

# Alcohols, Phenols and Ethers

## TOPIC 1 Alcohols and Phenols

When a hydrogen atom in a hydrocarbon (aliphatic or aromatic) is replaced by one or more—OH groups, the compound is known as alcohols or phenols. In other words, hydroxy derivatives of aliphatic hydrocarbons are called **alcohols** while hydroxy derivatives of benzene are called **phenols**.

### 1.1 Nomenclature

The common name of an alcohol is derived from common name of alkyl group and adding the word alcohol to it. In IUPAC system, the name of an alcohol is derived from the name of the alkane by replacing 'e' of the alkane with the suffix 'ol'.

For naming polyhydric alcohols, the 'e' of alkane is retained and the ending 'ol' is added.

Cyclic alcohols are named using the prefix cyclo and considering —OH group attached to C - 1.

#### Common and IUPAC name of some alcohols

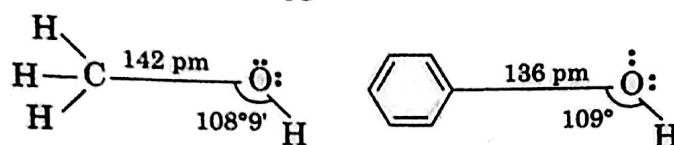
Compound	Common name	IUPAC name
$\text{CH}_3\text{OH}$	Methyl alcohol	Methanol
$\text{CH}_3\text{CH}_2\text{OH}$	Ethyl alcohol	Ethanol
$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	<i>n</i> -propyl alcohol	Propan-1-ol
$\begin{array}{c} \text{OH} \\   \\ \text{CH}_3 - \text{CH} - \text{CH}_3 \end{array}$	<i>Iso</i> -propyl alcohol	Propan-2-ol
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2 - \text{OH}$	<i>n</i> -butyl alcohol	Butan-1-ol
$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CH}_3 \\   \\ \text{OH} \end{array}$	<i>Sec</i> -butyl alcohol	Butan-2-ol

Compound	Common name	IUPAC name
	—	Cyclohexanol
	Phenol	Phenol
	Catechol	Benzene-1, 2-diol
	o-cresol	2-methyl phenol

### Structure of Alcohols and Phenols

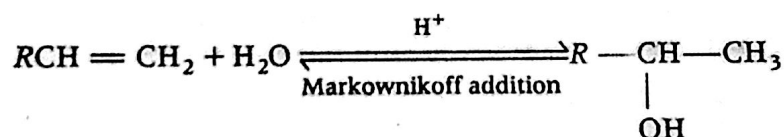
The C—O bond length in phenol is slightly less than that of alcohol due to following reasons.

- Partial double character due to resonance.
- $sp^2$  hybridised state of carbon to which oxygen is attached.

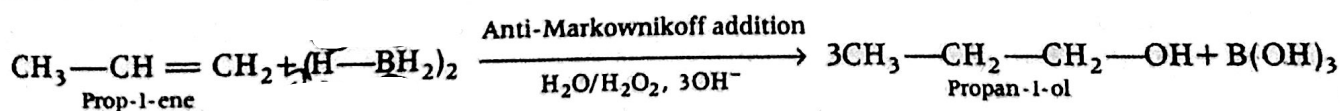


## 1.2 Preparation of Alcohols

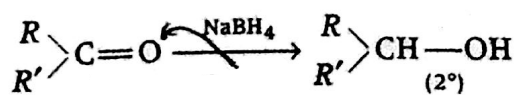
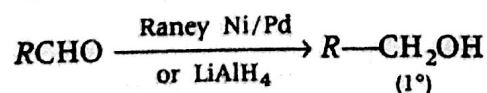
- By acid catalysed hydration of alkenes, i.e. addition of  $H_2O$  on alkenes in the presence of an acid as a catalyst. Unsymmetrical alkenes undergo Markownikoff's addition to yield secondary alcohols.



- By hydroboration-oxidation of unsymmetrical alkenes, i.e. addition of diborane on alkenes followed by oxidation of  $H_2O_2$  in presence of  $NaOH$  yields primary alcohols.

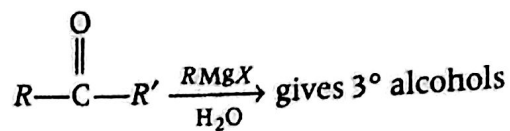
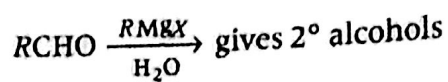
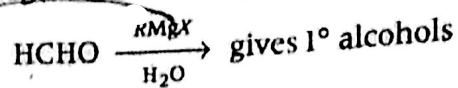


- By reduction of carbonyl compounds, i.e. aldehydes and ketones in presence of Raney Ni/Pd,  $LiAlH_4$ ,  $NaBH_4$ . Aldehydes give primary alcohols while ketones give secondary alcohols.



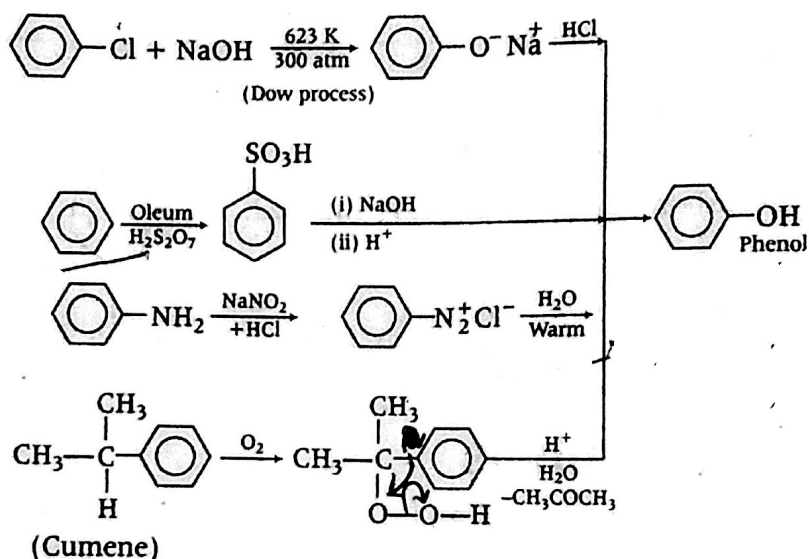
Carboxylic acids are reduced to primary alcohols in excellent yields by  $LiAlH_4$ , a strong reducing agent.

(iv) By the addition of Grignard's reagent followed by hydrolysis with dil. HCl,



(v) By hydrolysis of alkyl halides with aqueous NaOH or KOH through  $\text{S}_\text{N}$  reaction.

## 1.3 Preparation of Phenols



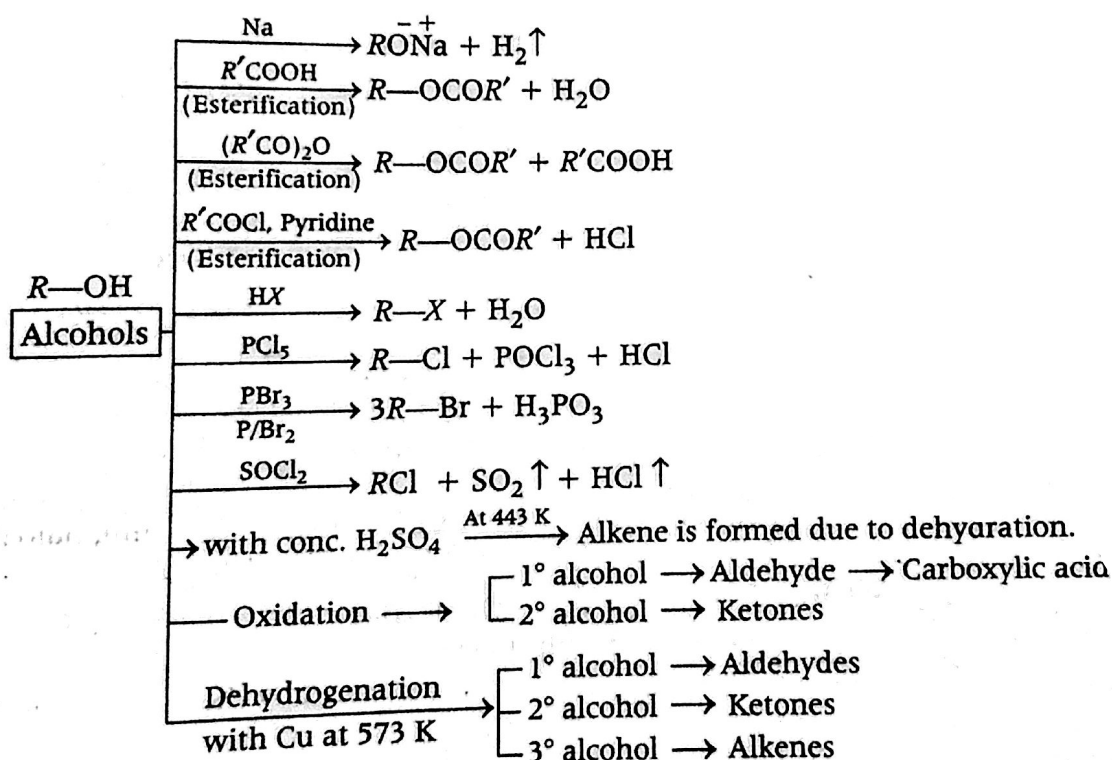
## 1.4 Properties of Alcohols and Phenols

- Boiling point of alcohols and phenols are much higher than those of corresponding haloalkanes, ethers and hydrocarbons due to intermolecular H-bonding. Boiling point of alcohols increases with increase in the number of carbon atoms and decreases with increase in branching.
- Alcohols and phenols are soluble in water due to intermolecular H-bonding.
- Alcohols are less acidic than phenols because phenoxide ion [formed by the loss of H-atom] is stabilised by resonance but alkoxide ion is not.
- Electron withdrawing groups like  $\text{NO}_2$ ,  $\text{X}$ , increases the acidic strength of phenols due to the effective delocalisation of negative charge in phenoxide ion and this effect is more pronounced at *o*- and *p*-positions than at *m*-positions. Therefore, correct order of acidity is *p*-nitrophenol > *o*-nitrophenol > *m*-nitrophenol.
- Electron donating groups like  $-\text{OCH}_3$ ,  $-\text{NH}_2$  do not favour the formation of phenoxide ion. Hence, decreases the acidic strength of phenols.

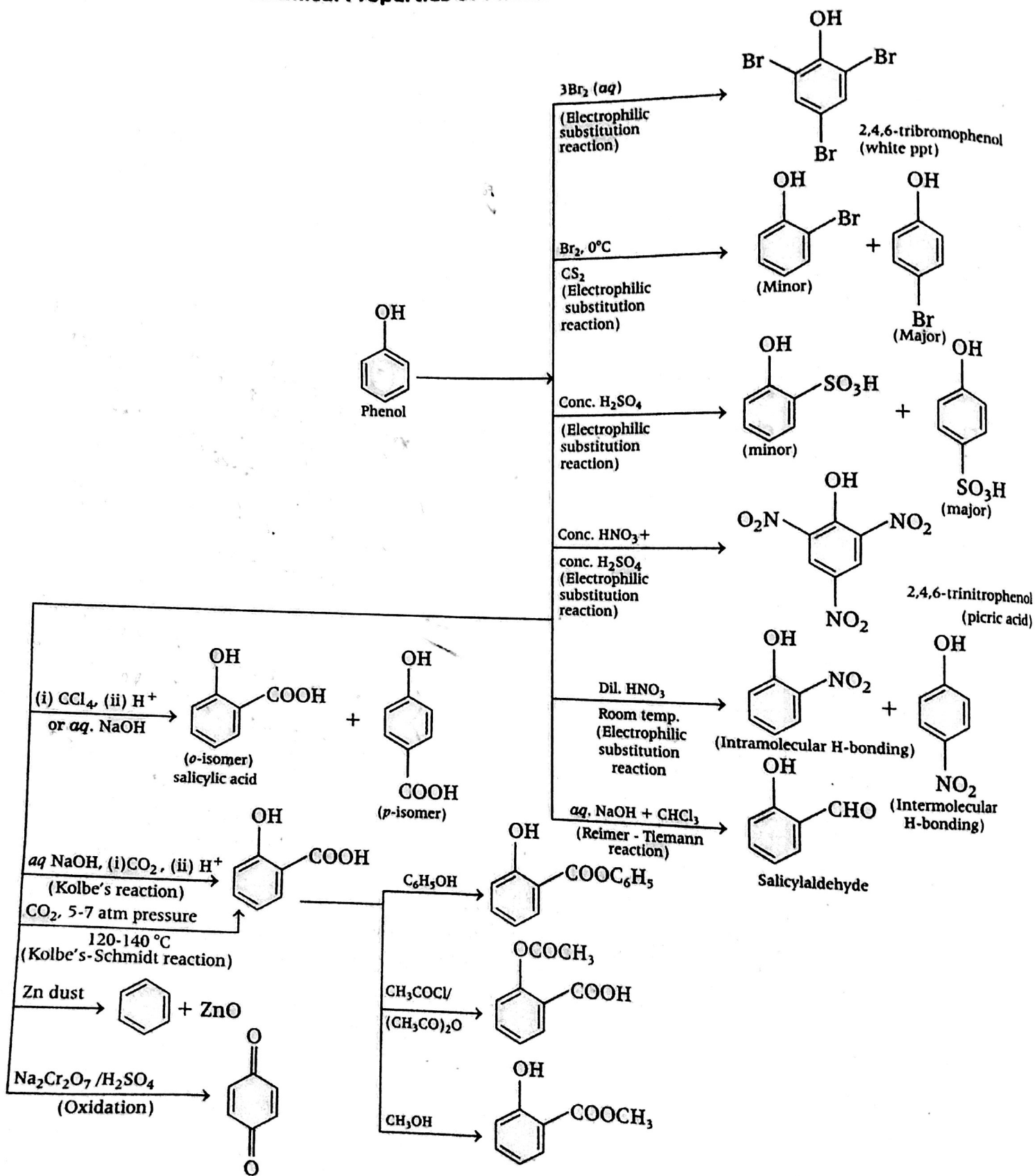
- Primary alcohols are oxidised to carboxylic acid by acidified  $K_2Cr_2O_7$  and to aldehydes by  $CrO_3$  or PCC. Secondary alcohols on oxidation gives ketones.  $3^\circ$  alcohols undergo oxidation only under strong conditions.
- Phenols readily undergo electrophilic substitution reactions due to strong activating  $-OH$  group.
- Phenol gives a mixture of *o* and *p* -nitrophenols on reaction with dil.  $HNO_3$  at 293K. *o*-nitrophenol forms weak intramolecular H-bonding due to which it has lower melting point and boiling point, lower solubility in water and it is more volatile than *p*-nitrophenol which forms intermolecular H-bonding and hence, has high melting and boiling point, more solubility in water. Thus, both types of nitrophenols can be separated by steam distillation.
- On treating phenol with  $CHCl_3$  (chloroform) in the presence of sodium hydroxide, a  $-CHO$  group is introduced at *o*-position of benzene ring. This reaction is called **Reimer-Tiemann reaction**.
- Sodium phenoxide (formed by reaction of phenol with  $NaOH$ ) when heated with  $CO_2$  at 400K under a pressure of 4-7 atm followed by acidification gives salicylic acid. This reaction is called **Kolbe's reaction**.

## 1.5 Chemical Properties

### (i) Flow Chart for the Chemical Properties of Alcohols



(ii) Flow Chart for Chemical Properties of Phenols

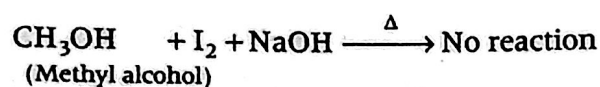
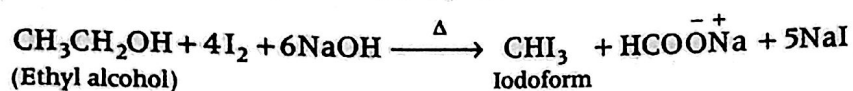


## 1.6 Methods to Distinguish Alcohols and Phenols

- (i) Phenols can be distinguished from alcohols by litmus test, phenols turn blue litmus red and produces violet colouration with neutral  $\text{FeCl}_3$  and white ppt. of 2, 4, 6-tribromophenol with bromine water, whereas alcohols does not give this test.
- (ii) **Coupling reaction** Phenols react with diazonium salts in weakly basic solution to form yellow or orange coloured azo dyes but alcohols do not react.

### Methods to distinguish between 1°, 2° and 3° alcohols

- (i) **Lucas test** Alcohols are soluble in Lucas reagent (conc.  $\text{HCl}$  and  $\text{ZnCl}_2$ ) while, their halides are immiscible and produces turbidity. 3° alcohols produces turbidity immediately, 2° alcohols produces after 5 minutes while 1° alcohols does not produce turbidity at room temperature.
- (ii) **Iodoform test** All alcohols containing the group  $\text{CH}_3\text{CH}(\text{OH})$  linked to carbon or hydrogen atom can be distinguished from other alcohols by the iodoform test.



Phenols and alcohols can also be distinguished using this test.

## 1.7 Some Commercially Important Alcohols and Uses of Alcohol and Phenols

- (i) 100% ethanol is **absolute alcohol** and 95% ethanol is **rectified alcohol**.
- A mixture of 20% ethanol and 80% gasoline is the **power alcohol**.
- (ii) **Uses**
- Alcohols are used as solvents, anti-freeze agent in the preparation of medicines as preservatives etc.
  - Phenols are used to prepare bakelite, plastic for manufacturing of dyes and drugs in medicines in the preparation of phenolphthalein, etc.



## [TOPIC 2] Ethers

- The substitution of a hydrogen atom in a hydrocarbon (aliphatic/aromatic) by an alkoxy ( $\text{—OR}$ ) or by aryloxy ( $\text{—OAr}$ ) group yield ethers. Ethers are represented as  $R\text{—OR}'$  and have general formula  $\text{C}_n\text{H}_{2n+2}\text{O}$ .
- Ethers are dialkyl derivatives of water or monoalkyl derivatives of alcohols.
- The IUPAC name of ether is alkoxy alkane. The ethereal oxygen is taken with smaller alkyl group and forms a part of alkoxy group while, the larger alkyl group is considered to be a part of the alkane. e.g. The IUPAC name for  $\text{CH}_3\text{—O—CH}_3$  is methoxy methane and for  $\text{CH}_3\text{—CH}_2\text{O—CH}_2\text{CH}_3$  is ethoxy ethane.
- The isomerism commonly exhibited by ethers is metamerism.

### 2.1 Preparation of Ethers

- (i) By dehydration of alcohols in presence of protic acids at 413 K.
- (ii) Both symmetrical and unsymmetrical ethers can be prepared by **Williamson's synthesis**. The order of reactivity of alkyl halides for Williamson's synthesis reaction is primary > secondary > tertiary.
- (iii) To obtain best yield of *tert*-butyl ether by Williamson's synthesis, the alkyl halide should be primary and alkoxide should be *tert*-butoxide.
- (iv) Aromatic ethers like anisole can be prepared by the reaction of sodium phenoxide with alkyl halides.

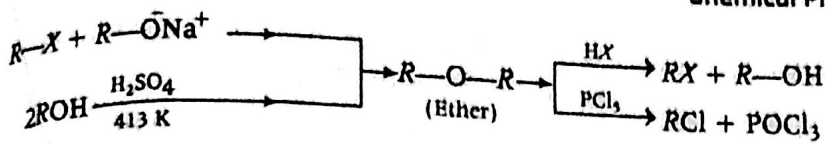
### 2.2 Properties of Ethers

- (i) Ethers have low boiling points than isomeric alcohols due to their inability to form H-bonds.
- (ii) Ethers are inert and thus are used as solvents in many reactions.
- (iii) Ethers on cleavage by acids give back alcohols and alkyl halides. The reaction proceed *via*  $\text{S}_{\text{N}}2$  mechanism. Due to steric hindrance, the alkyl halide is always obtained from smaller alkyl group.
- (iv) Aromatic ethers on cleavage give phenol and alkyl halide.

# Flow Chart for the Preparation and Chemical Reactions of Ether

## Preparation

## Chemical Properties



## Reactions of Anisole

### • Electrophilic Substitution Reactions

