

UNIT 11

ALCOHOLS PHENOLS AND ETHERS

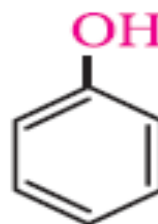
READING MATERIAL

Alcohols and Phenols

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



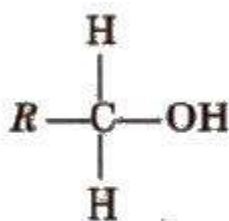
Alcohol
(R-OH)



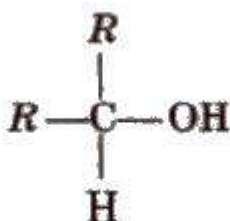
Phenol
(Ar-OH)

Classification of Alcohols and Phenols

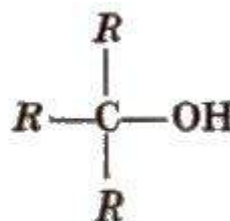
In alcohols, -OH group is attached to Sp^3 hybridised carbon. These alcohols are usually classified as primary, secondary and tertiary alcohols.



primary (1°)



secondary (2°)



tertiary (3°)

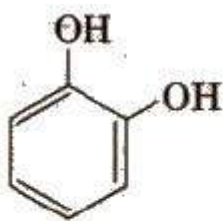
Alcohols may be

- (i) monohydric-containing one – OH group,
- (ii) dihydric-containing two – OH groups and
- (iii) polyhydric-containing three or more -OH groups.

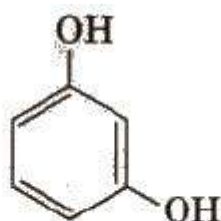
In phenols, -OH group is attached to Sp^2 hybridised carbon. These may also be monohydric, dihydric, etc. The dihydric phenol further found to be ortho, meta' or para derivative.



phenol



catechol



resorcinol



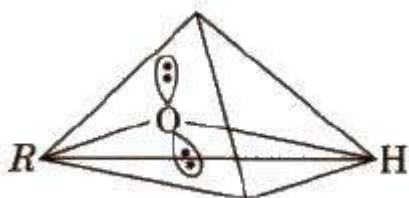
quinol or hydroquinone

In allylic alcohols, – OH group is attached to sp^3 hybridised carbon but next to $C=C$ bond.

e.g., $CH_2 = CH - CH_2OH$, Benzylic alcohol ($C_6H_5CH_2OH$)

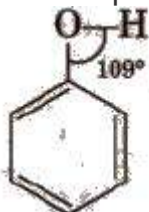
Structure of Alcohols and Phenols

The oxygen atom of alcohols is Sp^3 hybridised and they have tetrahedral position of hybrid atomic orbitals .



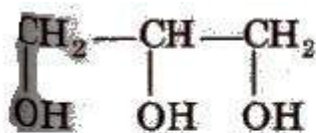
The value of $\angle ROH$ bond angle depends upon the R group. For methyl alcohol, it is ($\angle C - O - H$) 108.9° due to repulsion of lone pairs.

In phenols, the – OH group is attached to Sp^2 hybridised carbon and thus, the $C - O$ bond acquires a partial double bond character.

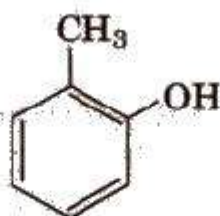


Nomenclature of Alcohols and Phenol

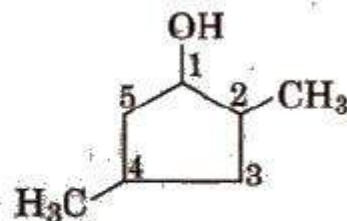
In IUPAC, system, alcohol or alkanols are named by replacing the last word 'e' of the corresponding alkane by 'ol'. e.g.,



propan-1,2,3-triol



2-methyl phenol

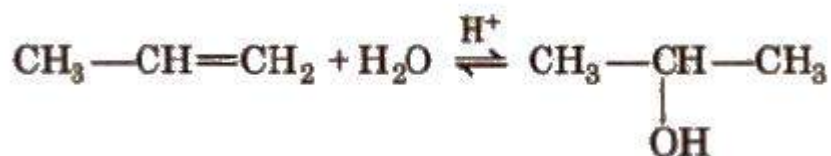
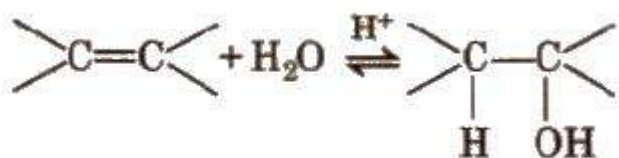


2,4-dimethylcyclopentanol

Preparation of Alcohols

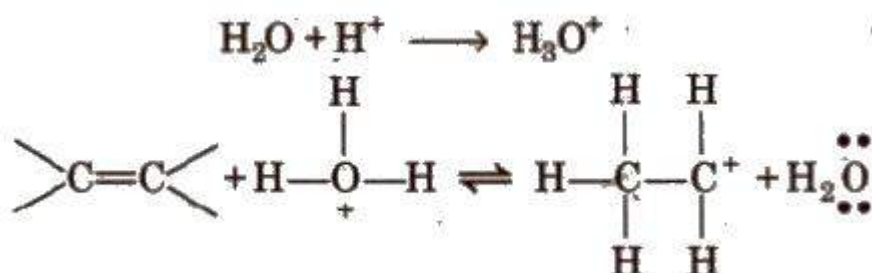
(i) From alkenes

(a) By acid catalysed hydration in accordance with Markownikoff's rule.

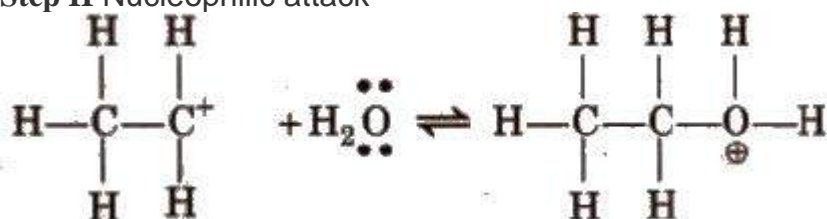


Mechanism

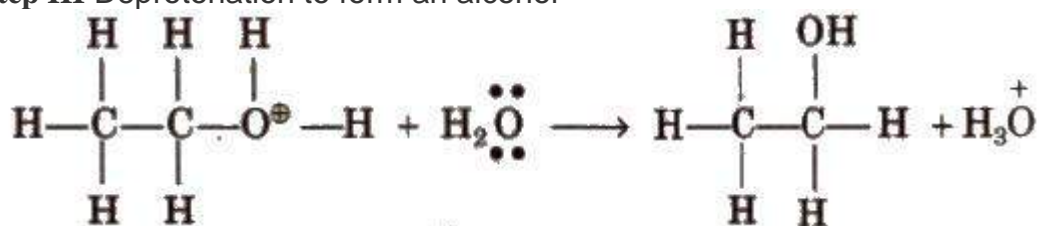
Step I Protonation of alkene by attack of H₃O⁺



Step II Nucleophilic attack

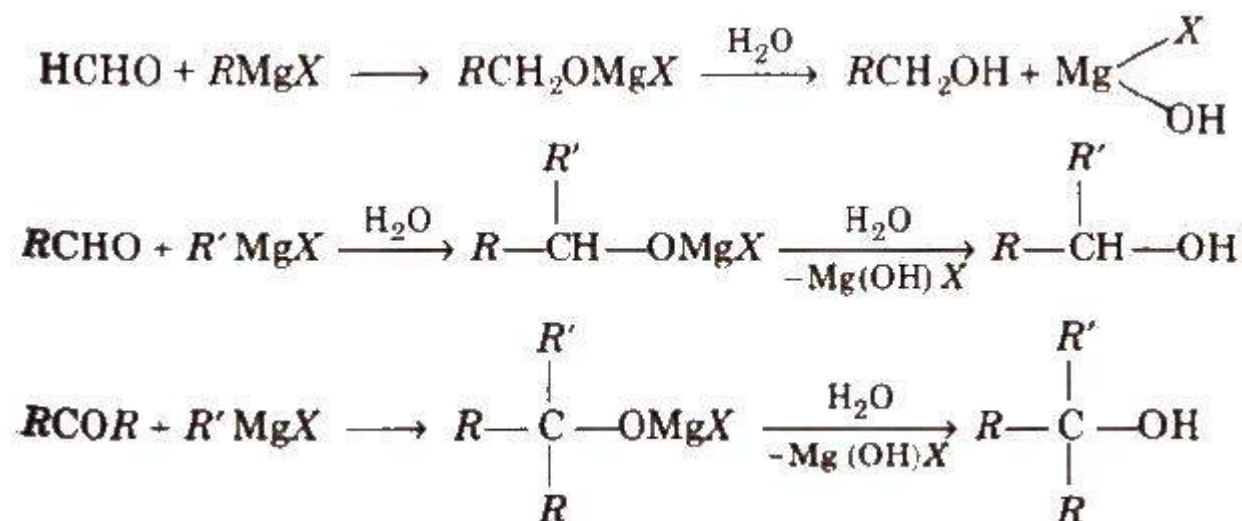


Step III Deprotonation to form an alcohol

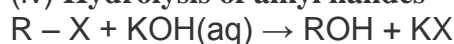


(b) By hydroboration-oxidation

The reaction produces a primary alcohol with methanol, a secondary alcohol with aldehydes (except methanal) and tertiary alcohol with ketones



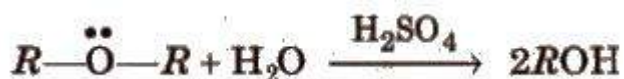
(iv) Hydrolysis of alkyl halides



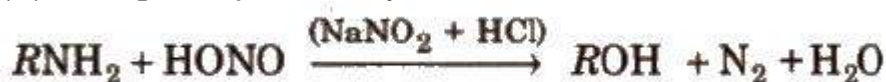
To avoid dehydrohalogenation of RX, mild alkalies like moist

Ease of hydrolysis of alkyl halides $\text{RI} > \text{R}-\text{Br} > \text{RCI} > \text{and } t > s > p$ alkyl halides.

(v) Hydrolysis of ethers

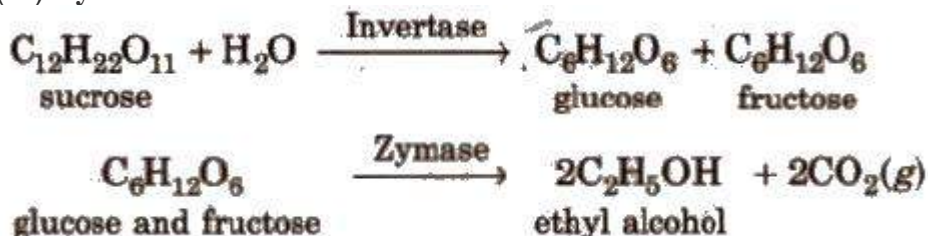


(vi) From primary amines By treatment with nitrous acid.



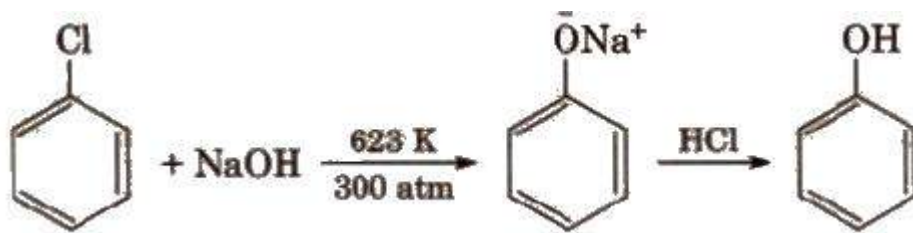
Methylamine does not give methyl alcohol when treated with HNO_2 . It gives CH_3OCH_3 and CH_3ONO .

(vii) By alcoholic fermentation

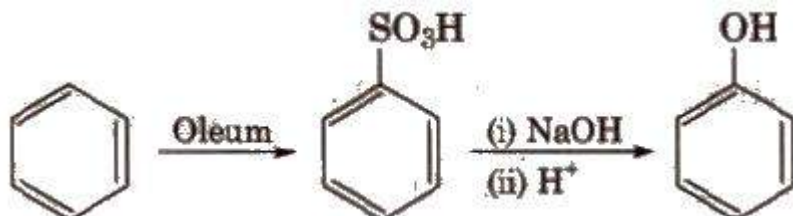


Preparation of Phenols

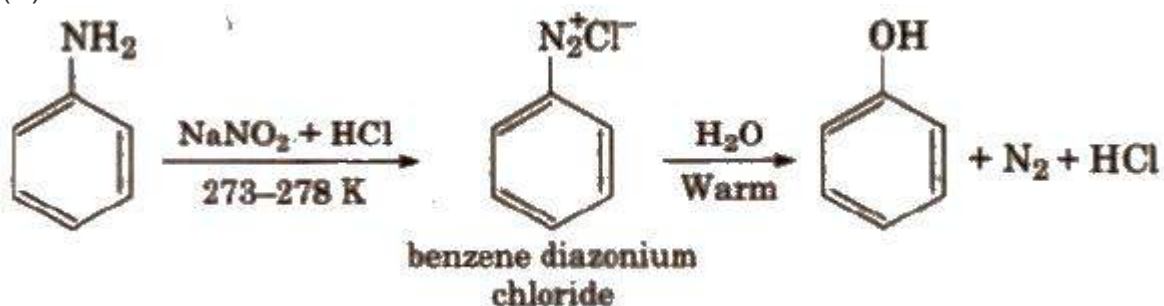
(i) From haloarenes



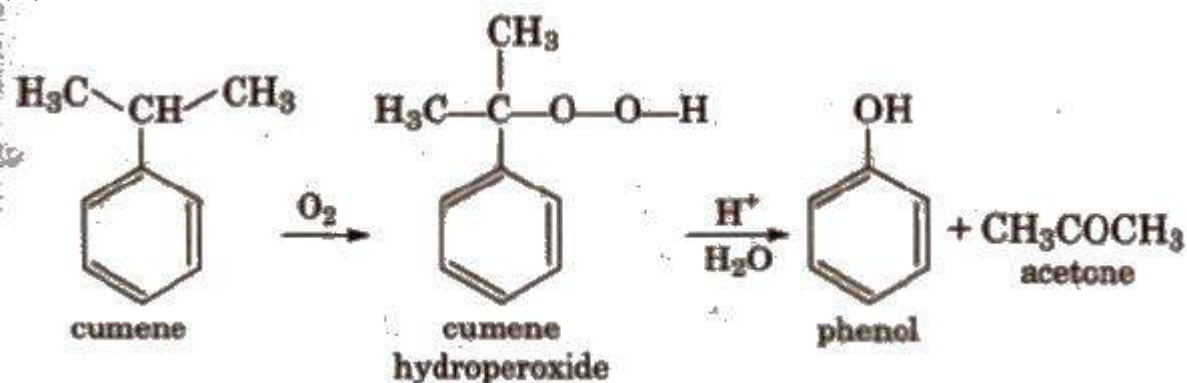
(ii) From benzene sulphonic acid



(iii) From diazonium salts

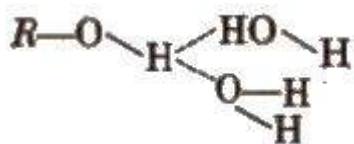


(iv) From cumene



Physical Properties of Alcohols

1. Lower alcohols are colourless liquids, members from C₅ – C₁₁ 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 $1^\circ > 2^\circ > 3^\circ$ as the van der Waals' forces of attraction decreases]

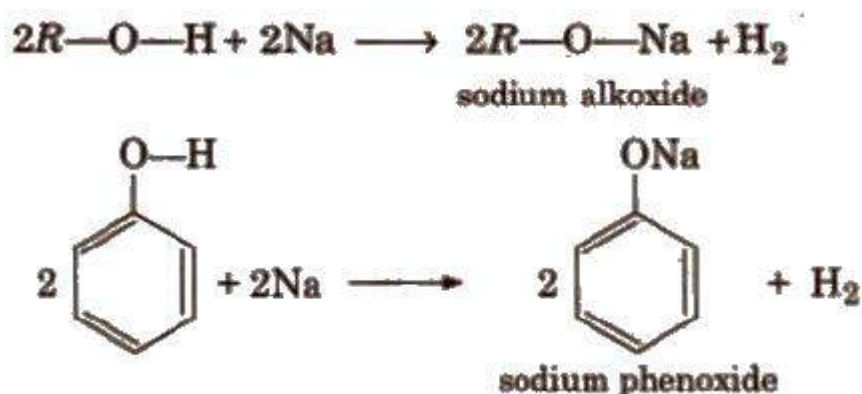
Physical Properties of Phenols

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.

Chemical Reactions of Alcohols and Phenols

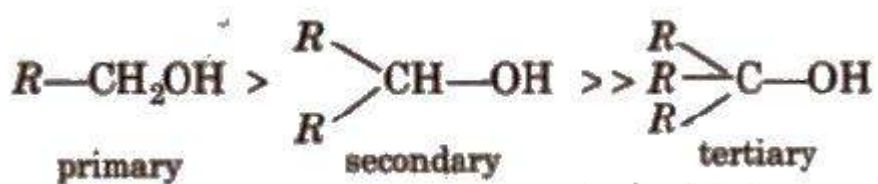
(i) Reactions involving cleavage of O – H Bond

(a) Acidity of alcohols and phenols



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

Acid strength of alcohols



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

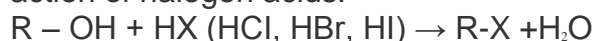
Order of acidity is



Phenol is more acidic than alcohols due to stabilisation of phenoxide ion through resonance. Presence of electron withdrawing group increases the acidity of phenol by ,

Alkyl group due to +I effect increases the electron density on the carbon and oxygen atom of C-OH bond. As a result, the bond cleavage becomes easy. Greater the number of alkyl groups present, more will be the reactivity of alcohol. Thus, the relative order of reactivity of the alcohols is justified.

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



For a given alcohol order of reactivity of HX is



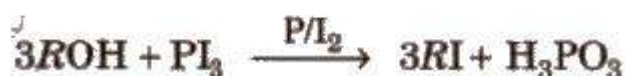
For a given halogen acid order of reactivity of alcohols

Tertiary > Secondary > Primary

Lucas test

Primary alcohols	Secondary alcohols	Tertiary alcohols
$RCH_2OH \xrightarrow[\text{Anhy. ZnCl}_2]{\text{Conc HCl}}$	$R_2CH-OH \xrightarrow[\text{Anhy. ZnCl}_2]{\text{Conc HCl}}$	$R_3C-OH \xrightarrow[\text{Anhy. ZnCl}_2]{\text{Conc HCl}}$
No reaction and hence, no white cloudiness or turbidity at room temperature.	R_2CHCl White cloudiness or turbidity appears with in about 5 minutes.	R_3CCl White cloudiness or turbidity appears immediately.

(b) **Reaction with phosphorus halides**

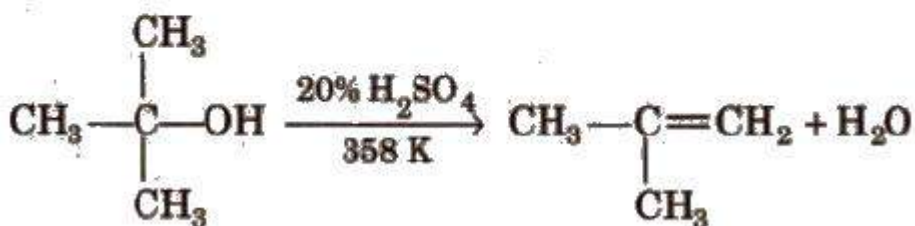
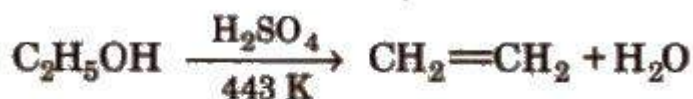


(c) **Reaction with thionyl chloride**



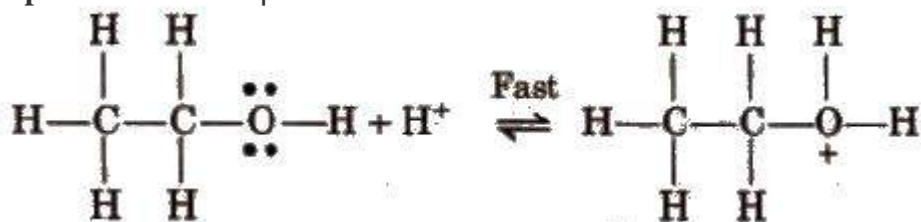
d) **Dehydration of alcohols** It requires acid catalyst and the reaction proceeds via intermediate carbonium ion. Acidic catalyst converts hydroxyl group into a good leaving group.

Since, the rate determining step is the formation of carbocation, the ease of dehydration is

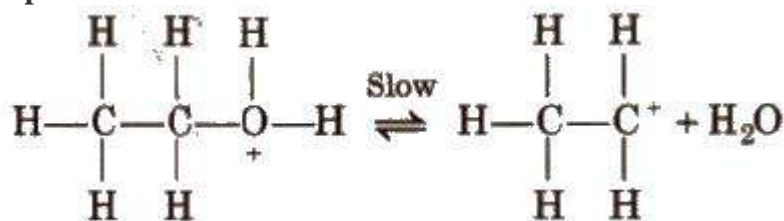


Mechanism

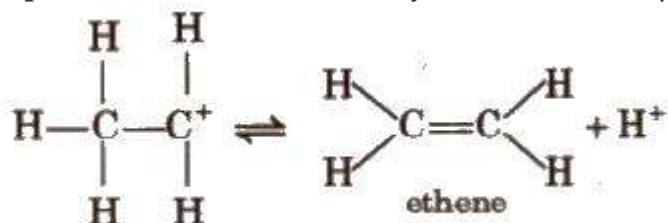
Step I Formation of protonated alcohol



Step II Formation of carbocation



Step III Formation of ethene by elimination of a proton

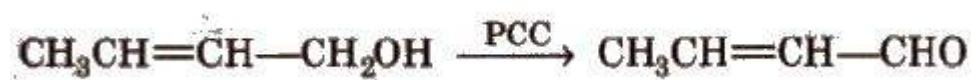


In dehydration reaction, highly substituted alkene is the major product and if the major product is capable of showing cis-trans isomerism, trans-product is the major product. (Saytzeff's rule).

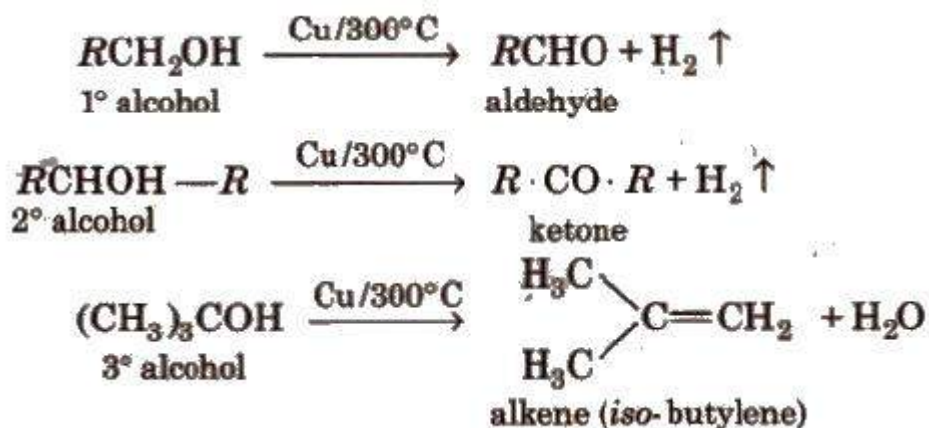
(iii) Oxidation reactions Oxidising reagents used for the oxidation of alcohols are neutral, acidic or alkaline KMnO_4 and acidified $\text{K}_2\text{Cr}_2\text{O}_7$.

Primary alcohols	Secondary alcohols	Tertiary alcohols
$\text{CH}_3\text{CH}_2\text{OH}$	$\text{CH}_3\text{CHOH}-\text{CH}_3$	$(\text{CH}_3)_3\text{C}-\text{OH}$
$\downarrow[\text{O}]$	$\downarrow[\text{O}]$	$\downarrow[\text{O}]$
CH_3CHO	CH_3COCH_3	$\text{CH}_3\text{COCH}_3 + \text{CO}_2 + \text{H}_2\text{O}$
$\downarrow[\text{O}]$	$\downarrow[\text{O}]$	$\downarrow[\text{O}]$
CH_3COOH	$\text{CH}_3\text{COOH} + \text{CO}_2 + \text{H}_2\text{O}$	$\text{CH}_3\text{COOH} + \text{CO}_2 + \text{H}_2\text{O}$

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



(iv) Dehydrogenation

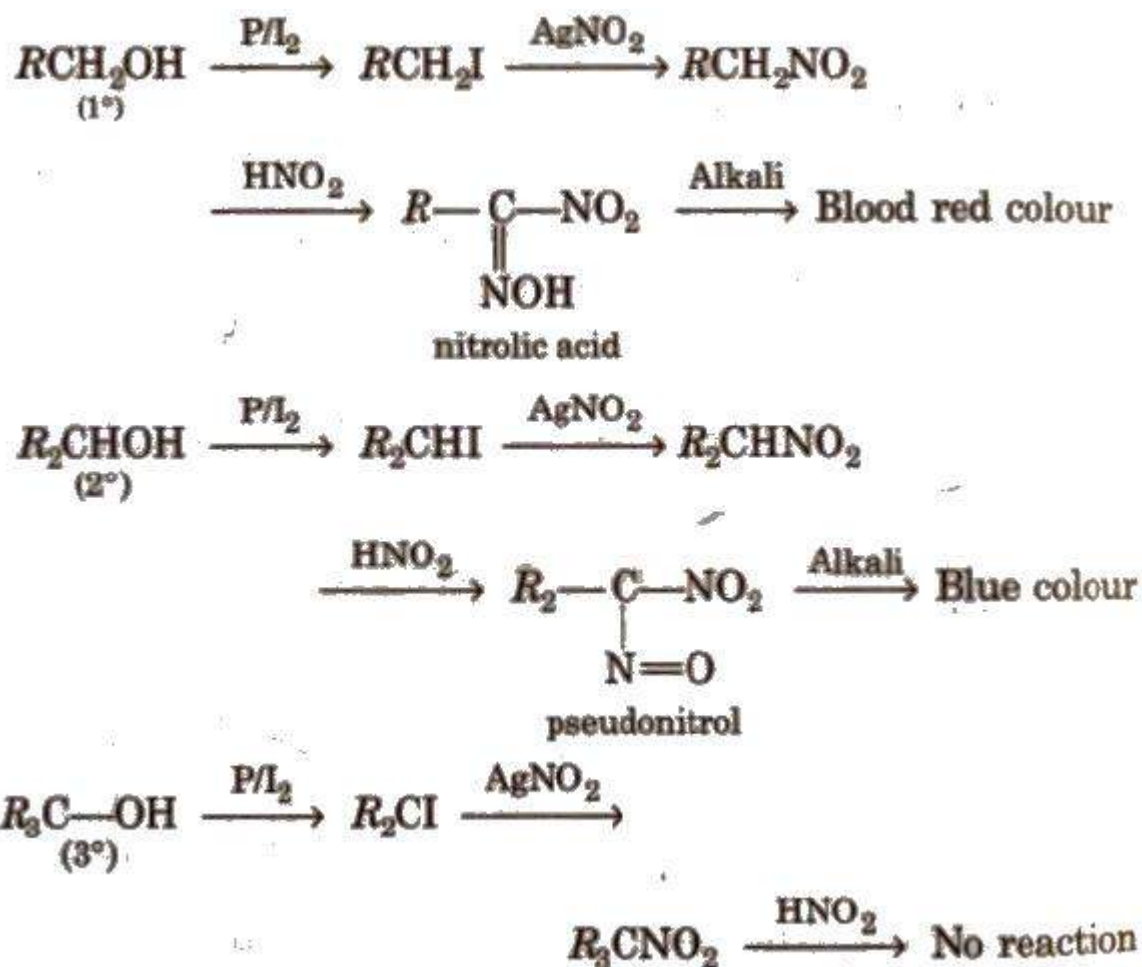


Distinction among 1°, 2° and 3° Alcohols

1°, 2° and 3° alcohols are distinguished by Lucas test, oxidation and reduced copper.

Victor Meyer's test is also used to distinguish them.

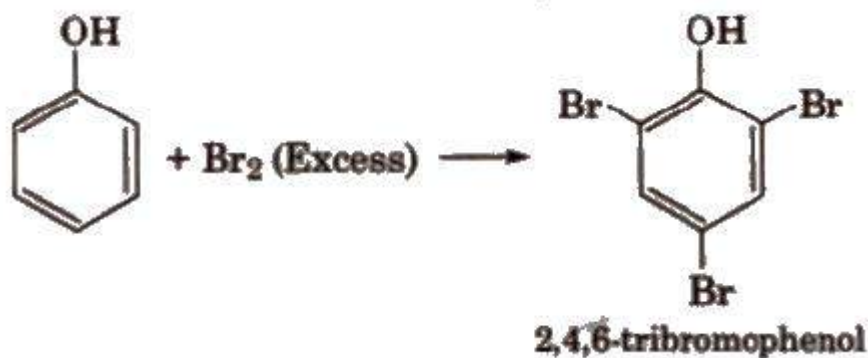
In this test, primary (1°) alcohols give red colour, secondary (2°) alcohols give blue colour and tertiary (3°) alcohols give no colouration.



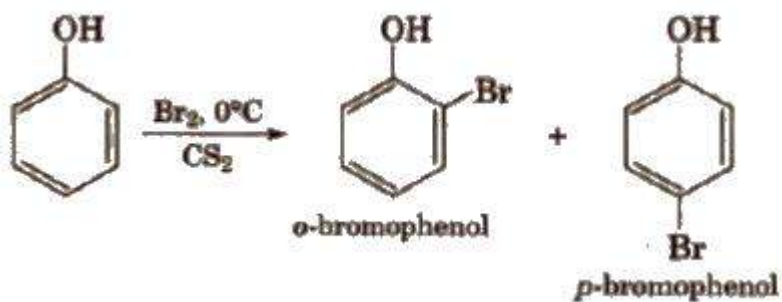
Reactions of Phenols

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

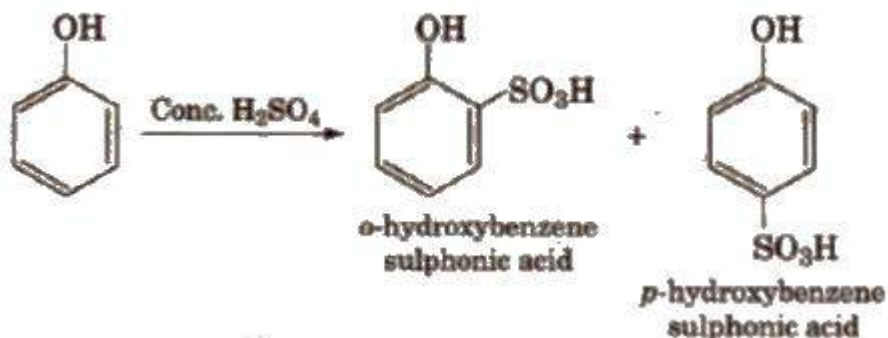
(a) **Halogenation**



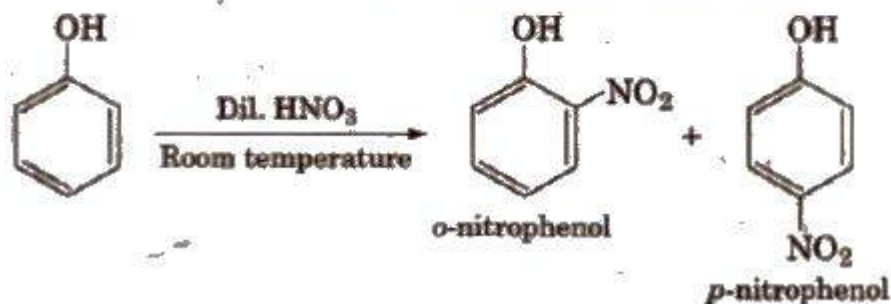
With calculated amount of Br₂ in CS₂ or CHCl₃, it gives ortho and para product.



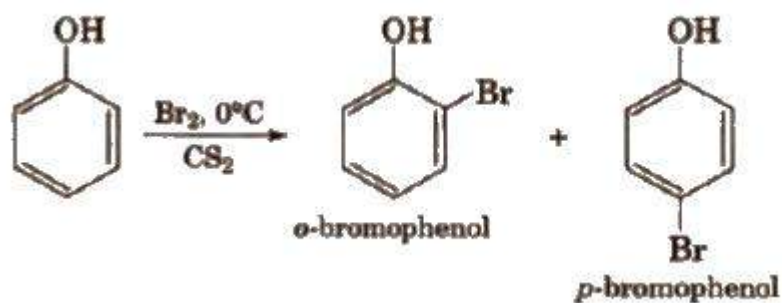
(b) Sulphonation



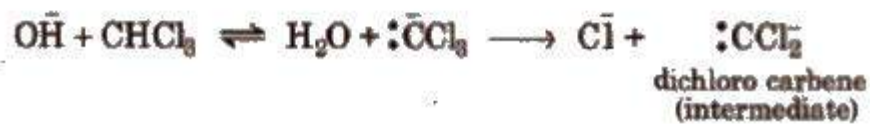
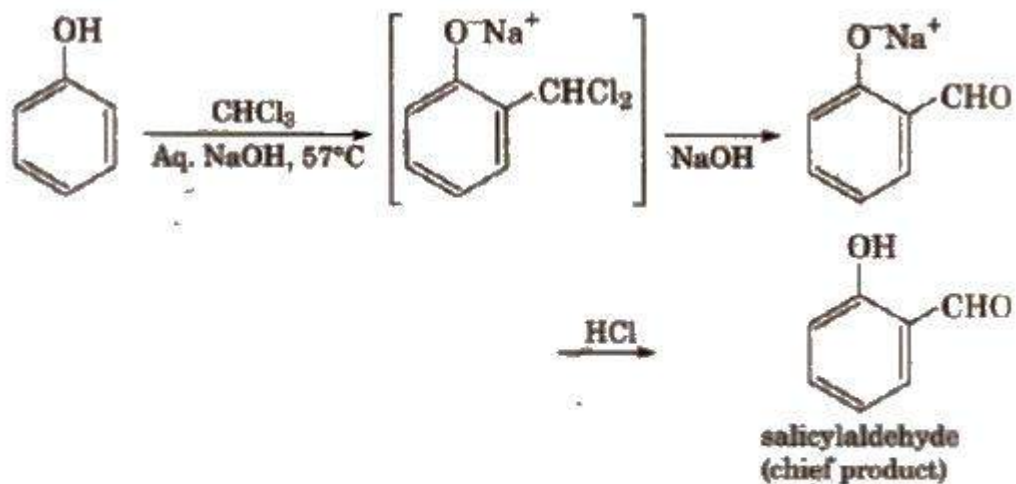
(c) Nitration



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.

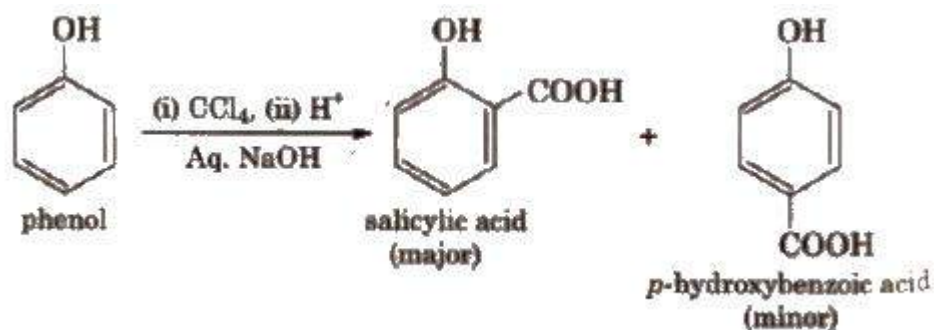


(d) Reimer-Tiemann reaction

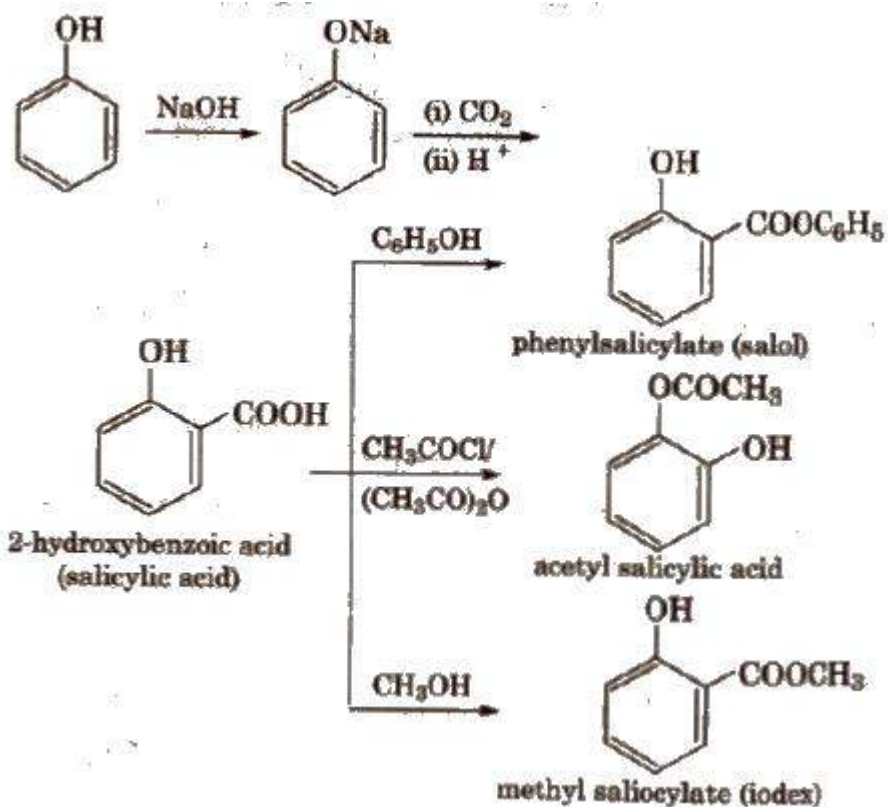


This reaction is an electrophilic substitution reaction and electrophile is dichlorocarbene.

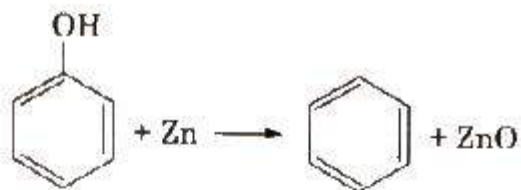
Similarly with carbon tetrachloride and alkali, *c*- and *p*-hydroxybenzoic acid are obtained



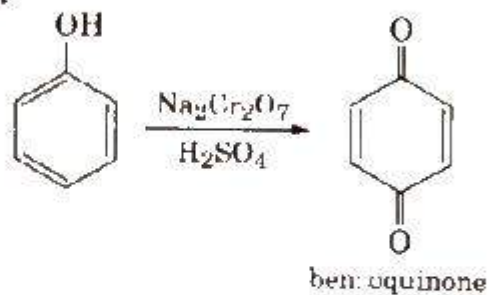
(ii) Kolbe's reaction



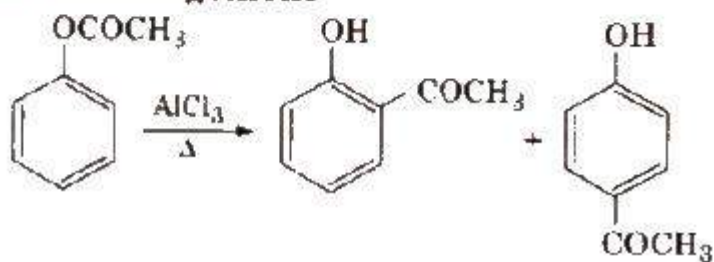
(iii) Reaction with zinc dust



(iv) Oxidation



(v) Fries rearrangement



Terms Related to Alcohols

(a) **Rectified spirit** It contains 95% ethyl alcohol and 45% water. It is an azeotrope (constant boiling mixture) and boils at 74°.

(b) **Absolute alcohol** Alcohol containing no water, i.e; 100% C₂H₅OH is known as absolute alcohol. It is prepared as follows.

(i) Quick lime process

(ii) Azeotropic method

(c) **Methylated spirit** The rectified spirit rendered poisonous by addition of 4-5% methyl alcohol, traces of pyridine and some copper sulphate and is known as methylated spirit or denatured alcohol.

(d) **Power alcohol** Alcohol mixed with petrol or fuel and used In internal combustion engines Is known as power alcohol.

(e) **Wood spirit** Methyl alcohol (CH₃OH) is also called wood spirit. It is obtained by destructive distillation of wood. Pyroligneous add, the product of destructive distillation of wood, contains acetic acid (10%), methyl alcohol (25%) and acetone (05%). Drinking of methanol causes blindness.

(f) **Grain alcohol** Ethyl alcohol C₂H₅OH is also called grain alcohol. It is used In the preparation of various beverages containing different percentages.

Dihydric Alcohols

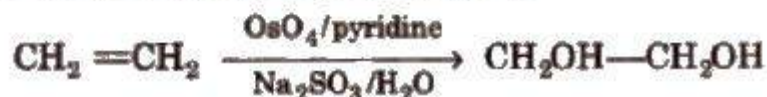
These are generally called glycols because of their sweet taste. Ethylene glycol (CH₂OH – CH₂OH) is the first and most important member of dihydric alcohol series.

Methods of Preparation

(i) From ethylene



(1% alkaline KMnO₄ is called Baeyer's reagent)



(ii) By reduction of glyoxal

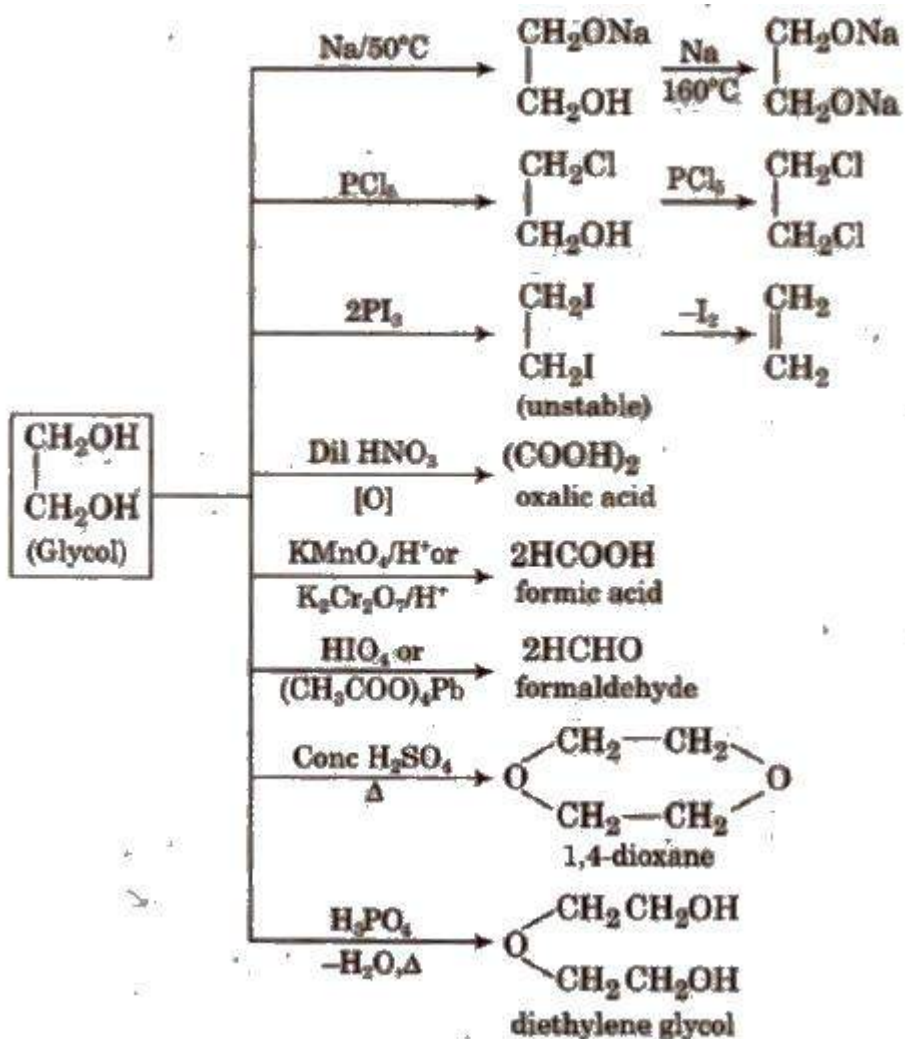


Physical Properties

1. It is a colourless, syrupy liquid with sweet taste.
2. Because of its tendency of formation of H-bonds, it is miscible with H₂O and ethanol but not with ether.

Chemical Properties

It gives all the general reactions of -OH group.



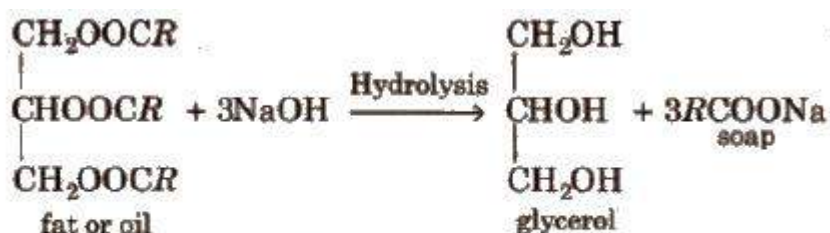
The per-iodic acid cleavage of 1,2-glycols is sometimes called Malaprade reaction.

Trihydric Alcohols

Glycerol or glycerine, $\text{CH}_2\text{OH} - \text{CH}(\text{OH}) - \text{CH}_2\text{OH}$ is the first member of this group. Its IUPAC name is propane-1,2,3-triol.

Method of Preparation

It is obtained as a by product in saponification reaction.



(where, $R = \text{C}_{17}\text{H}_{35}$ or $\text{C}_{15}\text{H}_{31}$ or $\text{C}_{17}\text{H}_{33}$)

Physical Properties

1. It is a colourless, odourless, viscous and hygroscopic liquid.
2. It is sweet in taste and steam volatile.

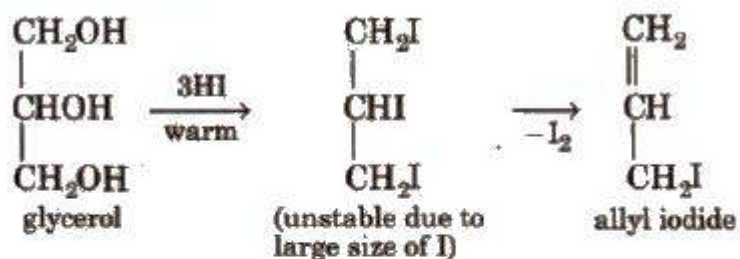
3. It is soluble in water but insoluble in ether.
4. Due to excessive H-bonding, it is highly viscous and has high boiling point.

Chemical Properties

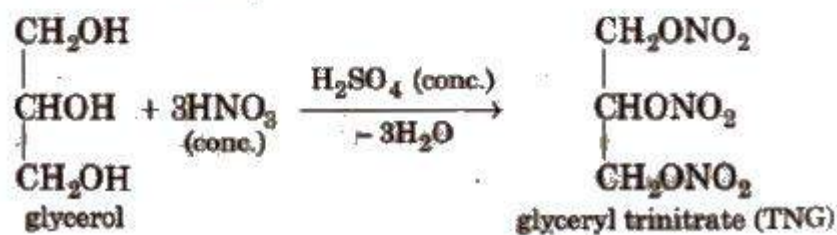
It gives all the general reactions given by -OR group but 2° OR is less reactive as compared to 1° .

Some of its specific reactions are :

(i) Reaction with HI



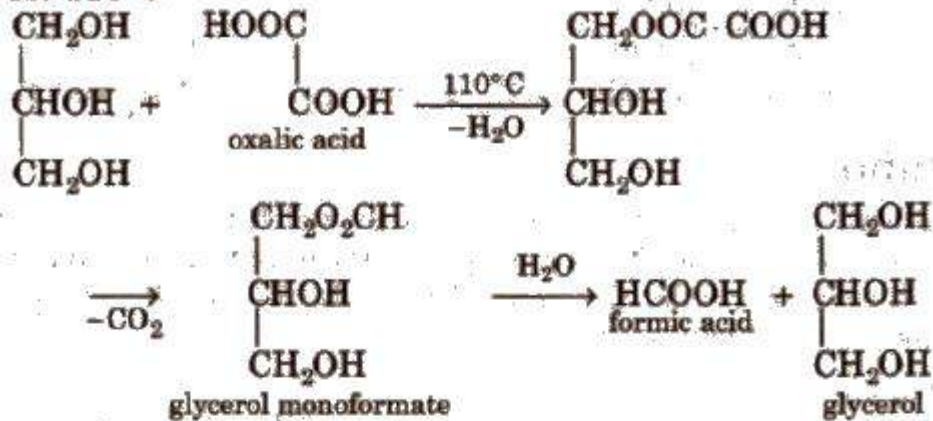
(ii) Reaction with HNO₃



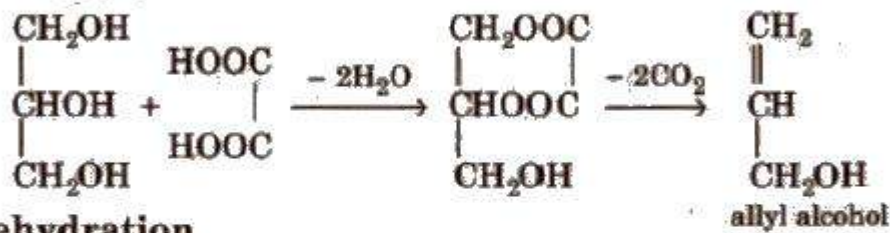
Glyceryl trinitrate or tri nitroglycerine, when adsorbed on Kieselguhr is known as dynamite. Mixture of TNG and cellulose trinitrate is called blasting gelatin.

(iii) Reaction with oxalic acid

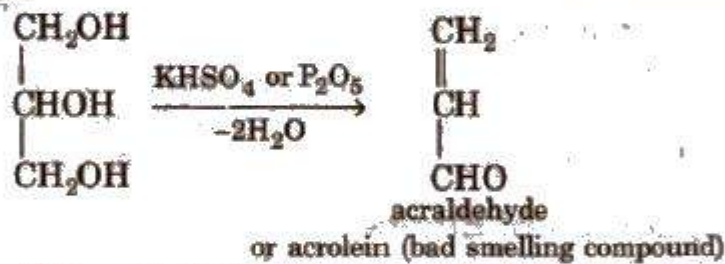
(a) At 110°C



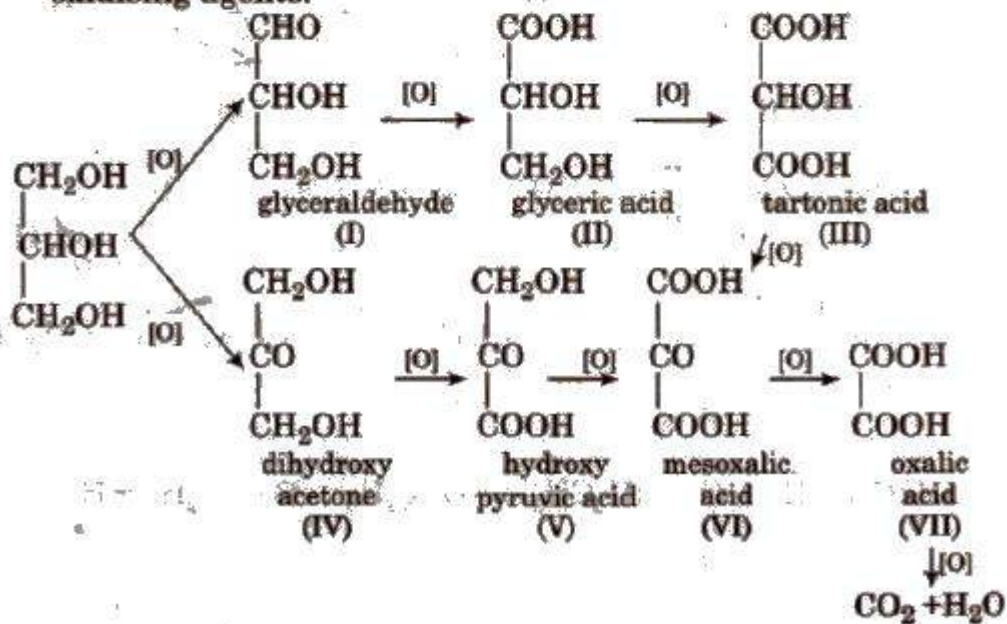
(b) At 260°C



(iv) Dehydration



(v) Oxidation Different products are obtained by different oxidising agents.



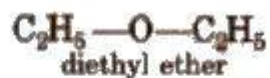
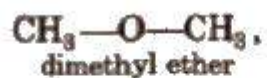
Cone HNO_3 gives II; dil HNO_3 gives II and III; $\text{Bi}(\text{NO}_3)_3$ or NaNO_3 gives VI; Fenton's reagent or NaOBr or Br_2 water in Na_2CO_3 gives a mixture of I and IV.

Solid KMnO_4 oxidises glycerol to VII and CO_2 and H_2O .

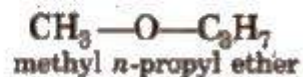
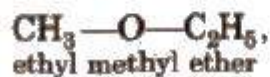
With HIO_4 (periodic acid). glycerol gives HCOOH and HCHO .

Ethers

Ethers are the organic compounds in which two alkyl or aryl groups are attached to a divalent oxygen. known as ethereal oxygen. These are represented by the general formula $\text{R}-\text{O}-\text{R}'$ where R may be alkyl or aryl groups. e.g.,



Mixed ethers



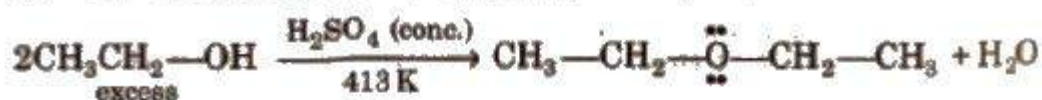
These are the functional isomers of alcohols. These also exhibit chain isomerism and metamerism.

Nomenclature of Ethers

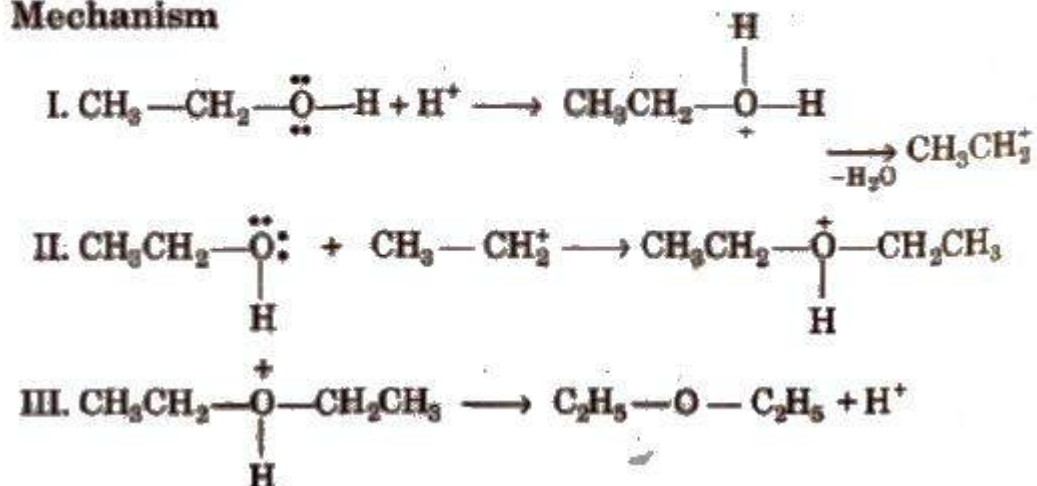
In the IUPAC system, ethers are regarded as 'alkoxy alkanes' in which the ethereal oxygen is taken along with smaller alkyl group while the bigger alkyl group is regarded as a part of the alkane.

Preparation of Ethers

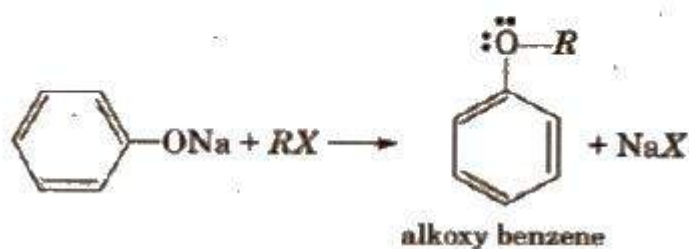
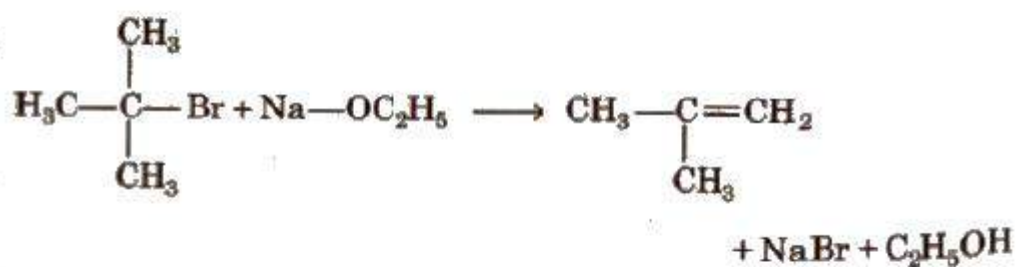
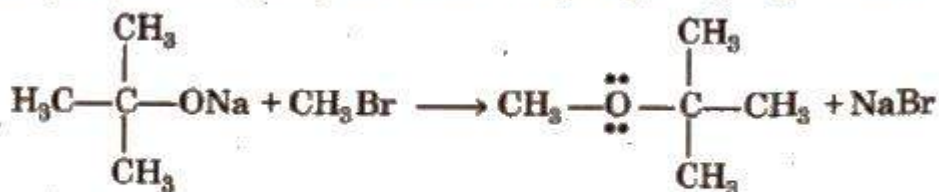
(i) By dehydration of alcohols



Mechanism



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

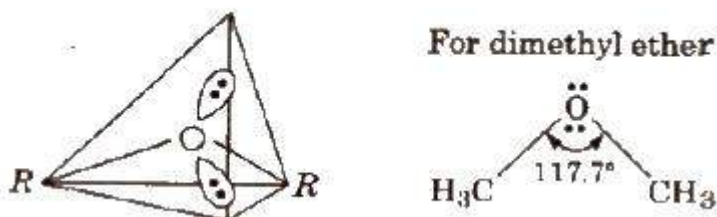


Physical Properties of Ethers

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.

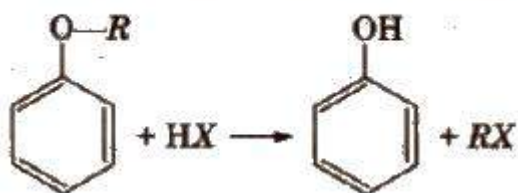
Structure of Ether

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

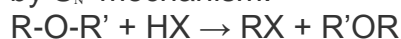


Chemical Reactions of Ether

(i) Reaction with HX



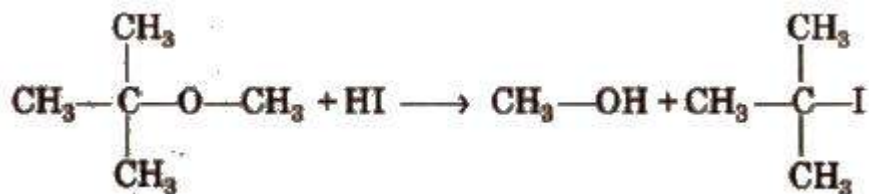
Ethers with two different alkyl groups are also cleaved in the same manner and results in the formation of a primary halide (or smaller and less complex alkyl halide) by S_N2 mechanism.



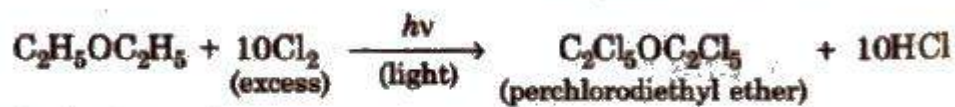
The order of reactivity of hydrogen halides is as follows



In ethers if one of the alkyl groups is a tertiary group, the halide formed is a tertiary halide by S_N1 mechanism.



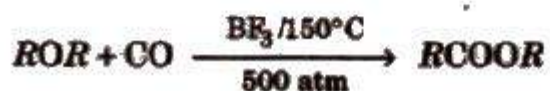
(ii) Halogenation



(iii) Reaction with PCl_5

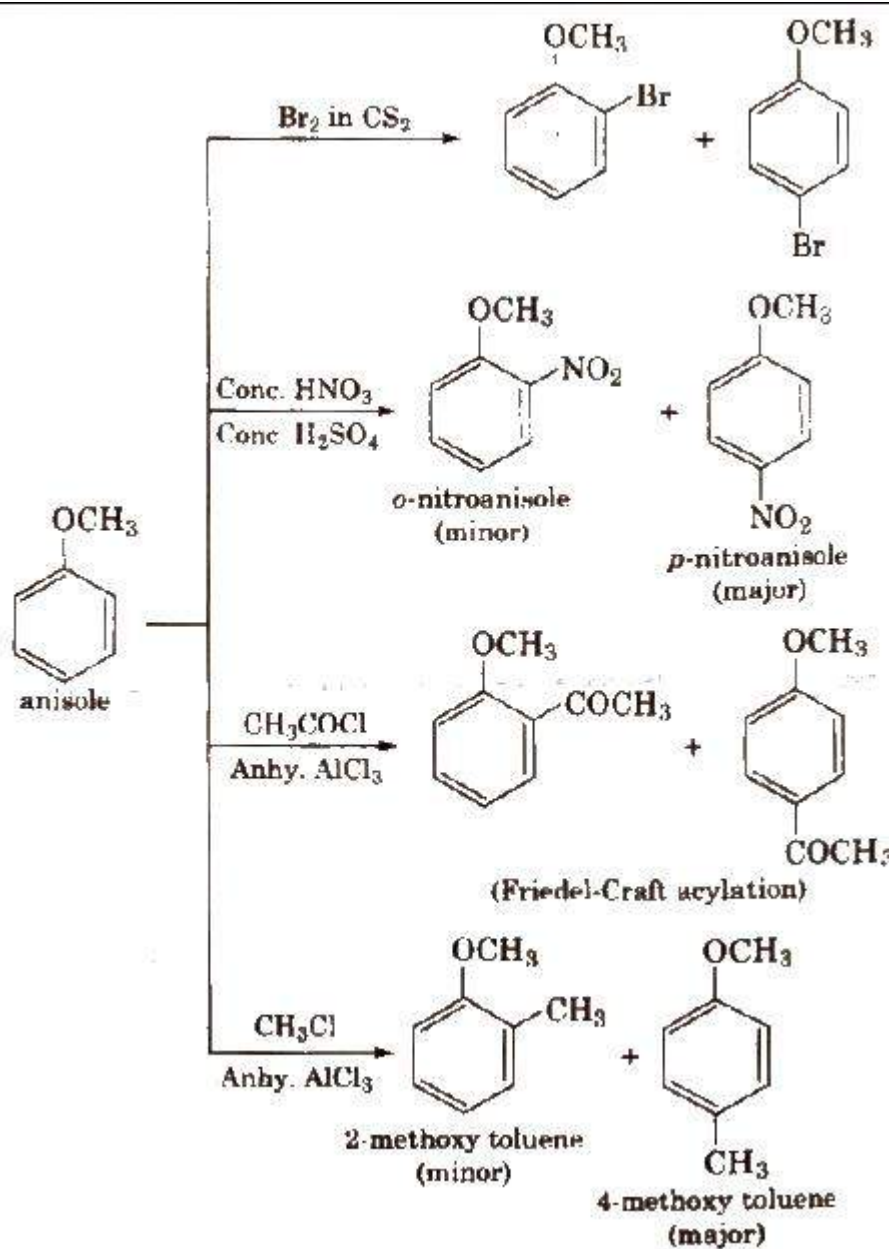


(iv) Reaction with CO



(v) Electrophilic substitution reactions in ethers:

-OR is ortho, para directing group and activate. the aromatic ring towards electrophilic substitution reaction.



Ethyl phenyl ester $\text{C}_6\text{H}_5\text{OC}_2\text{H}_5$ is also, known as phenetole.

Uses of Ethers

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