

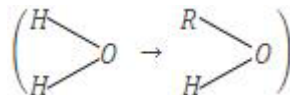
ORGANIC CHEMISTRY

TOPIC: 2 HYDROXY COMPOUNDS, ALCOHOLS AND PHENOLS

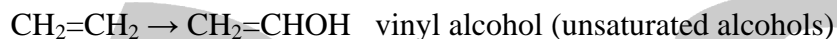
VERY SHORT ANSWER QUESTIONS

1. What are alcohols?

Alcohols are regarded as mono alkyl derivative of water



or hydroxyl derivative of hydrocarbons e.g.



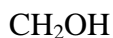
2. What are monohydric alcohols?

Ans: Monohydric alcohols: Containing two OH group e.g. CH_3OH methyl alcohol

3. What are dihydric alcohols?

Ans: Dihydric alcohols : Containing two OH group

e.g.



|



Glycol

4. What are polyhydric alcohols?

Ans: Polyhydric alcohols: Containing more than two OH group



Glycerol

5. Why alcohols with two hydroxyl groups present on the same carbon do not exist?

Ans: If two or more hydroxyl groups attached to same carbon atom, the compound is usually unstable and lose a molecule of water to give a stable compound and therefore two or more hydroxyl groups must be present on different carbon atoms.

6. What is power alcohol?

Ans: Power alcohol:

Rectified spirit + C_6H_6 + Petrol, for generation of power.

7. What is methylated spirit?

Methylated spirit:

(i) Methanol + Pyridine + mineral naphtha + Rectified spirit.

(ii) These are added to make sure that it will not be used for beverages. This process is known as denaturation & alcohol is known as denatured spirit.

Type:

(a) **Mineralized methylated spirit:** 90% Rectified spirit + 10% methanol or pyridine or naphtha

(b) **Industrial methylated spirit:** 95% Rectified spirit, 5% methanol.

8. What is proof spirit?

Proof spirit:

- (i) The % of alcohol is expressed in terms of proof spirit for tax levied on it.
- (ii) Proof spirit is ethanol (57.1%) + water
- (iii) The weakest possible alcohol % which allows gun powder to catch fire is known as proof spirit.
- (iv) 10° under proof means 100 volume of sample containing as 90 volume of proof spirit.
- (v) 10° over proof means 100 volume of sample containing as 110 volume of proof spirit.
- (vi) The determination of strength of alcohol is known as alcoholometry.
- (vii) A sample is called over under proof, as it is stronger or weaker than proof spirit.

SHORT ANSWER QUESTIONS

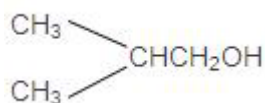
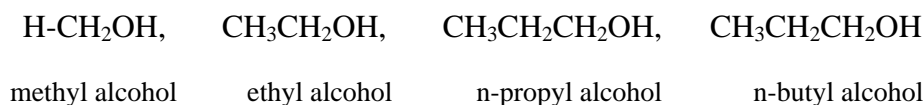
1. How monohydric alcohols are classified?

Ans; Monohydric alcohols:

General formula $C_nH_{2n+1}OH$ or $C_nH_{2n+2}O$; usually represented by $R-OH$ where R is alkyl group.

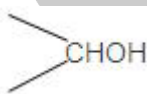
Monohydric alcohols are further classified as

(a) **Primary alcohols:** $-OH$ group attached on 1° carbon atom; group : $-CH_2OH$



isobutyl alcohol

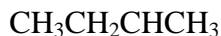
(b) **Secondary alcohols:** $-OH$ group attached on 2° carbon atom; group:



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OH

isopropyl alcohol

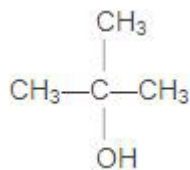


|

OH

sec. butyl alcohol

(c) **Tertiary alcohols:** $-OH$ groups attached on 3° carbon atom; group: $\begin{array}{c} \diagup \\ \diagdown \\ \text{C} \\ \diagup \\ \text{COH} \end{array}$



is tertiary butyl alcohol

2. Write the nomenclature of alcohols.

| Nomenclature : | Common name | Carbinol name | IUPAC name |
|---|-------------------|---------------------|---------------------|
| CH ₃ OH | methyl alcohol | carbinol | methanol |
| CH ₃ CH ₂ OH | ethyl alcohol | methyl carbinol | ethanol |
| CH ₃ CH ₂ CH ₂ OH | n-propyl alcohol | ethyl carbinol | propanol-1 |
| CH ₃ CHOHCH ₃ | isopropyl alcohol | dimethyl carbinol | propanol-2 |
| CH ₃ CH ₂ CH ₂ CH ₂ OH | n-butyl alcohol | propyl carbinol | butanol-1 |
| $\begin{array}{l} \text{CH}_3 \\ \diagdown \\ \text{CH} \\ \diagup \\ \text{CH}_3 \end{array} \text{CH}_2\text{OH}$ | isobutyl alcohol | isopropyl carbinol | 2-methylpropanol-1 |
| CH ₃ CH ₂ CHOHCH ₃ | sec.butyl alcohol | ethylmethylcarbinol | butan-2-ol |
| $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{COH} \\ \\ \text{CH}_3 \end{array}$ | t-butyl alcohol | trimethyl carbinol | 2-methylpropan-2-ol |

3. Explain the isomerism in alcohols.

Ans: Isomerism: Molecular formula C_nH_{2n+2}O of alcohols show following types of isomerism.

C₃H₈O : CH₃CH₂CH₂OH and CH₃CHOHCH₃ are position isomers

Alcohols

Ethers

C₄H₁₀O : (a) CH₃CH₂CH₂CH₂OH (e) CH₃CH₂OCH₂CH₃

(b) CH₃CH₂CHOHCH₃ (f) CH₃OCH₂CH₂CH₃

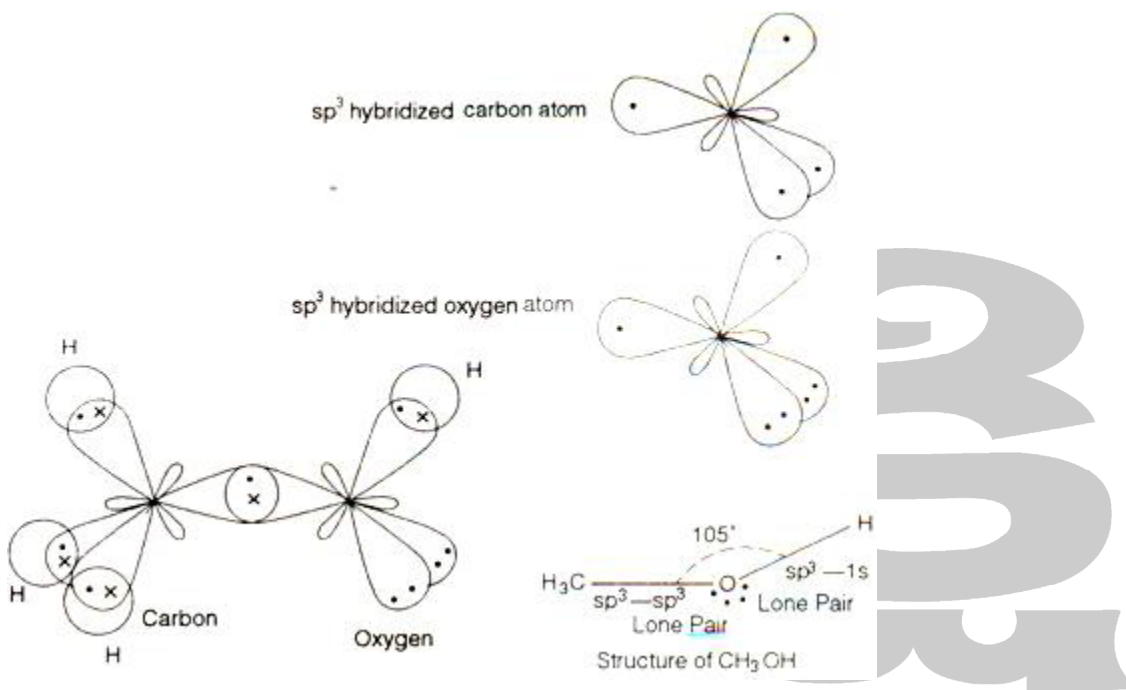
(c)
$$\begin{array}{l} \text{CH}_3 \\ \diagdown \\ \text{CH} \\ \diagup \\ \text{CH}_3 \end{array} \text{CH}_2\text{OH}$$
 (g)
$$\begin{array}{l} \text{CH}_3 \\ \diagdown \\ \text{CH}_3\text{OCH} \\ \diagup \\ \text{CH}_3 \end{array}$$

(d)
$$\begin{array}{l} \text{CH}_3 \\ | \\ \text{CH}_3\text{COH} \\ | \\ \text{CH}_3 \end{array}$$

In all 7 isomers of C₄H₁₀O are noticed among which are **chain isomers** (a & c), **position isomers** (a & b), **functional isomers** (an alcohol & an ether) as well as **metamers** (e, f, g). Also formula (b) shows **optical isomers** for butan-2-ol as it has one asymmetric carbon atom C*.

4. Explain the structure and chemical behaviour of alcohols.

Ans: Structure: In alcohols carbon as well as oxygen both show sp^3 hybridization. In carbon all the four sp^3 hybridized orbitals have one electron in each orbital whereas in oxygen two of the four sp^3 hybridized orbitals have one electron & rest two orbitals have one electron pair in each. These two completely filled orbitals in oxygen atom do not take part in bonding and give rise to contraction in bond angles due to lone pair effect and therefore the bond angle C-O-H is 105° which is lesser than the normal tetrahedral structure.



LONG ANSWER QUESTIONS

1. Explain the general methods of preparation of alcohols.

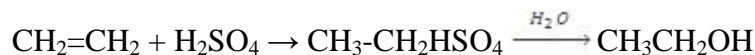
Ans: General methods of preparation of Alcohols

(i) **By the hydrolysis of alkyl halides:** A nucleophilic substitution.

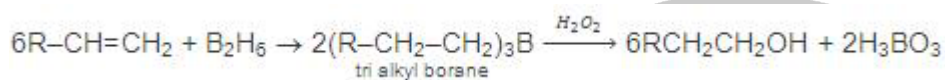


The method is not satisfactory as olefins are also formed as by-products. However better yields is obtained by using moist Ag₂O or aqueous K₂CO₃. Tertiary butyl halides mainly give alkene due to dehydrohalogenation.

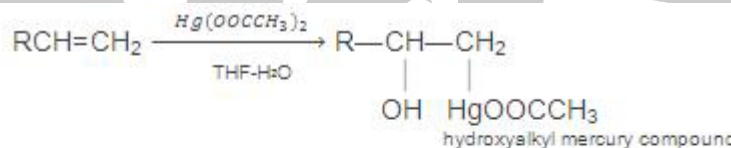
(ii) (a) **By the hydration of alkenes :** An electrophilic addition of H₂O.



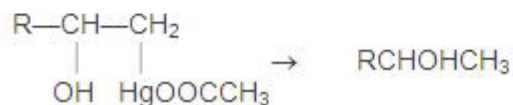
Except ethyl alcohol no other primary alcohol can be obtained by this method, however hydroboration of terminal alkenes give primary alcohols.



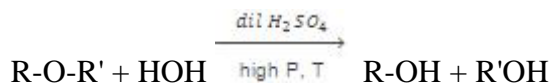
(b) **By oxymercuration and demercuration of alkenes :** Alkenes react with mercuric acetate in presence of H₂O and tetra hydrofuran to give alkyl mercury compounds.



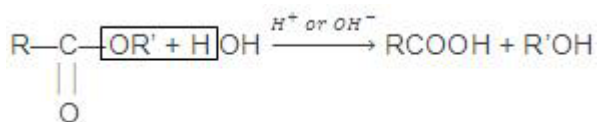
These mercury compounds on reducing with NaBH₄ give alcohols.



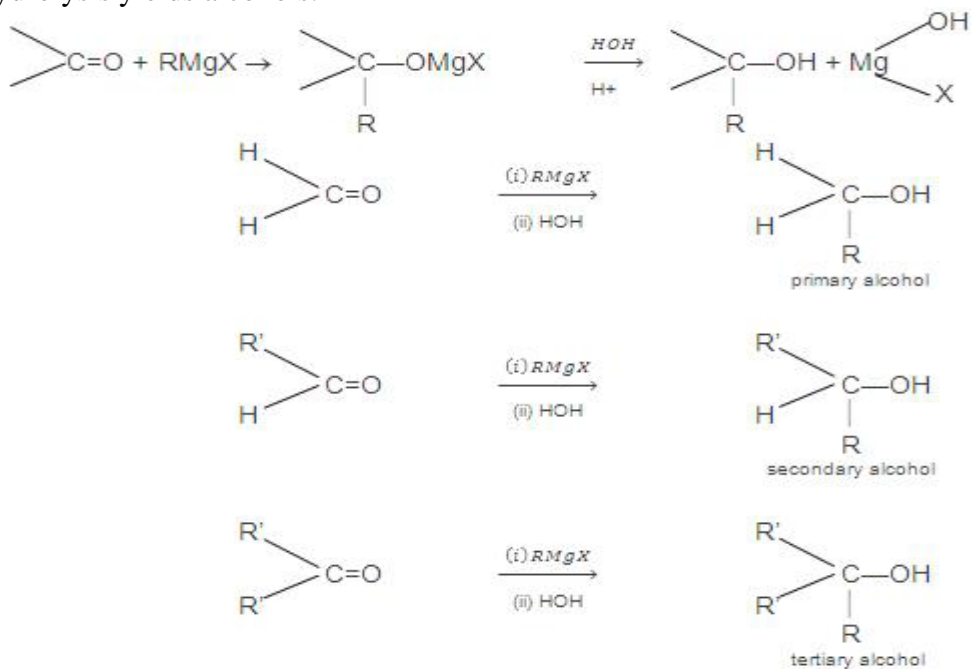
(iii) **By the hydrolysis of ethers:**



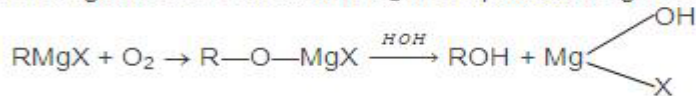
(iv) **By the hydrolysis of esters:**



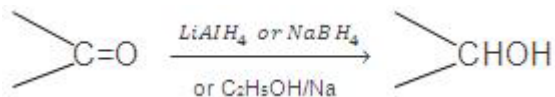
(v) **By Grignard reagents:** All the three types of monohydric alcohols (primary, secondary and tertiary alcohols) are obtained by the use of Grignard reagents and carbonyl compounds. The addition of RMgX on carbonyl compounds followed with hydrolysis yields alcohols.



Grignard reagents also reacts with O₂ and epoxides to give alcohols.



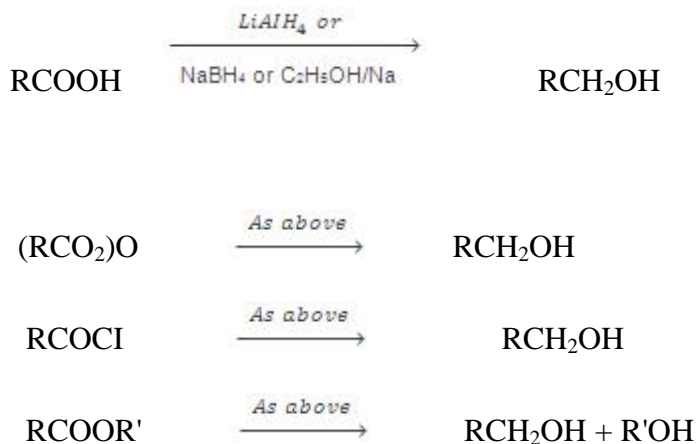
(vi) **By the reduction of carbonyl compounds:** Reduction of **aldehydes gives primary alcohol and**



Reduction of ketones gives secondary alcohol.

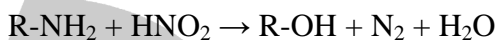
Note: tertiary alcohols can be obtained by this method.

(vii) **By the reduction of acids and their derivatives:**

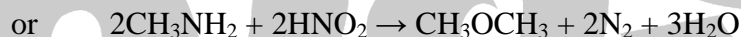


Note: If $\text{C}_2\text{H}_5\text{OH} + \text{Na}$ is used as reducing agent, the reduction is known as Bouveault-Blane reaction.

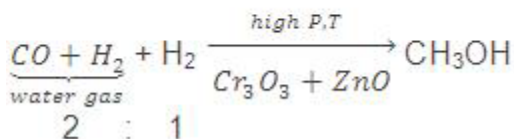
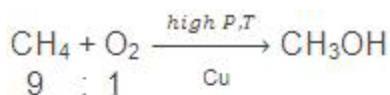
(viii) **By the action of nitrous acid on primary amines:**



However under similar conditions CH_3NH_2 gives $\text{CH}_3\text{-O-N=O}$ or CH_3OCH_3



(ix) Methanol can also be prepared as



2. **Explain how ethyl alcohol is prepared by fermentation?**

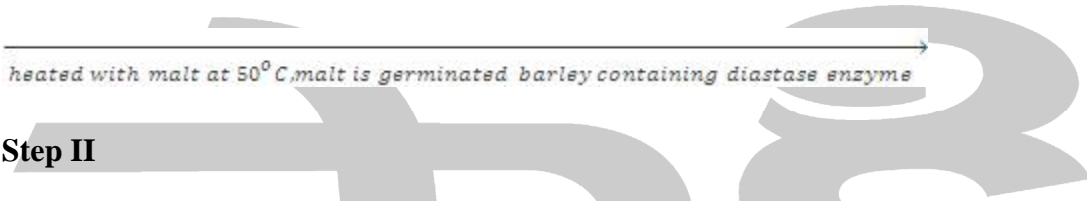
By fermentation:

(i) Fermentation is the slow decomposition of complex organic compounds into simpler organic compounds by the activity of enzymes. Enzymes are complex, nitrogenous (proteins), non living macro molecules of high molecular weight derived from living organisms. These are also known as biological catalysts.

- (ii) Fermentation process is generally accompanied with evolution of gases like CO_2 & CH_4 and is exothermic in nature.
- (iii) The alcoholic fermentation involves conversion of sugar into ethyl alcohol by yeast.
- (iv) The starting material for alcoholic fermentation is starch (potato, rice, barley, maize). The source of starch depends upon its availability in that country. In India, alcoholic fermentation is made by molasses i.e. the dark coloured syrupy liquid left after crystallization of sugar from sugar cane juice. Molasses contains about 50% sugar left after crystallization of sugar from cane juice.
- (v) An outline of alcoholic fermentation is given below.

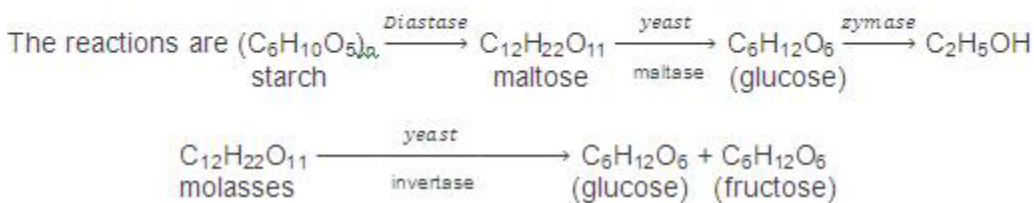
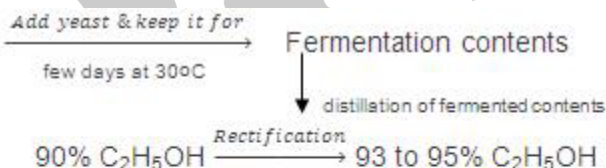
Step I

Starchy material, mashed with hot water and Maltose extracted solution is taken



Step II

Maltose obtained from starch or molasses solution diluted to the extent to have not more than 8 to 10% sugar



Conditions favorable for fermentation:

1. Optimum temperature range for fermentation is 25-30°C. At higher temperature enzymes are coagulated.
2. Certain inorganic substances, $(\text{NH}_4)_2\text{SO}_4$, phosphate etc are added as food for ferment cells.
3. Solution to be fermented should be dilute.

4. Substances like boric acid, mercury salts etc. should not be present as they retard fermentation.

5. Proper aeration should be maintained in fermentation.

Note: The name fermentation has been derived from Latin word ferver meaning to boil, because during fermentation there is lot of frothing due to evolution of CO_2 and this gives the appearance of boiling liquid.

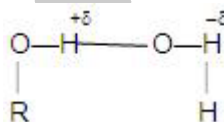
3. Explain the physical and chemical properties of alcohols.

Ans: Physical Properties of Alcohols

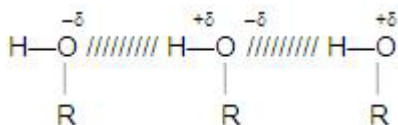
Properties:

(i) Lower alcohols are colourless, volatile, toxic, inflammable liquids with burning taste and spirituous odour. Above C_{12} , alcohols are solid.

(ii) Lower alcohols are soluble in water due to H-bonding, however their solubility decreases with increase in molecular weight of alcohols due to increasing nature of hydrophobic nature (to recedes away from H_2O) of alkyl chain.



(iii) Boiling point of alcohols are much higher than those of corresponding alkanes and thiols due to H-bonding.



However the isomeric alcohols shows the b.pt. order :

primary > secondary > tertiary.

(iv) Alcohols are neutral and do not influence the pH of solution and thus alcohols are weaker acids than water. The basic character: $\text{OC}_2\text{H}_5 > \text{OH}^-$

(v) Lower alcohols form solid derivatives with metallic salt in which alcohol molecule show solvation phenomenon. e.g.



That is why alcohols cannot be dried by anhydrous CaCl_2 .

Chemical nature:

(i) Reactions involving H atom of -OH group: All such reactions involving replacement of H atom of -OH group represent Bronsted acid nature of alcohols. The Bronsted acid nature shows the order:

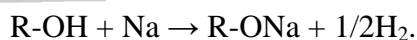
Methyl alcohols $> 1^\circ > 2^\circ > 3^\circ$ alcohol

The tendency to attract electron pair of O-H bond by O atom decreases by the +ve I.E. of CH_3 groups as it intensifies the partial -ve charge on oxygen atom & thus tendency to release H atom decreases in tertiary alcohols.

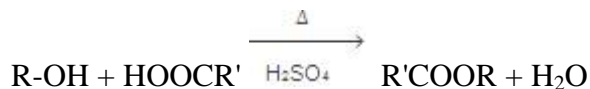


Following reactions of this category are noticed.

(a) **Action of active metals:** Strong electropositive metals like Na, K, Ca & Mg react with alcohols forming alkoxides with the liberation of H_2 gas.

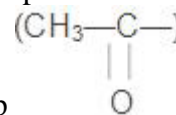


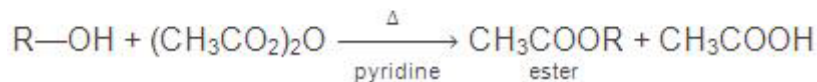
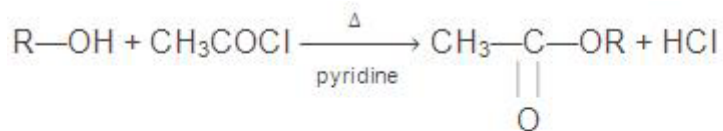
(b) **Action of carboxylic acids or esterification:** Alcohols on reacting with anhydrous acids in presence of conc. H_2SO_4 form esters. Concentrated H_2SO_4 acts as catalyst as well as dehydrating agent.



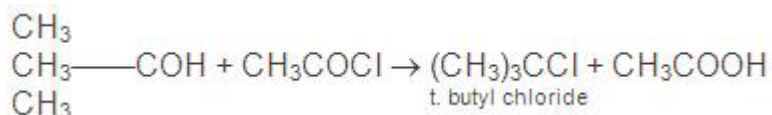
(c) **Action of acetyl chloride and acetic anhydride or acetylation:** Replacement of H

atom by acetyl group. The H atom of alcohol is replaced by acetyl group

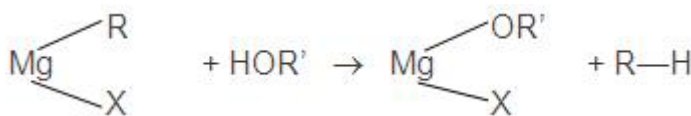




Tertiary alcohols are not acylated, however, they react with acetyl chloride to give alkyl chlorides and in some cases alkenes.



(d) Action of Grignard reagent:



All these reactions show the reactivity order P.A. > S.A. T.Alcohol

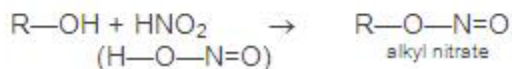
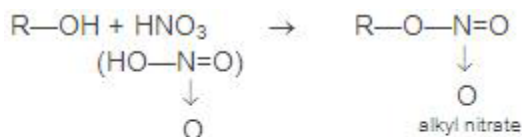
2. Reactions involving replacement of -OH group of alcohols: The -OH group of alcohol has two lone pair of electrons on O atom & thus behaves as Lewis base. The Lewis base nature of alcohols shows the order.

T.A. > S.A. > P. Alcohol

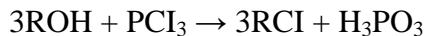
or $3^\circ > 2^\circ > 1^\circ > \text{methyl alcohol}$

K, tertiary alcohols the partial -ve charge on oxygen atom is intensified due to + I.E. of CH_3 groups. This increases the tendency of oxygen atom to donate electron pair or to show cleavage of C-O bond.

(a) Action of inorganic acids: Forms esters with inorganic acids

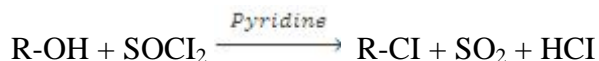


(b) Action of phosphorus halides:

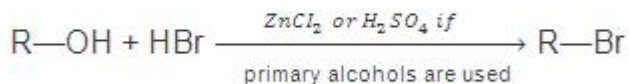
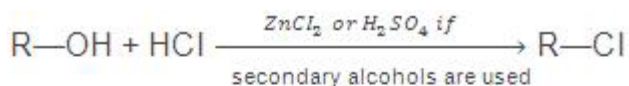


Similar reactions are obtained by using $\text{P} + \text{Br}_2$ and $\text{P} + \text{I}_2$ for alkyl bromide and iodide preparation because of less stable nature of PBr_3 & PI_3

(c) **Action of SOCl_2 :**



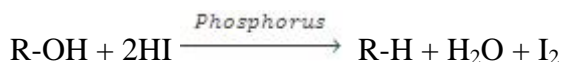
(d) **Action of halogen acids:**



The reactivity order for halogen acids is: $\text{HI} > \text{HBr} > \text{HCl}$

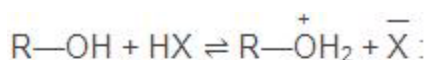
Note:

1. If alcohols are heated with conc. HI and red P, alkanes are formed

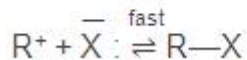
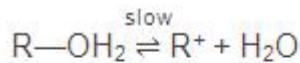
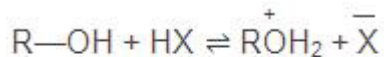


2. For getting bromo and iodo derivatives from alcohols, a mixture of $\text{KBr} + \text{H}_2\text{SO}_4$ and $\text{KI} + \text{H}_2\text{SO}_4$ respectively can be used.

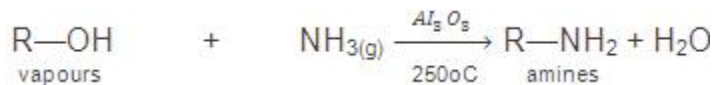
3. Primary alcohols follow $\text{S}_{\text{N}}2$ mechanism during replacement of OH group by halogen atom



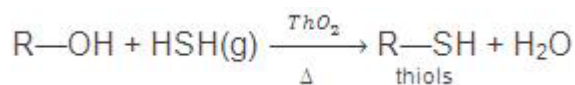
4. Secondary and tertiary alcohols follow $\text{S}_{\text{N}}1$ mechanism during replacement of OH group by halogen atom.



(e) Action of NH₃:



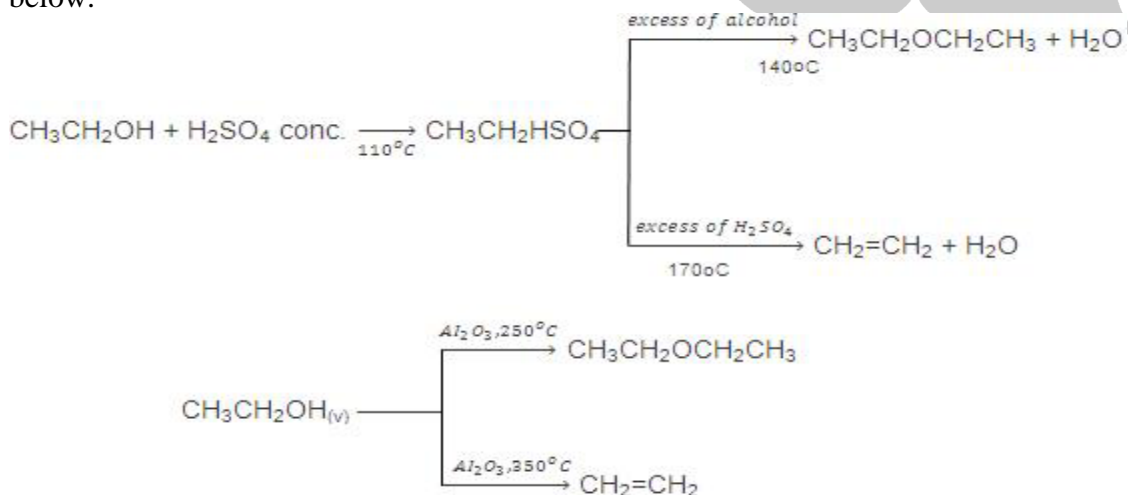
(f) Action of H₂S:



All these reactions (a) to (f) show the reactivity order T.A. > S.A. > P. Alcohol.

3. Reactions involving complete molecule of alcohols:

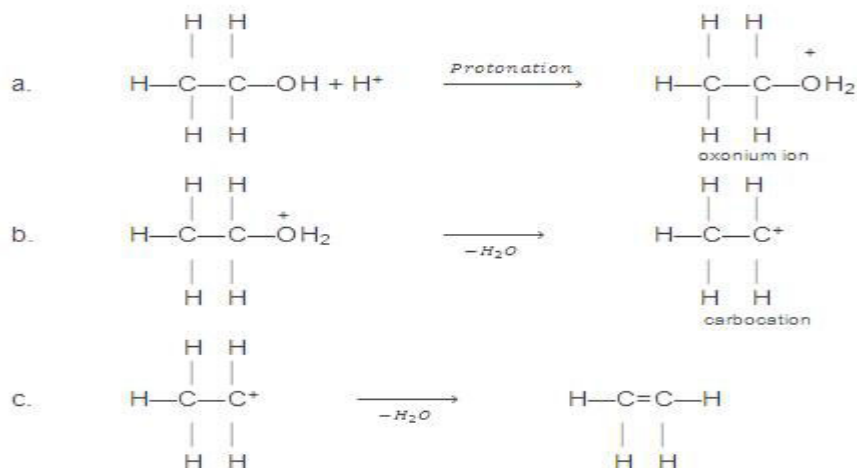
(a) Dehydration: Dehydration (removal of H₂O) of alcohols yields alkene or ether depending up-on the experimental conditions. The dehydration of alcohol favour the order T.A. > S.A. > P. Alcohol. The action of various dehydrating agents used are given below.



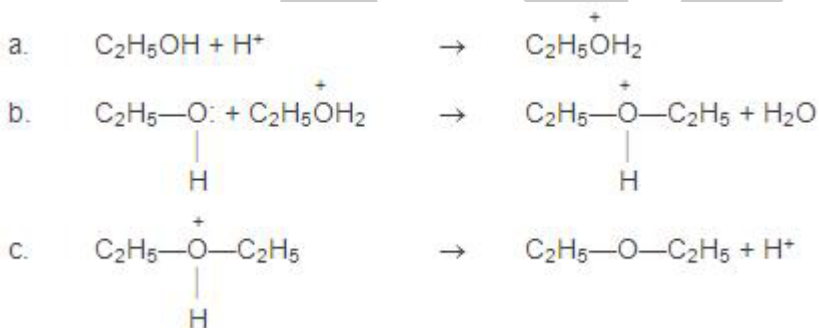
Note:

1. Normally secondary & tertiary alcohols give alkene as main product on dehydration.

2. The mechanism of dehydration of alcohols giving alkene involves protonation of the alcohol followed by loss of a water molecule and a proton.

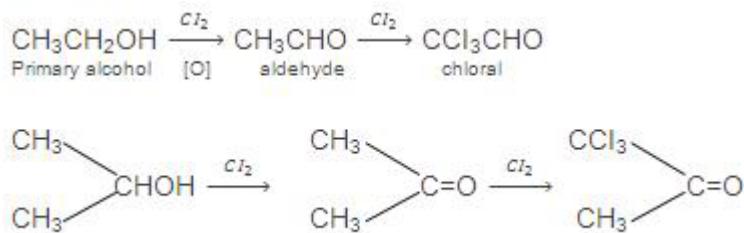


3. The mechanism of dehydration of alcohol giving ether involves protonation of alcohol. An unprotonated molecule of alcohol then combines with the protonated molecule of alcohol losing water molecule. The oxonium ion formed gives ether by a loss of a proton.



(b) Action of halogens:

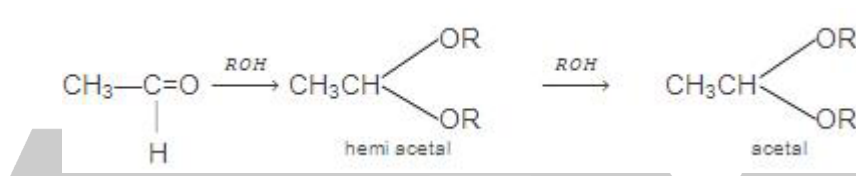
- (i) Halogens oxidize primary and secondary alcohols to aldehydes and ketones respectively.
- (ii) After oxidation, the halogens also show substitution at α -carbon atom of products.



Chemical Nature of Alcohols

Note: Tertiary alcohols are not oxidised by halogens and thus tertiary butyl alcohol does not give iodoform if heated with halogens and alkali.

(c) Acetal formation:



(d) **Haloform reaction:** Ethyl alcohol and all alkanol-2 (secondary alcohols only) undergo haloform reaction on heating with halogen and alkali. Follow haloform reaction.

Uses:

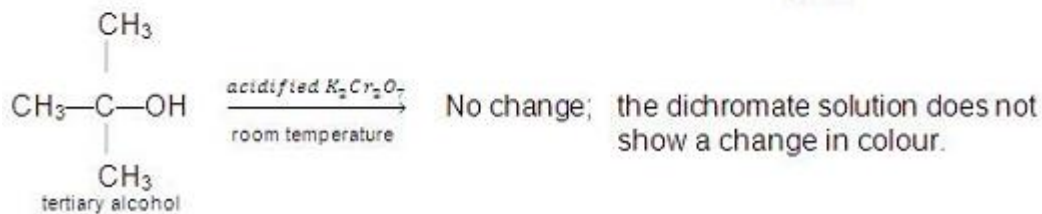
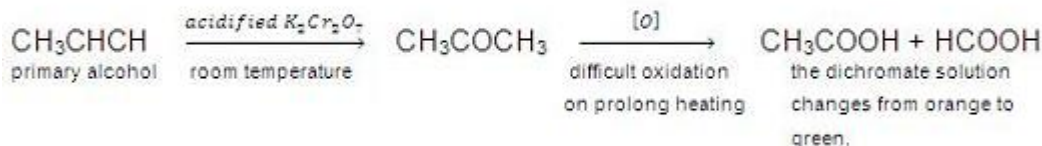
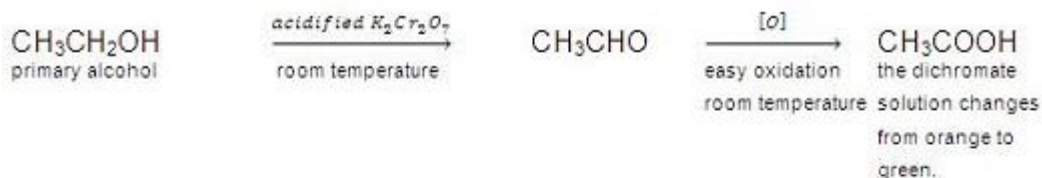
- (i) In beverage industry
- (ii) As antiseptic - spirit
- (iii) As fuel - spirit lamp
- (iv) As solvent for medicines
- (v) As an antifreeze; glycol and glycerols are used with water to form an antifreeze mixture to cool down the radiators.

4. How primary, secondary and tertiary alcohols are distinguished?

Distinction test for primary, secondary and tertiary alcohols

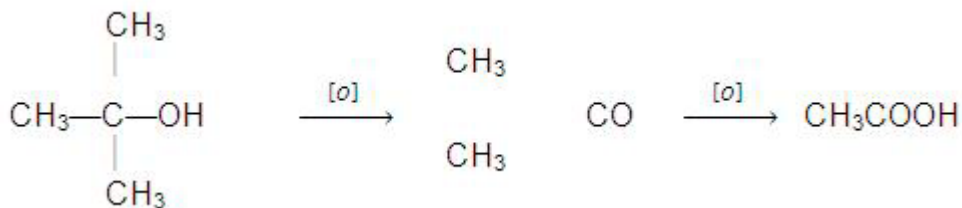
1. By oxidation:

The nature of the oxidation products of alcohols depends upon the nature of alcohol. The oxidizing agent used commonly are acidified $K_2Cr_2O_7$, alkaline or acidified $KMnO_4$ or dilute HNO_3 .

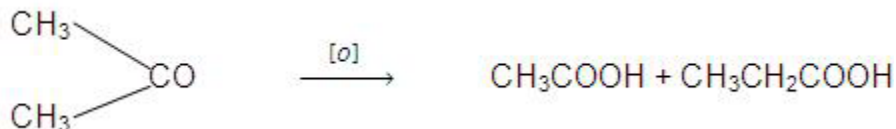


Note:

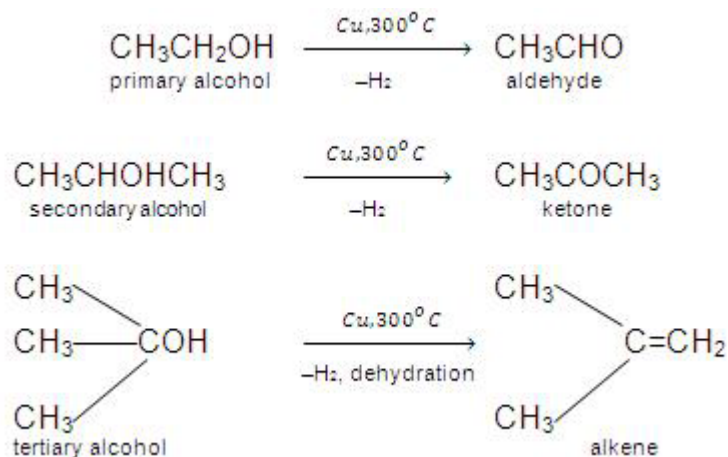
- (i) In case of primary alcohol, aldehyde and acid both have same no. of C atoms as parent alcohols have.
- (ii) In case of secondary alcohols, ketone has same no. of carbon atoms but acid has less carbon atom than alcohol and ketone.
- (iii) Tertiary alcohols are not oxidized in neutral or alkaline medium, however under drastic oxidation it gives ketone and acid both having lesser number of carbon atoms than the parent alcohol.



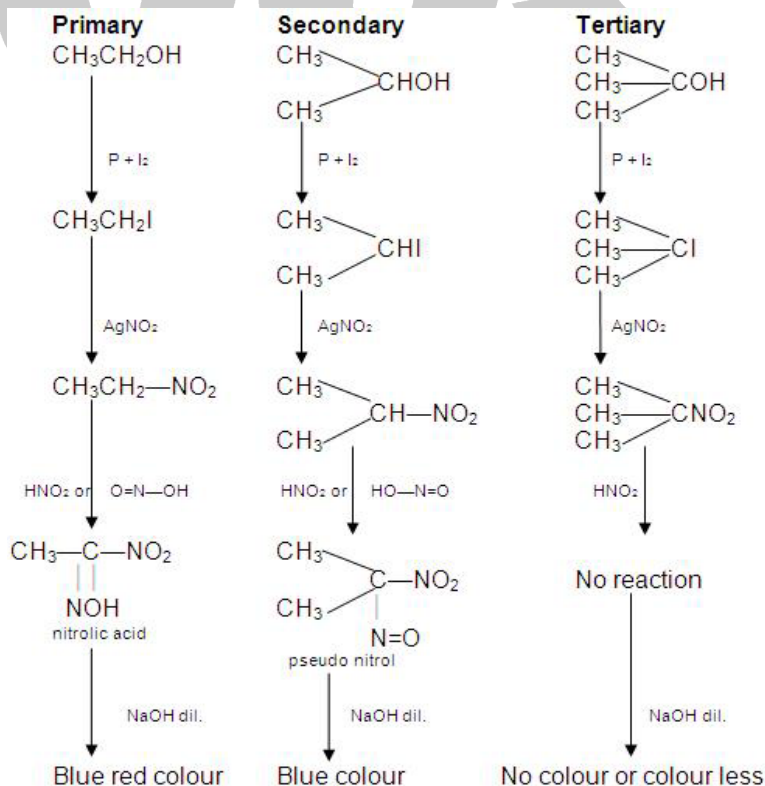
- (iv) In case of oxidation of unsymmetrical ketones, the splitting of the ketonic chain takes place according to **Popff's rule**, that the carbonyl group always remains attached to a smaller alkyl group.



2. By catalytic dehydrogenation: The dehydrogenation of alcohol vapours passed over reduced Cu at 300°C gives different products depending upon the nature of alcohols.

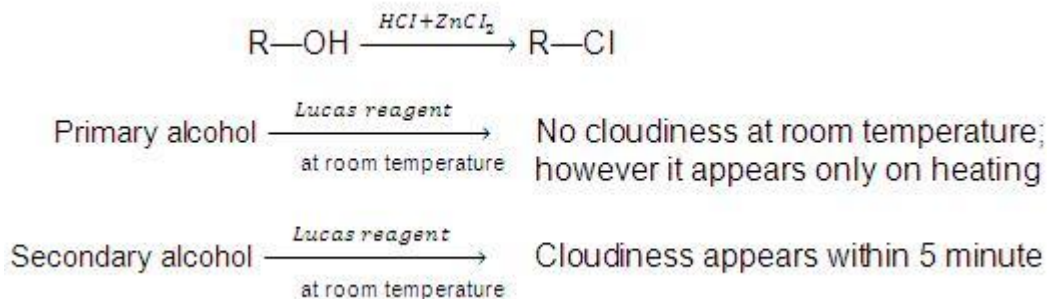


3. By Victor Meyer's test: Alcohols are subjected to a series of operations given below. The final colour of solution indicates the nature of alcohol.



Addition of NaOH simply increases the dissociation of nitric acid to increase the concentration of red coloured anions

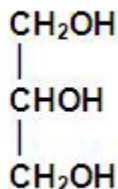
4. Lucas reagent test: This test is based on the reactivity order of alcohols to replace -OH group by halogen atom i.e. T.A. > S.A. > P.A. The alcohols are allowed to react with Lucas reagent (i.e. conc. HCl and $ZnCl_2$ anhydrous) and following observations are noticed.



5. Explain the preparation and properties of Glycerol.

Ans: Glycerol or Glycerin

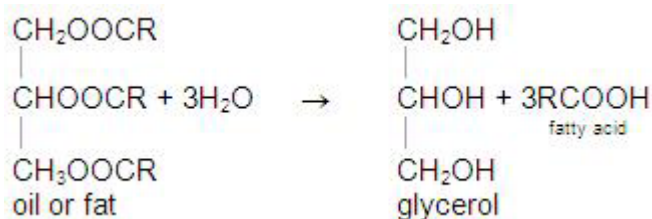
Glycerol or Glycerine



Glycerol is a trihydric alcohol. Its IUPAC name is propane-1, 2, 3-triol and in industry it is known as glycerine.

Manufacture

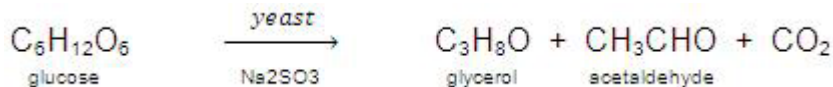
1. From Fats and Oils : On hydrolysis of fats and oils (i.e. glycerides or ester of higher fatty acids) glycerol and fatty acids are formed.



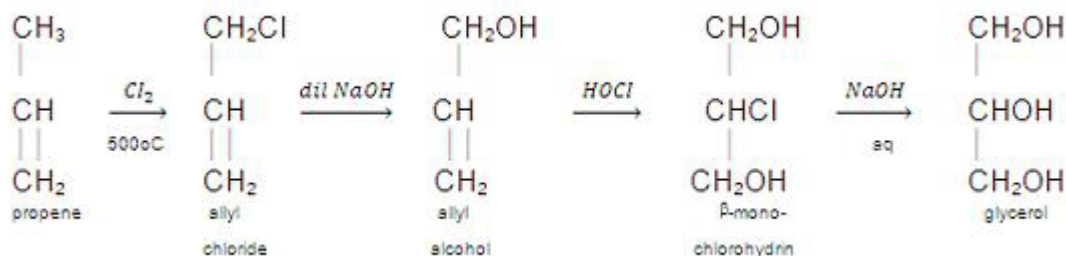
Glycerol is obtained as by-product in soap and candle industry.

2. By Fermentation of sugar:

Alcoholic fermentation of sugar gives 3% glycerol. However, if the fermentation is done in presence of sodium sulphite, the yield can be increased to 25%.



3. Synthesis (From Propene):



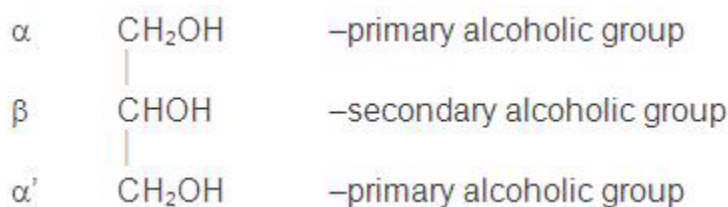
Properties

Physical

- It is a colourless, odourless, viscous and hygroscopic liquid, sweet in taste and non-toxic in nature.
- It is soluble in water and ethyl alcohol but insoluble in ether.
- The high viscosity and high boiling point of glycerol are due to strong hydrogen bonding.

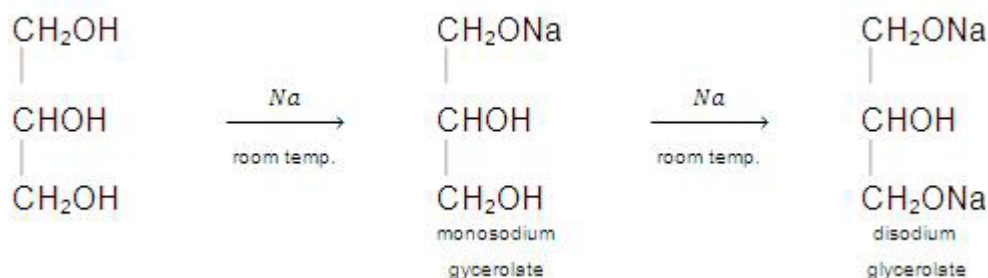
Chemical:

The molecule of glycerol contains two primary -OH groups and one secondary -OH group. The carbon atoms in glycerol are indicated as α , β and α' .

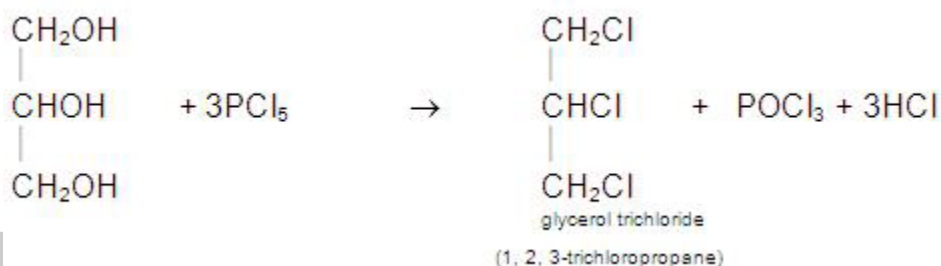


Primary -OH groups are more reactive than secondary -OH group.

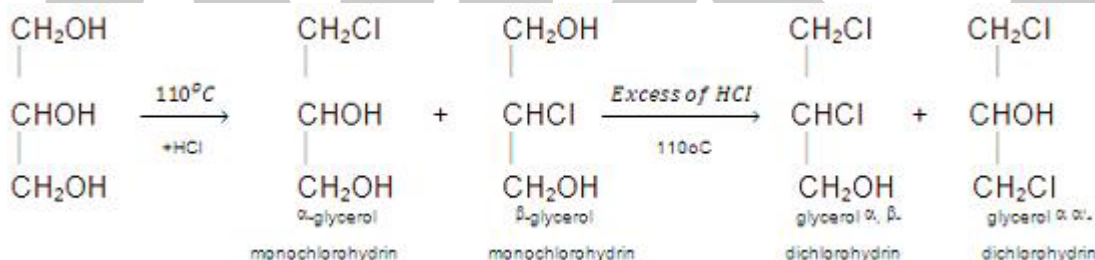
(i) **Action of sodium:** Only primary alcoholic groups are attacked one by one and secondary alcoholic group is not attacked.



(ii) **Action of PCl_5 :**

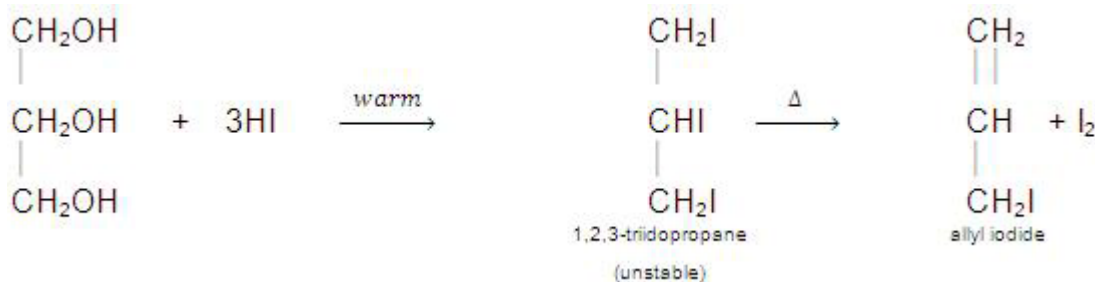


(iii) **Action of HCl or HBr:**

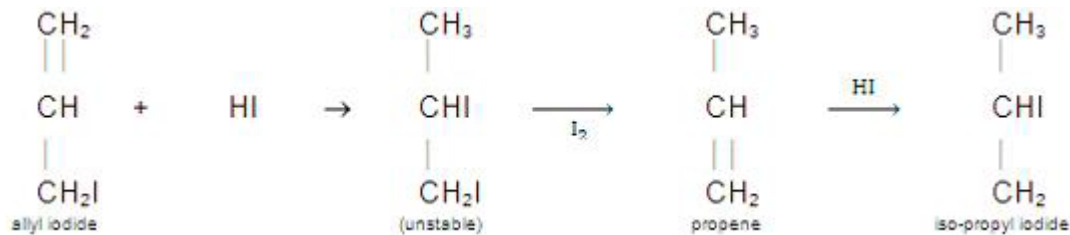


(iv) **Action of HI:** Glycerol reacts with HI in two ways:

(a) When glycerol is warmed a small amount of hydrogen iodide, allyl iodide is formed.

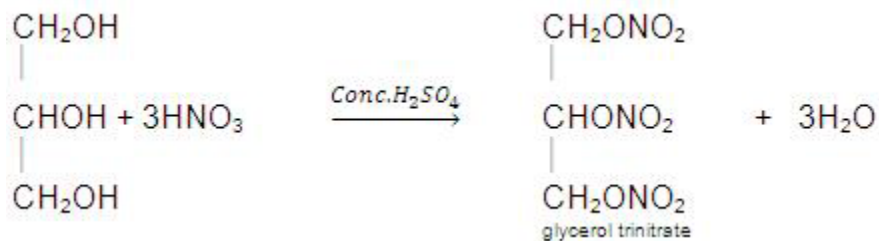


(b) When glycerol is heated with excess of HI, the allyl iodide formed first is reduced to propene. Propene in presence of excess of HI forms iso-propyl iodide.



Note: Same products are obtained when glycerol is treated with phosphorus tri-iodide.

(v) **Action of nitric acid:**



Glycerol trinitrate is a yellow oily, poisonous liquid and causes headache. It explodes violently when heated rapidly or subjected to sudden shock.

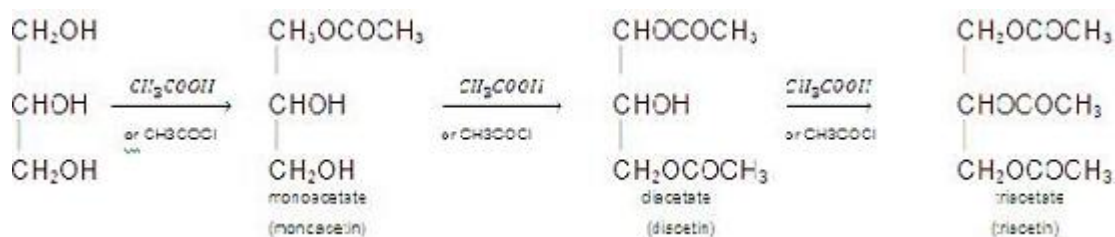


It is a safer explosive when absorbed on kieselguhr and known as dynamite. Some other important explosives prepared from glycerol trinitrate are :

(a) **Blasting gelatin:** A mixture of glycerol trinitrate and cellulose nitrate (gun cotton).

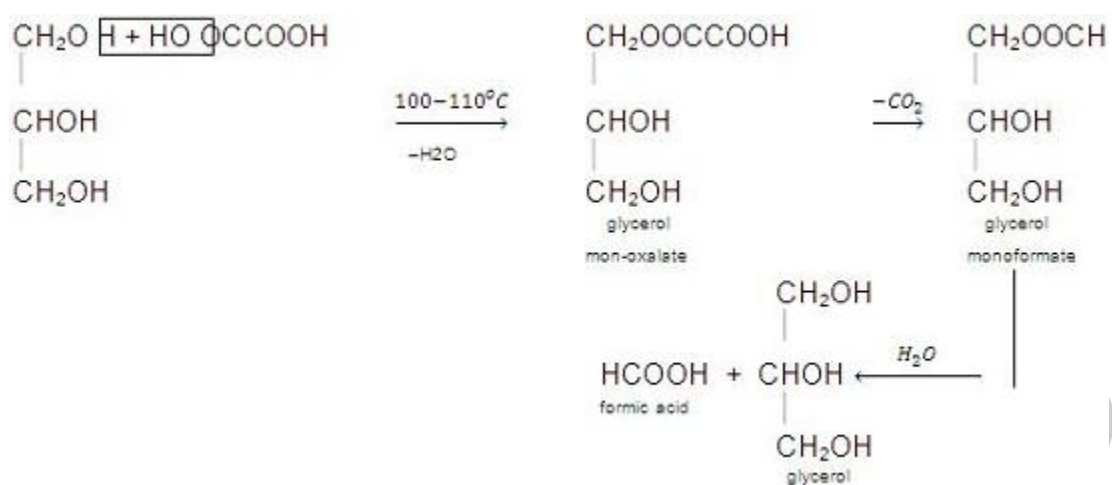
(b) **Cordite:** It is obtained by mixing glycerol trinitrate with gun cotton and Vaseline. It is smokeless explosive

(vi) **Action of CH₃COOH, acetic anhydride or acetyl chloride:** Mono, di and trimers of glycerol are formed.

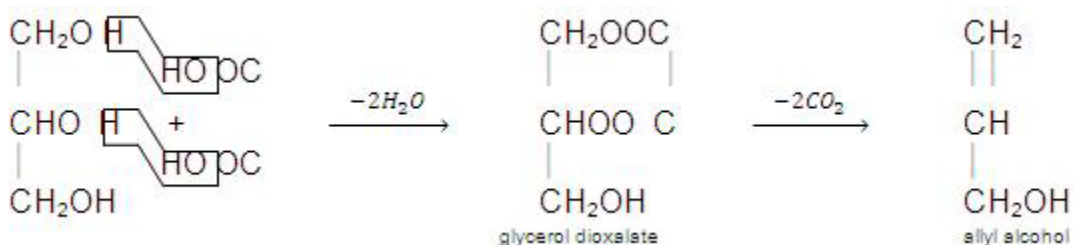


(vii) **Action of oxalic acid:** Different products are formed under different conditions.

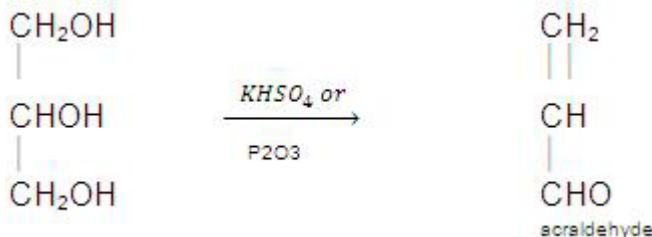
(a) At 110°C and with excess of oxalic acid, formic acid is formed.



(b) At 260°C, allyl alcohol is formed.

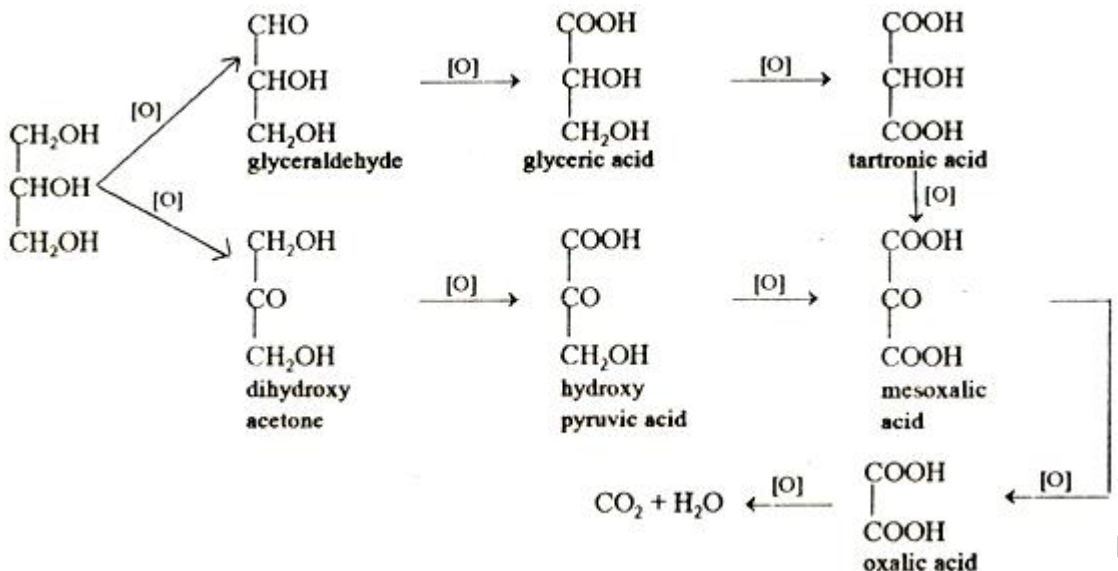


(viii) **Dehydration:** Glycerol on dehydration by potassium hydrogen sulphate or phosphorus pentoxide or concentrated sulphuric acid gives acrolein or acraldehyde which has a characteristic bad odour.



This reaction can be used as a test of glycerol.

(ix) **Oxidation:** Glycerol gives different oxidation products depending on the nature of oxidizing agent.



Oxidation of Glycerol with.....

- (a) Dilute HNO₃ gives mainly glyceric acid.
- (b) Conc. HNO₃ gives glyceric acid and tartronic acid.
- (c) Bismuth nitrate gives mainly mesoxalic acid.
- (d) Fenton's reagent (H₂O₂ + F₂SO₄) or NaOBr or Br₂-water in presence of Na₂CO₃ gives glyceraldehydes and dihydroxy acetone.
- (e) Solid KMnO₄, gives oxalic acid and carbon dioxide. The reaction is violent and explosion occurs.

Uses

- (a) As a sweetening agent in confectionary, beverages and medicines due to nontoxic nature.
- (b) As antifreeze in automobile radiators.
- (c) In the manufacture of plastics & synthetic fibres.
- (d) In the manufacture of explosives like dynamite and cordite.
- (e) As a lubricant in watches.
- (f) In the preparation of good quality of soaps, hand lotions, vanishing creams, shaving creams and tooth pastes.
- (g) In the manufacture of various organic compounds like, formic acid, allyl alcohol, acrolein, etc.
- (h) As a preservative.
- (i) In the preparation of non-drying inks, printing inks and stamp pad inks.

6. Explain the preparation and properties of Phenol.

PHENOL

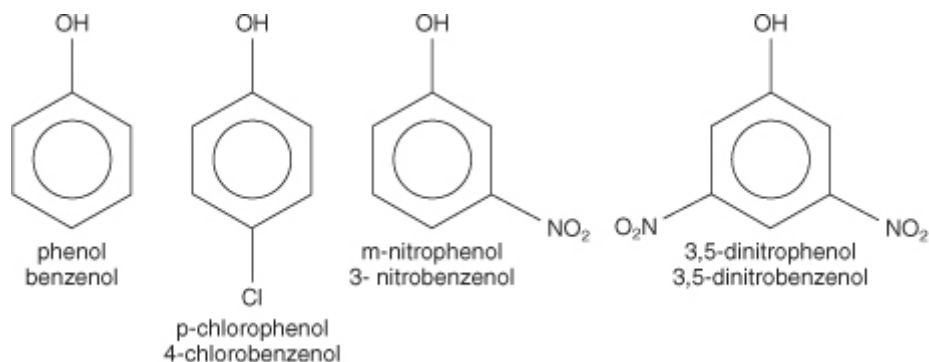
Phenols are molecules that have a hydroxyl group attached to the carbon atom of an aromatic ring.

Nomenclature:

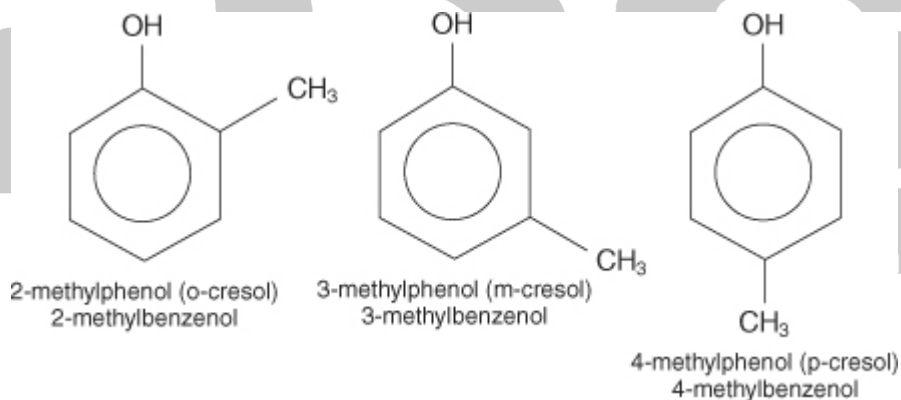
By definition, phenol is hydroxybenzene. Phenol is a common name for the compound. Its IUPAC name would be benzenol, derived in the same manner as the IUPAC names for aliphatic alcohols.

When a phenol molecule is substituted with additional groups, either the ortho, meta, para system or the numbering system can be employed. In either case, if the parent molecule is referred to as a *phenol*, the nomenclature being used is the common system.

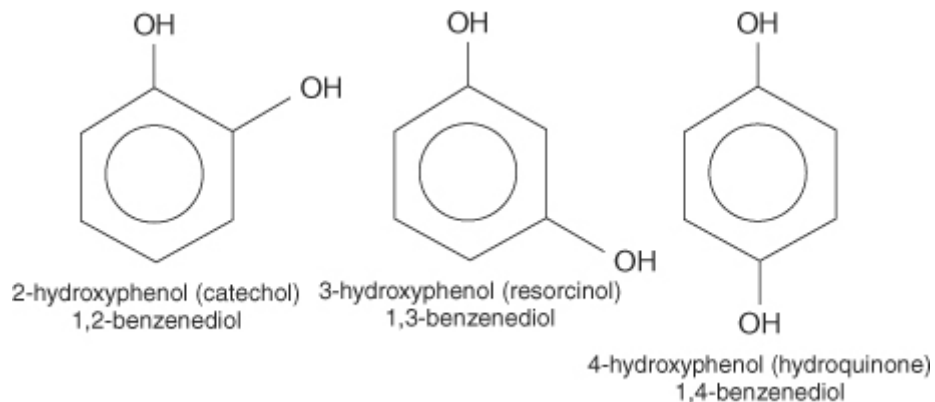
In IUPAC nomenclature, the parent molecule is called benzenol, and substituents are always numbered with the OH group being given the understood first position. For the compounds below, the first name listed is the common name and the second is the IUPAC name.



Certain phenols are referred to by common names. For example, methyl phenols are called *cresols*. In the illustrations below, the first name under each compound is its common name, and the bottom name is its IUPAC name.



Similarly, hydroxyphenols have common names, which are listed first under each of the following illustrations, while the IUPAC names are listed last.

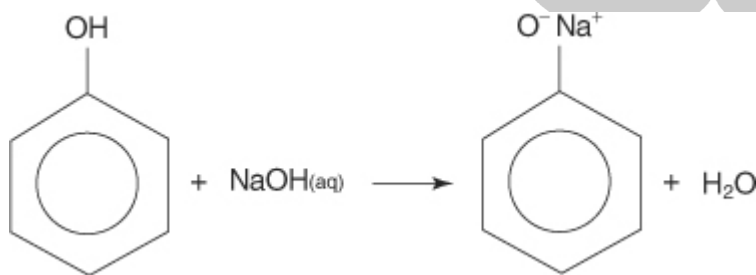


Physical properties

1. Low molecular weight phenols are normally liquids or low melting solids.
2. Due to hydrogen bonding, most low molecular weight phenols are water-soluble.
3. Phenols tend to have higher boiling points than alcohols of similar molecular weight because they have stronger intermolecular hydrogen bonding.

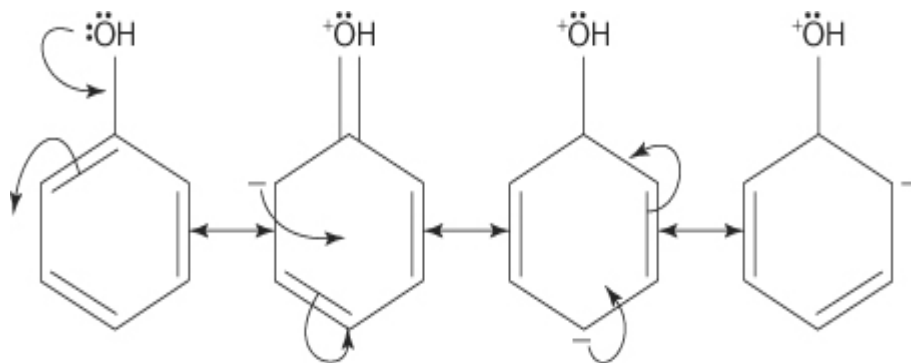
Acidity

Phenols show appreciable acidity ($p K_a = 8^{-10}$). For example, phenol reacts with aqueous NaOH as follows.



This is a typical neutralization reaction.

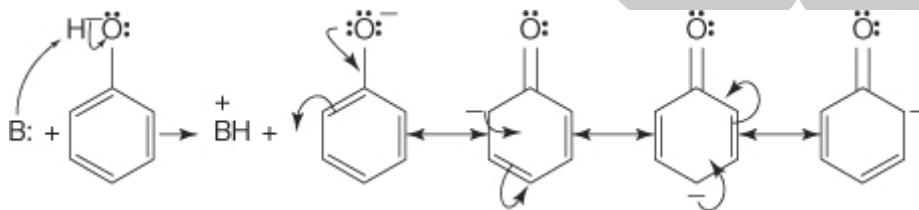
Because of their high acidity, phenols are often called **carbolic acids**. The phenol molecule is highly acidic because it has a partial positive charge on the oxygen atom due to resonance, and the anion that is formed by loss of a hydrogen ion is also resonance stabilized.



Resonance structures of phenol

Notice that three of the four contributing structures possess a positive charge on the oxygen atom of the molecule. Thus, the true hybrid structure must possess a partial positive charge. Because oxygen is an electronegative element, the electrons in the oxygen-hydrogen bond orbital are attracted to the oxygen atom, resulting in partially positive hydrogen.

Loss of a hydrogen ion to a base creates a phenoxide ion that is resonance stabilized.



Notice that upon removal of the hydroxy hydrogen by a base, the phenoxide anion results. This anion is resonance stabilized by delocalization of an electron pair throughout the molecule, as shown by the contributing structures.

Synthesis of Phenols

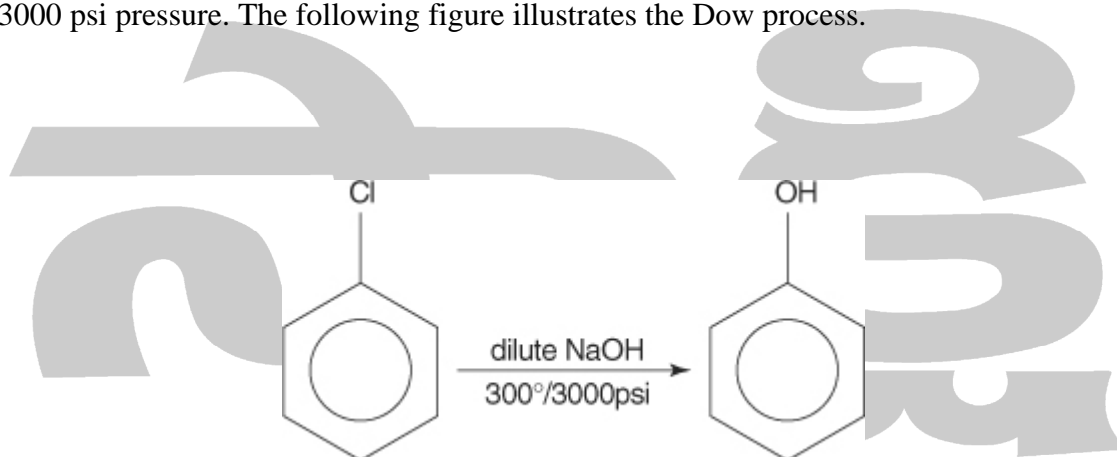
You can prepare phenols in large quantities by the pyrolysis of the sodium salt of benzene sulfonic acid, by the Dow process, and by the air oxidation of cumene. Each of these processes is described below. You can also prepare small amounts of phenol by the peroxide oxidation of phenylboronic acid and the hydrolysis of diazonium salts.

1. Pyrolysis of sodium benzene sulfonate

In this process, benzene sulfonic acid is reacted with aqueous sodium hydroxide. The resulting salt is mixed with solid sodium hydroxide and fused at a high temperature. The product of this reaction is sodium phenoxide, which is acidified with aqueous acid to yield phenol.

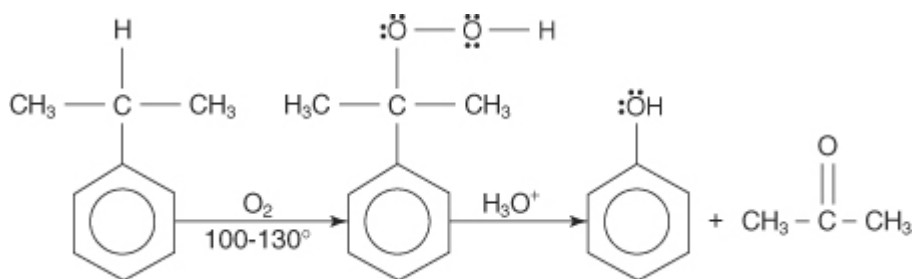
2. Dow process

In the Dow process, chlorobenzene is reacted with dilute sodium hydroxide at 300°C and 3000 psi pressure. The following figure illustrates the Dow process.



3. Air oxidation of cumene:

The air oxidation of cumene (isopropyl benzene) leads to the production of both phenol and acetone, as shown in the following figure. The mechanisms for the formation and degradation of cumene hydroperoxide require closer looks, which are provided following the figure.



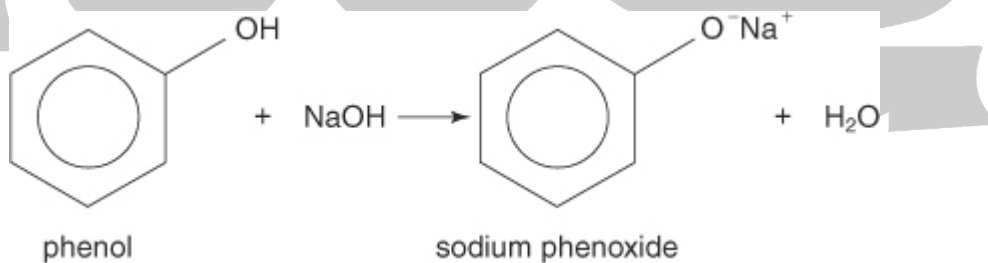
Chemical properties:

I. Reactions of Phenolic Hydrogen:

Phenols are acidic because of the ease with which the oxygen atom will release the hydrogen bonded to it. This section describes typical reactions that occur as a result of the acidity of phenols.

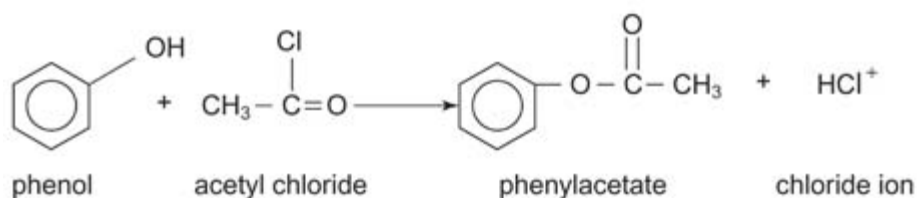
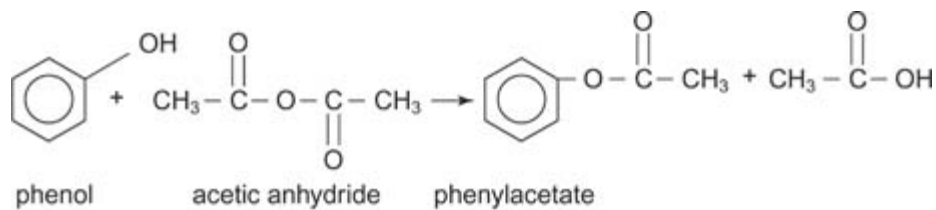
1. Reactions with bases:

Because phenol is acidic, it reacts with bases to form salts.



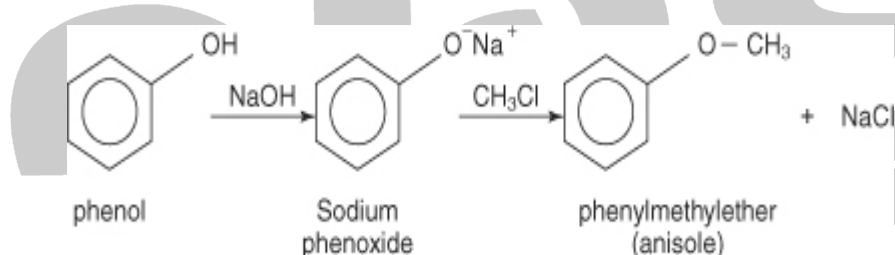
2. Esterification of phenol:

Phenols form esters with acid anhydrides and acid chlorides.



3. Williamson ether synthesis:

Ethers are produced from phenol by the Williamson method via an S_N mechanism.

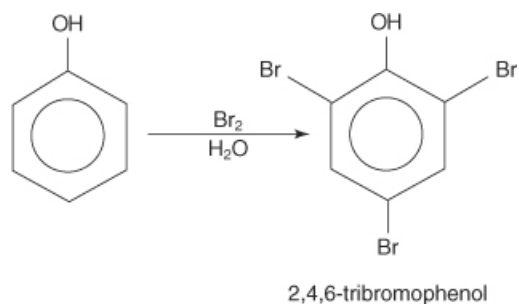


II. Reactions of Phenolic Benzene Rings:

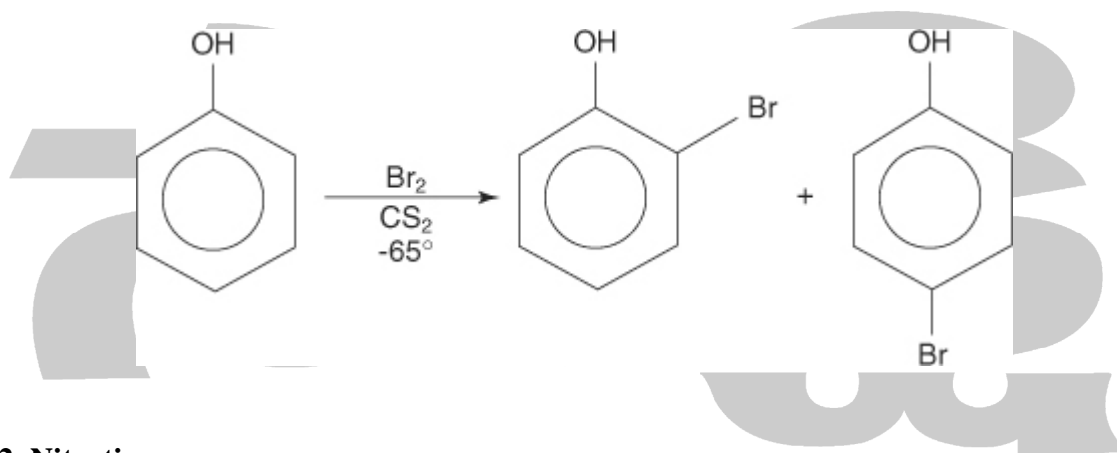
The hydroxy group in a phenol molecule exhibits a strong activating effect on the benzene ring because it provides a ready source of electron density for the ring. This directing influence is so strong that you can often accomplish substitutions on phenols without the use of a catalyst.

1. Halogenation:

Phenols react with halogens to yield mono-, di-, or tri-substituted products, depending on reaction conditions. For example, an aqueous bromine solution brominates all ortho and para positions on the ring.

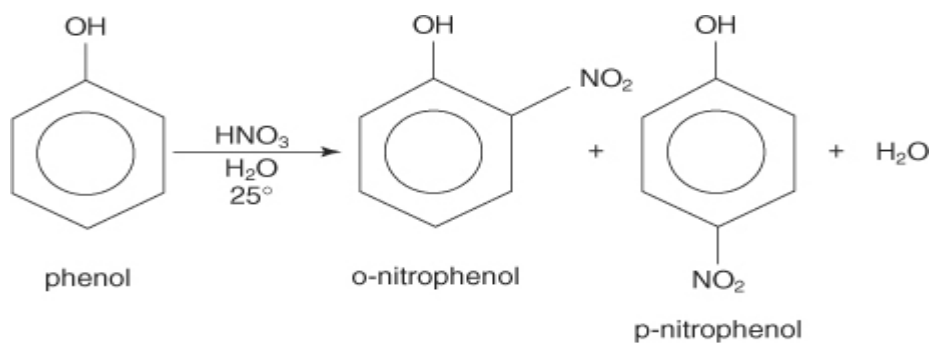


Likewise, you can accomplish monobromination by running the reaction at extremely low temperatures in carbon disulfide solvent.



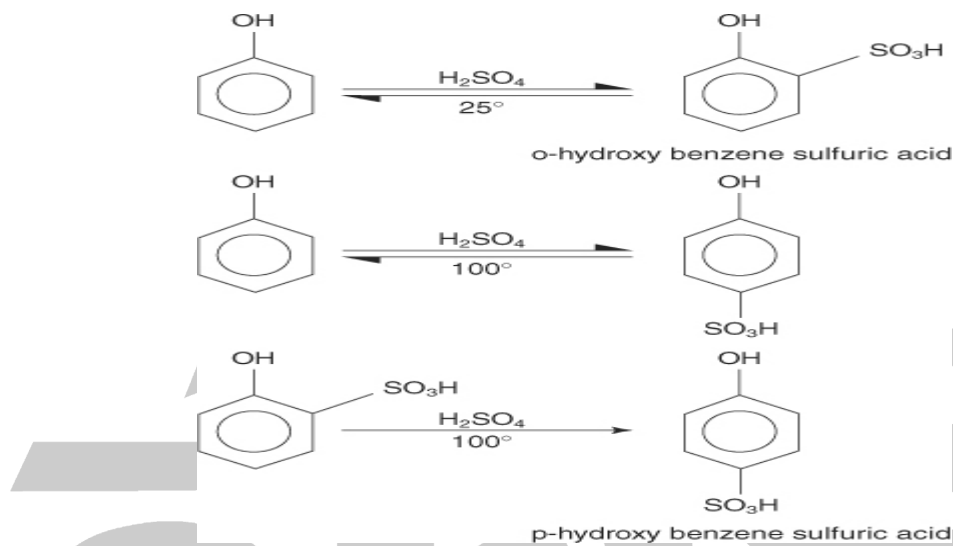
2. Nitration:

Phenol, when treated with dilute nitric acid at room temperature, forms ortho- and para-nitrophenol.



3. Sulfonation:

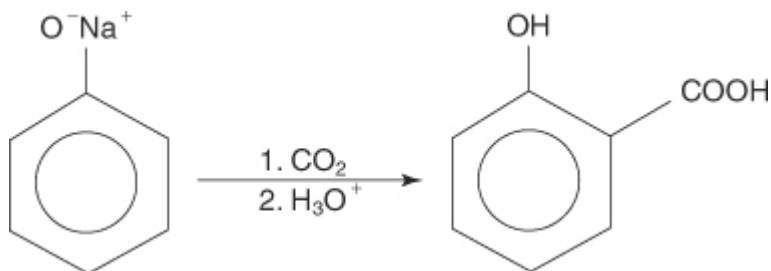
The reaction of phenol with concentrated sulfuric acid is thermodynamically controlled. At 25°C, the ortho product predominates while at 100°C, the para product is the major product.



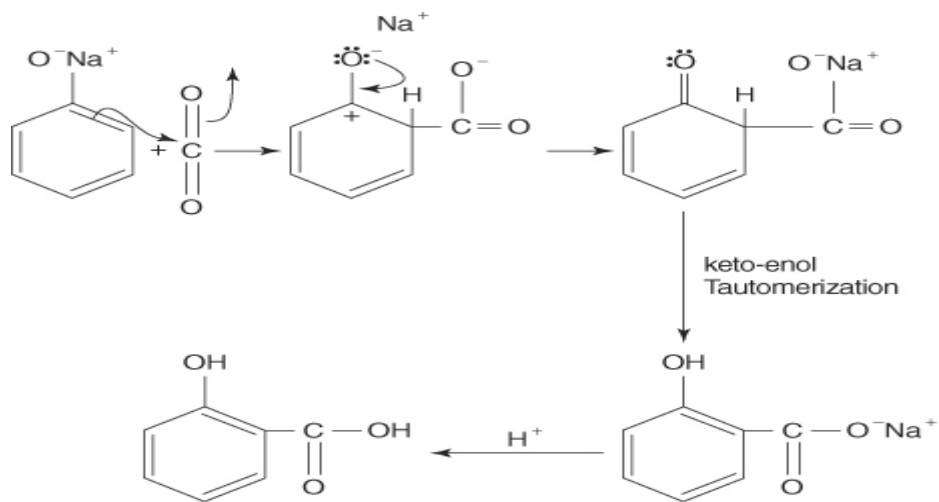
Notice that at both 25° and 100° , initially an equilibrium is established. However, at the higher temperature, the equilibrium is destroyed and the more thermodynamically stable product is produced exclusively.

4. Kolbe reaction:

The reaction of a phenoxide ion with carbon dioxide to produce a carboxylate salt is called the Kolbe reaction.



The Kolbe Reaction progresses via a carbanion intermediate.



In this reaction, the electron deficient carbon atom in carbon dioxide is attracted to the electron rich π system of the phenol. The resulting compound undergoes keto-enol tautomerization to create the product.