ALCOHOLS, PHENOLS AND ETHERS

Alcohols and Phenols

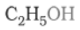
Alcohols and phenols are formed when a hydrogen atom in hydrocarbon (aliphatic and aromatic) is replaced by hydroxyl group (-OH group).

1. Alcohols and phenols may be classified as monohydric, dihydric, trihydric or polyhydric according to number of hydroxyl groups they contain one, two, three or many respectively in their molecules. Alcohols may be

(i) monohydric-containing one – OH group, Ethanol, C_2H_5OH

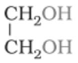
(ii) dihydric-containing two – OH groups, Ethylene glycol, $CH_2OH – CH_2OH$

(iii) polyhydric-containing three or more -OH groups. Glycerol, Propan-1, 2, 3-triol $CH_2OH – CHOH – CH_2OH$



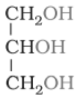
C_2H_5OH

Monohydric



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

Dihydric

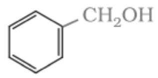


$$\begin{array}{c}CH_2OH\\ |\\ CHOH\\ |\\ CH_2OH\end{array}$$

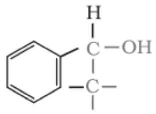
Trihydric

2.In phenols, -OH group is attached to Sp^2 hybridized carbon. These may also be monohydric, dihydric, etc. The dihydric phenol be ortho, Meta' or para derivative.

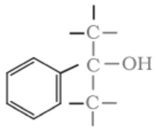
3.In Allylic alcohols, – OH group is attached to sp^3 hybridized carbon but next to C=C bond. e.g., $CH_2 = CH – CH_2OH$, Benzyl alcohol ($C_6H_5CH_2OH$).



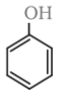
Primary



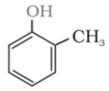
Secondary



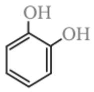
Tertiary



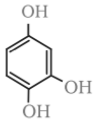
Monohydric



Monohydric



Dihydric



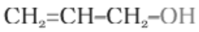
Trihydric

Classification of Alcohols and Phenols

In alcohols, -OH group is attached to Sp^3 hybridized carbon. These alcohols are usually classified as primary, secondary and tertiary alcohols.

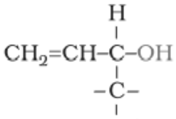
$R – CH_2 – OH$ (Primary), RR' CH – OH (Secondary), R R'R'' C – OH (Tertiary)

Allylic alcohols: classified as primary, secondary and tertiary alcohols.



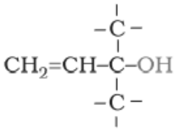
$CH_2{=}CH{-}CH_2{-}OH$

Primary



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

Secondary



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

Tertiary

Structures of Methanol, Phenols and Methoxymethane (Dimethyl ether)

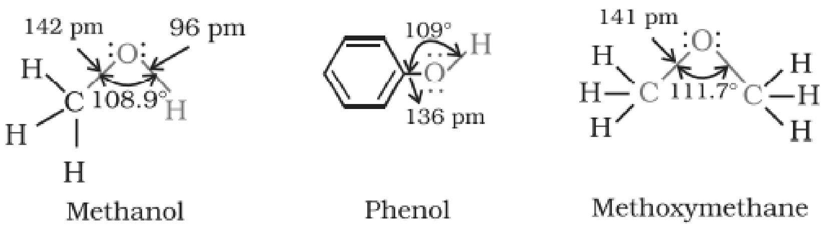


Fig. 11.1: Structures of methanol, phenol and methoxymethane

Isomerism in Alcohols: Alcohols exhibits four types of structural isomers:
(i)Chain isomer: $C_4H_{10}O$ Butan-1-ol, 2-methylpropan-1-ol
(ii)Position isomerism: C_3H_8O Propan-1-ol, propan-2-ol
(iii)Functional isomerism: C_2H_6O Ethanol, methoxy methane
(iv)Optical isomerism: Monohydric alcohols containing chiral carbon atoms exhibit optical isomerism. E.g. Butan-2-ol, Pentan-2-ol

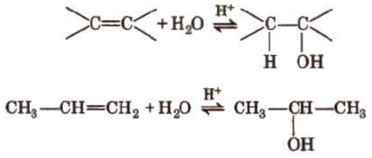
Nomenclature of Alcohols and Phenol:

In IUPAC, system, alcohol or alkanols are named by replacing the last word 'e' of the corresponding alkane by 'ol'. e.g., Propan-1, 2, 3-triol, 2-methyl phenol and 2, 4-dimethylcyclopentanol.

Preparation of Alcohols

(i) **From alkenes**

(a) By acid catalyzed hydration in accordance with Markovnikov's rule.

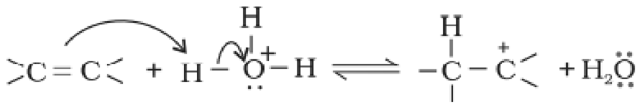


$$CH_3-CH=CH_2 + H_2O \overset{H^+}{\rightleftharpoons} CH_3-\underset{OH}{\underset{|}{CH}}-CH_3$$

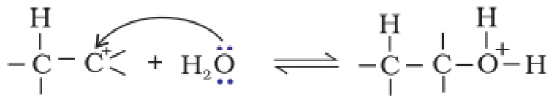
Mechanism (ref. ncert)

Step I Protonation of alkene to form carbocation by electrophilic attack of H_3O^+

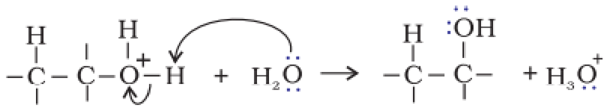
$$H_2O + H^+ \rightarrow H_3O^+$$



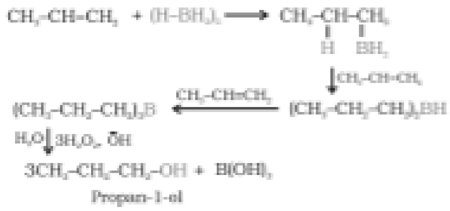
Step II Nucleophilic attack of water on carbocation forming protonated alcohol.



Step III Deprotonation to form an alcohol.



(b) **By hydroboration-oxidation:** Diborane B_2H_6 reacts with alkenes (prop-1-ene) to give trialkyl boranes as addition product. This is oxidised to alcohol (Propan-1-ol) by hydrogen peroxide in the presence of aqueous sodium hydroxide. (Ref. ncert)



(ii) **From carbonyl compounds**

(a) By reduction of aldehydes and ketones:

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

$R\ CO\ R' \xrightarrow{NaBH4} R - CH(OH) - R'$

(b) By reduction of carboxylic acids and ester

$R - COOH \xrightarrow{LiAlH4 /H2O} R - CH_2 - OH$

(iii) **From haloalkanes:**

$R - X + KOH(aq) \rightarrow ROH + KX$

(iv) **From primary amines** by treatment with nitrous acid.

$R - NH_2 + HONO \xrightarrow{NaNO + HCl} R - OH + N_2 + H_2O$

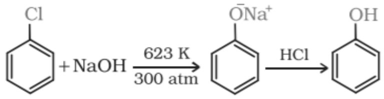
(v) **By alcoholic fermentation:**

Sucrose + H_2O $\xrightarrow{Invertase}$ glucose + fructose

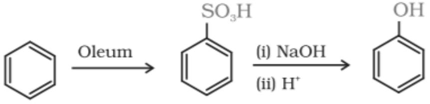
Glucose/Fructose $\xrightarrow{Zymase}$ Ethyl alcohol

Preparation of Phenols

(i) **From Haloarenes (Dow's process)**



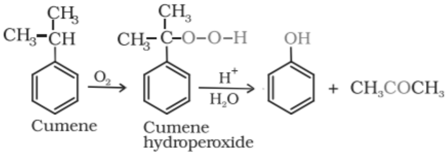
(ii) **From benzene sulphonic acid**



(iii) **From diazonium salts: Aniline to Phenol**

$C_6H_5 - NH_2 \xrightarrow{NaNO_2 + HCl} C_6H_5 - N_2^+Cl^- \xrightarrow{H2O} C_6H_5 - OH + N_2 + H_2O$

(iv) **From cumene**



Physical Properties of Alcohols

1. Lower alcohols are colourless liquids, members from $C_5 - C_{11}$ are oily liquids and higher members are waxy solids.

2. The hydroxyl groups in alcohols can form H-bonds with water, so alcohols are miscible with water. The solubility decreases with increase in molecular mass.

3. Boiling points of alkanes are higher than expected because of the presence of intermolecular hydrogen bonding in the polar molecules. The boiling point decreases in the order 1° > 2° > 3°, This is due to the fact that with branching, the surface area decreases and therefore, Vander walls forces decrease, consequently, boiling point also decreases.

Physical Properties of Phenols

1. These are colourless liquids or crystalline solids but become coloured due to slow oxidation with air.
2. Phenol is also called carbolic acid.
3. Because of the presence of polar -OH bond, phenols form intermolecular H-bonding with other phenol molecules and with water.
4. Boiling point of phenols are higher than the boiling points of aromatic hydrocarbons, due to the presence of intermolecular hydrogen bonding in phenols.

Chemical Reactions of Alcohols and Phenols

(i) **Reactions involving cleavage of O – H Bond**

(a) Acidity of alcohols and phenols: $R - OH + 2Na \longrightarrow 2R - ONa + H_2$

$$C_6H_5 - OH + 2Na \longrightarrow 2C_6H_5 - ONa + H_2$$

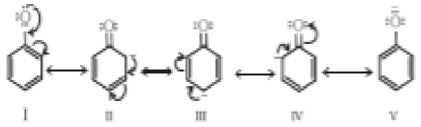
Alcohols are weaker acids than water due to (+I effect) group present in alcohols, which decreases the polarity of -O-H bond.

Acid strength of alcohols: 1° > 2° > 3°

Electron releasing group increases electron density on oxygen to decrease the polarity of – OH bond.

Order of acidity is: $RCOOH > H_2CO_3 > C_6H_5OH > H_2O > R - OH$.

Phenol is more acidic than alcohols due to stabilization of phenoxide ion through resonance.



Presence of electron withdrawing groups ($-NO_2$, -CN, -X) increases the acidity of phenol by stabilizing phenoxide ion while presence of electron releasing groups (-R, $-NH_2$, -OR) decreases the acidity of phenol by destabilizing phenoxide ion.

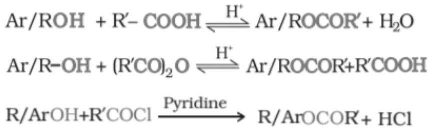
Thus, increasing acidic strength is

o-cresol < p-cresol < m-cresol < phenol < o-nitrophenol < 2, 4, 6 Trinitrophenol (picric acid)

Higher K_a and lower pK_a value correspond to the stronger acid.

(b) **Esterification:** The reaction with R'COOH and $(R'\,CO)_2\,O$ is reversible, so cone, H_2SO_4 is used to remove water.

The reaction with R' COCI is carried out in the presence of pyridine so as to neutralize HCI which is formed during the reaction.



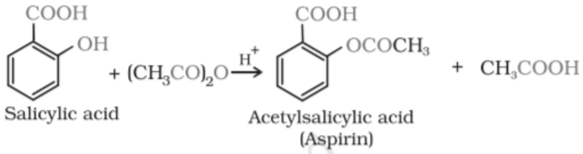
$$Ar/ROH + R'-COOH \overset{H^+}{\rightleftharpoons} Ar/ROCOR' + H_2O$$

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

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

The introduction of acetyl (CH_3CO-) group in phenols is known as acetylation.

Acetylation of salicylic acid produces aspirin.



(ii) **Reaction involving cleavage of C-O bond in alcohols** in these reactions, the reactivity order of alcohols: 3° > 2° > 1°

Alkyl group due to +1 effect increases the electron density on the carbon and oxygen atom of C-O bond. As a result, the bond cleavage becomes easy. Greater the number of alkyl groups present; more will be the reactivity of alcohol. 3° > 2° > 1° (Reactivity decreases)

(a) **Reaction with halogen acids:** Alcohols can be converted into haloalkanes by the action of halogen acids.

In this reaction anhydrous $ZnCl_2$ is used, $R – OH + HCI \rightarrow R\text{-}Cl + H_2O$

In this reaction conc. H_2SO_4 & reflux, $R – OH + HBr \rightarrow R\text{-}Br + H_2O$

In this reaction Red P at 423 K, $R – OH + HI \rightarrow R\text{-}H + I_2 + H_2O$

For a given alcohol order of reactivity of HX is H-1 > H-Br > H-Cl

This is because I^- ion is a better nucleophile than Br^- ion,

For a given halogen acid order of reactivity of alcohols: Tertiary > Secondary > Primary

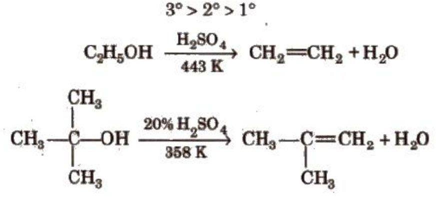
(b) **Reaction with phosphorus halides:**

$ROH + PCl_5 \rightarrow RCl + POCl_3 + HCl$

(c) **Reaction with thionyl chloride:**

$ROH + SOCl_2 \rightarrow RCl + SO_2 + HCl$

d) **Dehydration of alcohols** It requires acid catalyst and the reaction proceeds via intermediate carbonium ion. Acidic catalyst converts hydroxyl group into a good leaving group. Since, the rate determining step is the formation of carbocation, the ease of dehydration is ref. ncert



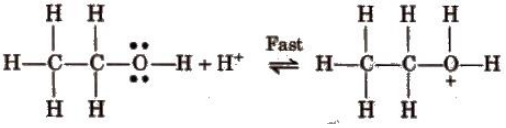
3° > 2° > 1°

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

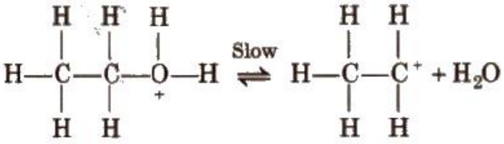
$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-OH \xrightarrow[358\ K]{20\%\ H_2SO_4} CH_3-\underset{CH_3}{\underset{|}{C}}{=}CH_2 + H_2O$$

Mechanism

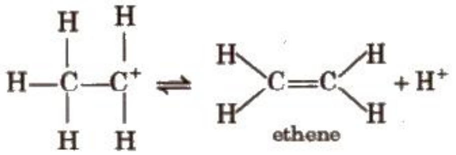
Step I Formation of protonated alcohol



Step II Formation of carbocation

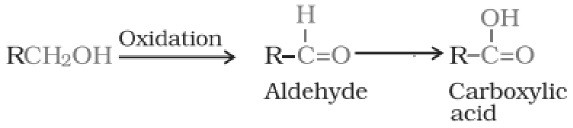


Step III Formation of Ethene by elimination of a proton



In dehydration reaction, highly substituted alkene is the major product and if the major product is capable of showing cis-trans isomerism, trans-product is the major product. (Saytzeff rule).

(iii) Oxidation reactions: Oxidizing reagents used for the oxidation of alcohols are neutral, acidic or alkaline $KMnO_4$ and acidified $K_2Cr_2O_7$.



$$RCH_2OH \xrightarrow{\text{Oxidation}} R\text{–}\overset{H}{\overset{|}{C}}{=}O \longrightarrow R\text{–}\overset{OH}{\overset{|}{C}}{=}O$$

Aldehyde

Carboxylic acid

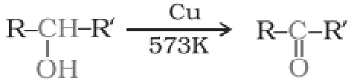
$$RCH_2OH \xrightarrow{CrO_3} RCHO$$

A common reagent that selectively oxidizes a primary alcohol to an aldehyde (and no further) is pyridinium chlorochromate (PCC).

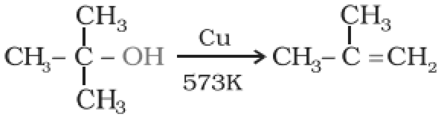
$$CH_3-CH=CH-CH_2OH \xrightarrow{PCC} CH_3-CH=CH-CHO$$

(iv) **Dehydrogenation:**

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



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



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

Distinction among 1°,2° and 3° Alcohols:

1°, 2° and 3° alcohols are distinguished by Lucas test. In this test with an equimolar concentrated HCl and anhydrous $ZnCl_2$ .The alcohols get converted into alkyl halides. Since the alkyl halides are insoluble in water, their formation is indicated by the appearance of turbidity in the reaction mixture.

If turbidity appears immediately, the alcohol is tertiary.

If turbidity appears within five minutes, the alcohol is secondary.

If turbidity appears only upon heating, the alcohol may be primary.

Victor Meyer's test is also used to distinguish them. This test involves the following steps:

(i)The given alcohol is treated with red phosphorous and iodine resulting in the formation of alkyl iodide.

(ii)The alkyl iodide is treated with silver nitrate to form nitroalkane.

(iii)The nitroalkane finally reacted with nitrous acid and resulting solution is made alkaline.

Formation of a blood red colour indicates the primary alcohol.

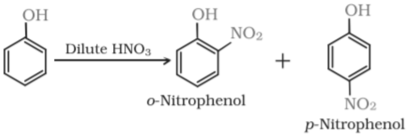
Formation of a blue colour shows the original alcohol to be secondary.

A colourless solution means that alcohol is tertiary alcohol.

Reactions of Phenols

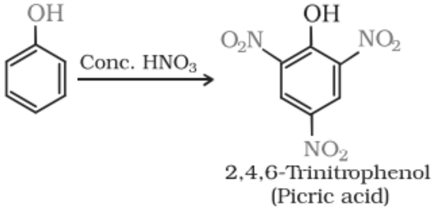
1. Electrophilic substitution reactions The -OH group attached to the benzene ring activates it towards electrophilic substitution at ortho and para positions.

(i)(a)**Nitration:** With dilute nitric acid at low temperature (298 K), phenol yields a mixture of ortho and para nitrophenol.

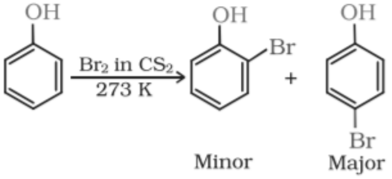


The ortho and para isomers can be separated by steam distillation. This is because o-nitrophenol is steam volatile due to intramolecular hydrogen bonding while p nitrophenol is less volatile due to intermolecular hydrogen bonding which causes the association of molecules.

(b)With concentrated nitric acid, phenol is converted to 2, 4, 6-trinitrophenol (Picric acid)

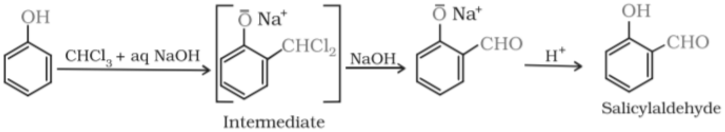


(ii) (a)**Halogenation:** With calculated amount of Br_2 in CS_2 or $CHCI_3$ it gives ortho and para product

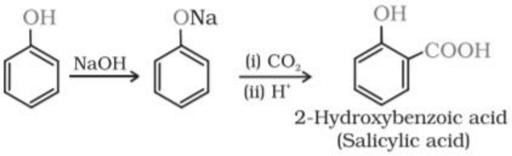


(b)When phenol is treated with bromine water, 2, 4, 6-tribromophenol is formed as white precipitate.

(d) **Reimer-Tiemann reaction:** On treating phenol with chloroform in the presence of sodium hydroxide, a –CHO group is introduced at ortho position of benzene ring. This reaction is known as Reimer - Tiemann reaction.



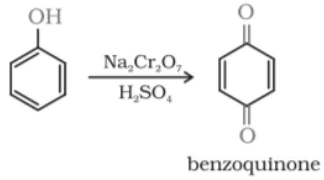
(ii) **Kolbe's reaction:**



(iii) **Reaction with zinc dust:** Phenol is converted to benzene on heating with zinc dust.

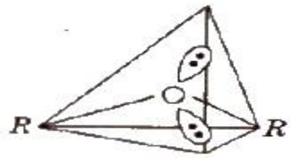
$C_6H_5OH + Zn \rightarrow C_6H_6 + ZnO$

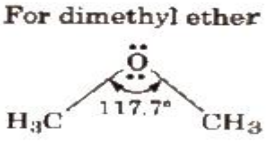
(iv) **Oxidation:** Oxidation of phenol with chromic acid produces a conjugated diketone known as benzoquinone.



ETHERS: Structure of Ether

The hybridization of oxygen atom in ethers is sp^3 (tetrahedral) and its shape is V-shape.





Ethers Classifications

Ethers can be classified into two categories; they are listed below.

- **Symmetrical Ethers**

If two identical groups are attached to either side of an oxygen atom, then it is referred to as symmetrical ethers. These are also known as Simple Ethers.
Examples are diethyl ether, dipropyl ether, dimethyl ether, and more.

- **Asymmetrical Ethers**

If two different groups are attached to either side of an oxygen atom, it is said to be asymmetrical ethers. These are also known as Mixed Ethers.
Examples are methyl phenyl ether, ethyl methyl ether, and more.

Nomenclature of Ethers:

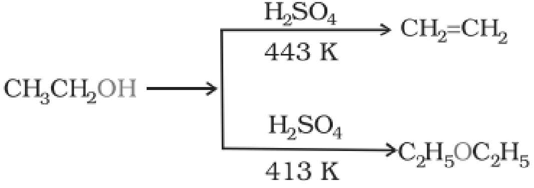
CH_3OCH_3 is named as “Dimethyl ether.”
$CH_3OC_2H_5$ is named as “Ethyl methyl ether.” “1-methoxy ethane.”
$CH_3OC_6H_5$ is named as “Methyl phenyl ether.”
$C_6H_5OC_2H_5$ is named as ‘’Ethyl phenyl ether’’ & also, known as phenetole.

Physical Properties of Ethers

Ethers are polar but insoluble in H_2O and have low boiling point than alcohols of comparable molecular masses because ethers do not form hydrogen bonds with water.

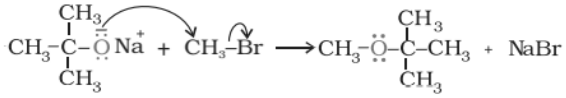
Preparation of Ethers: Ethers can be prepared

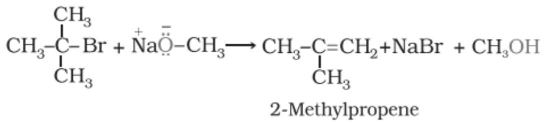
(a) by dehydration of alcohols



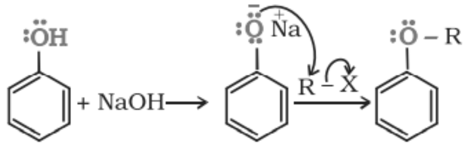
(b)Williamson’s synthesis: Only primary alkyl halides when react with sodium alkoxide give ether while tertiary alkyl halides give alkene due to steric hindrance.

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





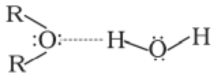
(c)For Aryl ethers, Phenol converted into ether.



Physical properties of ether: The C – O bond in ethers are polar. The boiling point of alkanes, alcohols and ethers as follows:

Formula	$CH_3(CH_2)_3CH_3$ n-Pentane	C_2H_5-O-C_2H_5 Ethoxyethane	$CH_3(CH_2)_3$-OH Butan-1-ol
b.p./K	309.1	307.6	390

The miscibility of ethers with water due to hydrogen bond with water.



Chemical properties:

(a) Cleavage of C-O bond in ethers:

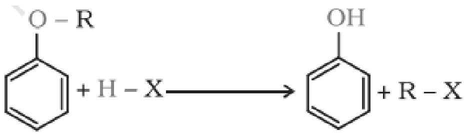
R – O – R’ + HX → RX + R’ – OH

R’ – OH + HX → R’ – X + H_2O

(b) Electrophilic substitution: In this, the alkoxy group activates the aromatic ring and directs the incoming group to ortho and para positions.

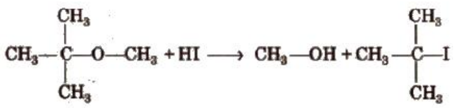
(i) **Reaction with HX:**

R – O – R + HX → RX + R – OH



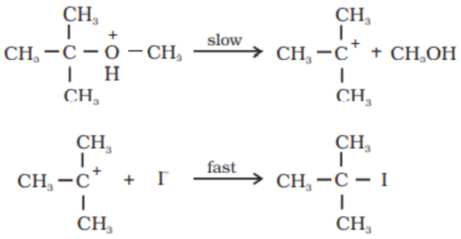
The order of reactivity of hydrogen halides is as follows: HI > HBr > HCl

In ethers if one of the alkyl groups is a tertiary group, the halide formed is a tertiary halide by $S_N{}^1$ mechanism.



$$CH_3-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}-O-CH_3 + HI \longrightarrow CH_3-OH + CH_3-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}-I$$

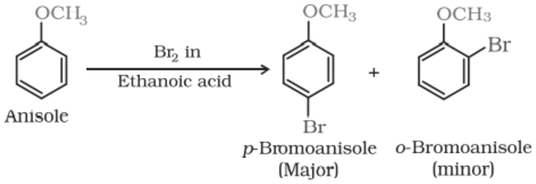
Mechanism:



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

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

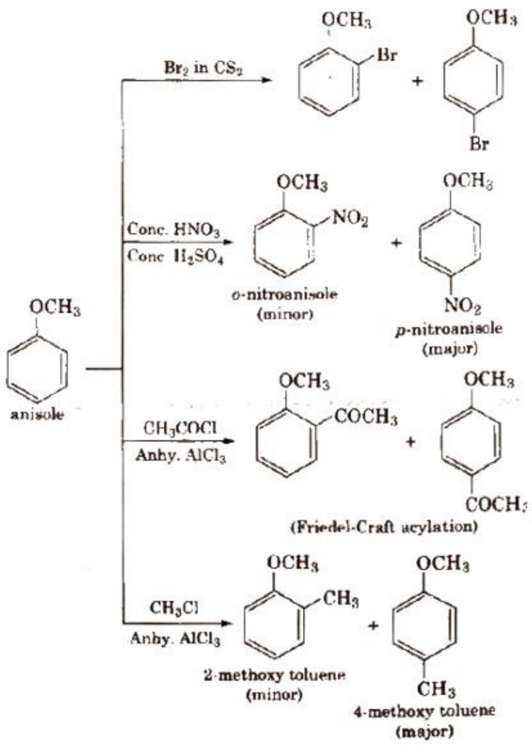
(ii)Halogenation: Bromination of Anisole**:**



(iii)Reaction with PCl_5:
Ethers on heating give alkyl halides
R – O – R +PCl_5 → RCl + $POCl_3$

(iv)Reaction with CO:
R – O – R + CO → RCOOR

(v) Electrophilic substitution reactions in ethers, -OR is ortho, para directing group and activate. the aromatic ring towards electrophilic substitution reaction.
1. Anisole reacts with Br_2 to give ortho- and para-bromo anisole (major)
2. Anisole reacts with concentrated nitric acid and concentrated Sulphuric acid to give ortho- and para-nitro anisole (major)
3. Anisole reacts with CH_3COCl in the presence of anhydrous $AlCl_3$ to give 2-methoxy acetophenone and 4-methoxy acetophenone (major) [Friedal Craft acylation]
4. Anisole reacts with CH_3Cl in the presence of anhydrous $AlCl_3$ to give 2-methoxy toluene and 4-methoxy toluene (major) [Friedal Craft alkylation]



Uses of Ethers

1. Dimethyl ether is used as refrigerant and as a solvent at low temperature.
2. Diethyl Ether is used as an anesthesia in surgery.

ASSIGNMENTS:

Q1. Give the structures and IUPAC names of the products expected from the following reactions:

(a) Catalytic reduction of butanal.

(b) Hydration of propene in the presence of dilute Sulphuric acid.

(c) Reaction of Propanone with methyl magnesium bromide followed by hydrolysis.

Ans.

(a) Butan-1-ol
(b) Propan-2-ol
(c) 2-methyl Propan-2-ol

Q2. Arrange the following sets of compounds in order of their increasing boiling points:

(a) Pentan-1-ol, butan-1-ol, butan-2-ol, ethanol, propan-1-ol, methanol.

(b) Pentan-1-ol, n-butane, pentanal, ethoxyethane.

Ans. (a) Methanol, ethanol, propan-1-ol, butan-2-ol, butan-1-ol, pentan-1-ol.

(b) n-Butane, ethoxyethane, pentanal and pentan-1-ol.

Q3. Arrange the following compounds in increasing order of their acid strength:

Propan-1-ol, 2, 4, 6-trinitrophenol, 3-nitrophenol, 3, 5-dinitrophenol, phenol, 4-methylphenol.

Ans. Propan-1-ol, 4-methylphenol, phenol, 3-nitrophenol, 3,5-dinitrophenol, 2,4, 6-trinitrophenol.

Q4. Give structures of the products you would expect when each of the following alcohol reacts with (a) HCl –$ZnCl_2$ (b) HBr and (c) $SOCl_2$.

(i) Butan-1-ol
(ii) 2-Methylbutan-2-ol

Ans. (a) HCl –$ZnCl_2$, it is a Lucas reagent.

(i) Turbidity appear upon heating (ii) white turbidity formed

(b) With HBr to give alkyl halides.

(c) Both alcohols react to give alkyl chlorides.

Q5. Predict the major product of acid catalyzed dehydration of

(i) 1-methylcyclohexanol
(ii) butan-1-ol

Ans. (i) 1- Methyl cyclohexene (ii) But-2-ene.

Q6. Ortho and para nitrophenols are more acidic than phenol. Draw the resonance structures of the corresponding phenoxide ions.

Ans. Draw the resonance structures of o- & p- phenoxide ions.

Due to –I and –R effect of –NO_2 group, o- & p- phenoxide ions are more stable. Hence, Ortho and para nitrophenol are more acidic than phenol.

Q7. Write the equations involved in the following reactions:

(i) Reimer - Tiemann reaction
(ii) Kolbe’s reaction

Ans. (i) Reimer - Tiemann reaction – when phenol reacts with chloroform in the presence of aqueous sodium hydroxide, salicyladehyde is formed.

(ii) Kolbe’s reaction- when sodium phenoxide is heated with carbon dioxide at about 400K and under 4 to 7 atmospheric pressure, sodium salicylate is formed. On acidification gives salicylic acid.

Q8. The following is not an appropriate reaction for the preparation of t-butyl ethyl ether.

$C_2H5Na + (CH_3)_3 - Cl \longrightarrow (CH_3)_3 - OC_2H_5$

(i) What would be the major product of this reaction?
(ii) Write a suitable reaction for the preparation of t-butyl ethyl ether.

Ans. (i) The major product of the given reaction is 2-methylprop-1-ene. It is because sodium ethoxide is a strong nucleophile as well as a strong base. Thus, elimination reaction predominates over substitution.

(ii) $(CH_3)_3 - O^- Na^+ + CH_3CH_2Cl \longrightarrow (CH_3)_3 - OC_2H_5$

Q9. Write the mechanism of hydration of Ethene to yield ethanol.

Ans. It is an example of electrophilic addition.

$CH_2 = CH_2 + H^+ \longrightarrow CH_3CH_2OH$

Q10. Write the names of reagents and equations for the preparation of the following ethers by Williamson’s synthesis:

(i) 1-Propoxypropane
(ii) Ethoxybenzene
(iii) 2-Methoxy-2-methylpropane
(iv) 1-Methoxyethane

Ans. (i) Sodium propoxide + 1-bromopropane

(ii) Sodium phenoxide + ethyl bromide

(iii)Sodium 2-methyl-2-propoxide + Bromomethane

(iv)Sodium ethoxide + Bromomethane