Class : 11

2023 – 24

ALCOHOLS PHENOLS AND ETHERS

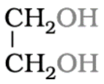
Classification:

Alcohols-Mono, Di, Tri or Polyhydric alcohols :

- Alcohols and phenols may be classified as mono-, di-, tri- or polyhydric compounds depending on whether they contain one, two, three or many hydroxyl groups respectively in their structures as given below:

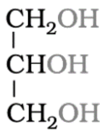
C_2H_5OH

Monohydric



$$\begin{array}{c} CH_2OH \\ | \\ CH_2OH \end{array}$$

Dihydric



$$\begin{array}{c} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

Trihydric

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

Compounds containing $C_{sp^3} - OH$ bond:

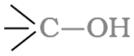
- In this class of alcohols, the $-OH$ group is attached to an sp^3 hybridised carbon atom of an alkyl group. They are further classified as follows:

  Primary, secondary and tertiary alcohols: In these three types of alcohols, the $-OH$ group is attached to primary, secondary and tertiary carbon atom, respectively as depicted below:

$-CH_2-OH$

Primary (1°)

Secondary (2°)

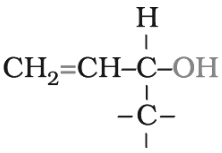


Tertiary (3°)

- **Allylic alcohols :** In these alcohols, the $-OH$ group is attached to a sp^3 hybridised carbon adjacent to the carbon-carbon double bond, that is to an allylic carbon.

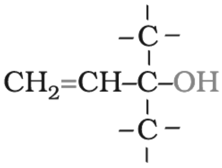
$CH_2=CH-CH_2-OH$

Primary



$$\begin{array}{c} H \\ | \\ CH_2=CH-C-OH \\ | \\ -C- \\ | \end{array}$$

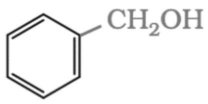
Secondary



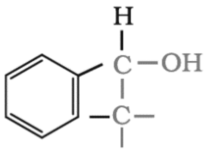
$$\begin{array}{c} | \\ -C- \\ | \\ CH_2=CH-C-OH \\ | \\ -C- \\ | \end{array}$$

Tertiary

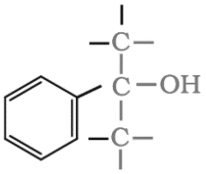
- **Benzylic alcohols**: In these alcohols, the $-OH$ group is attached to a sp^3-hybridised carbon atom next to an aromatic ring. For example.



Primary



Secondary



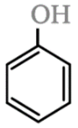
Tertiary

Compounds containing $C_{sp^2} - OH$ bond:

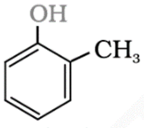
- These alcohols contain $-OH$ group bonded to a carbon-carbon double bond, i.e., to a vinylic carbon or to an aryl carbon. These alcohols are also known as vinylic alcohols.

  Vinylic alcohol: $CH_2 = CH - OH$

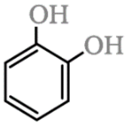
  Phenols-Mono, Di and trihydric phenols



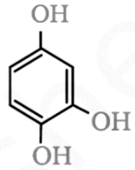
Monohydric



Monohydric



Dihydric



Trihydric

- **Ethers :** Ethers are classified as simple or symmetrical, if the alkyl or aryl groups attached to the oxygen atom are the same, and mixed or unsymmetrical, if the two groups are different.

Nomenclature:

Alcohols: The common name of an alcohol is derived from the common name of the alkyl group and adding the word alcohol to it. For example, $\mathrm{CH_3OH}$ is methyl alcohol.

According to IUPAC system the some of in alcohol is derived from the name of the alkane from which the alcohol is derived, by substituting ' e ' of alkane with the suffix '**ol**'.

For naming polyhydric alcohols, the ' e ' of alkane is retained and the ending 'ol' is added. The number of $-\mathbf{OH}$ groups is indicated by adding the multiplicative prefix, di, tri, etc., before 'ol'. Cyclic alcohols are named using the prefix cyclo and considering the $-\mathrm{OH}$ group attached to $\mathrm{C}-1$.

Phenols: The simplest hydroxy derivative of benzene is phenol. It is its common name and also an accepted IUPAC name. As structure

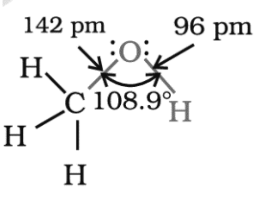
Ethers: Common names of ethers are derived from the names of alkyl/aryl groups written as separate words in alphabetical order and adding the word 'ether' at the end.

If both the alkyl groups are the same, the prefix ' di ' is added before the alkyl group. For example, $\mathrm{C_2H_5C_2H_5}$ is diethyl ether.

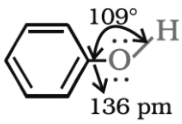
According to IUPAC system of nomenclature, ethers are regarded as hydrocarbon derivatives in which a hydrogen atom is replaced by an $-\mathrm{OR}$ or $-\mathrm{OAr}$ group, where R and Ar represent alkyl and aryl groups, respectively. The larger (R) group is chosen as the parent hydrocarbon.

Structures of Functional Groups:

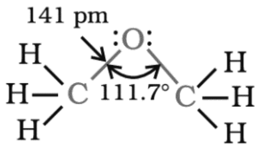
In alcohols, the oxygen of the $-\mathrm{OH}$ group is attached to carbon by a sigma (σ) bond formed by the overlap of a sp^3 hybridised orbital of carbon with a sp^3 hybridised orbital of oxygen.



Methanol



Phenol



Methoxymethane

The bond angle: In alcohols is slightly less than the tetrahedral angle $(109^\circ - 28')$. It is due to the repulsion between the unshared electron pairs of oxygen.

In phenols, the $-\mathrm{OH}$ group is attached to sp^2 hybridised carbon of an aromatic ring.

The carbon-oxygen bond length in phenol is slightly less than that in methanol.

This is due to (i) partial double bond character on account of the conjugation of unshared electron pair of oxygen with the aromatic ring and (ii) sp^2 hybridised state of carbon to which oxygen is attached.

In ethers, the four electron pairs, i.e., the two bond pairs and two lone pairs of electrons on oxygen are arranged approximately in a tetrahedral arrangement.

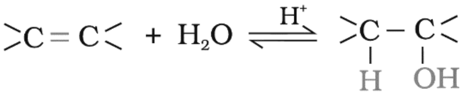
The bond angle is slightly greater than the tetrahedral angle due to the repulsive interaction between the two bulky $(-R)$ groups.

Alcohols and Phenols

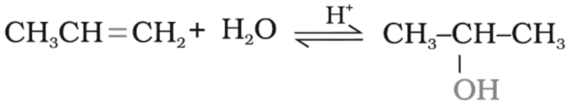
Preparation of Alcohols

From alkenes :

- **By acid catalysed hydration:** Alkenes react with water in the presence of acid as catalyst to form alcohols.



$$>C=C< + H_2O \underset{}{\overset{H^+}{\rightleftharpoons}} >\underset{H}{C}-\underset{OH}{C}<$$



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

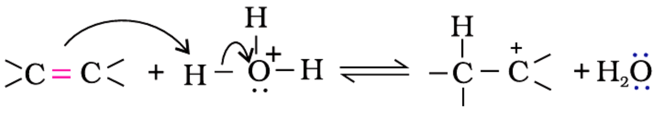
In case of unsymmetrical alkenes, the addition reaction takes place in accordance with Markovnikov's rule.

- **Mechanism**

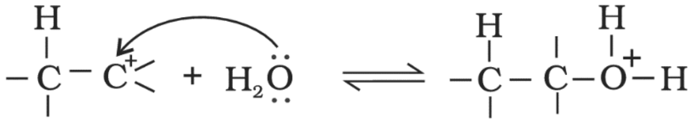
Step 1: Protonation of alkene to form carbocation by electrophilic attack of H_3O^+.

$$H_2O + H^+ \rightarrow H_3O^+$$

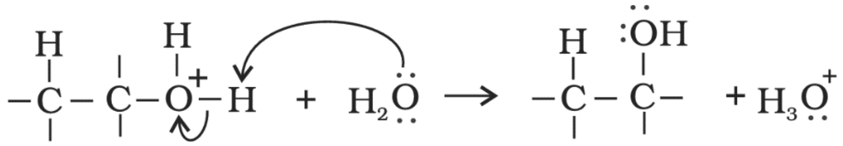
$$H_2O + H^+ \rightarrow H_3O^+$$



Step 2: Nucleophilic attack of water on carbocation.

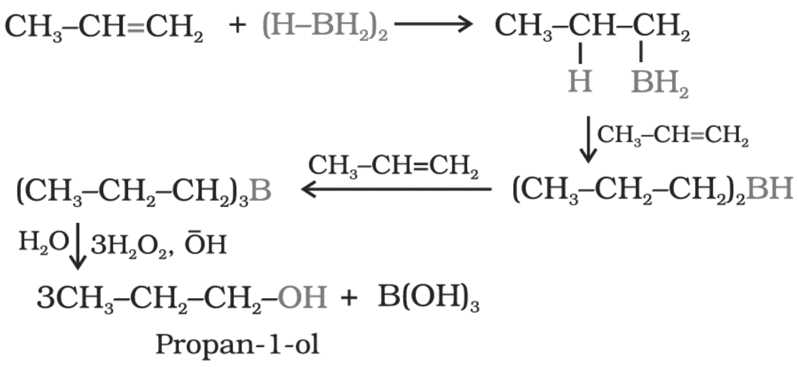


Step 3: Deprotonation to form an alcohol.



By hydroboration-oxidation: Diborane $(BH_3)_2$ reacts with alkenes to give trialkyl boranes as addition product. This is oxidised to alcohol by hydrogen peroxide in the presence of aqueous sodium hydroxide.

- The addition of borane to the double bond takes place in such a manner that the boron atom gets attached to the sp^2 carbon carrying greater number of hydrogen atoms.
- The alcohol so formed looks as if it has been formed by the addition of water to the alkene in a way opposite to the Markovnikov's rule.



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

From carbonyl compounds

By reduction of aldehydes and ketones:

Aldehydes and ketones are reduced to the corresponding alcohols by addition of hydrogen in the presence of catalysts (catalytic hydrogenation).

- The usual catalyst is a finely divided metal such as platinum, palladium or nickel.
- Aldehydes yield primary alcohols whereas ketones give secondary alcohols.

$$\mathrm{RCHO} + \mathrm{H_2} \overset{\mathrm{Pd}}{\rightarrow} \mathrm{RCH_2OH}$$

- It is also prepared by treating aldehydes and ketones with sodium borohydride $(\mathrm{NaBH_4})$ or lithium aluminium hydride $(\mathrm{LiAlH_4})$.

$$RCOR' + \overset{\mathrm{NaBH4}}{\rightarrow} R - \underset{\substack{| \\ \mathrm{C}}}{CH}{-}R'$$

- **By reduction of carboxylic acids and esters:** Carboxylic acids are reduced to primary alcohols in excellent yields by lithium aluminium hydride, a strong reducing agent.

$$\mathrm{RCOOH} \underset{\mathrm{H2O}}{\overset{\mathrm{LiAlH4}}{\rightarrow}} \mathrm{RCH_2OH}$$

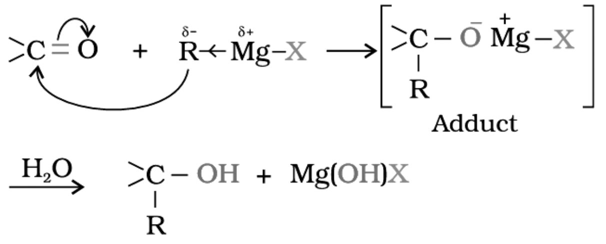
- However, $\mathrm{LiAlH_4}$ is an expensive reagent, and therefore, used for preparing special chemicals only.
- Commercially, acids are reduced to alcohols by converting them to the esters, followed by their reduction using hydrogen in the presence of catalyst (catalytic hydrogenation).

$$\mathrm{RCOOH} \underset{\mathrm{H}}{\overset{\mathrm{R'OH}}{\rightarrow}} \mathrm{RCOOR'} \underset{\mathrm{Catalyst}}{\overset{\mathrm{H2}}{\rightarrow}} \mathrm{RCH_2OH} + \mathrm{R'OH}$$

From Grignard reagents

Alcohols are produced by the reaction of Grignard reagents with aldehydes and ketones.

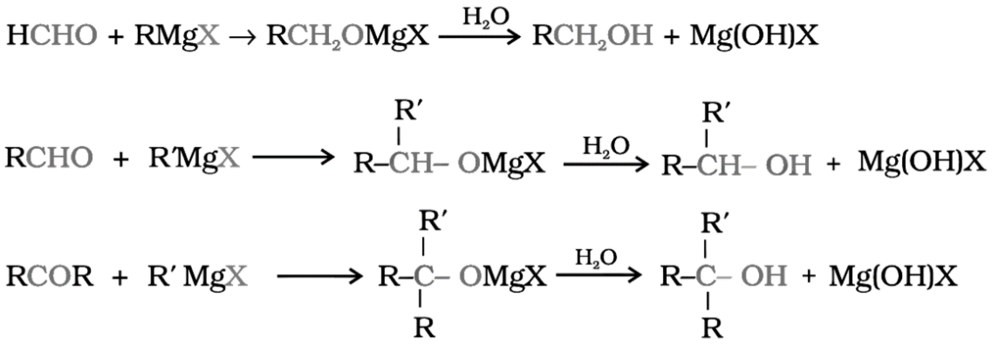
- The first step of the reaction is the nucleophilic addition of Grignard reagent to the carbonyl group to form an adduct. Hydrolysis of the adduct yields an alcohol the adduct yields an alcohol.



… (i)

…(ii)

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



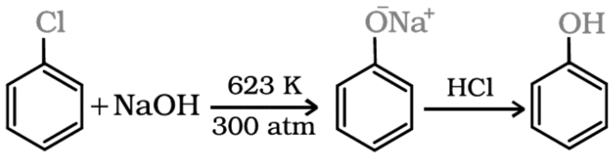
$$\mathrm{HCHO} + \mathrm{RMgX} \rightarrow \mathrm{RCH_2OMgX} \xrightarrow{\mathrm{H_2O}} \mathrm{RCH_2OH} + \mathrm{Mg(OH)X}$$

$$\mathrm{RCHO} + \mathrm{R'MgX} \longrightarrow \mathrm{R{-}\overset{\overset{\textstyle R'}{|}}{CH}{-}OMgX} \xrightarrow{\mathrm{H_2O}} \mathrm{R{-}\overset{\overset{\textstyle R'}{|}}{CH}{-}OH} + \mathrm{Mg(OH)X}$$

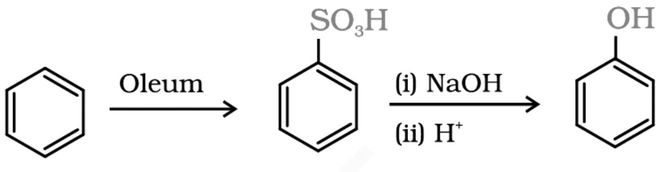
$$\mathrm{RCOR} + \mathrm{R'MgX} \longrightarrow \mathrm{R{-}\underset{\underset{\textstyle R}{|}}{\overset{\overset{\textstyle R'}{|}}{C}}{-}OMgX} \xrightarrow{\mathrm{H_2O}} \mathrm{R{-}\underset{\underset{\textstyle R}{|}}{\overset{\overset{\textstyle R'}{|}}{C}}{-}OH} + \mathrm{Mg(OH)X}$$

Preparation of Phenols:

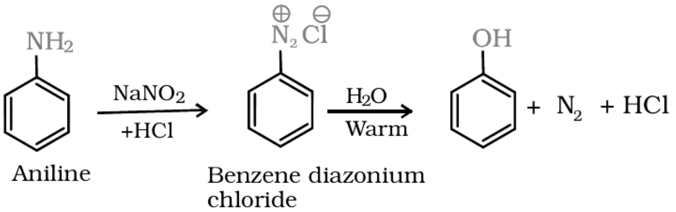
From haloarenes: Chlorobenzene is fused with NaOH at 623 K and 320 atmospheric pressure to give sodium phenoxide which on acidification gives phenols.



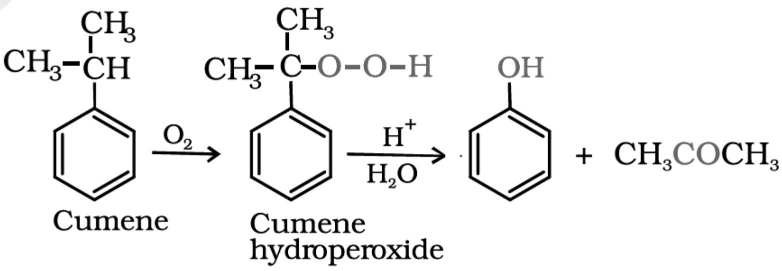
From benzenesulphonic acid : Benzene is sulphonated with oleum and benzene sulphonic acid so formed is converted to sodium phenoxide on heating with molten sodium hydroxide. Acidification of the sodium salt gives phenol.



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



- **From cumene :** Phenol is manufactured from the hydrocarbon, cumene. Cumene (isopropylbenzene) is oxidised in the presence of air to cumene hydroperoxide which on treatment with dil. acid gives phenol, acetone.

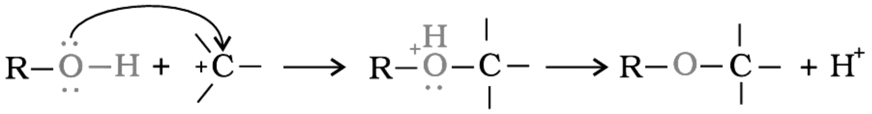


- **Physical Properties :** Alcohols and phenols consist of two parts, an alkyl/ aryl group and a hydroxyl group. The properties of alcohols and phenols are chiefly due to the hydroxyl group.
- The boiling points of alcohols and phenols increase with increase in the number of carbon atoms (increase in van der Waals forces).
- In alcohols, the boiling points decrease with increase of branching in carbon chain (because of decrease in van der Waals forces with decrease in surface area).

Boiling points of alcohols and phenols are higher in comparison to other classes of compounds. The high boiling points of alcohols are mainly due to the presence of intermolecular hydrogen bonding in them which is lacking in esters at of hydrocarbons.
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 Reactions: Alcohols are versatile compounds. They react both as nucleophiles and electrophiles. The bond between $0 - H$ is broken when alcohols react as nucleophiles.

Alcohols as nucleophiles

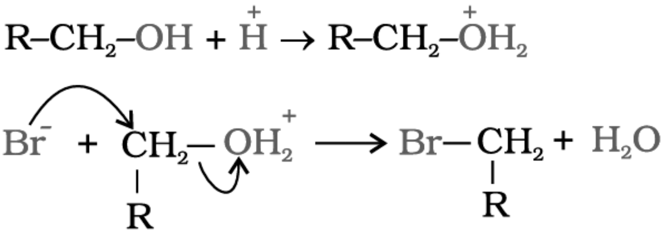


(i)

(ii) The bond between $\mathrm{C-O}$ is broken when they react aselectrophiles Protonated alcohols react in this manner.

- **Protonated alcohols as electrophiles**

$$\mathrm{R-CH_2-OH} + \overset{+}{\mathrm{H}} \rightarrow \mathrm{R-CH_2-\overset{+}{O}H_2}$$

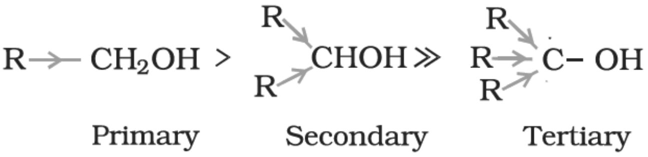


Acidity of alcohols and phenols

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

$$\mathrm{2R-O-H + 2Na \rightarrow 2R-O-Na + H_2}$$

- **Acidity of alcohols:** The acidic character of alcohols is due to the polar nature of $\mathrm{O-H}$ bond.
- An electron-releasing group $(-\mathrm{CH_3}, -\mathrm{C_2H_5})$ increases electron density on oxygen tending to decrease the polarity of $\mathrm{O-H}$ bond. The acid strength of alcohols decreases in the following order:



- Alcohols are, weaker acids than water.
- Alcohols act as Bronsted bases as well. It is due to the presence of unshared electron pairs on oxygen, which makes them proton acceptors.
- **Acidity of phenols**: The reactions of phenol with metals (e.g. sodium, aluminium) and sodium hydroxide indicate its acidic nature.
- The reaction of phenol with aqueous sodium hydroxide indicates that phenols are stronger acids than alcohols and water
- Due to the higher electronegativity of sp^2 hybridised carbon of phenol to which $-\mathrm{OH}$ is attacbed, electron density decreases on oxygen. This increases the polarity of $\mathrm{O-H}$ bond and results in an increase in ionisation of phenols than that of alcohols. Therefore phenol is more acidic than alcohol.
- In alkoxide ion, the negative charge is localised on oxygen while in phenoxide ion, the charge is delocalised. The delocalisation of negative charge makes pentoxide ion more stable and favours the ionisation of phenol. Although there is also charge delocalisation in phenol, its resonance structures have charge separation due to which the phenol molecule is less stable than phenoxide ion.
- In substituted phenols, the presence of electron withdrawing groups such as nitro group, enhances the acidic strength of phenol.
- It is due to the effective delocalisation of negative charge in phenoxide ion when substituent is at ortho or para position. On the other hand, electron releasing groups, such as alkyl groups, in general, do not favour the formation of phenoxide ion resulting in decrease in acid strength.

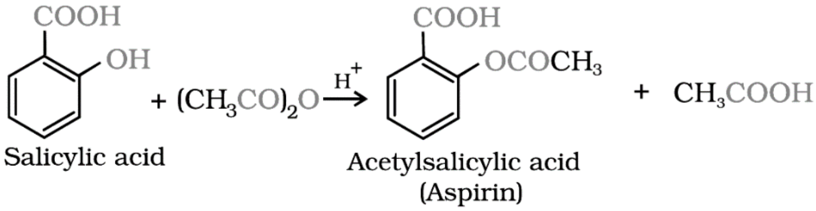
- **Esterification :** Alcohols and phenols react with carboxylic acids, acid chlorides and acid anhydrides to form esters.

$$Ar/ROH + R' - COOH \overset{H^+}{\rightleftharpoons} Ar/ROCOR' + H_2O$$

$$Ar/R - OH + (R'CO)_2O \overset{H^+}{\rightleftharpoons} Ar/ROCOR' + R'COOH$$

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

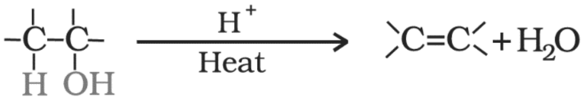
- The reaction with acid chloride is carried out in the presence of a base (pyridine) so as to neutralise HCl which is formed during the reaction.
- The introduction of acetyl (CH_2CO) group in alcohols or phenols is known as acetylation. Acetylation of salicylic acid produces aspirin.



- The difference in reactivity of three classes of alcohols with HCl distinguishes them from one another (Lueas test) Alcohols are soluble in Lucas reagent (cone. HCl and $ZnCl_2$) while their halides alcohols, turbidity is produced immediately as they form the hatides aicobols, turbidary is produced immeduce turbidity at room temperature.

- **Reaction with phosphorus trihalides:**
  Alcohols are converted to alkyl bromides by reaction with phosphorus tribromide,

Dehydration: Alcohols undergo dehydration (removal of a molecule of water) to form alkenes on treating with a protic acid.

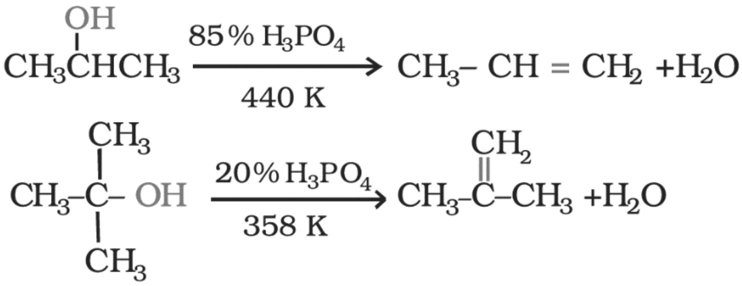


$$-\underset{H}{\overset{|}{C}}-\underset{OH}{\overset{|}{C}}- \xrightarrow[Heat]{H^+} >C=C< + H_2O$$

Ethanol under goes dehydration by heating it with concentrated H_2SO_3, at 443 K.

$C_2H_5OH \rightarrow CH_2 = CH_2 + H_2O$

- Secondary and tertiary alcohols are dehydrated under milder conditions.



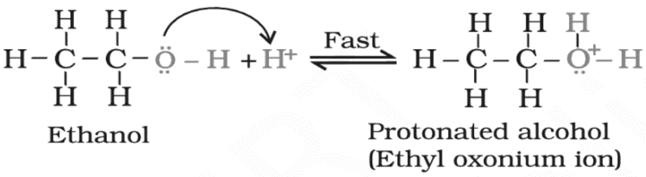
$$CH_3\overset{OH}{\overset{|}{C}}HCH_3 \xrightarrow[440\ K]{85\%\ H_3PO_4} CH_3-CH=CH_2 + H_2O$$

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

- The relative ease of dehydration of alcohols follows the following order: Tertiary > Secondary > Primary

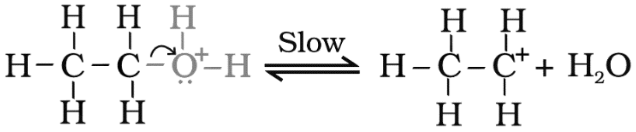
Mechanism

Step 1: Formation of protonated alcohol.

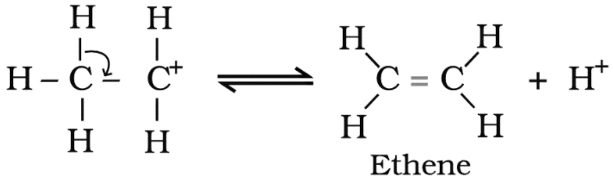


Protonated alcohol (Ethyl oxonium ion)

- **Step 2:** Formation of carbocation: It is the slowest step and hence, the rate determining step of the reaction.

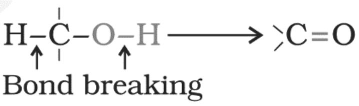


- **Step 3:** Formation of ethene by elimination of a proton.

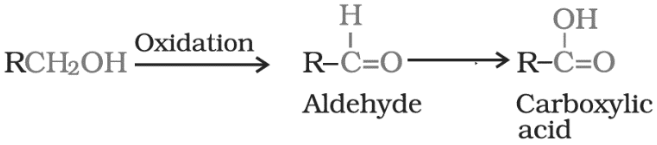


The acid used in step I is released in step 3. To drive the equilibrium to the right, ethene is removed as it is formed.

Oxidation: Oxidation of alcohols involves the formation of a carbon oxygen double bond with cleavage of an $O-H$ and $C \cdot H$ bonds.



- These are also known as dehydrogenation reactions as these involve loss of dihydrogen from an alcohol molecule.
- Depending on the oxidising agent used, a primary alcohol is oxidised to an aldehyde which in turn is oxidised to a carboxylic acid.



Strong oxidising agents such as acidified potassium permanganate are used for getting carboxylic acids from alcohols directly.

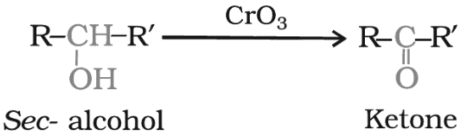
- CrO_3 in anhydrous medium is used as the oxidising agent for the isolation of aldehydes.

$$RCH_2OH \rightarrow RCHO$$

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

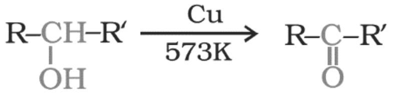
$$CH_3-CH=CH-CH_2OH \rightarrow CH_3-CH=CH-CHO$$

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

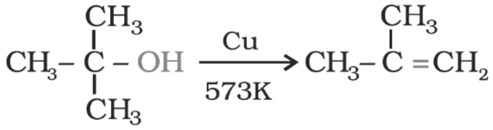


Tertiary alcohols do not undergo oxidation reaction. Under strong reaction conditions such as strong oxidising agents ($KMnO_4$) and elevated temperatures, cleavage of various $C-C$ bonds takes place and a mixture of carboxylic acids containing lesser number of carbon atoms is formed.

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



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



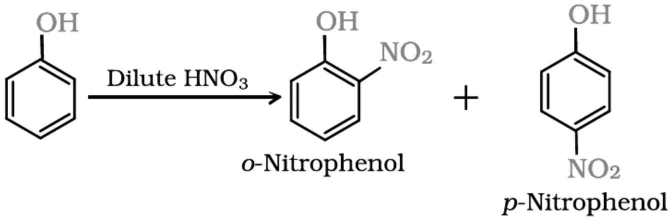
$$CH_3{-}\overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_3}}{C}}{-}OH \xrightarrow[573K]{Cu} CH_3{-}\overset{\substack{CH_3\\|}}{C}{=}CH_2$$

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

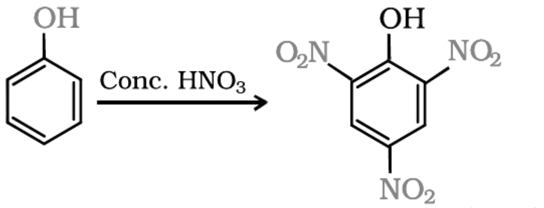
Reactions of phenols

Electrophilic aromatic substitution : In phenols, the reactions that take place on the aromatic ring are electrophilic substitution reactions. Common electrophilic aromatic substitution reactions taking place in phenol are as follows:

- **Nitration:** With dilute nitric acid at low temperature phenol yields a mixture of ortho and para nitrophenols.



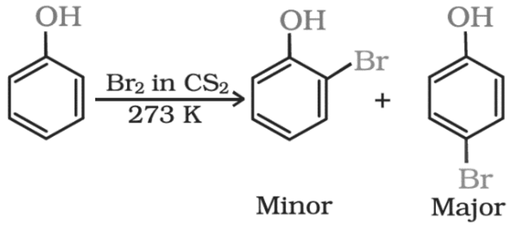
- The ortho and para isomers can be separated by steam distillation.
- *o*-Nitrophenol is steam volatile due to intramolecular hydrogen bonding while *p*-nitrophenol is less volatile due to intermolecular hydrogen bonding which causes the association of molecules.
- With concentrated nitric acid, phenol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



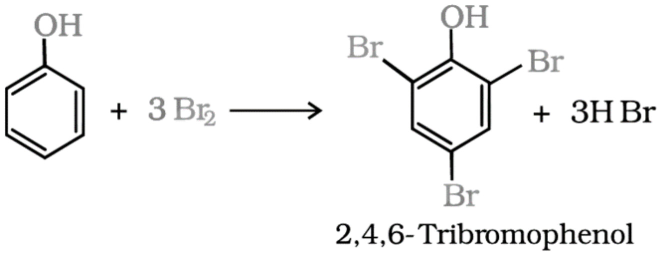
2,4,6-Trinitrophenol
(Picric acid)

- Nowadays picric acid is prepared by treating phenol first with concentrated sulphuric acid which converts it to phenol-2,4disulphonic acid, and then with concentrated nitric acid to get 2,4,6-trinitrophenol.

- **Halogenation:** When the reaction is carried out in solvents of low polarity such as $CHCl_3$ or CS_2 and at low temperature. monobromophenols are formed.

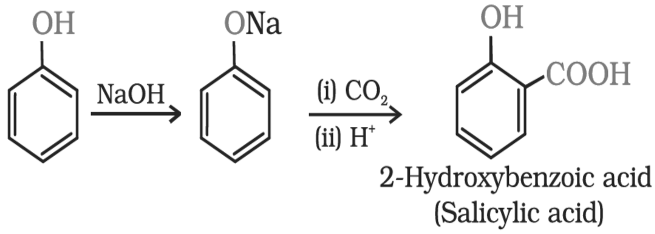


- The usual halogenation of benzene takes place in the presence of a Lewis acid, such as $FeBr_3$, which polarises the halogen molecule.
  In case of phenol, the polarisation of bromine molecule takes place even in the absence of Lewis acid. It is due to the highly activating. effect of $-OH$ group attached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



2,4,6-Tribromophenol

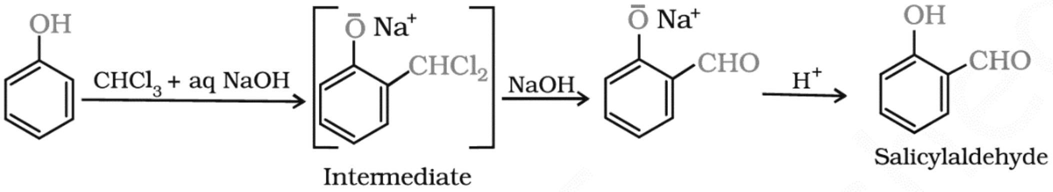
- **Kolbe's reaction :** Phenoxide ion generated by treating phenol with sodium hydroxide is even more reactive than phenol towards electrophilic aromatic substitution.



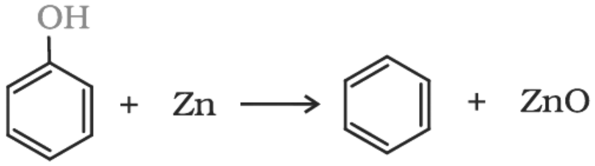
2-Hydroxybenzoic acid (Salicylic acid)

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

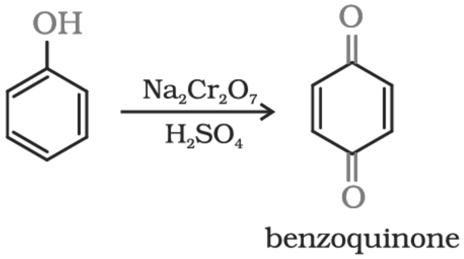
- The intermediate substituted benzal chloride is hydrolysed in the presence of alkali to produce salicylaldehyde.



Reaction of phenol with zinc dust : Phenol is converted to benzene on heating with zinc dust.



Oxidation : Oxidation of phenol with chromic acid produces a conjugated diketone known as benzoquinone.



Some Commercially Important Alcohols

Methanol :

Methanol, $\mathrm{CH_3OH}$, also known as 'wood spirit', was produced by destructive distillation of wood. Today, most of the methanol is produced by catalytic hydrogenation of carbon monoxide at high pressure and temperature and in the presence of $\mathrm{ZnO}-\mathrm{Cr_2O_3}$ catalyst.

$$CO + 2H_2 \xrightarrow[200-300atm]{ZnO-Cr2O3} CH_3OH$$

Methanol is a colourless liquid and boils at 337 K. It is highly poisonous in nature.
Methanol is used as a solvent in paints, varnishes and chiefly for making formaldehyde.

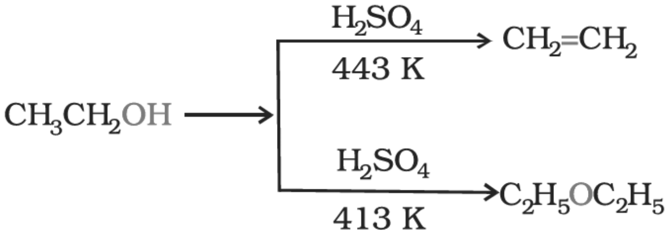
Ethanol :

- Ethanol, C_2H_5OH, is obtained commercially by fermentation, the oldest method is from sugars.
  Glucose and fructose undergo fermentation in the presence of another enzyme, zymase, which is found in yeast.
- $$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$
  $$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2$$
- The action of zymase is inhibited once the percentage of alcohol formed exceeds 14 percent. Ethanol is a colourless liquid with boiling point 351 K. It is used as a solvent in paint industry and in the preparation of a number of carbon compounds.
- The commercial alcohol is made unfit for drinking by mixing in it some copper sulphate (to give it a colour) and pyridine (a foul smelling liquid). It is known as **denaturation** of alcohol.
- Nowadays, large quantities of ethanol are obtained by hydration of ethene.

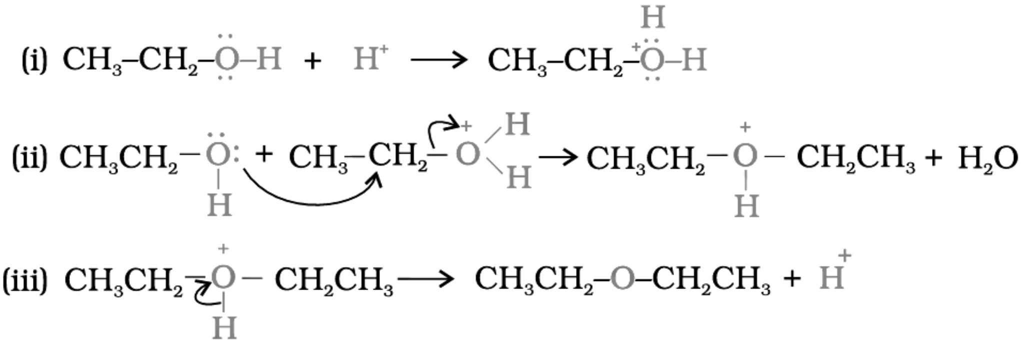
Ethers

Preparation of Ether by dehydration of Alcohols:

- Alcohols undergo dehydration in the presence of protic acids (H_2SO_2, H_3PO_4).
  The formation of the reaction product, alkene or ether depends on the reaction condition.



- The formation of ether is a nucleophilic bimolecular reaction (S_N2) involving the attack of alcohol molecule on a protonated alcohol, as indicated below:



$$\text{(i)}\ CH_3-CH_2-\ddot{O}-H + H^+ \longrightarrow CH_3-CH_2-\overset{H}{\overset{|}{\overset{+}{O}}}-H$$

$$\text{(ii)}\ CH_3CH_2-\underset{H}{\ddot{O}}: + CH_3-CH_2-\overset{+}{O}\begin{matrix}H\\H\end{matrix} \rightarrow CH_3CH_2-\underset{H}{\overset{+}{O}}-CH_2CH_3 + H_2O$$

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

- Acidic dehydration of alcohols, to give an alkene is also associated with substitution reaction to give an ether. 6. The method is suitable for the preparation of ethers having primary alkyl groups only. The alkyl group should be unhindered and the temperature be kept low. Otherwise the reaction favours the formation of alkene.
- The reaction follows &. I pathway when the alcohol is secondary of tertiary.
- The dehydration of secondary and tertiary alcohols to give corresponding ethers is unsuccessful as elimination compounds over substitution and as a consequence, alkenes are easily formed.

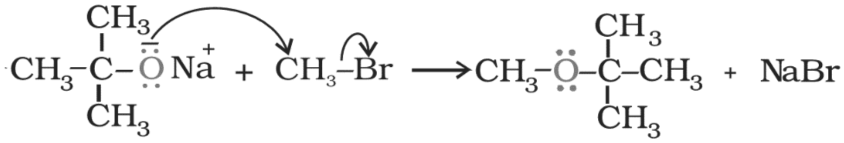
Williamsen synthesis :

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

$$R–X + R'–\overset{-}{\ddot{O}}\overset{+}{Na} \longrightarrow R–\ddot{O}–R' + Na\,X$$

- Ethers containing substituted alkyl groups (secondary or tertiary) may also be prepared by this method.

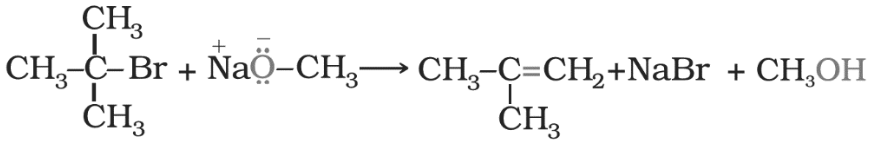
  The reaction involves $S_N{}^2$ attack of an alkoxide ion on primary alky halide.



$$CH_3–C(CH_3)_2–\overset{-}{\ddot{O}}\overset{+}{Na} + CH_3–Br \longrightarrow CH_3–\ddot{O}–C(CH_3)_2–CH_3 + NaBr$$

Better results are obtained if the alkyl halide is primary. In case of secondary and tertiary alkyl halides, elimination competes over substitution.

- If a tertiary alkyl halide is used, an alkene is the only reaction product and no ether is formed.



$$CH_3–C(CH_3)_2–Br + \overset{+}{Na}\overset{-}{\ddot{O}}–CH_3 \longrightarrow CH_3–C(CH_3){=}CH_2 + NaBr + CH_3OH$$

2-Methylpropene

It is because alkoxides are not only nucleophiles but strong bases as well.

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

Physical Properties :

The C-O bonds in ethers are polar and thus, ethers have a net dipole moment.

- The weak polarity of ethers do not appreciably affect their boiling points which are comparable to those of the alkanes of comparable molecular masses.

  Formula

  $CH_3(CH_2)_3CH_3C_2H_5 - O - C_2H_5CH_3(CH_2)_3 - OH$

  n-Pentane Ethoxyethane Butan-1-ol

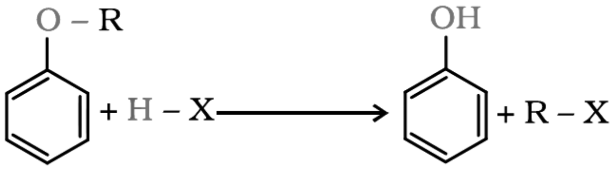
  B.p. /K 309.1 307.6 390

- The large difference in boiling points of alcohols and ethers is due to the presence of hydrogen bonding in alcohols.
- The miscibility of ethers with water resembles those of alcohols of the same molecular mass. This is due to the fact that just like alcohols, oxygen of ether can also form hydrogen bonds with water molecule as shown:
- **Chemical Reactions**

  Cleavage of $C - O$ bond in ethers : Ethers are the least reactive of the functional groups. The cleavage of $C - O$ bond in ethers takes place under drastic conditions with excess of hydrogen halides.

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

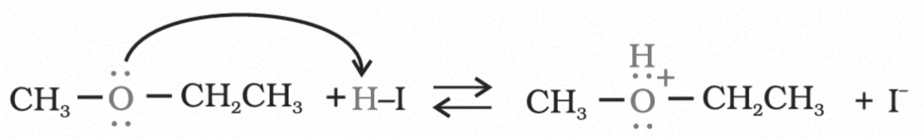
Alkyl aryl ethers are cleaved at the alkyl-oxygen bond due to the more stable aryl-oxygen bond. The reaction yields phenol and alkyl halide.



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

- The reaction of an ether with concentrated HI starts with protonation of ether molecule.

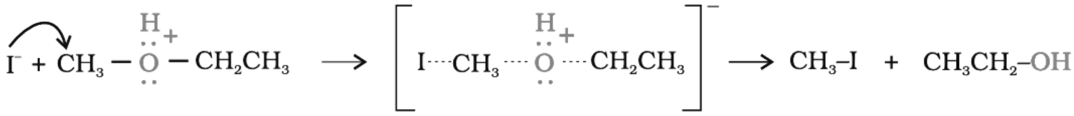
Step 1:



The reaction takes place with HBr or HI because these reagents are sufficiently acidic.

Step 2:

Iodide is a good nucleophile. It attacks the least substituted carbon of the oxonium ion formed in step 1 and displaces an alcohol molecule by $S_N{}^2$ mechanism.

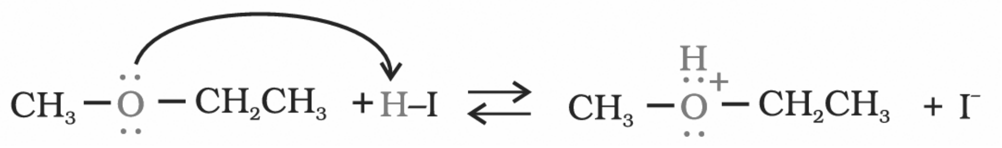


In the cleavage of mixed ethers with two different alkyl groups, the alcohol and alkyl iodide formed, depend on the nature of alkyl groups. When primary or secondary alkyl groups are present, it is the lower alkyl group that forms alkyl iodide ($S_N{}^2$ reaction).

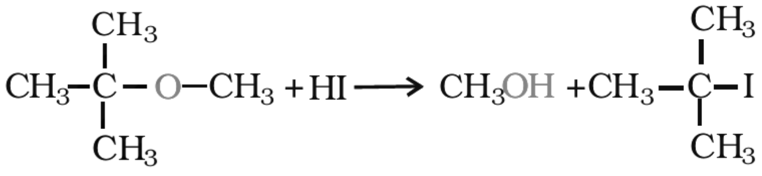
$$\longrightarrow CH_3-I+CH_3CH_2-OH$$

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

Step 3:

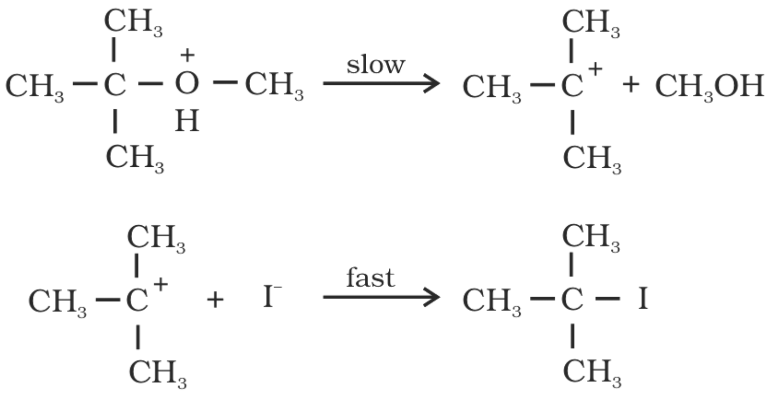


When one of the alkyl group is a tertiary group, the halide formed is a tertiary halide.



$$CH_3-C(CH_3)_2-O-CH_3+HI\longrightarrow CH_3OH+CH_3-C(CH_3)_2-I$$

- It is because in step 2 of the reaction, the departure of leaving group $(HO-CH_3)$ creates a more stable carbocation $[(CH_3)_3C^-]$ and the reaction follows S_N1 mechanism.



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{H}{\overset{+}{O}}-CH_3 \xrightarrow{slow} CH_3-\underset{CH_3}{\overset{CH_3}{C^+}} + CH_3OH$$

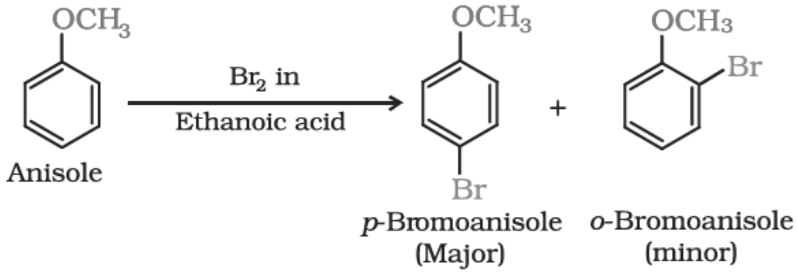
$$CH_3-\underset{CH_3}{\overset{CH_3}{C^+}} + I^- \xrightarrow{fast} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-I$$

-

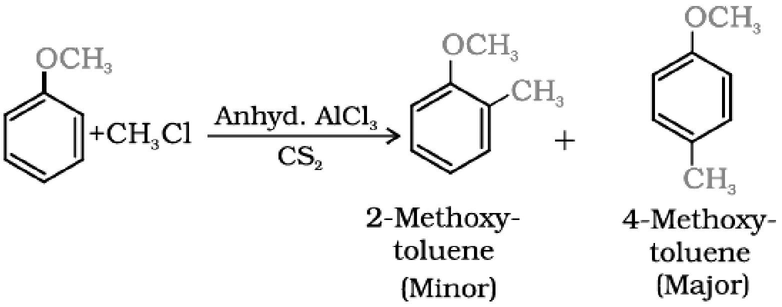
- In case of anisole, methylphenyl oxonium ion, is formed by protonation of ether. The bond between O^-CH_3 is weaker than the bond between 0 C_6H_5 because the carbon of phenyl group is sp^2 hybridised and there is a partial double bond character. Therefore the attack by I-ion breaks $O-CH_3$ bond to form CH_3I.

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

Halogenation:

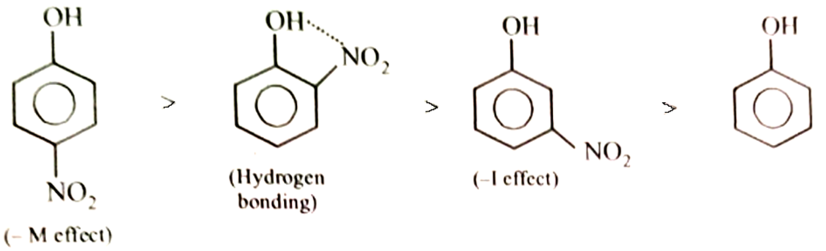


Friedel – Crafts reaction:



Past Years One – Liners
NEET/JEE Main/Board

- **Acidity of isomers of substituted Phenols:-**



- Ketones gives tertiary alcohols with ethyl magnesium bromide.
- In anisole $-\mathrm{OCH_3}$ group is attached to the sp^2 hybridized carbon of the phenyl ring. Due to partial bond character the $\mathrm{C-O}$ is not easy to break. So $\mathrm{-O-CH_3}$ bond will break and gives phenol and methyl iodide with HI.
- In phenol, the lone pairs of oxygen atom are involved in conjugation with benzene ring so they are not available for protonation and hence difficult to protonate the phenol.
- Ethyl alcohol gives sodium ethoxide by ionic reaction with alkali metal followed by reaction with $\mathrm{PCl_5}$ gives ethyl chloride.

  The acidity of phenol increases as the number of $\mathrm{NO_2}$ group attached to the benzene ring increases and thus 2,4,6 trinitrophenol is more acidic than phenol, mono and di substituted phenol.
- In case of ether, unsymmetrical ether is formed by any pathway the reaction will always called as Williamson ether synthesis reaction.
- Tertiary and secondary alcohols undergo acid-catalyzed dehydration by an $\mathrm{E_1}$ mechanism; primary alcohols are dehydrated by an E_2 mechanism. In either mechanism, the first step is the rapid protonation of the lone pair electrons of the oxygen atom to produce an alkyloxonium ion. Therefore, in case of tertiary carbocation the eliminating hydrogen atom will be alpha not beta.
- Lucas test is generally used to differentiate different type of alcohols. Tertiary alcohol instantly gives turbidity with Lucas reagent ($\mathrm{ZnCl_2}$ + con. HCl).
- Epoxide ring opening may occur via $\mathrm{S_N}1$ and $\mathrm{S_N}2$ pathway, when medium is acidic S_N1 pathway is followed otherwise S_N2. 1-Methyl ethylene oxide can be opened via $\mathrm{S_N}1$ pathway by using 1 molar equivalent of HBr and yields 2 bromopropane but when excess HBr is used further reaction take place and yields 1,2 dibromopropane.
- In presence of HI, cleavage of ethers occurs. In $\mathrm{-C-O-C-}$ linkage $-\mathrm{CO}$ bond is not break in case of phenolic ether due to its partial double bond character.

Tips/Tricks/Techniques ONE-LINERS

(Exam Special)

Tests of Phenols

(i) Ferric chloride test: Phenol $+1\%\mathrm{FeCl_3}$ solution → Violet colour

(ii) Bromine water: Phenol + bromine water → Curdy precipitate

(iii) Phenolphthalein test: (Phenol + phthalic anhydride + conc. $\mathrm{H_2SO_4}$)

$+\mathrm{NaOH} \xrightarrow{\text{heat}}$ Pink colour

Appearance of red colour confirms the presence of peroxide, i.c.,

$\mathrm{Fe^{2+}} \xrightarrow{\text{peroxide}} \mathrm{Fe^{3+}} \xrightarrow{\text{3KCNS}}$ Red colour $[\mathrm{Fe(CNS)_3}]$

(iv) Reaction of Ether with HX

(a) $\mathrm{CH_3-O-CH_2-CH_3+HX\,(cold)\longrightarrow CH_3-X+C_2H_5OH}$

If we take unsymmetrical ether with cold $\mathrm{H-X}$, then smaller alkyl group forms alkyl halide.

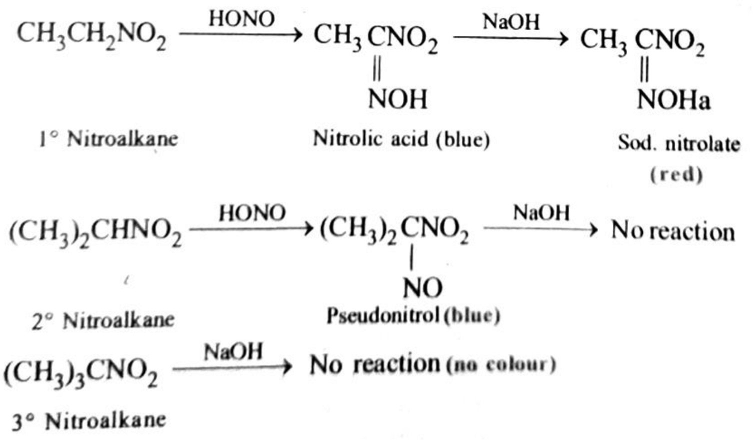
$$\text{(b) } \mathrm{CH_3-CH_2-O-CH_2-CH_3+2H-X(Hot)\xrightarrow{\Delta}2CH_3-CH_2-X+H_2O}$$

$$\mathrm{CH_3-O-CH_2-CH_3+2H-X\xrightarrow{\Delta}CH_3-X+C_2H_5X+H_2O}$$

The above reaction is called 'Ziesel's method estimation'.

Distinction Between Primary, Secondary and Tertiary Alcohols:

Victor Meyer test: This test is based upon the fact that the three types $(1^\circ, 2^\circ$ or $3^\circ)$ of nitroalkanes (formed by alcohols) react differently with nitrous acid followed by sodium hydroxide.



$$\underset{\text{1° Nitroalkane}}{CH_3CH_2NO_2} \xrightarrow{HONO} \underset{\text{Nitrolic acid (blue)}}{\underset{\underset{NOH}{\|}}{CH_3CNO_2}} \xrightarrow{NaOH} \underset{\text{Sod. nitrolate (red)}}{\underset{\underset{NOHa}{\|}}{CH_3CNO_2}}$$

$$\underset{\text{2° Nitroalkane}}{(CH_3)_2CHNO_2} \xrightarrow{HONO} \underset{\text{Pseudonitrol (blue)}}{\underset{\underset{NO}{|}}{(CH_3)_2CNO_2}} \xrightarrow{NaOH} \text{No reaction}$$

$$\underset{\text{3° Nitroalkane}}{(CH_3)_3CNO_2} \xrightarrow{NaOH} \text{No reaction (no colour)}$$

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PW Web/App - https://smart.link/7wwosivoicgd4

Library- https://smart.link/sdfez8ejd80if