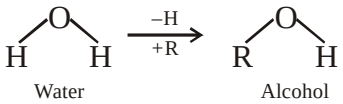


Country's Best Online Test Platform

Visit now https://quizrr.in

ALCOHOL PHENOL ETHER

- Alcohols are derivatives of water molecule replacing one hydrogen atom by an alkyl group

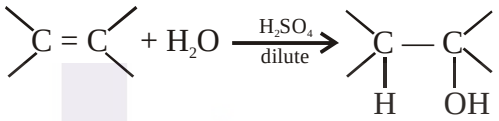


An alcohol is a compound containing one or more hydroxyl group (OH) directly attached to aliphatic carbon atoms.

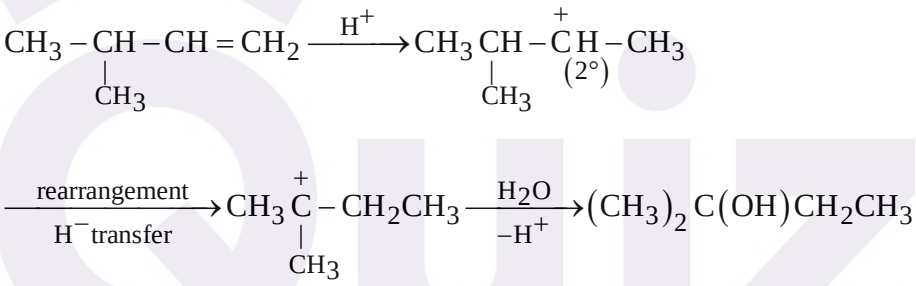
The simplest alcohol is methyl alcohol, (CH_3OH) also called carbinol.

• GENERAL METHODS OF PREPARATION OF ALCOHOLS

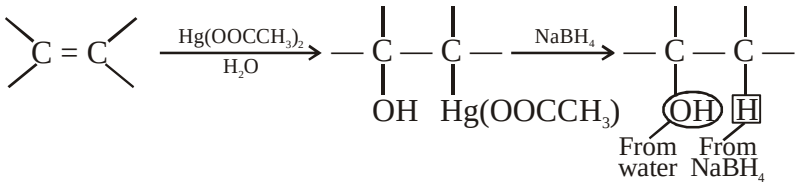
(A) From alkanes by hydration (addition of water)

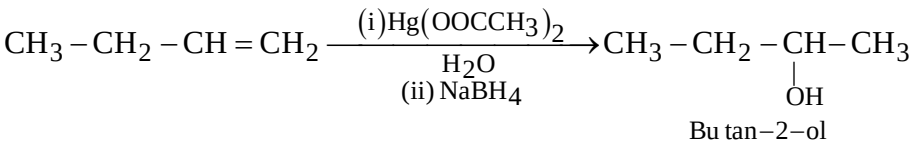
(i) 

Acid catalyzed hydration follows Markonikov's rule but rearrangement may also take place. e.g.,

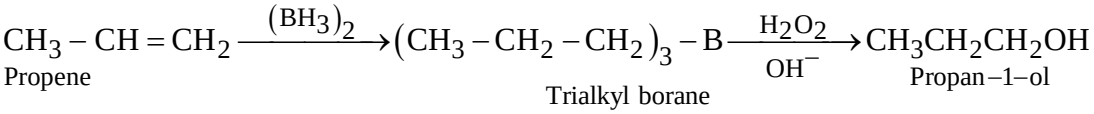


(ii) Hydration using mercuric acetate/$NaBH_4$ (oxymercuration-demercuration) follows Markovnikov's rule but no rearrangement.





(iii) Hydroboration oxidation using B_2H_6/H_2O_2 & OH^-, addition of water takes place according to anti Markonikov's rule



(B) Reduction method

(i) $\left.\begin{matrix} R-CHO \\ R-COCl \\ R-COOH \end{matrix}\right] \rightarrow$ All on reduction with $LiAlH_4/H_2O$ or H_2/Pd gives primary alcohols

While ketone RCOR' yields secondary alcohols.

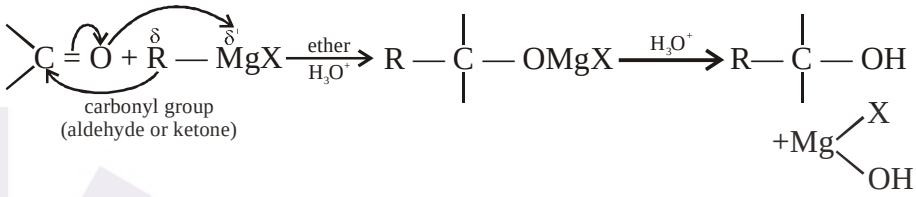
$NaBH_4$, reduces only aldehyde, ketones and acid halide.

$$\underset{\text{Ester}}{R-CO_2R'} \xrightarrow{Na/C_2H_5OH} RCH_2OH + R'OH$$

(C) From Grignard reagent (RMgX)

R—MgX is an organometallic compound. As carbon is more electronegative than metal, R group is present as negative group or Nu^- and attack at the e** deficient carbon.

The reaction is an example of nucleophilic addition reaction.



$$\underset{\text{Methanol}}{HCHO} + R-MgX \xrightarrow[(ii)H_3O^+]{(i)\text{ether}} \underset{1^\circ\text{ alcohol}}{R-CH_2OH}$$

$$\underset{\text{Aldehyde}}{R'-CHO} + R-MgX \xrightarrow[(ii)H_3O^+]{(i)\text{ether}} \underset{2^\circ\text{ alcohol}}{R'-\underset{\displaystyle OH}{\underset{|}{CH}}-R}$$

$$\underset{\text{ketone}}{R'-COR} + R''-MgX \xrightarrow[(ii)H_3O^+]{(i)\text{ether}} \underset{3^\circ\text{ alcohol}}{R'-\underset{\displaystyle OH}{\underset{|}{\overset{\displaystyle R}{\overset{|}{C}}}}-R''}$$

$$\underset{\text{Ester}}{H/R-\overset{\displaystyle O}{\overset{\|}{C}}-OR'} \xrightarrow{2R''MgX} H/R-\underset{\displaystyle R''}{\underset{|}{\overset{\displaystyle OH}{\overset{|}{C}}}}-R''$$

(Either 2° or 3° alcohol)

(D) Methanol is commercially prepared from CO + H_2 in the presence of Cu — ZnO — Cr_2O_3 as a catalyst at high temperature and pressure.

$CO + 2H_2 \rightarrow CH_3OH$ CH_3OH is called wood alcohol.

Ethanol is commercially manufactured by using fermentation process. Fermentation of sucrose gives ethanol.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Inverse}} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

$$\underset{\text{glucose}}{C_6H_{12}O_6} \xrightarrow{\text{zymase}} \underset{\text{ethanol}}{2C_2H_5OH} + 2CO_2$$

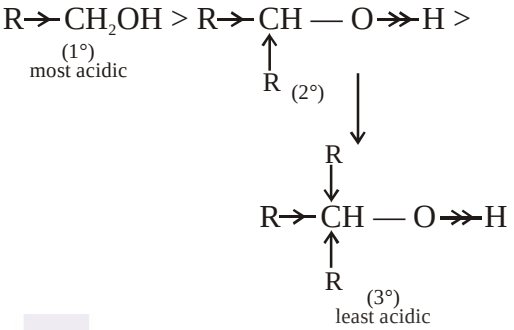
(i) Boiling point : Alcohols have a higher boiling point than haloalkanes of same number of C-atom. This is due to the fact that alcohols are associated via intermolecular hydrogen bonding. B.P. of alcohols increases

down the homologous series. For the same alcohol, as the branching increases, b.p. decreases due to decrease in surface area. Vander waal forces holding the molecules together decreases, b.p. decreases.

(ii) Solubility : Lower alcohols are completely miscible in water due to their ability to form hydrogen bonds with water.

The solubility of alcohols decreases down the homologous series, for the same alcohol, as the branching increases, solubility increases, t-butanol is more soluble in water than n-butanol.

(iii) Alcohols are weaker acids than water : O—H bond in alcohol is less polar as compared to O—H bond in water. The acidic strength of alcohols decreases as the number of e^- donating R groups increases at α-carbon.



The increasing O—H bond strength order is 1°RO—H < 2°RO—H < 3°RO—H and increasing C—O bond strength order is 3°R—OH < 2°R—OH < 1°R—OH

- Reactions of alcohols involving cleavage of O—H bond

(i) $RO-H \xrightarrow{Na} RO^-Na^+ + \frac{1}{2}H_2$

(ii) $\underset{\text{only 1°alcohol}}{RO-H} + R'-MgBr \rightarrow \underset{\text{alkane}}{R'-H} + RO-MgBr$

- Reaction involving cleavage of C—O bond toward these type of reactions, the reactivity order is

1°R—OH < 2°R—OH < 3°R—OH

All these reactions require the presence of Lewis's acid because OH is not a good leaving group as it is a very strong base. Before removing OH, we have to decrease its basicity by developing a positive charge on oxygen and decreasing C—O bond strength.

(i) $R-OH \xrightarrow{PCl_5} R-Cl + POCl_3 + \underset{\text{white fumes}}{HCl}$

(ii) $3R-OH \xrightarrow[X=Cl, Br]{PX_3} 3R-X + H_3PO_3$

(iii) $R-OH \xrightarrow{P+I_2} R-I + H_3PO_3$

(iv) $R-OH \xrightarrow{SOCl_2} R-Cl + SO_2 + HCl$

- Reaction with Lucas reagent

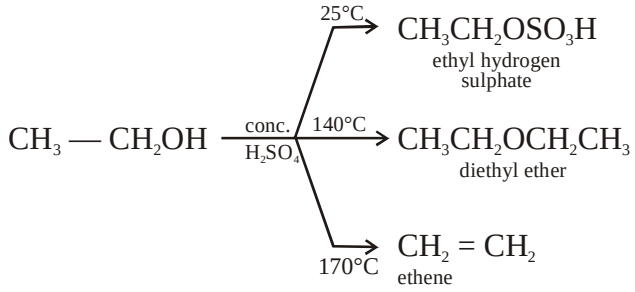
Lucas reagent is conc. HCl/anhyd. $ZnCl_2$. The reagent is used to distinguish 1°, 2° and 3° alcohol.

$\Rightarrow$ 3° ROH gives cloudiness or turbidity with Lucas reagent immediately.

$\Rightarrow$ 2° R—OH gives cloudiness or turbidity after 5-10 minute.

$\Rightarrow$ 1° R—OH does not give cloudiness or turbidity at room temperature.

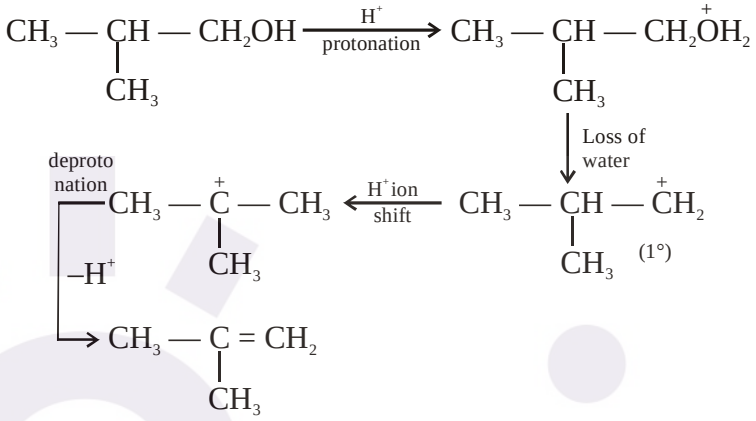
- Dehydration of alcohol (loss of H_2O) gives different products at different temperatures with conc. H_2SO_4. For example-



The ease of dehydration of three alcohols increases in the order

$$1° \text{ ROH} < 2° \text{ ROH} < 3° \text{ ROH}$$

- Dehydration of alcohol to alkene proceeds via the formation of carbonium ion (which can undergo rearrangement) e.g.



- Dehydrogenation (loss of H_2) with copper at 573K is used to distinguish 1°, 2° and 3° alcohol.

1° alcohol gives an aldehyde with same number of C-atoms

$$R - \underset{(1°)}{CH_2OH} \xrightarrow[573\ K]{Cu} \underset{\text{an aldehyde}}{R - CHO} + H_2$$

2° alcohol gives ketones

$$R - \underset{R}{CHOH} \xrightarrow[573\ K]{Cu} R - \underset{R}{\underset{\text{(Ketone)}}{CO}} + H_2$$

3° alcohol undergo dehydration to form alkene (as there is no carbinol hydrogen)

$$CH_3 - \underset{CH_3}{\overset{CH_3}{C}} - OH \xrightarrow[573\ K]{Cu} \underset{\text{2–methyl propene–2–ol}}{CH_3 - \underset{CH_3}{C} = CH_2} + \underset{\text{2–methyl propene}}{H_2O}$$

- Oxidation of alcohols involves the cleavage of O—H and C—H, final product of oxidation depends upon the structure of the alcohol and the oxidizing agent used.

The ease of oxidation follows a order

$$3°R — OH < 2°R—OH < 1°R — OH$$

(3° alcohols do not have any α-hydrogen)

$$R-CH_2OH \xrightarrow[K_2Cr_2O_7/H_2SO_4]{[O]} \underset{\text{same no. of C-atoms}}{R-CHO} \xrightarrow[K_2Cr_2O_7/H_2SO_4]{[O]} \underset{\text{acid with same no. of carbon}}{R-CHO}$$

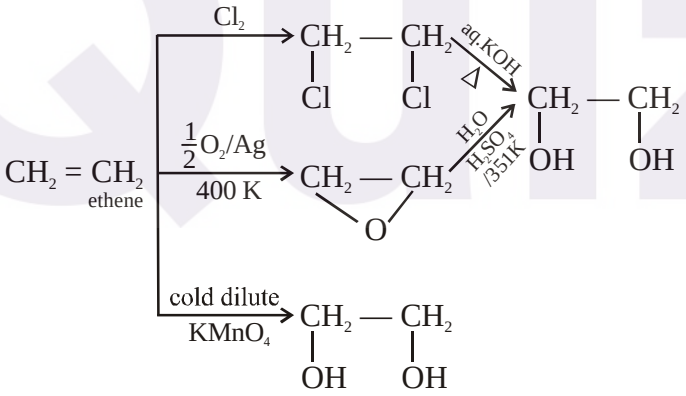
$$\underset{\substack{|\\ R'\\ (2^\circ)}}{R-CHOH} \xrightarrow[K_2Cr_2O_7/H_2SO_4]{[O]} \underset{\text{ketone with same no. C-atoms}}{R-CO-R'} \xrightarrow[K_2Cr_2O_7/H_2SO_4]{[O]} \underset{\text{each acid contains lesser no. of C-atoms}}{RCOOH + R'COOH}$$

$$\underset{\substack{|\\ R\\ (3^\circ)}}{\overset{\overset{R}{|}}{R-C-OH}} \xrightarrow{[O]} \text{No reaction}$$

- Properties and uses of methanol
    1. It is a colourless liquid and highly poisonous.
    2. It is completely soluble in water.
    3. It is used as solvent for paints, varnishes, and for making fomaldehyde.
- Ehtanol is a colourless liquid, higher b.p. than methanol. It is used as a solvent in paints industry. Denaturation of ethanol (or alcohol) means making it unfit for drinking purposes by adding $CuSO_4$ and pyridine.
- Ethylene glycol is an example of dihydric alcohol. Its IUPAC name is ehtane-1,2-diol. Its structureal formula is

$$\underset{|}{\overset{|}{CH_2-CH_2}}\\ OH \quad OH$$

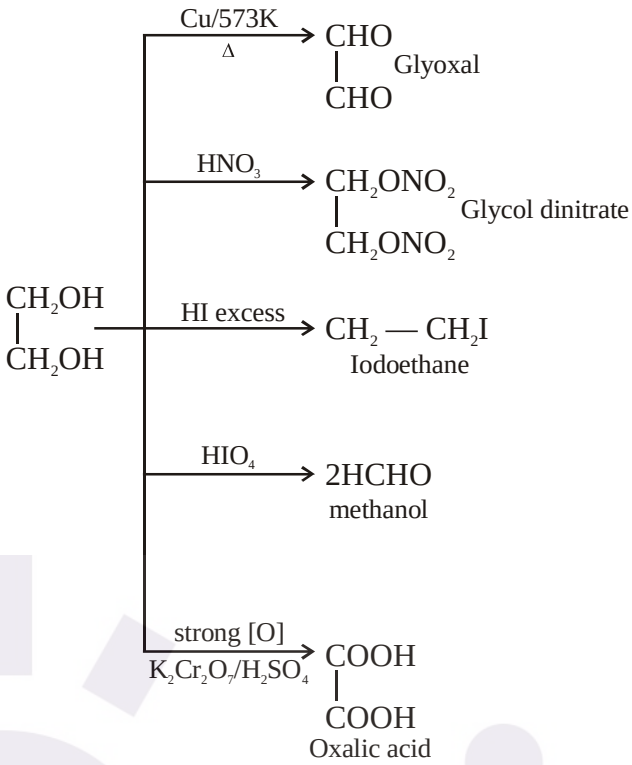
- Preparation of ethylene glycol



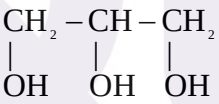
- Properties of ethylene glycol
    (i) It is colourless syrupy liquid
    (ii) It has a high b.p. than ehtanol due to more network of intermolecular hydrogen bonding.

  Uses of ethylene glycol
    (i) It is used as antifreeze in car radiator.
    (ii) It is used in the preparation of polyester.
    (iii) It is used as solvent.
- Reaction of Glycol

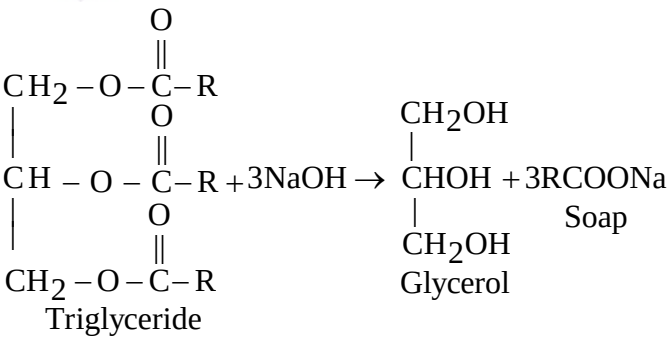
  In glycol, both the OH groups are primary alcoholic groups.



- Glycerol or glycerine is an example of trihydric alcohol. Its IUPAC name is propane-1,2,3-triol. Its structural formula is



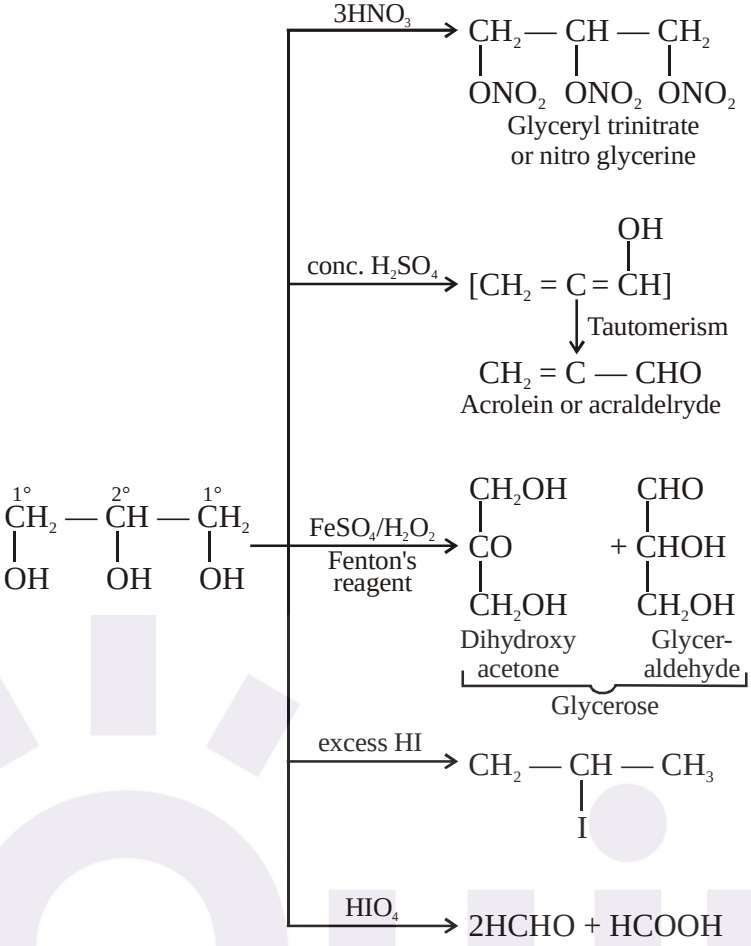
- Glycerol is prepared commercially by the alkaline hydrolysis of fat or oil (which are called triglycerides).



The alkaline hydrolysis of an ester is called saponification.

- Properties of Glycerol
  - (i) It is highly viscous liquid with high b.p. This is due to extensive network of inter molecular hydrogen bonding.
  - (ii) It is colourless, hygroscopic liquid.
  - (iii) Glycerol is used in the preparation of polyesters, dyanamite and for medicines, cosmetics and the textile processing.

- Reactions of glycerol

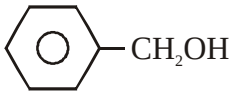


PHENOL

- Phenols are compounds with an OH group attached directly to a carbon of an aromatic ring. The compound phenol is C_6H_5OH.

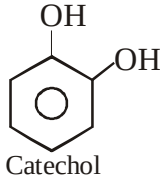


If OH group is present on the side chain, then it is called aliphatic alcohol. For example

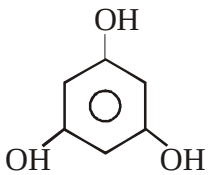


- Phenols may be

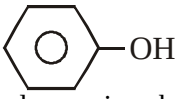
(i) monohydric, 

(ii) dihydric, 

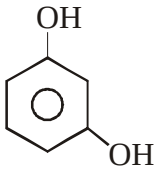
Catechol

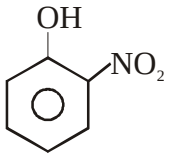
(iii) trihydric, 

Phloroglucinol

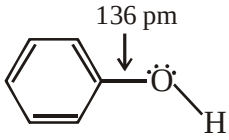
- Phenol name for  is also accepted in IUPAC system. IUPAC and common names of some of the phenolic compounds are given below :


p-cresol
(4-methylphenol)


Resorcinol
(Benzene-1,3-diol)

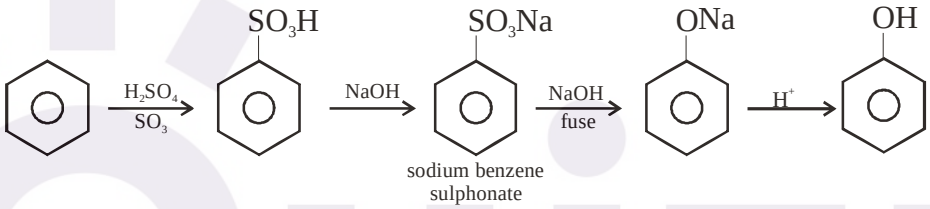

o-nitrophenol
(2-nitrophenol)

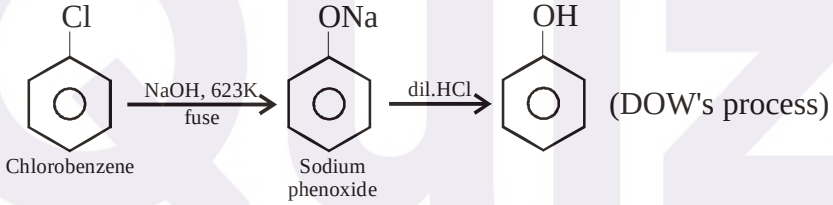
- The structure of phenol is

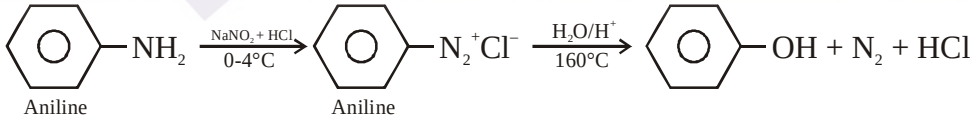


The C—O bond is slightly shorter than the C—O bond present in methanol. This is due to partial double bond character as lone pair of electrons on oxygen participates into resonance with the benzene ring.

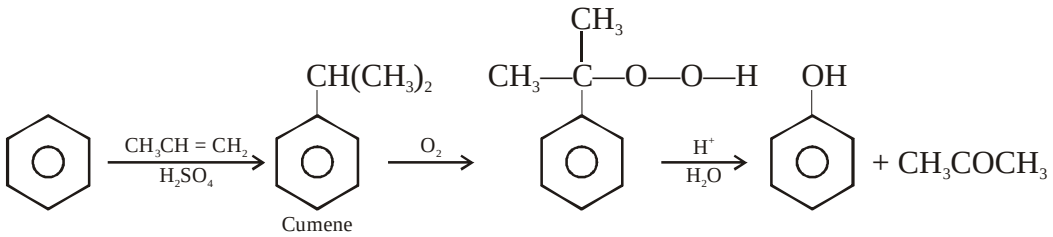
- Preparation of phenol

(i) 
sodium benzene sulphonate

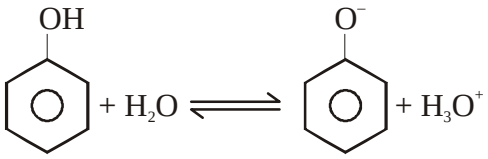
(ii) 
Chlorobenzene
Sodium phenoxide
(DOW's process)

(iii) 
Aniline
Aniline

- Phenol is prepared commercially by cumene-phenol process.

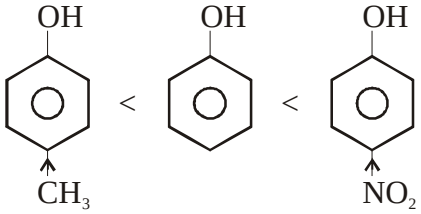

Cumene

- Phenols have a higher boiling point than the corresponding hydrocarbon or aryl halides. This is due to the presence of intermolecular hydrogen bonding. Due to their ability to forms H-bonds with water, phenols are moderately soluble in H_2O.
- The phenols are acidic in nature and stronger acids than alcohols.

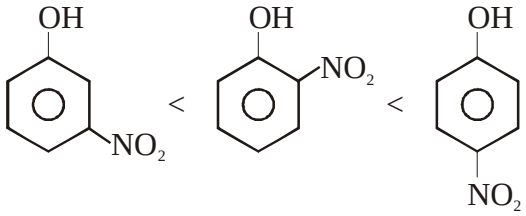


The pair of oxygen in phenol is delocalized with the benzene ring. As a result, the strength of O—H bond decreases and H as H^+ ion can easily be removed.

- The presence of electrons withdrawing group (EWG) like NO_2 group, increases the acidic strength and electron donating groups (EDG) like R group decreases the acidic strength. Therefore, the acidic strength order is



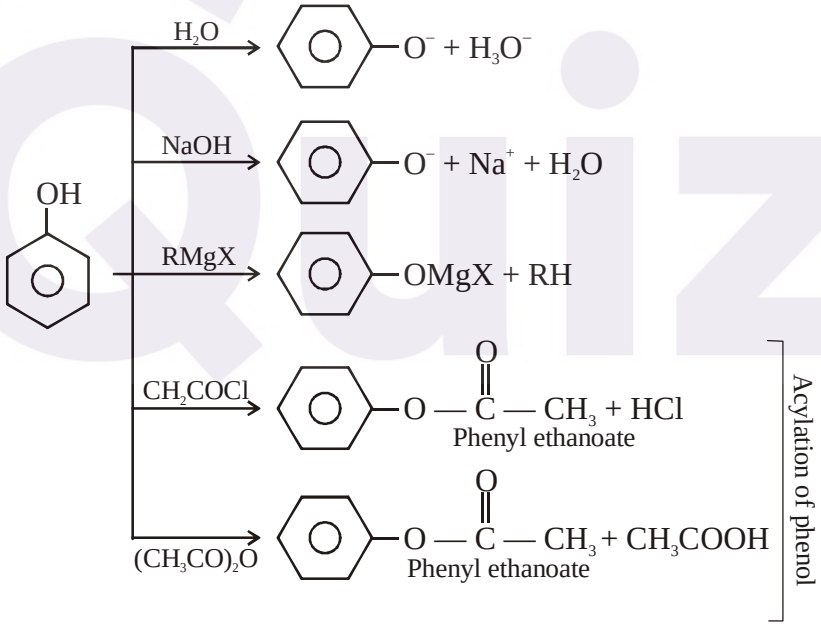
The increasing acidic strength order of the three nitrophenols is



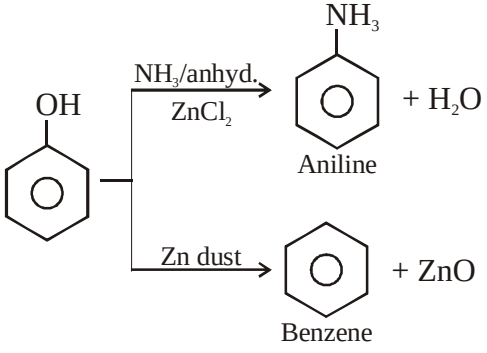
In m-nitro phenol, only –I effect no –R of NO_2 present. In o-nitro phenol. –I, –R effect of NO_2 both present but weaker than para as there exists an intra molecular hydrogen bonding.

p-nitrophenol is the strongest acid due to –R, –I effect of NO_2.

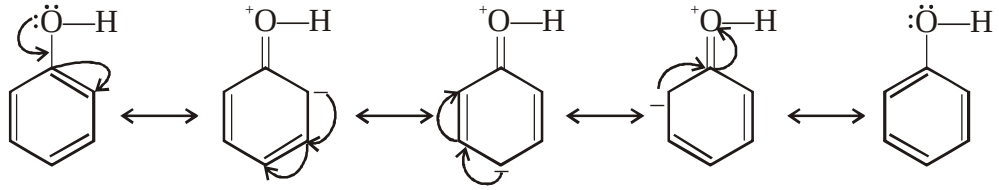
- Reaction of phenol involving the cleavage of O—H bond.



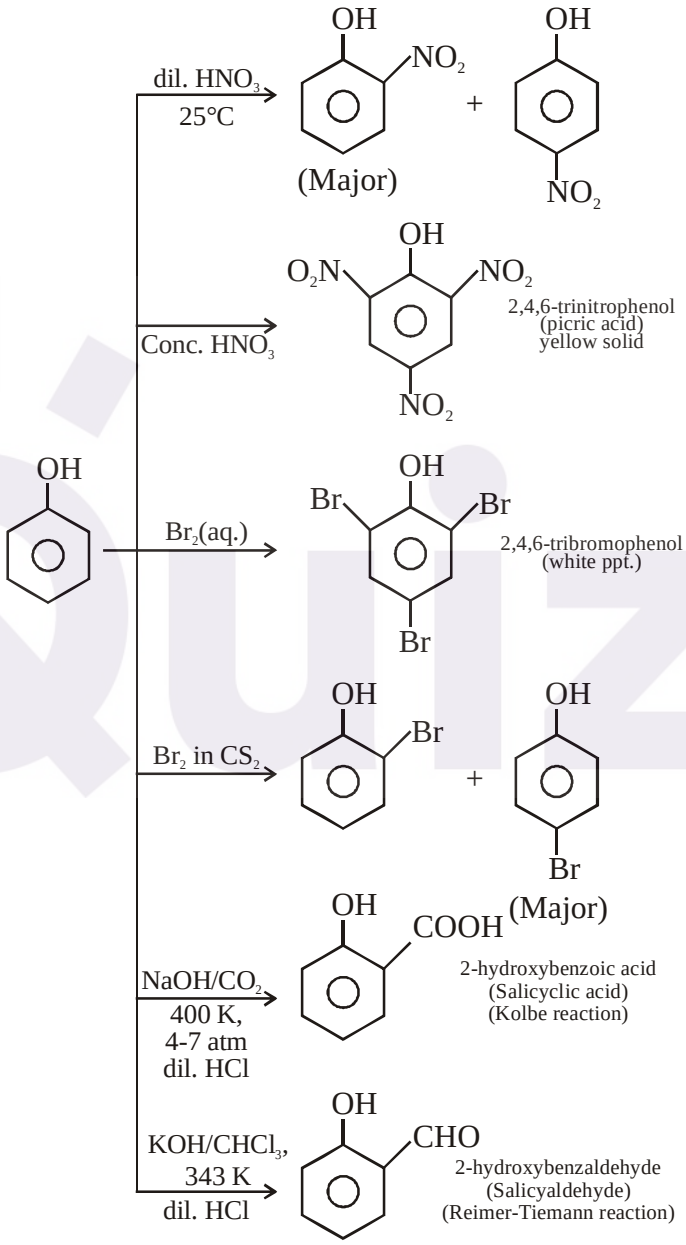
- Reactions of phenol involving cleavage of C—O bond



- The presence of OH group on benzene increases the electron density on the benzene ring making it more susceptible to attract by an electrophile. The reactions involving benzene ring are electrophilic substitution reactions. The presence of OH group makes the ortho and para-carbon of benzene more electron rich than meta position. The OH group is called o-, p-directing group.

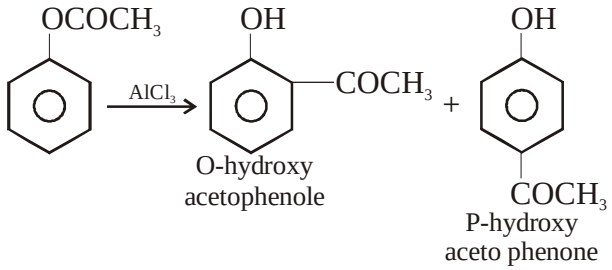


- Electrophilic substitution reactions of phenol



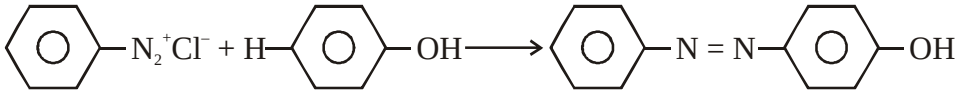
- Esters of phenol gives phenolic ketones on rearrangement in the presence of anhydrous $AlCl_3$. The reaction is called Fires rearrangement.

  Phenyl acetate yield phenolic ketones on treatment with anhydrous $AlCl_3$.



- Condensation reaction of phenol

  With benzene diazonium chloride (Diazo coupling)

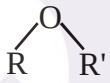


p-hydroxyazobenzene
(azodye)

- Uses of Phenol
  (i) It is used as an antiseptic, disinfectant.
  (ii) It is used in the preparation of dyes, drugs.
  (iii) It is used in the preparation of bakelite, Novalac.

ETHERS

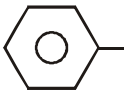
- Ethers are derivatives of water, H_2O, replacing both hydrogen by alkyl or aryl groups.



If R = R', then the ether is called simple ether. The common name is dialkyl ether. $CH_3CH_2OCH_2CH_3$ is diethyl ether.

If $R \neq R'$, then ether is called mixed ether. Then arrange the alkyl groups alphabetically and write a suffix ether.

$CH_3-O-\underset{\underset{CH_3}{|}}{CH}-CH_3$ is isopropyl methyl ether. In IUPAC system, ethers are called alkoxy alkane.

CH_3—OCH_2CH_3 is methoxy ethane and  is methoxy benzene. Its common name is methyl phenyl ether (anisole).

Phenetole is a common name of ethoxy benzene.

- Preparation of ethers
  (i) Dehydration of 1° alcohols

$$2CH_3CH_2OH \xrightarrow[413]{H_2SO_4} CH_3CH_2OCH_2CH_3$$

2° and 3° alcohols on dehydration gives alkenes and not ethers.

(ii) From alkyl halides.

$$2RX \xrightarrow[dry]{Ag_2O} R_2O + 2AgX$$

(iii) From alkyl halides using Williamson's synthesis (SN_2 reaction).

$$RX + NaOR' \longrightarrow R - O - R' + NaX$$

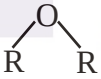
(R = CH_3,1°) sodium alkoxide

(R' = 1°, 2°, 3° or Ar)

The important method to prepare any type of ether. With 3° RX, alkenes are formed as alkoxide ion is also a strong base, alkyl halide then undergoes elimination reaction.

$$CH_3Br + CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-O^-Na^+ \rightarrow CH_3-O-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_3 + NaBr$$

$$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-Br + Na^+OCH_3 \longrightarrow CH_3-\underset{\displaystyle CH_3}{\overset{}{\underset{|}{C}}}=CH_2 + NaBr + CH_3OH$$

- Ethers and monohydric alcohols are functional isomers but ethers have a lower b.p. than alcohols due to their inability to associate via intermolecular hydrogen bonding. Ethers are volatile.
- Ethers are polar in nature and have a net dipole moment even if the R groups are similar. This is due to their bent structure. 

  The oxygen atom is sp^3 hybridized and C—O—C bond angle is more than 109° due to the repulsions between the bulky large size R groups.
- Lower ethers (containing upto three carbon atoms) are completely miscible in water. The solubility of ethers decreases as the number of carbon atoms increases.
- Due to the presence of electron donating R groups and lone pair on oxygen atoms, ethers are Bronsted bases as well as Lewis bases.

$$R_2O + HX \rightarrow R_2OH^+X^-$$

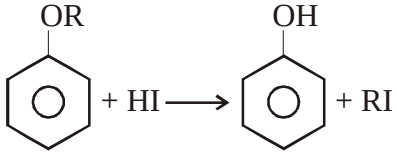
(X = Cl,Br) dialkyl oxonium halide

$$\underset{\text{Lewis base}}{R_2O} + \underset{\text{Lewis acid}}{BF_3} \rightarrow [R_2O \rightarrow BF_3]$$

- Reactions of ethers involving C—O bond cleavage R—O—R + HI $\rightarrow$ ROH + RI simple ether

  For a given ether, the reactivity of hydrogen halides follows a order:

  HCl < HBr < HI (Strongest acid)
- In case of aromatic ether, reaction with HI results in the cleagvage of R—O bond because Ar—O bond has a double bond character and is strong. Also breaking R—O bond results in the formation of phenoxide ion which is resonance stabilized.

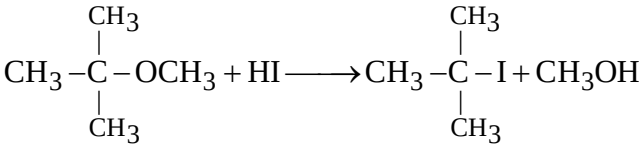


- In case of mixed ether with the different R groups, the product depends on the nature of R groups.

  When 1° or 2° R groups present, the lower R groups from alkyl iodide with HI (This is an S_N2 reaction)

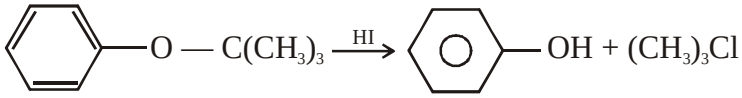
$$CH_3OCH_2CH_3 + HI \rightarrow CH_3I + CH_3CH_2OH$$

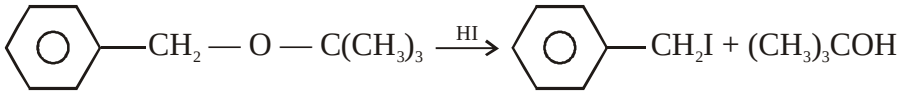
When one of the R group is 3° R group, then tertiary alkyl iodide is formed with HI.



Because 3° carbonium ion is more stable.

Some more examples :

(i) 

(ii) 

- The most important simple ether is ethoxy ethane. It is used as a solvent for oils, gums, resins, etc.

  It is also used as an inhalation anaesthetic. Ethrane and isoflurane are also used as anaesthetic. Phenyl ether used as a heat transfer medium because of its high boiling point.

- Some more reactions of ether

  (i) $R_2O + PCl_5 \rightarrow 2RCl + POCl_3$

  (ii) $R_2O + H_2O \xrightarrow{H^+} 2ROH$

  (iii) $CH_3OCH_3 + O_2 \longrightarrow CH_3-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-O-O-H$

  dimethyl ether peroxide
  (present as an impurity in ethers)

- RO-group on benzene ring is activating and o-, p-directing. Electrophilic substitution reactions of aromatic ether are

