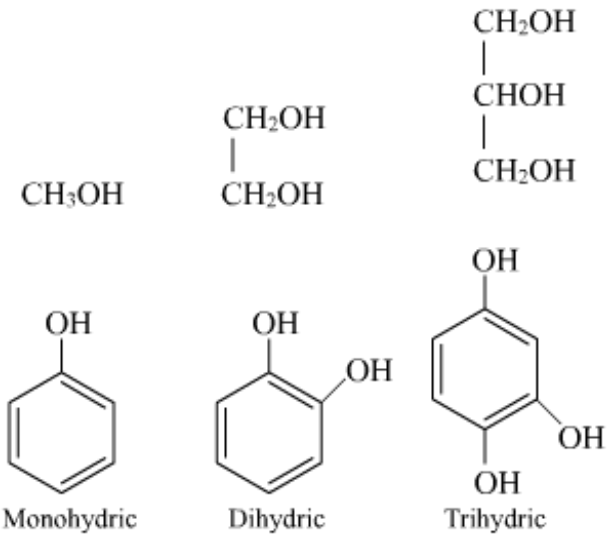
Alcohols, Phenols and Ethers

Classification of alcohols and phenols:

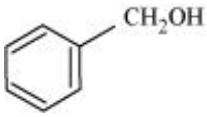
- Mono, di, tri or polyhydric –



- On the basis of hybridisation –

1. C_{sp^3} – OH
   a. Primary, secondary and tertiary
   b. Allylic alcohols

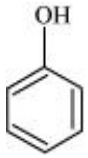
   1. Benzylic alcohols



2. C_{sp^2} – OH

   a. Vinylic alcohol

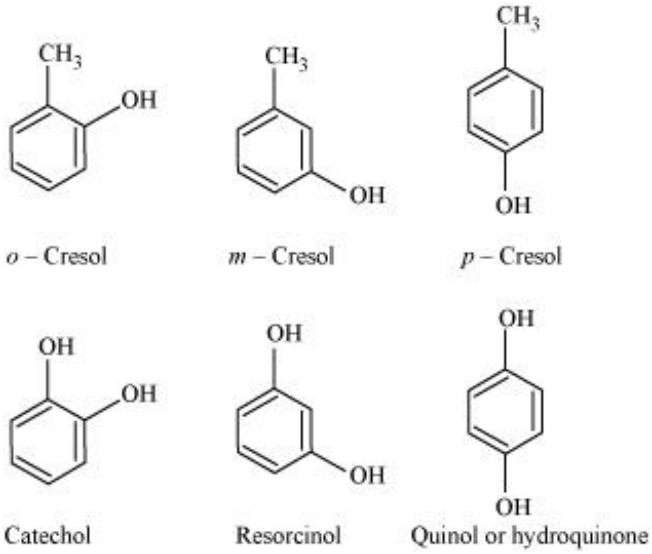
   b. Phenol



Classification of ethers:

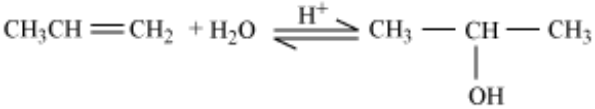
- Simple or symmetrical – $C_2H_5OC_2H_5$, $C_6H_5OC_6H_5$
- Mixed or unsymmetrical – $C_2H_5OCH_3$, $CH_3OC_6H_5$

Common names of some phenols:



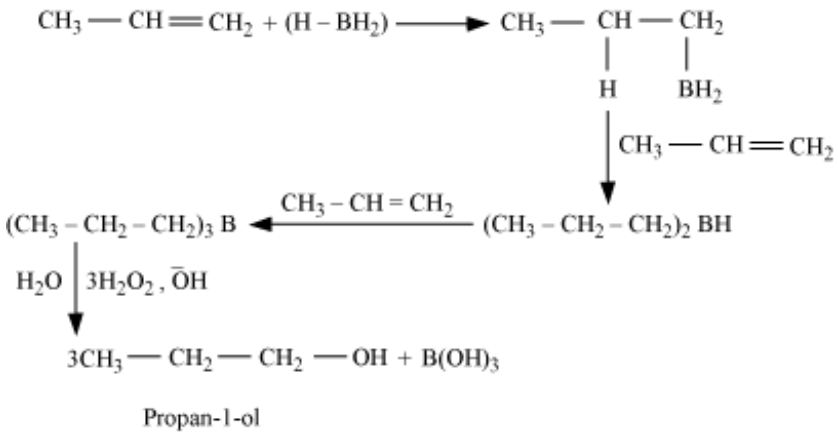
- **Preparation of alcohols –**

1. **From alkenes**
2. Acid catalysed hydration



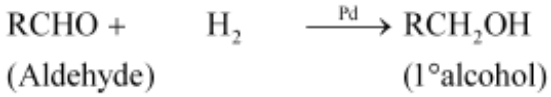
[According to Markovnikov's rule]

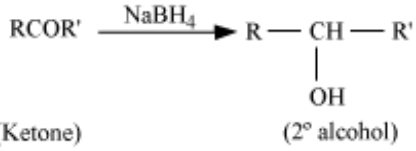
1. Hydroboration – oxidation



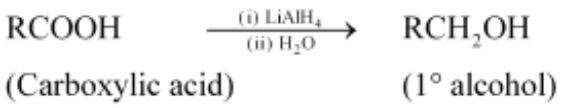
1. From carbonyl compounds
2. By reduction of aldehydes and ketones.

Aldehydes give 1° and ketones give 2°alcohols.

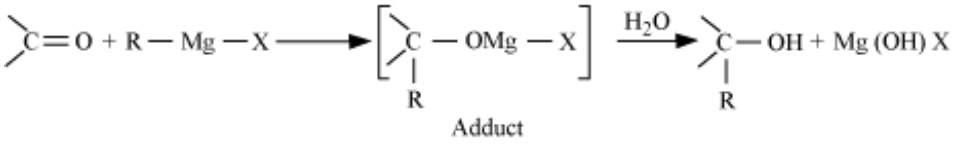




1. By reduction of carboxylic acids and esters



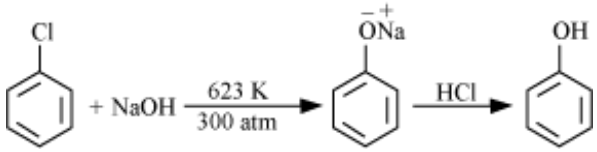
1. From Grignard reagents



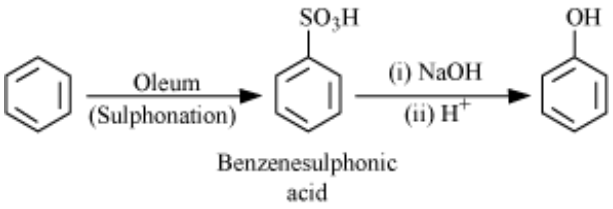
Methanol gives 1°, other aldehydes give 2°, and ketones give 3° alcohols.

- **Preparation of phenols –**

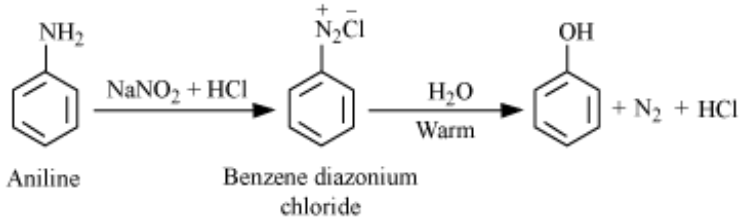
1. **From haloarenes**



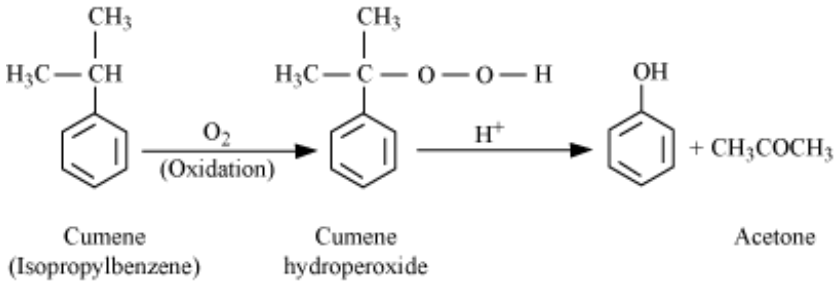
1. From benzenesulphonic acid



1. From diazonium salts



1. From cumene



Boiling points:

1. The boiling points of alcohols and phenols increase with increase in number of carbon atoms as it involves increase in van der Waals forces.
2. The boiling points of alcohols decrease with increase of branching. This is because van der Waals forces decrease with decrease in surface area.

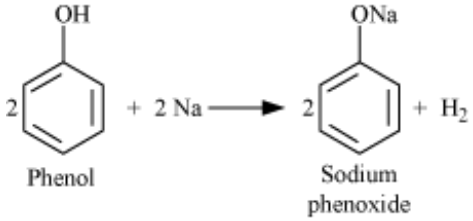
Solubility:

1. Alcohols and phenols form H-bonds, so they are soluble in water.
2. Their solubility decreases with increase in size of alkyl/aryl groups.

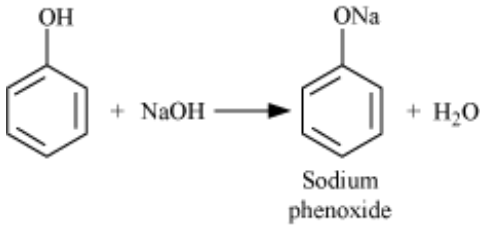
- **Reactions that involve cleavage of O – H bond**

1. **Acidity of alcohols and phenols**
2. Reaction with metals

$$2R-O-H + 2Na \longrightarrow \underset{\text{Sodium alkoxide}}{2R-O-Na} + H_2$$

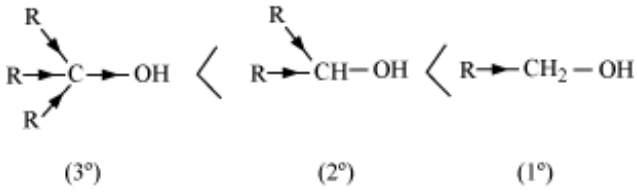


- Phenols react with aq. NaOH to form sodium phenoxides.



Acidity of alcohols

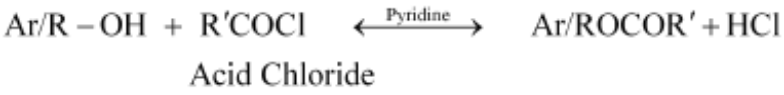
The increasing order of acidity of alcohols is



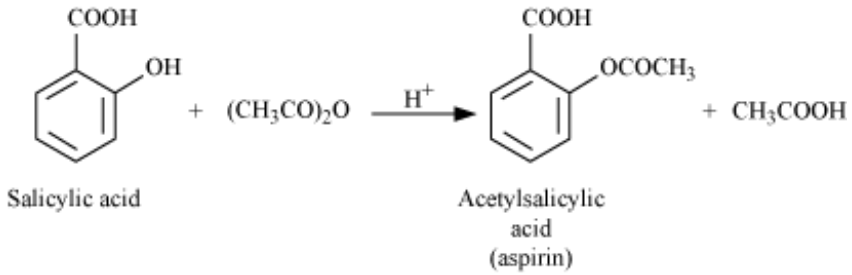
Acidity of phenols

Phenols are more acidic than alcohols and water.
Electron-withdrawing groups increase the acidity of phenols while electron-releasing groups decrease the acidity of phenols.

Esterification



Acetylation of salicylic acid



- **Reactions that involve cleavage of C – O bond in alcohols**

Reaction with hydrogen halide

$$R-OH+HX \xrightarrow{ZnCl_2} R-X+H_2O$$

Lucas test – Used for distinguishing between 1°, 2° and 3° alcohols. (Lucas reagent – Concentrated HCl and anhydrous $ZnCl_2$)

Reaction with phosphorus trihalide

$$3R-OH+PX_3 \longrightarrow 3R-X+H_3PO_3 (X=Cl,Br)$$

Dehydration

Treated with concentrated H_2SO_4 or H_3PO_4 or Anhyd. $ZnCl_2$, or Al_2O_3

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

The order of increasing reactivity towards dehydration is
1° alcohol < 2°alcohol < 3° alcohol

Oxidation (also known as dehydrogenation)

It involves formation of a carbon–oxygen double bond.

Oxidising agent – Acidified $KMnO_4$

$$\text{Alcohol} \xrightarrow{\text{(directly)}} \text{Carboxylic acid}$$

Oxidising agent is Anhyd. CrO_3

1° alcohol → Aldehyde
2°alcohol → Ketone

Pyridinium chlorochromate (PCC)

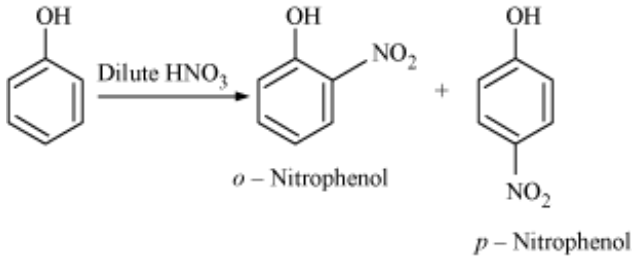
1° alcohol → Aldehyde

Oxidising agent → Heated Cu at 573 K

1° alcohol → Aldehyde
2°alcohol → Ketone

3° alcohols do not undergo oxidation

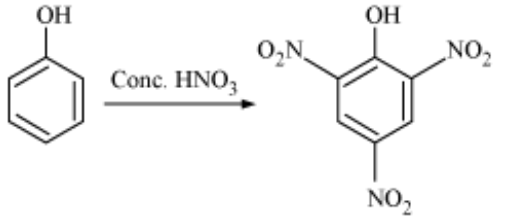
1. Electrophilic aromatic substitution reaction
2. Nitration



o – Nitrophenol

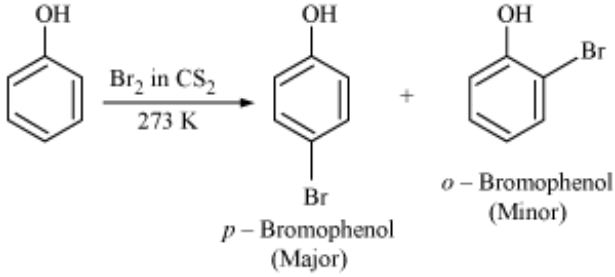
p – Nitrophenol

The *o*-isomer is steam volatile due to intramolecular H-bonding while the *p*-isomer is less volatile due to intermolecular H-bonding. So, they can be separated by steam distillation.



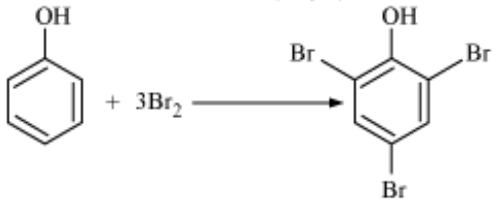
2, 4, 6 – Trinitrophenol
(Picric acid)

1. Halogenation



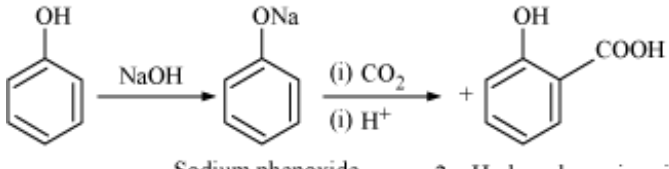
p – Bromophenol
(Major)

o – Bromophenol
(Minor)



2, 4, 6 – Tribromophenol

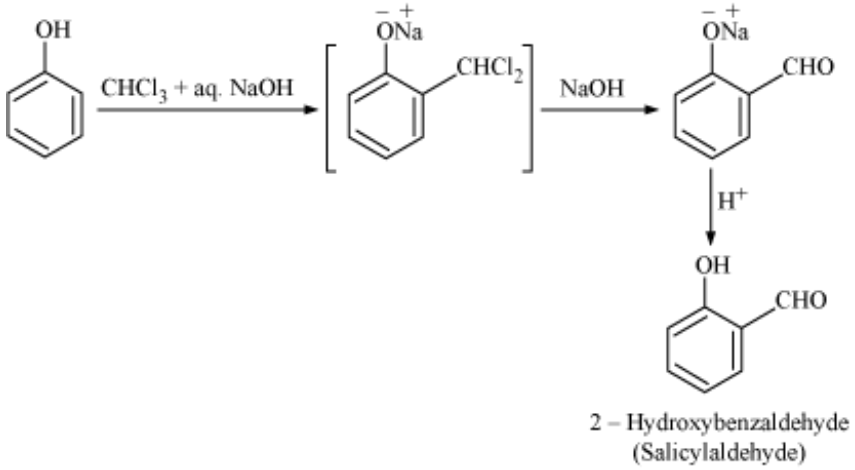
1. Kolbe's reaction



Sodium phenoxide

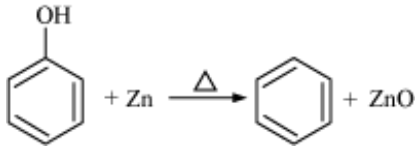
2 – Hydroxybenzoic acid
(Salicylic acid)

1. Reimer–Tiemann reaction

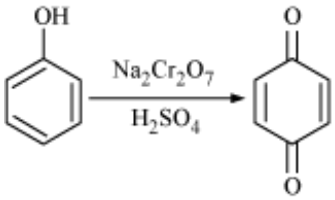


2 – Hydroxybenzaldehyde
(Salicylaldehyde)

1. Reaction of phenol with zinc dust



1. Oxidation



Benzoquinone

Methanol (CH_3OH)

Preparation

- Earlier produced by destructive distillation of wood
- Catalytic hydrogenation of carbon monoxide

Properties

- Colourless liquid
- Boiling point = 337 K
- Highly poisonous – Small quantities cause blindness and large quantities cause even death.

Uses

- As a solvent in paints and varnishes
- In the preparation of formaldehyde (HCHO)

Ethanol (C_2H_5OH)

Preparation

- By fermentation
- By hydration of ethane

Properties

- Colourless liquid
- Boiling point = 351 K

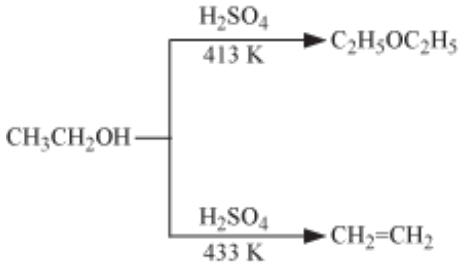
Uses

- As a solvent in manufacture of paint and a number of carbon compounds
- Denaturation of alcohol – Commercial alcohol becomes unfit for drinking by mixing methanol in it

Ethers:

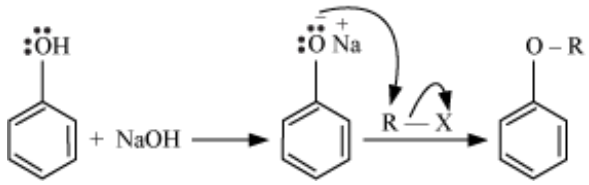
- **Preparation of ethers –**

1. **By dehydration of alcohols**



1. Williamson synthesis

1. But in case of 2° and 3° halides, instead of substitution, elimination takes place, resulting in alkenes.
2. Phenols are converted into ethers.



- **Physical properties of ethers –**

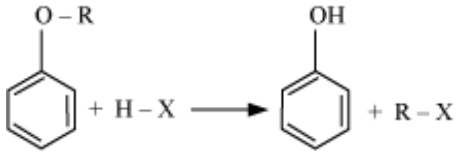
1. **Boiling points:**

   The boiling points of ethers are lower than those of alcohols of comparable molecular masses due to the presence of H-bonding in alcohols.

- **Chemical reactions of ethers:**

1. **Cleavage of C – O bond**
2. Least reactive; under drastic conditions with excess of hydrogen halides, the C – O bond is cleaved

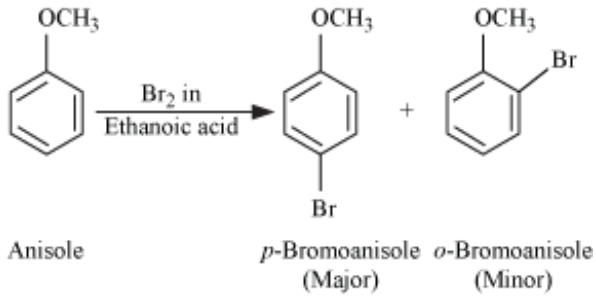
$$R-O-R+HX \longrightarrow RX+R-OH$$
$$R-OH+HX \longrightarrow R-X+H_2O$$



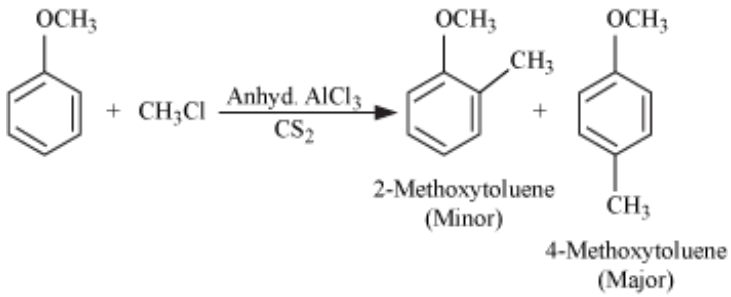
1. The order of increasing reactivity of hydrogen halides is

   HCl < HBr < HI

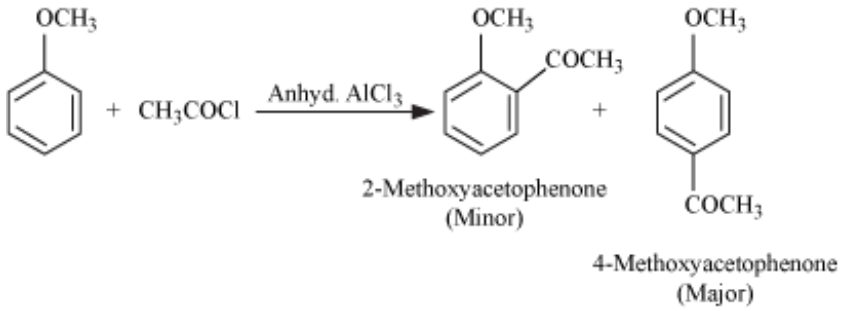
1. Electrophilic substitution
2. Halogenation



1. Friedel Craft's alkylation



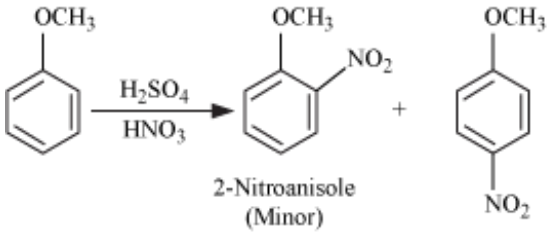
1. Friedel Craft's acylation



2-Methoxyacetophenone
(Minor)

4-Methoxyacetophenone
(Major)

1. Nitration



2-Nitroanisole
(Minor)

4-Nitroanisole
(Major)