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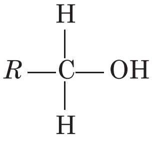
Alcohols, Phenols and Ethers

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).

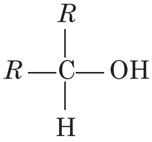
Classification of Alcohols and Phenols

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



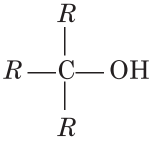
$$\begin{array}{c} \text{H} \\ | \\ R\text{—C—OH} \\ | \\ \text{H} \end{array}$$

primary (1°)



$$\begin{array}{c} R \\ | \\ R\text{—C—OH} \\ | \\ \text{H} \end{array}$$

secondary (2°)



$$\begin{array}{c} R \\ | \\ R\text{—C—OH} \\ | \\ R \end{array}$$

tertiary (3°)

Alcohols may be

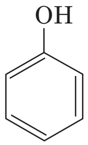
(i) monohydric-containing one —OH group,

(ii) dihydric-containing two —OH groups and

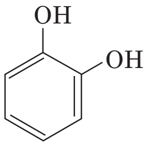
(iii) polyhydric-containing three or more —OH groups.

In allylic alcohols, —OH group is attached to sp^3-hybridised carbon but next to C═C bond. e.g. $CH_2{=}CH—CH_2OH$, in benzylic alcohol the — OH group is attached to sp^3 hybridised carbon atom next to an aromatic ring e.g. ($C_6H_5CH_2OH$).

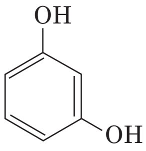
In phenols, — OH group is attached to sp^2-hybridised carbon. These may also be monohyric, dihydric, etc. The dihydric phenol further may be *ortho*, *meta*, or *para* derivative.



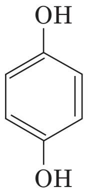
phenol



catechol



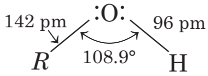
resorcinol



quinol or hydroquinone

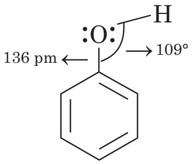
Structure of Alcohols and Phenols

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



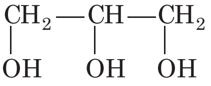
The value of ∠ROH bond angle depends upon the R group. For methyl alcohol, it is (∠C—$\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}}$—H) 108.9° due to repulsion of lone pairs.

In phenols, the —OH group is attached to sp^2-hybridised carbon and thus, the C—O bond acquires a partial double bond character due to resonance.



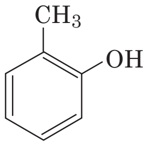
Nomenclature of Alcohol and Phenols

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

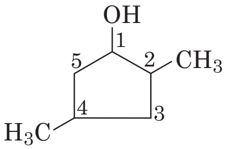


$\underset{OH}{\underset{|}{CH_2}}-\underset{OH}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH_2}}$

propane-1,2,3-triol



2-methylphenol

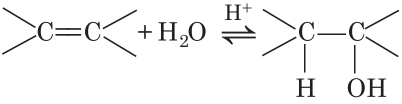


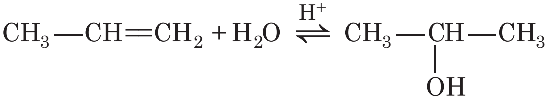
2,4-dimethylcyclopentanol

Preparation of Alcohols

(i) **From alkenes**

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



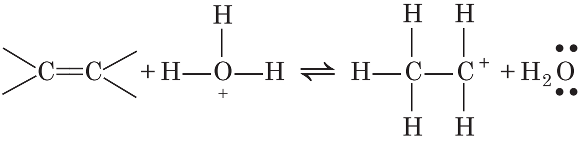


$$CH_3-CH=CH_2 + H_2O \overset{H^+}{\rightleftharpoons} CH_3-\underset{OH}{CH}-CH_3$$

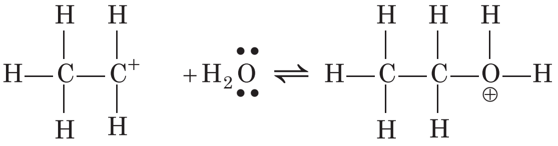
Mechanism

***Step* I** Protonation of alkene by attack of H_3O^+

$$H_2O + H^+ \longrightarrow H_3O^+$$

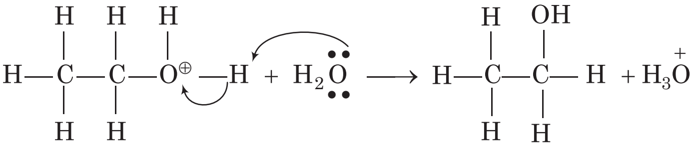


***Step* II** Nucleophilic attack



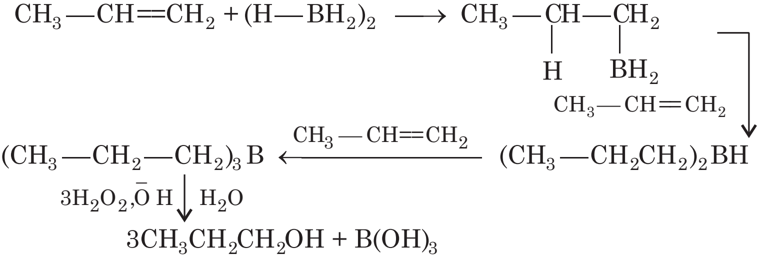
$$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C^+}} + H_2\ddot{\underset{..}{O}} \rightleftharpoons H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{\oplus}{\overset{H}{O}}-H$$

***Step* III** Deprotonation to form an alcohol



$$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\overset{H}{O^{\oplus}}-H + H_2\ddot{\underset{..}{O}} \longrightarrow H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{OH}{C}}-H + H_3\overset{+}{O}$$

(b) **By hydroboration-oxidation**



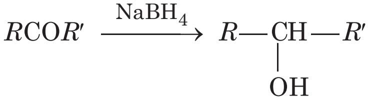
$$CH_3-CH=CH_2 + (H-BH_2)_2 \longrightarrow CH_3-\underset{H}{CH}-\underset{BH_2}{CH_2} \xrightarrow{CH_3-CH=CH_2} (CH_3-CH_2CH_2)_2BH$$

$$(CH_3-CH_2CH_2)_2BH \xrightarrow{CH_3-CH=CH_2} (CH_3-CH_2-CH_2)_3B \xrightarrow[H_2O]{3H_2O_2, \bar{O}H} 3CH_3CH_2CH_2OH + B(OH)_3$$

(ii) **From carbonyl compounds**

(a) By reduction of aldehydes and ketones

$$R\text{—CHO} + H_2 \xrightarrow{\text{Pd}} R\text{CH}_2\text{—OH}$$



$$R\text{COR}' \xrightarrow{\text{NaBH}_4} R\text{—}\underset{\substack{|\\ \text{OH}}}{\text{CH}}\text{—}R'$$

Aldehydes yield primary alcohols whereas ketones give secondary alcohols, when subjected to reduction.

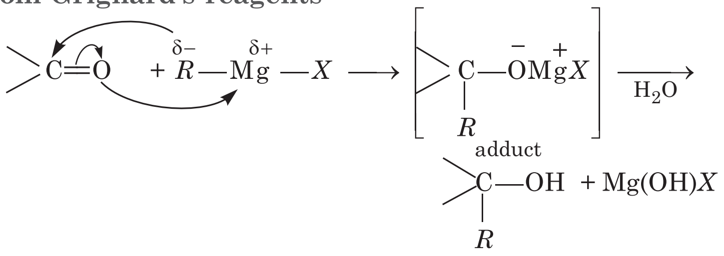
(b) By reduction of carboxylic acids and ester

$$R\text{COOH} \xrightarrow[\text{(ii) } H_2O]{\text{(i) LiAlH}_4} R\text{CH}_2\text{OH}$$

$$R\text{COO}R' \xrightarrow[\text{Catalyst}]{H_2} R\text{CH}_2\text{OH} + R'\text{OH}$$

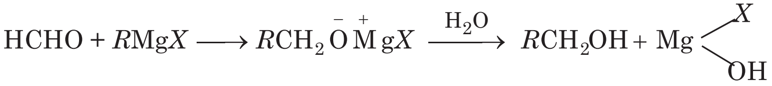
Reduction of aldehyde, ketones and esters with Na/alcohol is called Bouvaoult-blanc reduction.

(iii) **From Grignard's reagents**

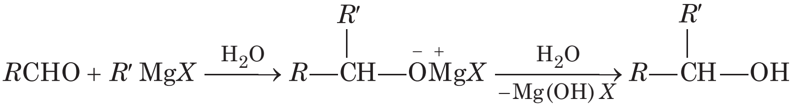


$$>\text{C}{=}\text{O} + \overset{\delta-}{R}\text{—}\overset{\delta+}{\text{Mg}}\text{—}X \longrightarrow \left[>\underset{\substack{|\\ R}}{\text{C}}\text{—}\overset{-}{\text{O}}\overset{+}{\text{Mg}}X\right]_{\text{adduct}} \xrightarrow[H_2O]{} >\underset{\substack{|\\ R}}{\text{C}}\text{—OH} + \text{Mg(OH)}X$$

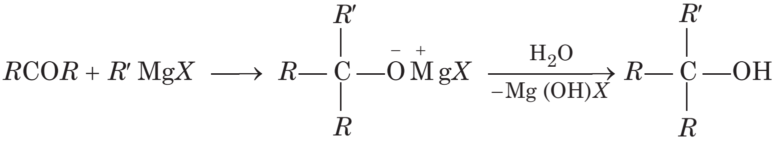
The reaction produces a primary alcohol with methanal, a secondary alcohol with aldehydes (except methanal) and tertiary alcohol with ketones.



$$\text{HCHO} + R\text{Mg}X \longrightarrow R\text{CH}_2\overset{-}{\text{O}}\overset{+}{\text{M}}\text{g}X \xrightarrow{H_2O} R\text{CH}_2\text{OH} + \text{Mg}\begin{smallmatrix} X \\ \text{OH}\end{smallmatrix}$$



$$R\text{CHO} + R'\,\text{Mg}X \xrightarrow{H_2O} R\text{—}\overset{\substack{R'\\ |}}{\text{CH}}\text{—}\overset{-}{\text{O}}\overset{+}{\text{Mg}}X \xrightarrow[-\text{Mg(OH)}\,X]{H_2O} R\text{—}\overset{\substack{R'\\ |}}{\text{CH}}\text{—OH}$$



$$R\text{CO}R + R'\,\text{Mg}X \longrightarrow R\text{—}\underset{\substack{|\\ R}}{\overset{\substack{R'\\ |}}{\text{C}}}\text{—}\overset{-}{\text{O}}\overset{+}{\text{M}}\text{g}X \xrightarrow[-\text{Mg (OH)}X]{H_2O} R\text{—}\underset{\substack{|\\ R}}{\overset{\substack{R'\\ |}}{\text{C}}}\text{—OH}$$

(iv) **Hydrolysis of alkyl halides**

$$R{-}X + \text{KOH}(aq) \longrightarrow R\text{OH} + \text{K}X$$

To avoid dehydrohalogenation of RX, mild alkalies like moist silver oxide is used.

Ease of hydrolysis of alkyl halides $R\text{I} > R\text{Br} > R\text{Cl} >$ and $t(3°) > s(2°) > p(1°)$ alkyl halides.

(v) **Hydrolysis of ethers**

$$R{-}\ddot{\text{O}}{-}R + \text{H}_2\text{O} \xrightarrow{\text{H}_2\text{SO}_4} 2R\text{OH}$$

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

$$R\text{NH}_2 + \text{HONO} \xrightarrow{(\text{NaNO}_2 + \text{HCl})} R\text{OH} + \text{N}_2\uparrow + \text{H}_2\text{O}$$

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

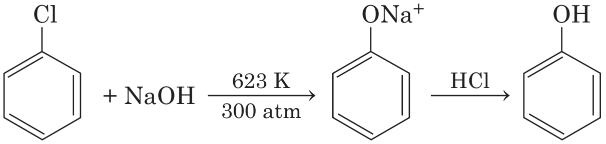
(vii) **By alcoholic fermentation**

$$\underset{\text{sucrose}}{\text{C}_{12}\text{H}_{22}\text{O}_{11}} + \text{H}_2\text{O} \xrightarrow{\text{Invertase}} \underset{\text{glucose}}{\text{C}_6\text{H}_{12}\text{O}_6} + \underset{\text{fructose}}{\text{C}_6\text{H}_{12}\text{O}_6}$$

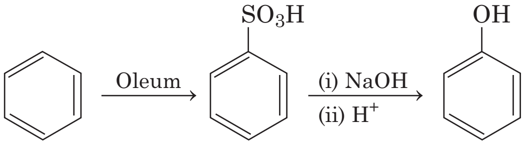
$$\underset{\text{glucose and fructose}}{\text{C}_6\text{H}_{12}\text{O}_6} \xrightarrow{\text{Zymase}} \underset{\text{ethyl alcohol}}{2\text{C}_2\text{H}_5\text{OH}} + 2\text{CO}_2(g)$$

Preparation of Phenols

(i) **From haloarenes**

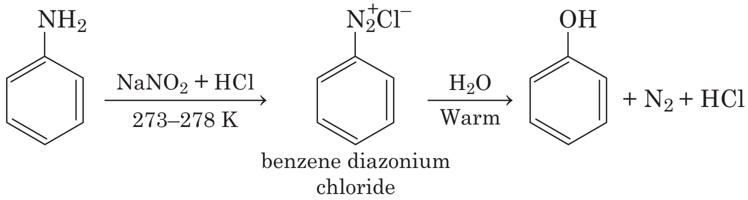


(ii) **From benzene sulphonic acid**

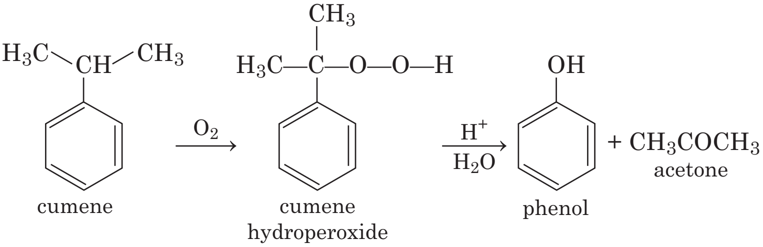


Benzene
sulphonic acid

(iii) **From diazonium salts**

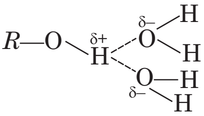


(iv) **From cumene**



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 alkanols 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° 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.

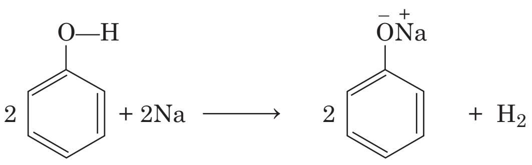
Chemical Reactions Common to Alcohols and Phenols

(i) Reactions involving cleavage of O—H Bond

(a) Acidity of alcohols and phenols

$$2R\text{—O—H} + 2\text{Na} \longrightarrow 2R\text{—}\overset{-}{\text{O}}\text{—}\overset{+}{\text{N}}\text{a} + \text{H}_2$$

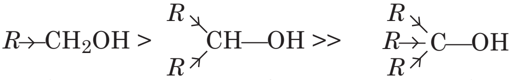
sodium alkoxide



sodium phenoxide

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 and decreases the polarity of —OH bond.

Order of acidity is

$$R\text{COOH} > \text{H}_2\text{CO}_3 > \text{C}_6\text{H}_5\text{OH} > \text{H}_2\text{O} > R\text{—OH}.$$

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 stabilising phenoxide ion while presence of electron releasing group decreases the acidity of phenol by destabilising 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 corresponds to the stronger acid.

(b) Esterification

$$\text{Ar}/R\text{—O—H} + R'\text{COOH} \overset{\text{H}^+}{\rightleftharpoons} \text{Ar}/R\text{—OCO}R' + \text{H}_2\text{O}$$

$$\text{Ar}/R\text{—OH} + (R'\text{CO})_2\text{O} \overset{\text{H}^+}{\rightleftharpoons} \text{Ar}/R\text{—OCO}R' + R'\text{COOH}$$

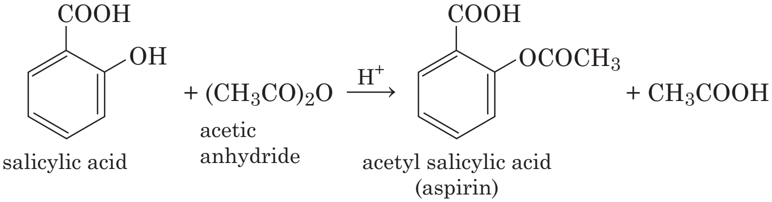
$$R/\text{Ar—OH} + R'\text{COCl} \xrightarrow[\text{Pyridine}]{} R/\text{Ar—OCO}R' + \text{HCl}$$

The reaction with $R'COOH$ and $(R'CO)_2O$ is reversible, so conc. H_2SO_4 is used to remove water.

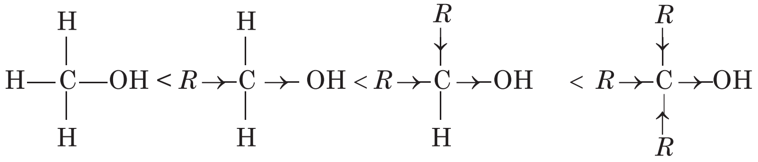
The reaction with $R'COCl$ is carried out in the presence of pyridine so as to neutralise HCl which is formed during the reaction.

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 different alcohols is :



$$H—\underset{H}{\overset{H}{C}}—OH < R\rightarrow\underset{H}{\overset{H}{C}}\rightarrow OH < R\rightarrow\underset{H}{\overset{R\downarrow}{C}}\rightarrow OH < R\rightarrow\underset{\uparrow R}{\overset{R\downarrow}{C}}\rightarrow OH$$

methyl alcohol primary alcohol secondary alcohol tertiary alcohol

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.

$$R—OH + HX\ (HCl, HBr, HI) \longrightarrow R—X + H_2O$$

For a given alcohol order of reactivity of H*X* is

H—I > H—Br > H—Cl

For a given halogen acid order of reactivity of alcohols

Tertiary > Secondary > Primary

Mixture of anhyd. $ZnCl_2$ and conc.HCl (Lucas reagent) is used to distinguish 1°, 2° and 3° alcohols (discussed later).

(b) **Reaction with phosphorus halides**

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

$$3ROH + PBr_3 \longrightarrow 3RBr + H_3PO_3$$

$$3ROH + PI_3 \longrightarrow 3RI + H_3PO_3$$

(c) **Reaction with thionyl chloride**

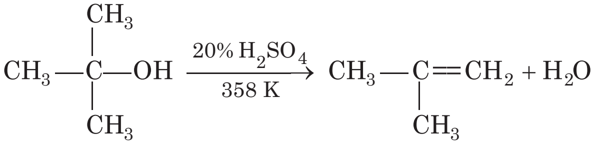
$$ROH + SOCl_2 \longrightarrow RCl + SO_2\uparrow + HCl\uparrow$$

(d) **Dehydration of alcohols** It requires acid as 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

$$3° > 2° > 1°$$

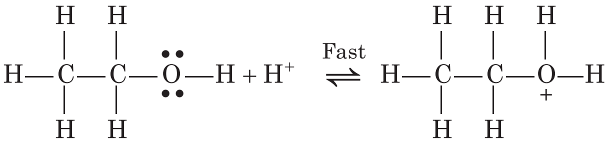
$$C_2H_5OH \xrightarrow[443\ K]{H_2SO_4} CH_2{=}CH_2 + H_2O$$



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

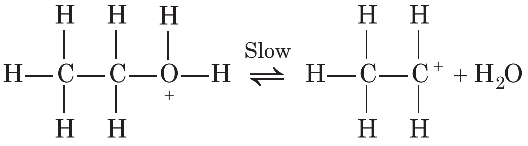
Mechanism

***Step* I** Formation of protonated alcohol



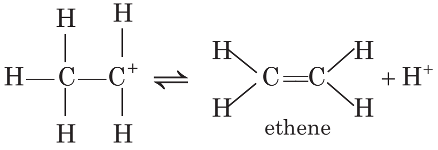
$$H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\bullet\bullet}{\overset{\bullet\bullet}{O}}-H + H^+ \overset{\text{Fast}}{\rightleftharpoons} H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{+}{\overset{\overset{H}{|}}{O}}-H$$

***Step* II** Formation of carbocation



$$H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{+}{\overset{\overset{H}{|}}{O}}-H \overset{\text{Slow}}{\rightleftharpoons} H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C^+}} + H_2O$$

***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)**.

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

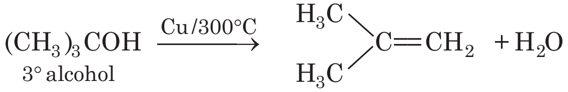
$$CH_3CH{=}CH{-}CH_2OH \xrightarrow{PCC} CH_3CH{=}CH{-}CHO$$

(e) **Oxidation reaction** This reaction is used to distinguish between 1°, 2° and 3° alcohols. Generally , alk. $KMnO_4$ and acid. $K_2Cr_2O_7$ is used as reagent (discussed later in this chapter)

(f) **Dehydrogenation**

$$\underset{1^\circ\text{ alcohol}}{RCH_2OH} \xrightarrow{Cu/300^\circ C} \underset{\text{aldehyde}}{RCHO} + H_2\uparrow$$

$$\underset{2^\circ\text{ alcohol}}{RCHOH-R} \xrightarrow{Cu/300^\circ C} \underset{\text{ketone}}{R\cdot CO\cdot R} + H_2\uparrow$$



alkene (*iso*- butylene)

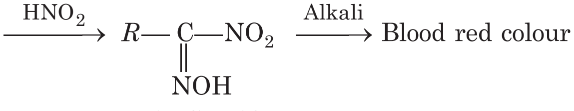
Distinction among Primary (1°), Secondary (2°) and Tertiary (3°) Alcohols

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.

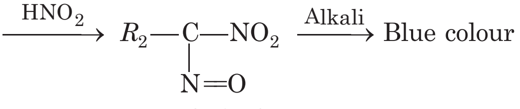
$$\underset{(1^\circ)}{RCH_2OH} \xrightarrow{P/I_2} RCH_2I \xrightarrow{AgNO_2} RCH_2NO_2$$



$$\xrightarrow{HNO_2} R-\underset{\underset{NOH}{\|}}{C}-NO_2 \xrightarrow{Alkali} \text{Blood red colour}$$

nitrolic acid

$$\underset{(2^\circ)}{R_2CHOH} \xrightarrow{P/I_2} R_2CHI \xrightarrow{AgNO_2} R_2CHNO_2$$



$$\xrightarrow{HNO_2} R_2-\underset{\underset{N=O}{|}}{C}-NO_2 \xrightarrow{Alkali} \text{Blue colour}$$

pseudonitrol

$$\underset{(3°)}{R_3C\text{—}OH} \xrightarrow{P/I_2} R_2CI \xrightarrow{AgNO_2} R_3CNO_2 \xrightarrow{HNO_2} \text{No reaction}$$

Lucas reagent (mixture of anhyd. $ZnCl_2$ and conc. HCl) is used to distinguish 1°, 2° and 3° alcohols.

Lucas test

Primary alcohols	Secondary alcohols	Tertiary alcohols
$RCH_2OH \xrightarrow[\text{Anhy.ZnCl}_2]{\text{Conc HCl}} (X)$	$R_2CH\text{—}OH \xrightarrow[\text{Anhy.ZnCl}_2]{\text{Conc HCl}}$	$R_3C\text{—}OH \xrightarrow[\text{Anhy.ZnCl}_2]{\text{Conc HCl}}$
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.

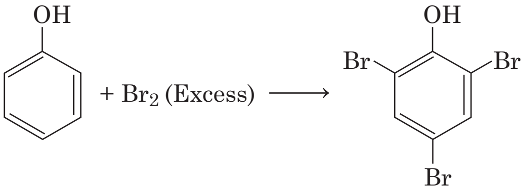
Oxidation reactions Oxidising reagents used for the oxidation of alcohols are neutral, acidic or alkaline $KMnO_4$ and acidified $K_2Cr_2O_7$.

Primary alcohols	Secondary alcohols	Tertiary alcohols
CH_3CH_2OH $\downarrow[O]$ CH_3CHO $\downarrow[O]$ CH_3COOH	$CH_3CH(OH)\text{—}CH_3$ $\downarrow[O]$ CH_3COCH_3 $\downarrow[O]$ $CH_3COOH + CO_2 + H_2O$	$(CH_3)_3C\text{—}OH$ $\downarrow[O]$ $CH_3COCH_3 + CO_2 + H_2O$ $\downarrow[O]$ $CH_3COOH + CO_2 + H_2O$

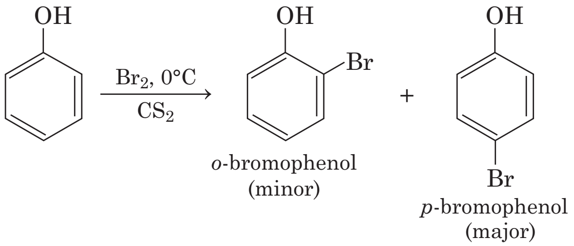
Chemical Reactions only for Phenols

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

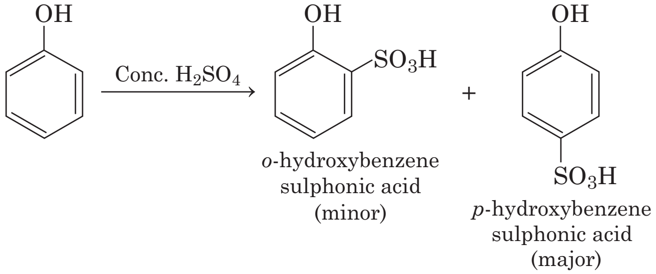
(a) **Halogenation**



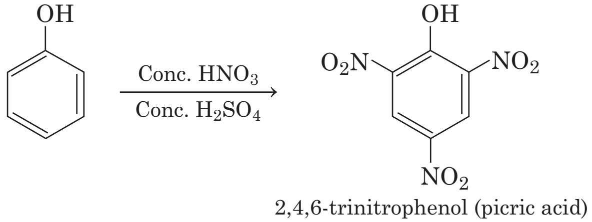
With calculated amount of Br_2 in CS_2 or $CHCl_3$, it gives *ortho* and *para* product.

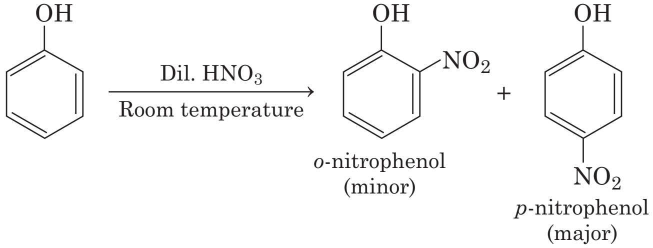


(b) **Sulphonation**

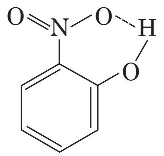


(c) **Nitration**

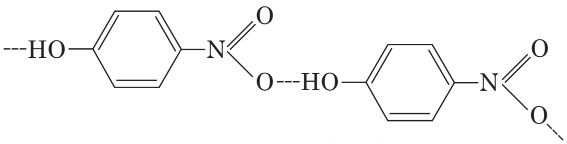




The *ortho* and *para* isomers can be separated by steam distillation. This is because *o*-nitrophenol is steam volatile due to intramolecular hydrogen bonding while *p*-nitrophenol is less volatile due to intermolecular hydrogen bonding which causes the association of molecules.

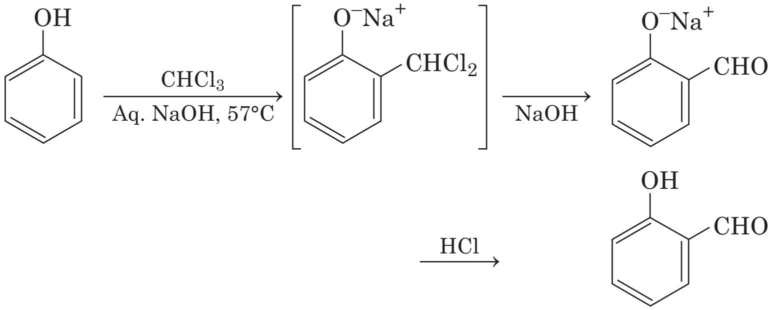


o-nitrophenol



p-nitrophenol

(d) **Reimer-Tiemann reaction**

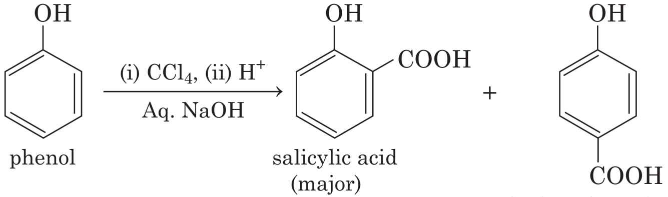


salicylaldehyde
(main product)

$$\bar{O}H + CHCl_3 \rightleftharpoons H_2O + :\bar{C}Cl_3 \longrightarrow \bar{Cl} + \underset{\substack{\text{dichlorocarbene}\\\text{(electrophile)}}}{:CCl_2}$$

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

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

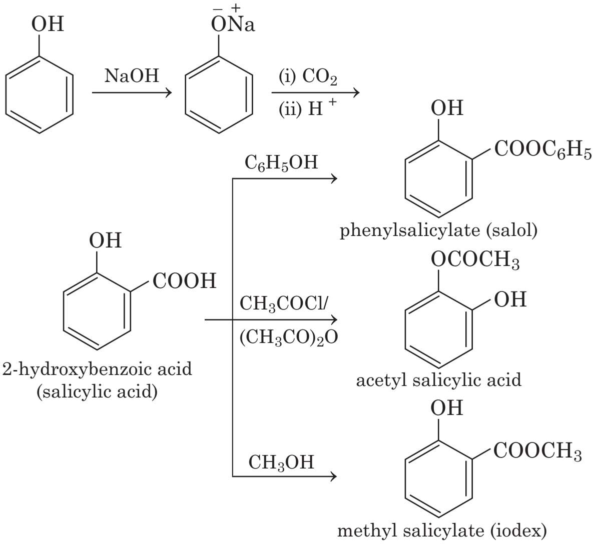


phenol

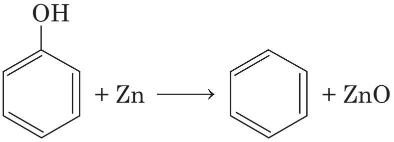
salicylic acid
(major)

p-hydroxybenzoic acid
(minor)

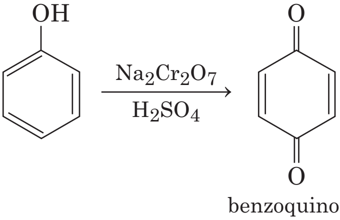
(ii) **Kolbe's reaction**



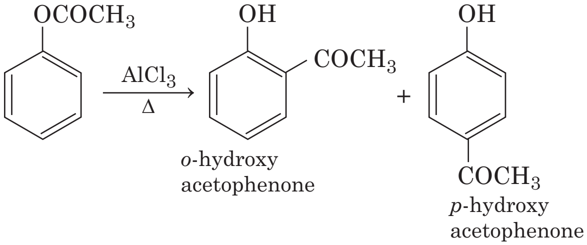
(iii) **Reaction with zinc dust**



(iv) **Oxidation**



(v) **Fries rearrangement**



Terms Related to Alcohols

(a) **Rectified spirit** It contains 9.5% ethyl alcohol and 4.5% water. It is an azeotrope (constant boiling mixture) and boils at 74°C.

(b) **Absolute alcohol** Alcohol containing no water, i.e. 100% C_2H_5OH 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.

Some Commercially Important Alcohols

Methanol

Methanol is a colourless liquid and boils at 337 K. It is also known as 'wood spirit' as it was produced by destructive distillation of wood. It is highly poisonous in nature. Ingestion of even small quantities of methanol is hazardous and large quantities causes even death. It is used as a solvent in paints, varnishes and for manufacturing formaldehyde dyes, medicines and perfumes.

Ethanol

Ethanol is a colourless liquid with boiling point 351 K. It is used in alcoholic beverages, produced by fermentation of sugars by yeast. It is used as a solvent in paint industry. It is also a good industrial solvent, hence, it is made unfit for drinkable purposes, by addition of a denaturant like CH_3OH which is poisonous. It gives carbon dioxide and water on burning. Thus, it is used as a fuel. It is safe and can be used to dissolve many organic compounds which are insoluble in water. Ethanol is used for medical purposes as a Central Nervous System (CNS) depressant.

Dihydric Alcohols

These are generally called glycols because of their sweet taste. Ethylene glycol ($CH_2OH—CH_2OH$) is the first and most important member of dihydric alcohol series.

Methods of Preparation

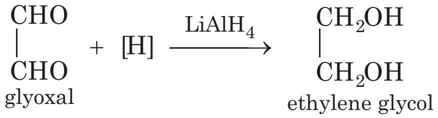
(i) **From ethylene**

$$CH_2{=}CH_2 + [O] + H_2O \xrightarrow{\text{Baeyer's reagent}} CH_2OH—CH_2OH$$

(1% alkaline $KMnO_4$ is called Baeyer's reagent)

$$CH_2{=}CH_2 \xrightarrow[Na_2SO_3/H_2O]{OsO_4/pyridine} CH_2OH{-}CH_2OH$$

(ii) **By reduction of glyoxal**



$$\begin{array}{c}CHO\\|\\CHO\end{array} + [H] \xrightarrow{LiAlH_4} \begin{array}{c}CH_2OH\\|\\CH_2OH\end{array}$$

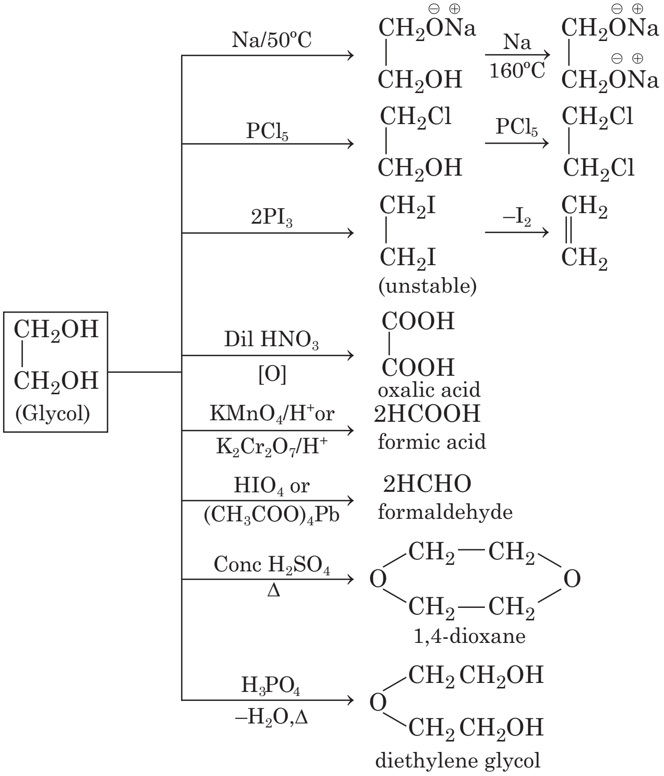
glyoxal ethylene glycol

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 H_2O and ethanol but not with ether.

Chemical Properties

It gives all the general reactions of —OH group.



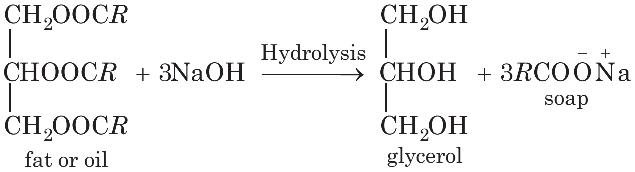
The per-iodic acid cleavage of 1,2-glycols is sometimes called Malaprade reaction.

Trihydric Alcohols

Glycerol or glycerine, $CH_2OH—CH(OH)—CH_2OH$ 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.



$$\underset{\text{fat or oil}}{\begin{array}{l}CH_2OOCR\\ |\\ CHOOCR\\ |\\ CH_2OOCR\end{array}} + 3NaOH \xrightarrow{\text{Hydrolysis}} \underset{\text{glycerol}}{\begin{array}{l}CH_2OH\\ |\\ CHOH\\ |\\ CH_2OH\end{array}} + \underset{\text{soap}}{3RCO\overset{-}{O}\overset{+}{N}a}$$

(where, $R = C_{17}H_{35}$ or $C_{15}H_{31}$ or $C_{17}H_{33}$)

Physical Properties

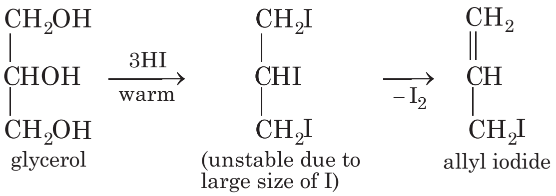
1. It is a colourless, odourless, viscous and hygroscopic liquid.
2. It is sweet in taste and steam volatile.
3. It is soluble in water but insoluble in ether.
4. Due to excessive H-bonding, it is highly viscous and has high boiling point.

Chemical Properties

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

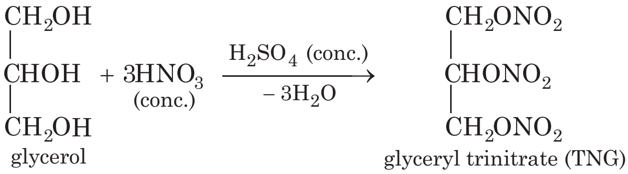
Some of its specific reactions are :

(i) **Reaction with HI**



$$\underset{\text{glycerol}}{\begin{array}{l}CH_2OH\\ |\\ CHOH\\ |\\ CH_2OH\end{array}} \xrightarrow[\text{warm}]{3HI} \underset{\text{(unstable due to large size of I)}}{\begin{array}{l}CH_2I\\ |\\ CHI\\ |\\ CH_2I\end{array}} \xrightarrow[-I_2]{} \underset{\text{allyl iodide}}{\begin{array}{l}CH_2\\ \|\\ CH\\ |\\ CH_2I\end{array}}$$

(ii) **Reaction with HNO_3**

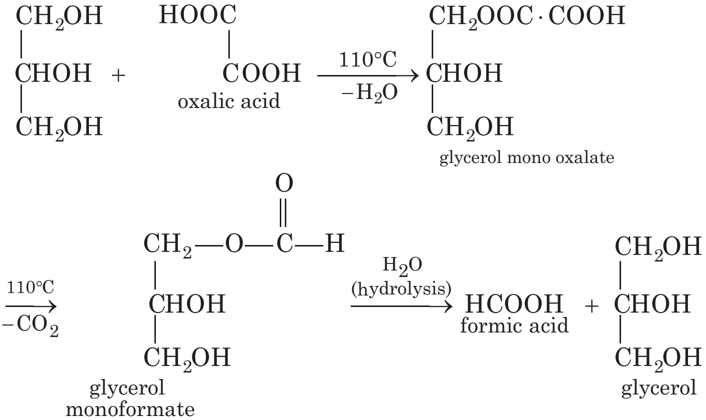


$$\underset{\text{glycerol}}{\begin{array}{l}CH_2OH\\ |\\ CHOH\\ |\\ CH_2OH\end{array}} + \underset{\text{(conc.)}}{3HNO_3} \xrightarrow[-3H_2O]{H_2SO_4\text{ (conc.)}} \underset{\text{glyceryl trinitrate (TNG)}}{\begin{array}{l}CH_2ONO_2\\ |\\ CHONO_2\\ |\\ CH_2ONO_2\end{array}}$$

Glyceryl trinitrate or trinitroglycerine, when adsorbed on Keiselghur is known as **dynamite**. Mixture of TNG and cellulose trinitrate is called **blasting gelatin**.

(iii) **Reaction with oxalic acid**

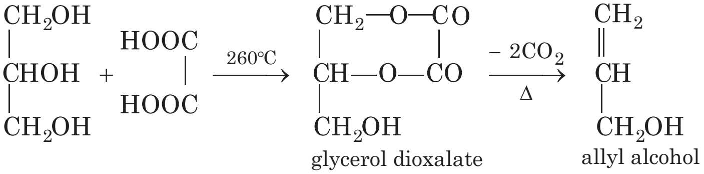
(a) **At 110°C**



$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + \begin{array}{r} HOOC \\ | \\ COOH \end{array} \xrightarrow[-H_2O]{110°C} \begin{array}{l} CH_2OOC\cdot COOH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

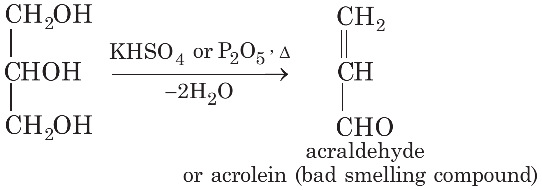
$$\xrightarrow[-CO_2]{110°C} \begin{array}{l} CH_2—O—\overset{\overset{\displaystyle O}{\|}}{C}—H \\ | \\ CHOH \\ | \\ CH_2OH \end{array} \xrightarrow{\substack{H_2O \\ (hydrolysis)}} HCOOH + \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

(b) **At 260°C**



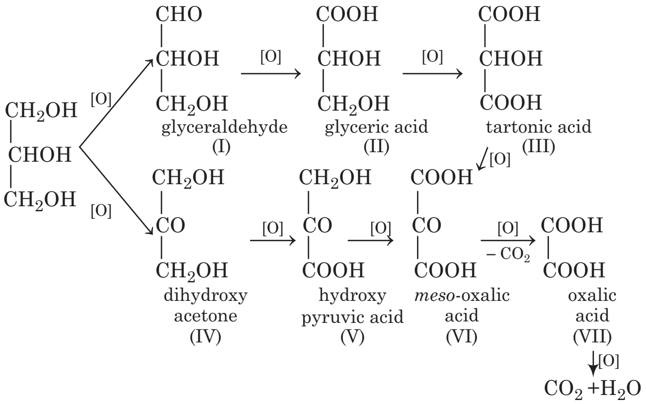
$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + \begin{array}{r} HOOC \\ | \\ HOOC \end{array} \xrightarrow{260°C} \begin{array}{l} CH_2—O—CO \\ |\qquad\qquad | \\ CH—O—CO \\ | \\ CH_2OH \end{array} \xrightarrow[\Delta]{-\ 2CO_2} \begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ CH_2OH \end{array}$$

(iv) **Dehydration**



$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} \xrightarrow[-2H_2O]{KHSO_4 \text{ or } P_2O_5,\ \Delta} \begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ CHO \end{array}$$

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



In the above reaction conc. HNO_3 gives II; dil HNO_3 gives II and III; $Bi(NO_3)_3$ 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 $R—O—R'$ where R may be alkyl or aryl groups. e.g.

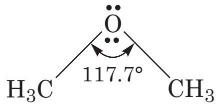
Simple ethers	$CH_3—O—CH_3$, dimethyl ether	$C_2H_5—O—C_2H_5$ diethyl ether
Mixed ethers	$CH_3—O—C_2H_5$, ethyl methyl ether	$CH_3—O—C_3H_7$ methyl n-propyl ether

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

Structure of Ether

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

For dimetnyl ether



Nomenclature of Ethers

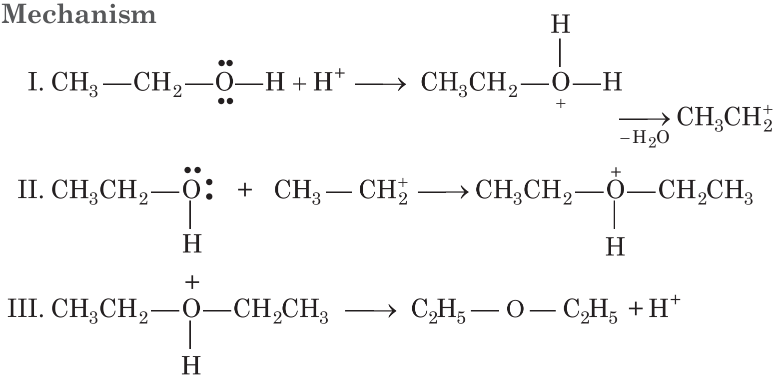
In the IUPAC system, ethers are regarded as ‘alkoxyalkanes’ in which the ethereal oxygen is taken along with smaller alkyl group while the bigger alkyl group is regarded as a part of the alkane.

Preparation of Ethers

(i) **By dehydration of alcohols**

$$\underset{\text{excess}}{2CH_3CH_2-OH} \xrightarrow[413\text{ K}]{H_2SO_4\text{ (conc.)}} CH_3-CH_2-\ddot{\underset{\cdot\cdot}{O}}-CH_2-CH_3 + H_2O$$

Mechanism



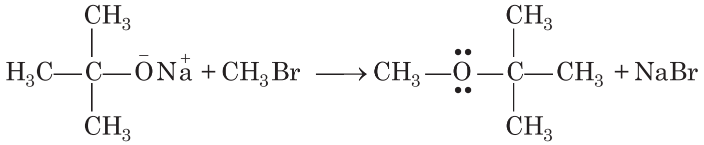
$$\text{I. } CH_3-CH_2-\ddot{\underset{\cdot\cdot}{O}}-H + H^+ \longrightarrow CH_3CH_2-\overset{\overset{H}{|}}{\underset{+}{O}}-H \xrightarrow[-H_2O]{} CH_3CH_2^+$$

$$\text{II. } CH_3CH_2-\underset{\underset{H}{|}}{\ddot{O}}: + CH_3-CH_2^+ \longrightarrow CH_3CH_2-\underset{\underset{H}{|}}{\overset{+}{O}}-CH_2CH_3$$

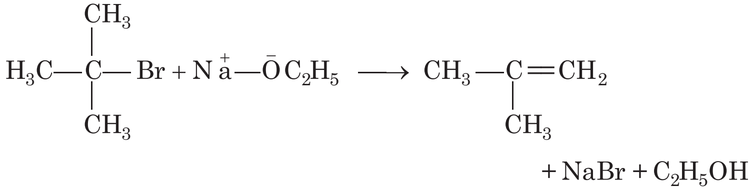
$$\text{III. } CH_3CH_2-\underset{\underset{H}{|}}{\overset{+}{O}}-CH_2CH_3 \longrightarrow C_2H_5-O-C_2H_5 + H^+$$

(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.

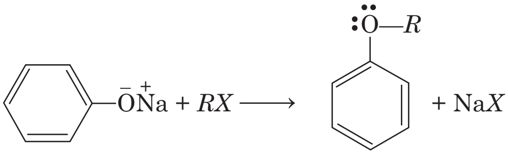
$$CH_3CH_2Br + CH_3CH_2\overset{-}{O}\overset{+}{N}a \longrightarrow CH_3CH_2OCH_2CH_3 + NaBr$$



$$H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\overset{-}{O}N\overset{+}{a} + CH_3Br \longrightarrow CH_3-\ddot{\underset{\cdot\cdot}{O}}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 + NaBr$$



$$H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-Br + N\overset{+}{a}-\overset{-}{O}C_2H_5 \longrightarrow CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2 + NaBr + C_2H_5OH$$



alkoxy benzene

Physical Properties of Ethers

(i) Ethers are polar but insoluble in H_2O.

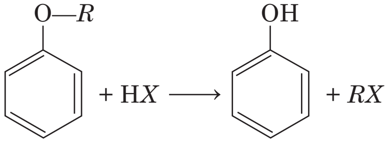
(ii) They have low boiling point than alcohols of comparable molecular masses because ethers do not form hydrogen bonds with water.

(iii) Dimethyl ether and ethyl methyl ether are both gases.

Chemical Reactions of Ether

(i) **Reaction with HX**

$$R\text{—O—}R + HX \longrightarrow RX + R\text{—OH}$$



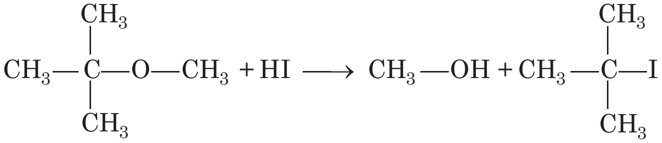
Ethers with two different alkyl groups are also cleaved in the same manner and results in the formation of a primary halide (or smaller and less complex alkyl halide) by S_N2 mechanism.

$$R\text{—O—}R' + HX \longrightarrow RX + R'OH$$

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_N1 mechanism.



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

(ii) **Halogenation**

$$CH_3CH_2OCH_2CH_3 \xrightarrow[\text{Dark}]{Cl_2} \underset{(\alpha\text{-monochloro diethyl ether})}{CH_3CHClOCH_2CH_3}$$

$$C_2H_5OC_2H_5 + \underset{(\text{excess})}{10Cl_2} \xrightarrow[(\text{light})]{h\nu} \underset{(\text{perchlorodiethyl ether})}{C_2Cl_5OC_2Cl_5} + 10HCl$$

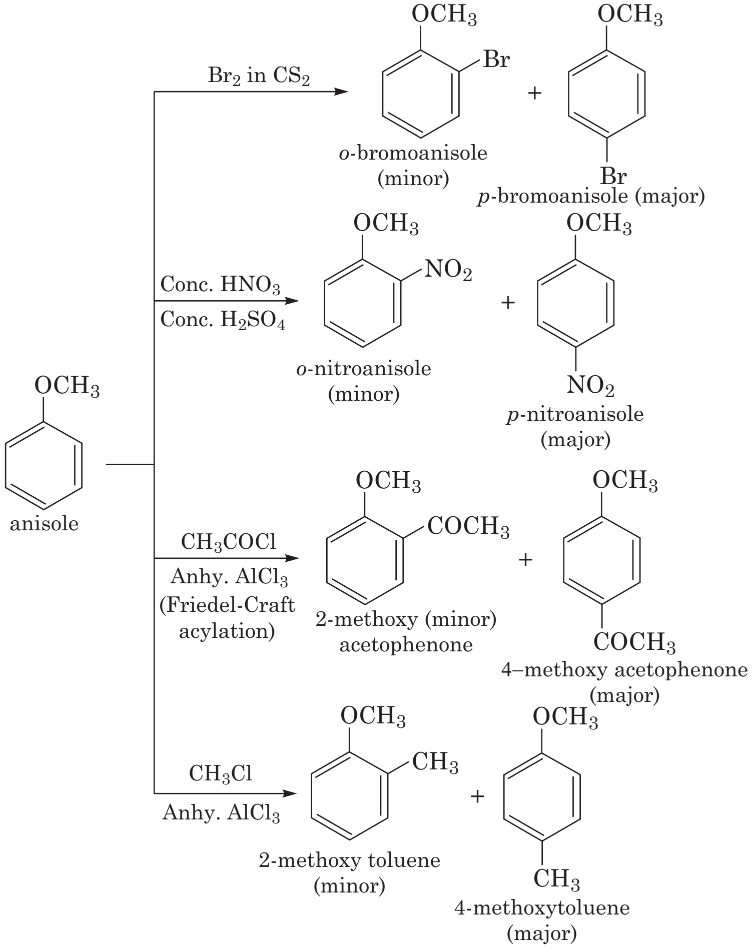
(iii) **Reaction with PCl_5**

$$R\text{—O—}R + PCl_5 \xrightarrow{\Delta} 2RCl + POCl_3$$

(iv) **Reaction with CO**

$$ROR + CO \xrightarrow[500\text{ atm}]{BF_3/150°C} RCOOR$$

(v) **Electrophilic substitution reactions** In ethers, —O*R* is *ortho*, *para* directing group and activates the aromatic ring towards electrophilic substitution reaction.



Ethyl phenyl ester $C_6H_5OC_2H_5$ is also, known as phenetole.

Uses of Ethers

1. Dimethyl ether is used as refrigerant and as a solvent at low temperature.
2. Diethylether is used as an anaesthesia in surgery.