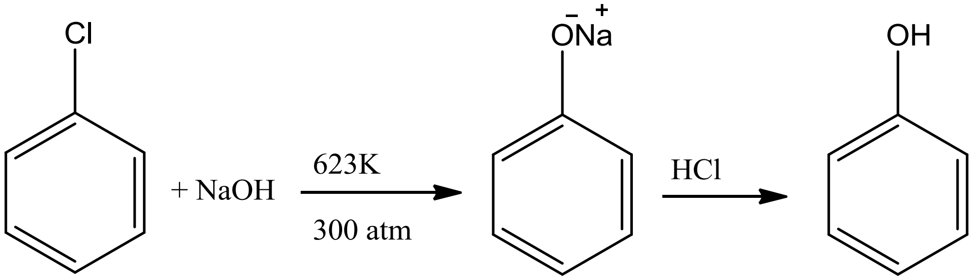


$$RCHO + R'MgX \longrightarrow R-\underset{R'}{\overset{H}{C}}-OMgX \xrightarrow{H_2O} R-\underset{R'}{\overset{H}{C}}-OH + Mg(OH)X$$

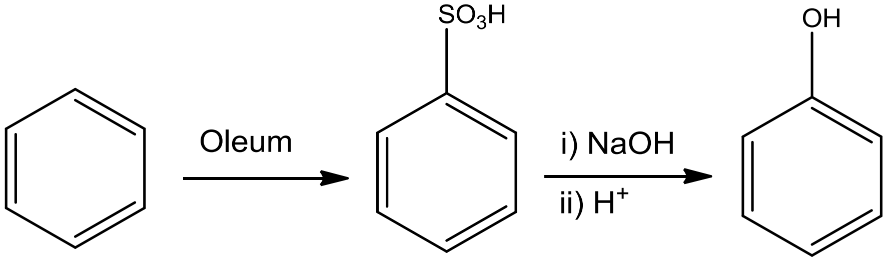
$$RCOR + R'MgX \longrightarrow R-\underset{R}{\overset{R'}{C}}-OMgX \xrightarrow{H_2O} R-\underset{R}{\overset{R'}{C}}-OH + Mg(OH)X$$

Preparation of Phenols

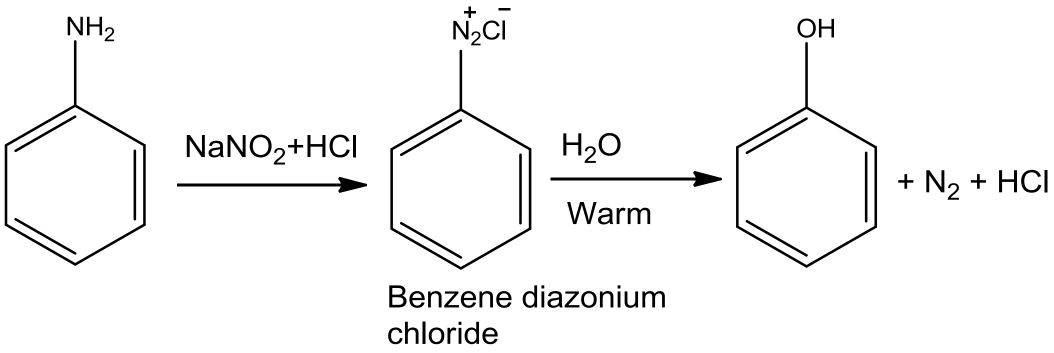
- **From Haloarenes**
  Chlorobenzene on fusing with NaOH at 623 K and 320 atmospheric pressure gives sodium phenoxide which on acidification yields phenol.



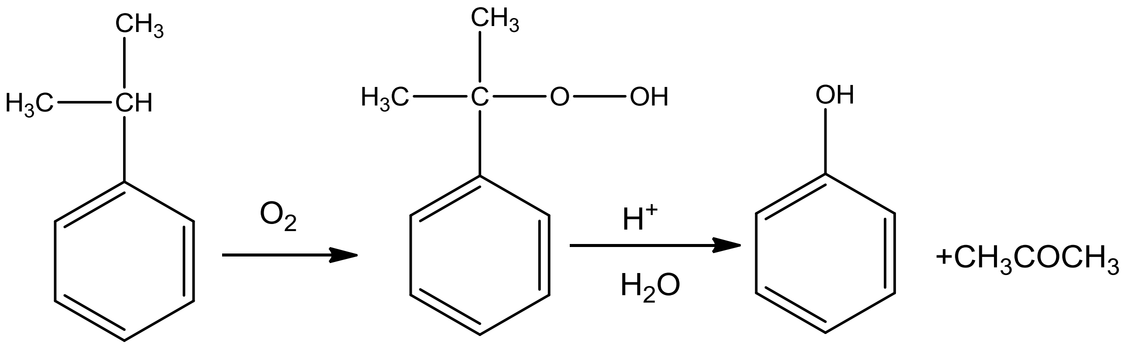
- **From Benzenesulphonic Acid**
  Benzene on sulphonation with oleum gives benzene sulphonic acid which on heating with molten sodium hydroxide gives sodium phenoxide. Acidification of the sodium phenoxide gives phenol.



- **From Diazonium Salts**
  Aniline on treatment with nitrous acid at 273-278K gives benzene diazonium chloride which on hydrolysis with warm water or treatment with dilute acids is converted to phenols.



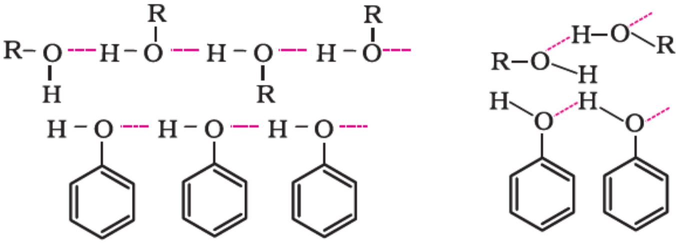
- **From Cumene**
  Cumene(isopropylbenzene) on oxidation with air gives cumene hydroperoxide which on treatment with dilute acid is converted to phenol.



Physical Properties

- **Boiling points**

- Boiling points of alcohols and phenols are higher in comparison to other classes of compounds, namely hydrocarbons, ethers, haloalkanes and haloarenes of comparable molecular masses. This is because the –OH group in alcohols and phenols is involved in intermolecular hydrogen bonding.

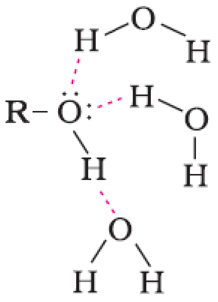


- The boiling points of alcohols and phenols increase with increase in the number of carbon atoms. This is because of increase in van der Waals forces with increase in the surface area.

- In alcohols, the boiling points decrease with increase in branching in the carbon chain. This is because of decrease in van der Waals forces with decrease in the surface area.

- **Solubility**

- Alcohols and phenols are soluble in water due to their ability to form hydrogen bonds with water molecules.



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

Chemical Properties

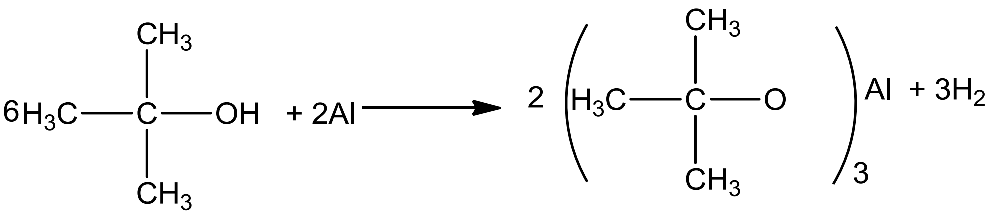
Alcohols react both as nucleophiles and electrophiles.

A) Reactions involving cleavage of O-H bond

(i) Reaction with Metals

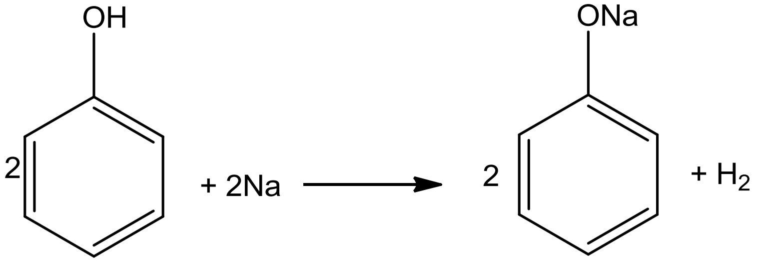
Alcohols and phenols react with active metals like Na, K and Al to give corresponding alkoxides/phenoxides with the evolution of hydrogen.

$2R\text{-}OH + 2Na \rightarrow 2R\text{-}O\text{-}Na + H_2$



tert. -butyl alcohol

Aluminium tert. butoxide



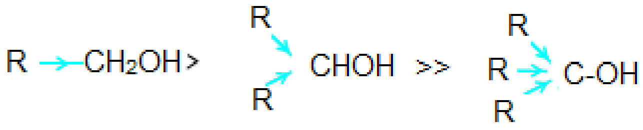
Phenol

Sodium phenoxide

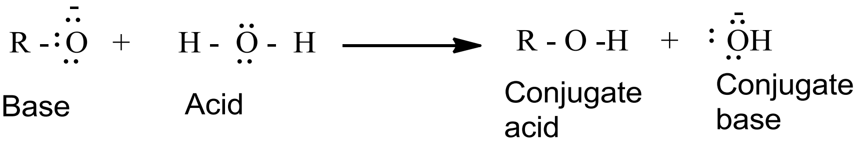
(ii) Acidity of Alcohols

- The acidity of alcohols depends on the polar nature of O-H bond.
- The electron releasing groups ($-CH_3$, $-C_2H_5$) increases the electron density on oxygen and thus decrease the polarity of O-H bond which decreases the acid strength.

- The acid strength of alcohols decreases in the following order:



- Alcohols are weaker acids than water which can be seen in the following reaction.



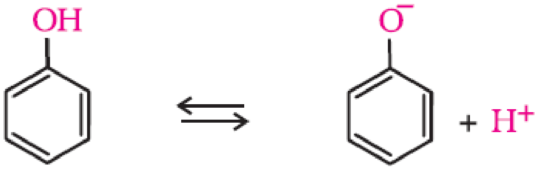
In the reaction, water is a better proton donor (i.e., stronger acid) than alcohol. Over here the alkoxide ion is a better proton acceptor than hydroxide ion which suggests that alkoxides are stronger bases.

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

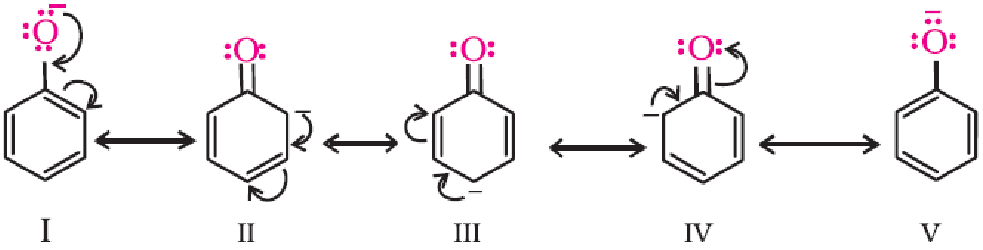
(iii) Acidity of Phenols

- In phenol, the hydroxyl group is directly attached to the sp^2 hybridised carbon of the benzene ring which acts as an electron-withdrawing group. Whereas in alcohols, the hydroxyl group is attached to the alkyl group which has an electron-releasing inductive effect.
- In phenol, the hydroxyl group is directly attached to the sp^2 hybridised carbon of the benzene ring. Whereas in alcohols, the hydroxyl group is attached to the sp^3 hybridised carbon of the alkyl group. The sp^2 hybridised carbon has higher electronegativity than the sp^3 hybridised carbon. Thus, the polarity of the O–H bond of phenols is higher than that of alcohols. Hence, the ionisation of phenols is higher than that of alcohols.
- The ionisation of an alcohol and a phenol occurs as follows:

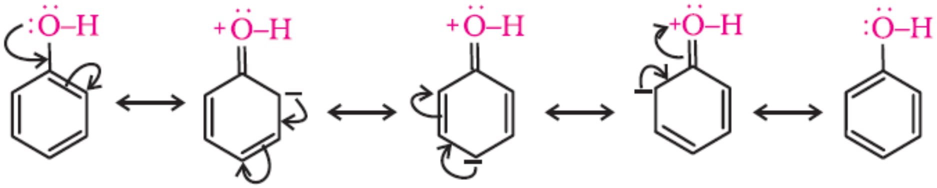
$$R-\ddot{\underset{\cdot\cdot}{O}}-H \rightleftharpoons R-\ddot{\underset{\cdot\cdot}{O}}:^{-} + H^{+}$$



- In alkoxide ion, the negative charge is localised on oxygen, while in phenoxide ion, the charge is delocalised.



- The delocalisation of the negative charge makes the phenoxide ion more stable and favours the ionisation of phenol. Although there is charge delocalisation in phenol, its resonance structures have charge separation due to which the phenol molecule is less stable than the phenoxide ion.



- In substituted phenols, the presence of electron-withdrawing groups such as the nitro group enhances the acidic strength of phenol. On the other hand, electron-releasing groups, such as alkyl groups, decrease the acidic strength. It is because electron-withdrawing groups lead to effective delocalisation of the negative charge in the phenoxide ion.

(iv) Esterification

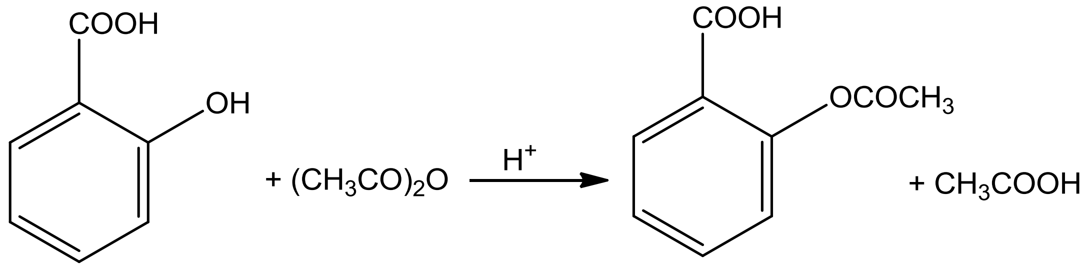
- Esters are formed when alcohols and phenols react with carboxylic acids, acid chlorides and acid anhydrides.

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

$$Ar/RO\text{-}H + (R'CO)_2O \xrightleftharpoons{H^+} Ar/ROCOR' + R'COOH$$

$$R/ArOH + R'COCl \xrightarrow{Pyridine} R/ArOCOR' + HCl$$

- In case of acid chloride, the reaction is carried out in the presence of base called pyridine to neutralise the HCl formed and to shift the equilibrium to the right.



Salicylic acid

Acetylsalicylic acid
(Aspirin)

B) Reactions involving cleavage of Carbon-Oxygen(C-O) bond in alcohols

Only alcohols show reactions involving cleavage of C-O bond. Phenols exhibit this type of reaction only with zinc.

i) Reaction with hydrogen halides

Alcohols on treatment with hydrogen halides form alkyl halides.

$ROH + HX \rightarrow R\text{-}X + H_2O$

How to distinguish between Primary, Secondary and Tertiary Alcohols?

Lucas reagent test:

$$ROH + HCl \xrightarrow[\text{Lucas reagent}]{\text{conc.HCl} + ZnCl_2} RCl + H_2O$$

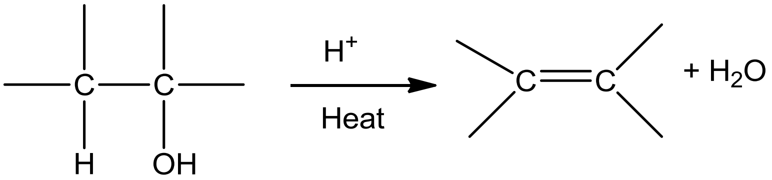
- If it is a primary alcohol, then no turbidity appears at room temperature. Turbidity appears only on heating.
- If it is a secondary alcohol, then turbidity appears in 5 minutes.
- If it is a tertiary alcohol, then turbidity appears immediately.

ii) Reaction with Phosphorus trihalides

Alcohols get converted into alkyl bromides on treatment with PBr_3.
$3R\text{-}OH + PBr_3 \rightarrow 3R\text{-}Br + H_3PO_3$

iii) Dehydration

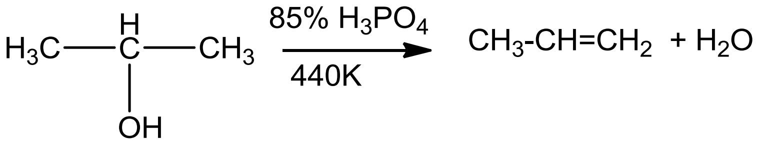
- Alcohols undergo dehydration to form alkenes in the presence of conc. H_2SO_4 or H_3PO_3 or catalysts such as anhydrous zinc chloride or alumina.



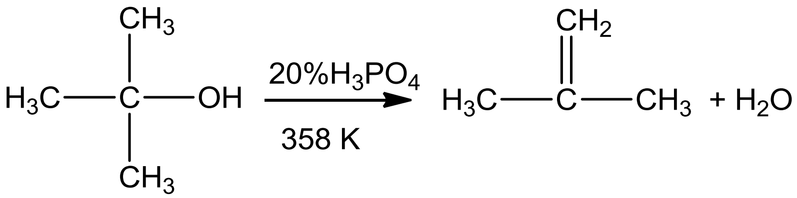
- Primary alcohol undergoes dehydration by heating it with conc. H_2SO_4 at 443K.

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

- Secondary and tertiary alcohols undergo dehydration in milder conditions.



$$H_3C-\overset{H}{\underset{OH}{C}}-CH_3 \xrightarrow[440K]{85\%\ H_3PO_4} CH_3\text{-}CH{=}CH_2 + H_2O$$

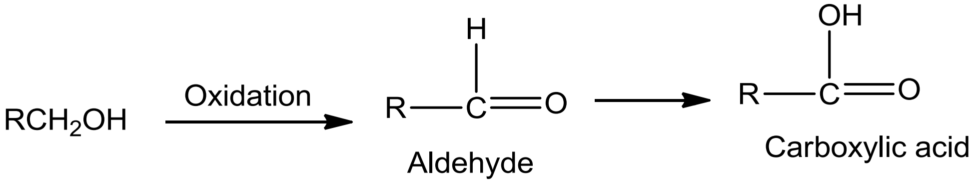


$$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-OH \xrightarrow[358\ K]{20\%H_3PO_4} H_3C-\overset{CH_2}{\overset{\|}{C}}-CH_3 + H_2O$$

- Thus the ease of dehydration of alcohols follows the order:
  Tertiary > Secondary > Primary

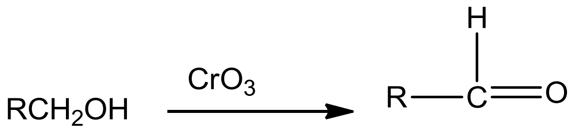
iv) Oxidation

- The oxidation of alcohols results in the formation of a carbon-oxygen double bond with the cleavage of an O-H and C-H bonds. The reaction is known as dehydrogenation reaction as it involves loss of dihydrogen from an alcohol molecule.



$$RCH_2OH \xrightarrow{\text{Oxidation}} \underset{\text{Aldehyde}}{R-\overset{H}{\overset{|}{C}}=O} \longrightarrow \underset{\text{Carboxylic acid}}{R-\overset{OH}{\overset{|}{C}}=O}$$

- Use of strong oxidising agents like acidified $KMnO_4$ is done to obtain carboxylic acids from alcohols directly. CrO_3 in anhydrous medium is used for obtaining aldehydes.



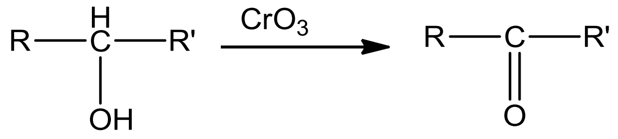
$$RCH_2OH \xrightarrow{CrO_3} R-\overset{H}{C}=O$$

Aldehyde

- Pyridinium chlorochromate (PCC), a complex of chromium trioxide with pyridine and HCl is a better oxidizing agent for oxidation of primary alcohols to aldehydes in good yield.

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

- CrO_3 is used to oxidize secondary alcohols to ketones.

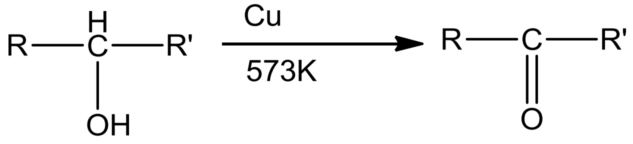


$$R-\underset{OH}{\overset{H}{C}}-R' \xrightarrow{CrO_3} R-\underset{O}{\underset{\|}{C}}-R'$$

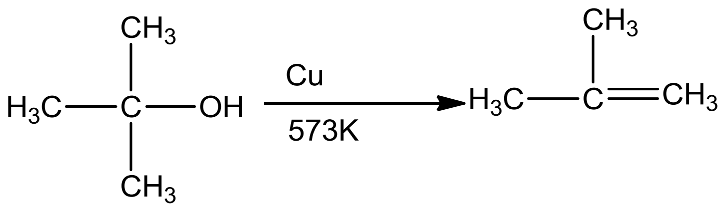
Sec-alcohol Ketone

- Tertiary alcohols do not undergo oxidation reaction. In presence of strong oxidizing agents ($KMnO_4$) and elevated temperatures, cleavage of C-C bonds takes place and a mixture of carboxylic acids containing lesser number of carbon atoms is formed.
- On passing vapours of a primary or a secondary alcohol over heated copper at 573K, dehydrogenation takes place and an aldehydes or a ketone is formed whereas tertiary alcohols undergo dehydration.

$$RCH_2OH \xrightarrow[573K]{Cu} RCHO$$



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



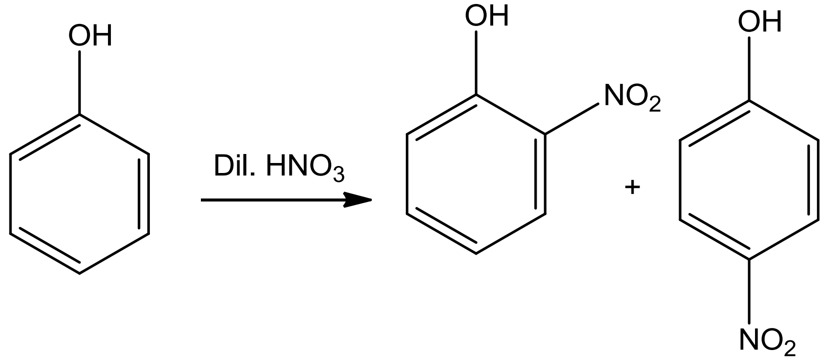
$$H_3C-\underset{CH_3}{\overset{CH_3}{C}}-OH \xrightarrow[573K]{Cu} H_3C-\overset{CH_3}{C}=CH_3$$

Characteristics of Phenols

- Phenols show electrophilic substitution reactions.
- The –OH group activates the benzene ring towards electrophilic substitution and also directs the incoming group to ortho and para positions in the ring as these positions become electron rich due to the resonance effect caused by –OH group.

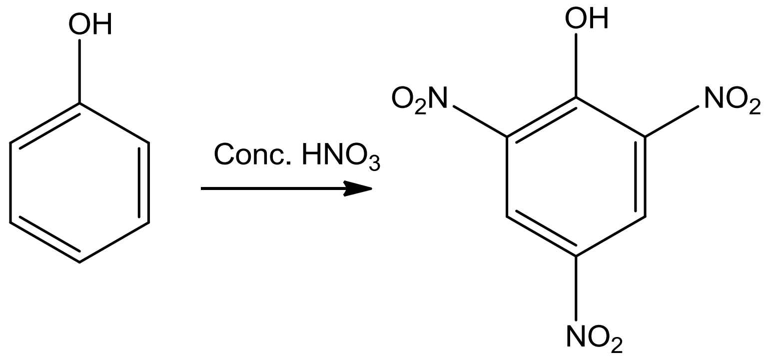
(i) Nitration

Phenol on treatment with dil.HNO_3 at low temperature yields a mixture of ortho and para nitrophenols.



o-Nitrophenol p-Nitrophenol

With conc. nitric acid, phenol is converted into 2, 4, 6-trinitrophenol.

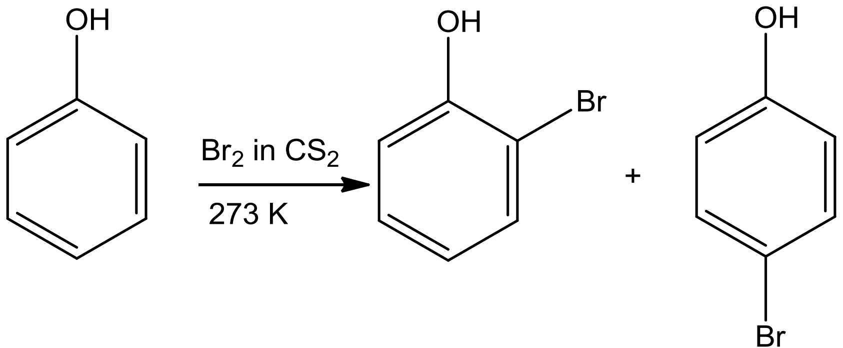


2,4,6-Trinitrophenol
(Picric acid)

(ii) Halogenation

(a) Bromine in $CHCl_3$ or CS_2

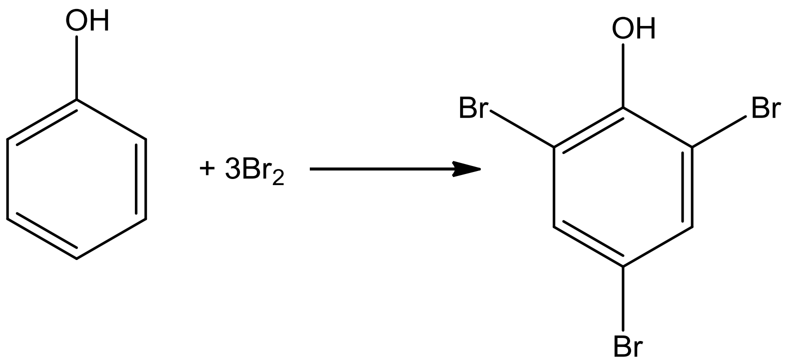
Monobromophenols are formed when phenol is treated with bromine in $CHCl_3$ or CS_2 at low temperature.



Minor Major

(b) Action of Bromine water

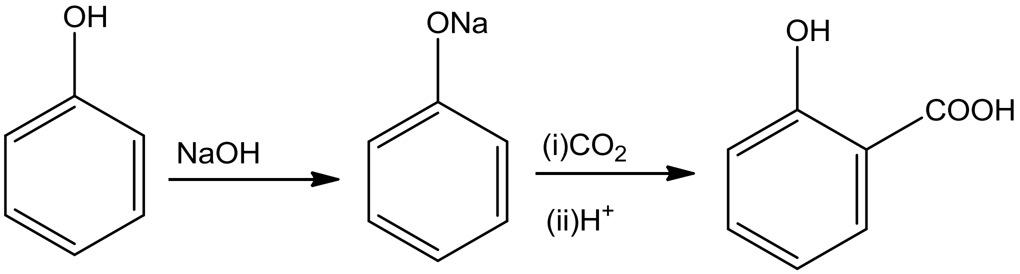
On treating phenol with bromine water, a white precipitate of 2, 4, 6-tribromophenol is formed.



2,4,6-Tribromophenol

(iii) Kolbe's Reaction

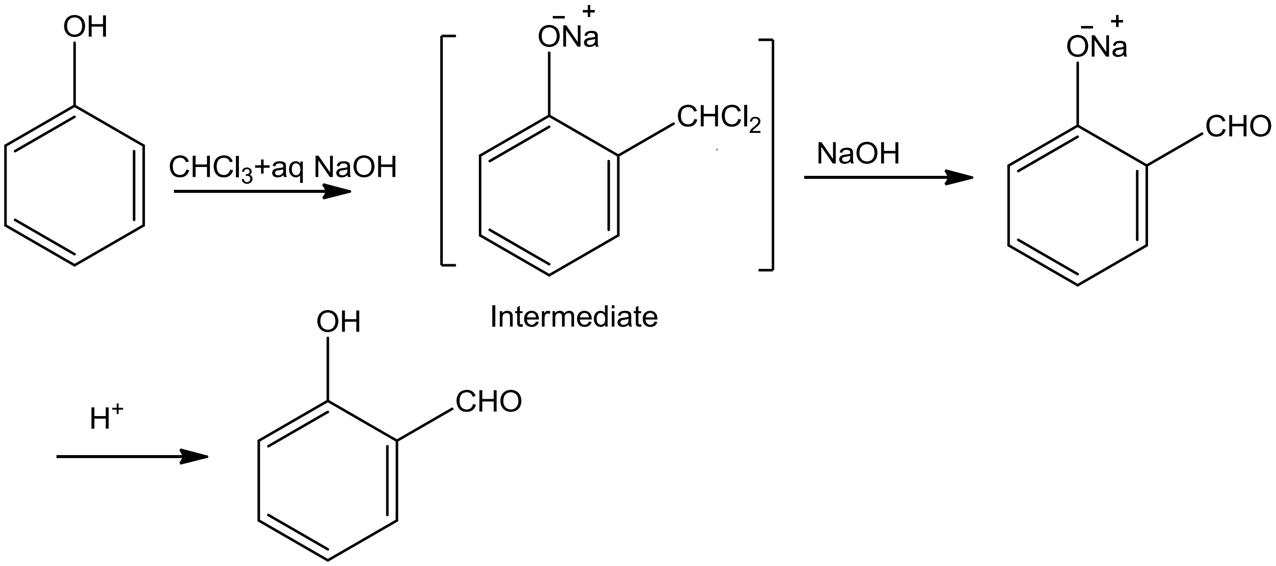
Phenols on treatment with NaOH produces phenoxide ion which is even more reactive than phenol towards electrophilic aromatic substitution and therefore it undergoes electrophilic substitution with carbon dioxide. Ortho hydroxybenzoic acid is obtained as the main product.



2-Hydroxybenzoic acid
(Salicylic acid)

(iv) Reimer-Tiemann Reaction

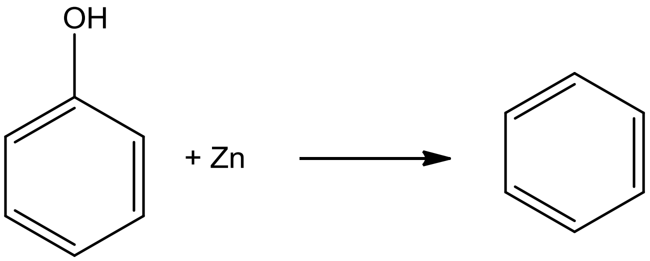
Phenols on treatment with chloroform in the presence of NaOH, a –CHO group is introduced at ortho position of benzene ring. The substituted benzal chloride formed as intermediate on hydrolysis with alkali produce salicylaldehyde.



Salicyaldehyde

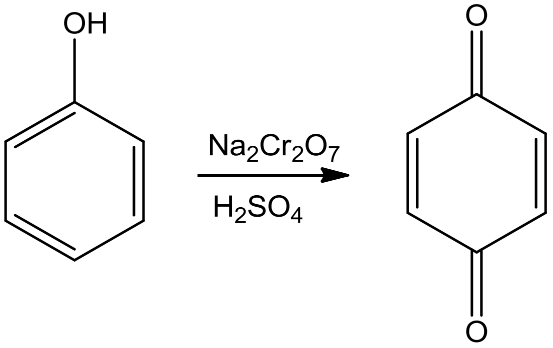
(v) Action of Zinc dust

Phenol on heating with zinc dust produces benzene.



(vi) Oxidation

Phenols on oxidation with chromic acid gives out conjugated diketone known as benzoquinone.



Some Commercially Important Alcohols

Methanol and ethanol are two commercially important alcohols.

Methanol

- Methanol also known as ‘wood spirit’ was produced by destructive distillation of wood.
- Now methanol is produced by catalytic hydrogenation of carbon monoxide at high pressure and temperature in the presence of $ZnO\text{-}Cr_2O_3$ catalyst.

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

Ethanol

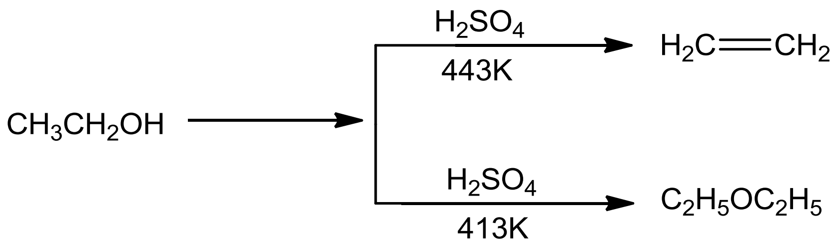
- It is commercially obtained by fermentation from sugars.
- The sugar in molasses, sugarcane or fruits like grapes is converted to glucose and fructose in the presence of an enzyme invertase.
- Glucose and fructose undergo fermentation in the presence of another enzyme, zymase, which is found in the yeast.

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

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

Preparation of Ethers

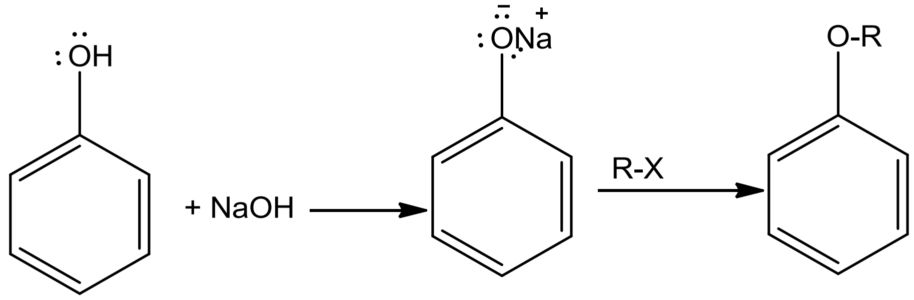
- **By Dehydration of Alcohols**
  - Alcohols on dehydration with protic acids like H_2SO_4, H_3PO_4 give alkene or ether depending on the reaction conditions.



- **Williamson Synthesis**
  - This method is used for the preparation of symmetrical and unsymmetrical ethers.
  - In this reaction, an alkyl halide is allowed to react with sodium alkoxide.

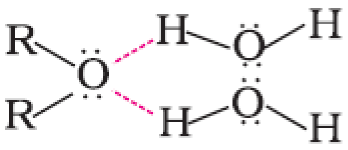
$$R\text{-}X + R'\text{-}\overset{-}{\underset{\cdot\cdot}{\ddot{O}}}\overset{+}{Na} \longrightarrow R\text{-}\underset{\cdot\cdot}{\ddot{O}}\text{-}R' + Na\,X$$

  - Phenols can also be converted into ethers using this method. In this, phenol is used as the phenoxide moiety.

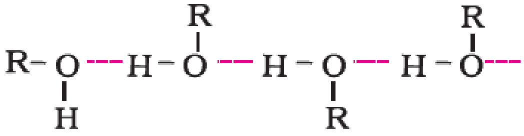


Physical Properties of Ethers

- **Miscibility**
  Miscibility of ethers with water resembles those of alcohols of the same molecular mass. This is because similar to alcohols; oxygen of ether can also form hydrogen bonds with the water molecule.



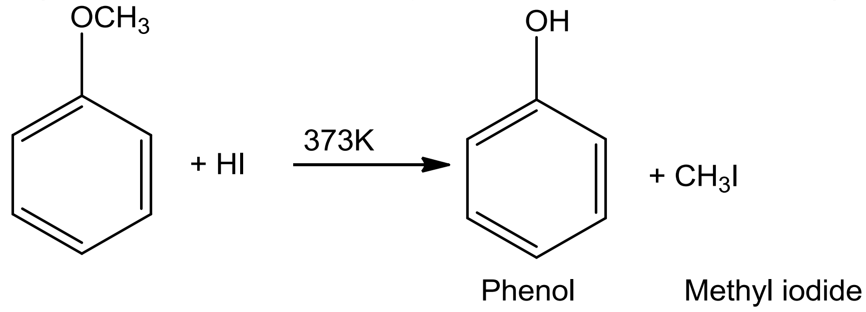
- **Boiling points**
  Ethers have much lower boiling points than alcohols. This is due to the presence of hydrogen bonding in alcohols. Hydrogen bonding is absent in ethers.



Chemical Properties of Ethers

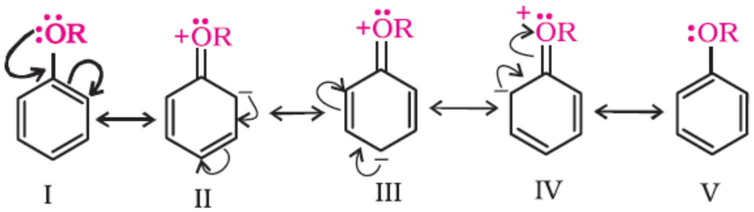
A. Cleavage of C–O bond in ethers

- Since ethers are least reactive of the functional groups, the cleavage of C-O bond in ethers takes place in excess of hydrogen halides.
  $$R\text{-}O\text{-}R + HX \longrightarrow RX + R\text{-}OH$$
- The cleavage of ethers with two different alkyl groups also takes place in the same manner.
  $$R\text{-}O\text{-}R' + HX \longrightarrow R\text{-}X + R'\text{-}OH$$
- In phenolic ethers, the cleavage occurs with the formation of phenol and alkyl halide.



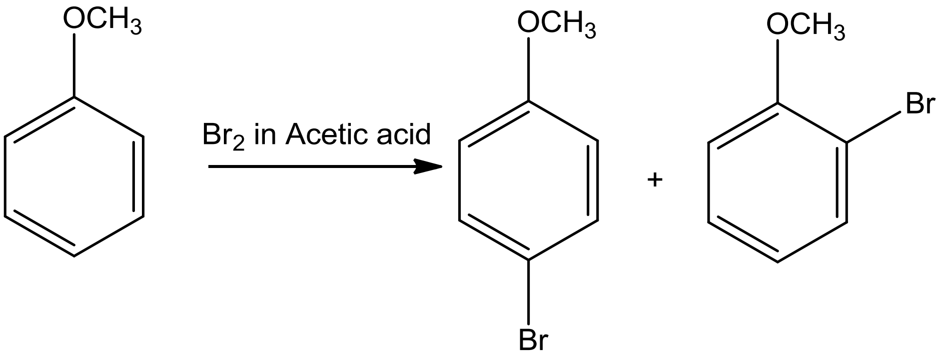
B. Electrophilic Substitution

The alkoxy group (-OR) is ortho,para directing and activates the benzene ring for aromatic substitution.



(i) Halogenation

Phenyl alkyl ethers undergo halogenation reaction.



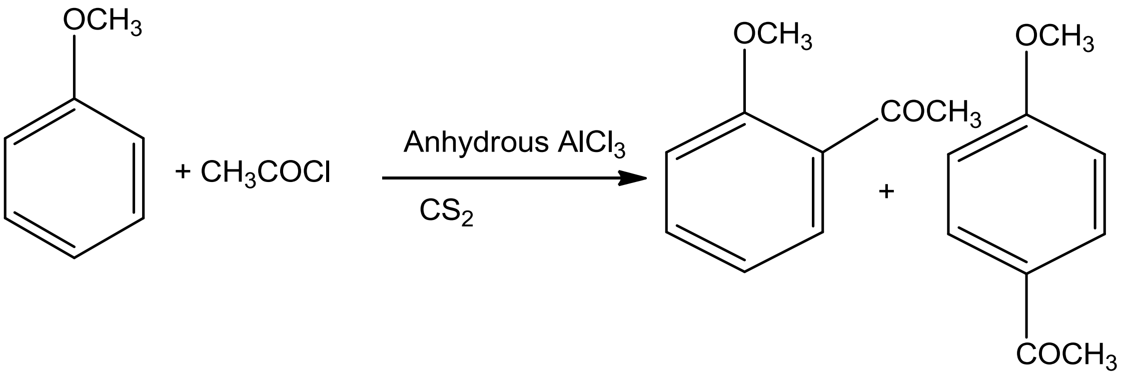
Anisole

p-Bromoanisole (Major)

o-Bromoanisole (Minor)

(ii) Friedel-Crafts reaction

In this reaction the alkyl groups and acyl groups are introduced at ortho and para position by treating anisole with alkyl halide and acyl halide in the presence of anhydrous chloride as catalyst.



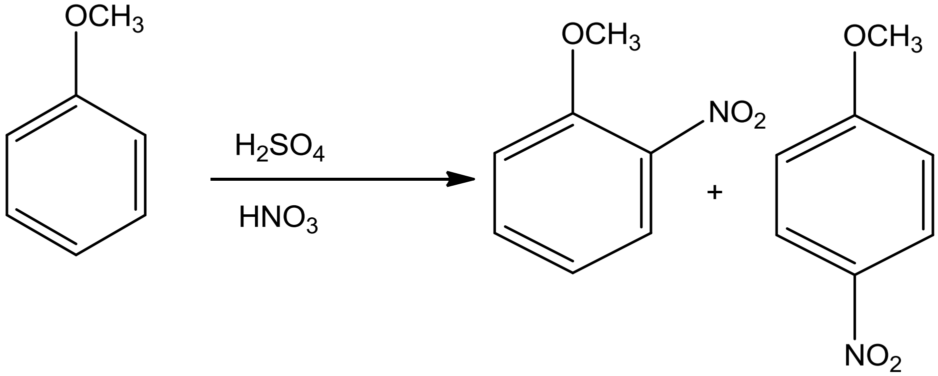
Anisole

2-Methoxy acetophenone

4-Methoxy acetophenone

(iii) Nitration

Anisole on treating with a mixture of sulphuric acid and nitric gives a mixture of ortho and para nitroanisole.



Anisole

2-Nitroanisole

(Minor)

4-Nitroanisole

(Major)