

ORGANIC HYDROXY COMPOUNDS

Organic compounds containing hydroxy group are called **hydroxy derivatives**. They are alcohols, phenols and carbohydrates.

Alcohols

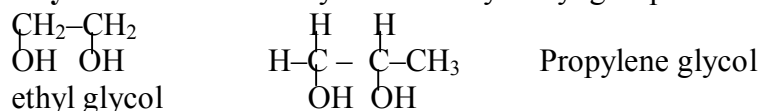
Definitions: Alcohols are defined as hydroxy derivatives of alkanes in which one or more hydrogen atoms of alkanes are replaced by corresponding number of hydroxyl groups.

Ex. (i) $\text{CH}_3\text{—OH}$ (ii) $\begin{array}{c} \text{CH}_2\text{—CH}_2 \\ | \quad | \\ \text{OH} \quad \text{OH} \end{array}$

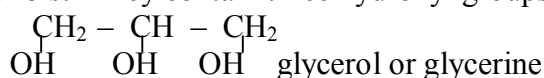
Classification of alcohols:- Alcohols are classified on the basis of number of hydroxyl groups.

a) Monohydric alcohols: They contain one hydroxyl groups. Ex:- R—OH , $\text{CH}_3\text{—OH}$, $\text{C}_2\text{H}_5\text{—OH}$

b) Dihydric alcohols:- They have two hydroxyl groups on two separate carbon atoms.

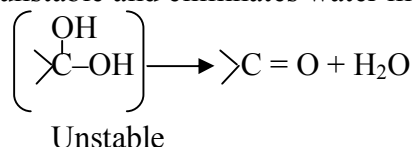


c) Trihydric alcohols:- They contain three hydroxyl groups on separate carbon atoms.



d) Polyhydric alcohols:- These alcohols have many (more than three) hydroxyl groups but on separate carbon atoms.

Rule:- If more than one hydroxyl groups are attached to the same carbon atom. The compound becomes unstable and eliminates water molecule.



Nomenclature of alcohols.

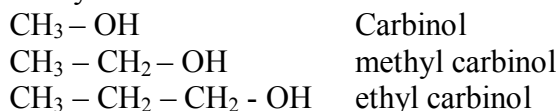
Common names or Trivial names.

Common names of alcohols are given on the basis of alkyl radicals directly attached to the hydroxyl group.

1)	$\text{CH}_3\text{—OH}$	Methyl alcohol
2)	$\text{C}_2\text{H}_5\text{—OH}$ or $\begin{array}{c} \text{CH}_3\text{—CH}_2 \\ \\ \text{OH} \end{array}$	ethyl alcohol
3)	$\text{CH}_3\text{CH}_2\text{—CH}_2\text{—OH}$	n propyl alcohol
4)	$\begin{array}{c} \text{H} \\ \\ \text{CH}_3\text{—C—OH} \\ \\ \text{CH}_3 \end{array}$	isopropyl alcohol OR secondary propyl alcohol
5)	$\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—OH}$	n butyl alcohol
6)	$\begin{array}{c} \text{H} \\ \\ \text{CH}_3\text{—C—CH}_2\text{—CH}_3 \\ \\ \text{OH} \end{array}$	secondary butyl alcohol
7)	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{—C—CH}_2 \\ \quad \\ \text{H} \quad \text{OH} \end{array}$	isobutyl alcohol
8)	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{—C—CH}_3 \\ \\ \text{OH} \end{array}$	tertiary butyl alcohol

Carbinol system:

In this system methyl alcohol is called carbinol & other alcohols considered as derivatives of methyl alcohol.

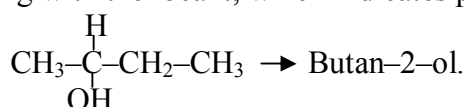


IUPAC system of Nomenclature

Rule (1):- Select the longest chain of carbon atoms containing that carbon to which hydroxyl group is attached. Count the number of carbon atoms in it. This gives the name of parent alkane.

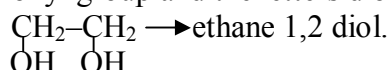
Rule (2):- Give numbers to the carbon atoms in the longest chain from that end which is nearest to the functional group. Thus carbon carrying hydroxyl group gets minimum possible number, called as **locant**.

Rule (3):- From the name of the parent alkanes, the last letter 'e' should be replaced by the letters 'ol' along with the locant, which indicates position of functional group.

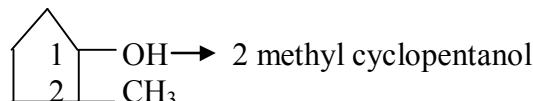


Rule (4):- The names and the numbers of remaining branches are prefixed to the name of alcohol in alphabetical order.

Rule (5):- While giving names to polyhydric alcohols, the letter 'e' from the alkane should be **retained**. Then, number of alcoholic groups are indicated by diol, triol, etc. The locants carrying the hydroxyl group and the letters diol, triol, etc. are suffixed to the parent alkane.



Rule (6):- Cyclic alcohols are named by replacing last letter 'e' by 'ol' from the name of cycloalkane. The -OH group is always considered to be on first carbon.



Structural formula	Common/ Trivial Name	IUPAC Name
$\text{H}_3\text{C}-\text{OH}$	Methyl alcohol	Methanol
$\text{H}_3\text{C}-\text{CH}_2-\text{OH}$	Ethyl alcohol	Ethanol
$\text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{OH}$	n-Propyl alcohol	Propan-1-ol
$\begin{array}{c} \text{H}_3\text{C}-\text{CH}_2-\text{CH}-\text{OH} \\ \\ \text{CH}_3 \end{array}$	sec-Butyl alcohol	Butan-2-ol
$\begin{array}{c} \text{H}_3\text{C}-\text{CH}-\text{CH}_2-\text{OH} \\ \\ \text{CH}_3 \end{array}$	Isobutyl alcohol	2-Methylpropanol
$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C}-\text{C}-\text{OH} \\ \\ \text{CH}_3 \end{array}$	tert-Butyl alcohol	2-Methylpropan-2-ol
$\begin{array}{c} \text{H}_2\text{C}-\text{CH}_2 \\ \quad \\ \text{OH} \quad \text{OH} \end{array}$	Ethylene glycol	Ethane-1,2-diol
$\begin{array}{c} \text{H}_2\text{C}-\text{CH}-\text{CH}_2 \\ \quad \quad \\ \text{OH} \quad \text{OH} \quad \text{OH} \end{array}$	Propylene glycerol	Propane-1,2,3-triol
$\text{H}_3\text{CCH}=\text{CHCH}_2\text{OH}$	Crotonyl alcohol	But-2-en-1-ol

Exercise

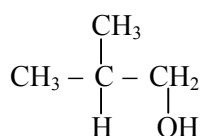
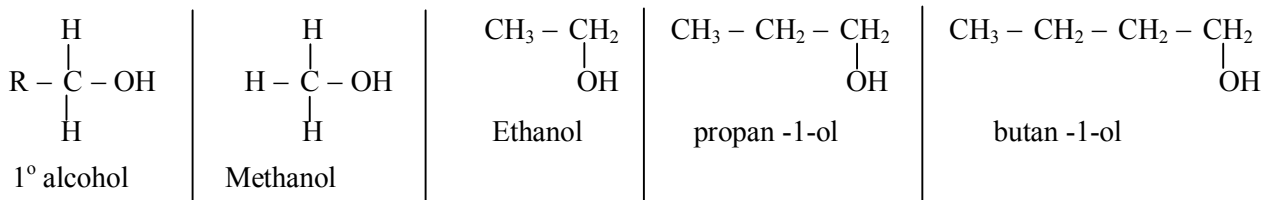
Que. Give IUPAC names of the following compounds.

Monohydric alcohols:- (R-OH, or C_n H_{2n+2}O)

Classification of monohydric alcohols on the basis of nature of carbon.

1) Primary alcohols:

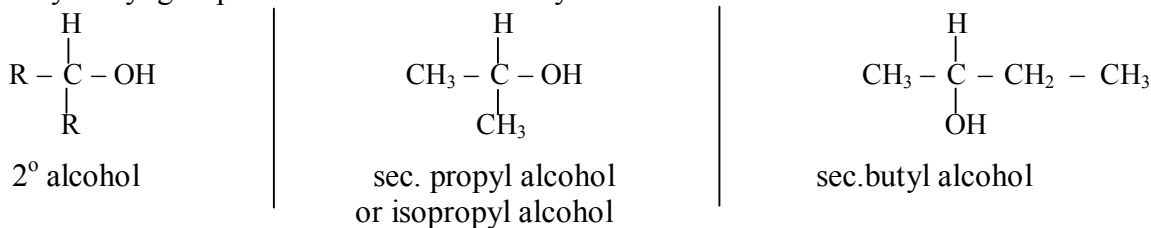
In these compounds hydroxyl group is attached to a primary carbon atom.



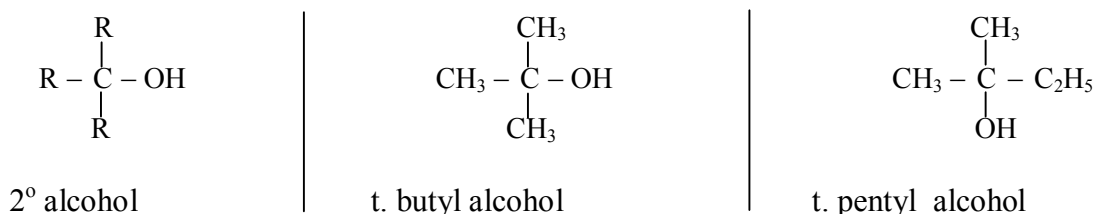
isobutyl alcohol or 2 methyl propan -1-ol

2) Secondary alcohols:

Hydroxyl group is attached to a secondary carbon atom.



3) Tertiary alcohols: hydroxyl group is attached to a tertiary carbon atom.



Primary alcoholic group → - CH₂OH

Secondary alcoholic group → >CHOH

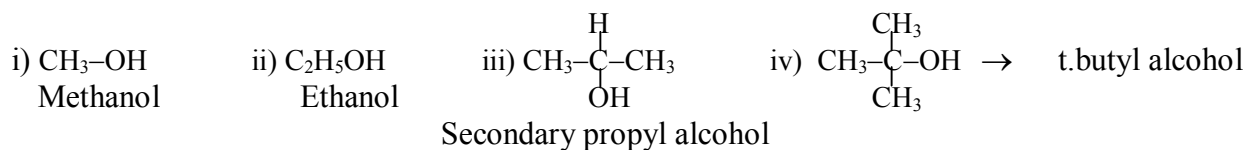
Tertiary alcoholic group → >C-OH

Classification Based on Hybridised state of carbon

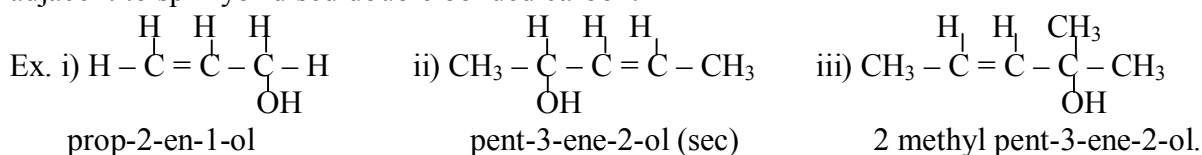
These monohydric alcohols are classified into four types depending upon hybridized state of carbon atom.

A) Alcohols having Sp³ C – OH bond

1) Alkyl alcohols:- In these compounds, hydroxyl group is attached to sp³ hybridised carbon. In fact, these alcohols are saturated alcohols.

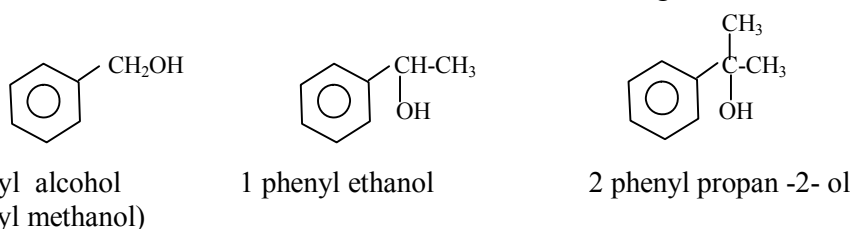


2) Allylic alcohols: In these compounds, hydroxyl group is attached to sp^3 hybridised carbon which is adjacent to sp^2 hybridised double bonded carbon.



3) Benzylic alcohols: These are aromatic alcohols in which hydroxyl group is attached to sp^3 hybridized carbon, which is also attached to a benzene ring.

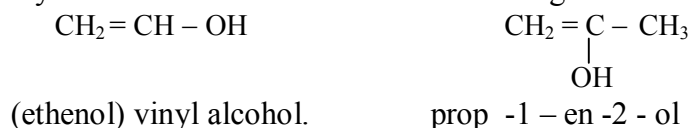
Ex.



B) Alcohols having sp^2 C – OH bond

Vinylic alcohols: In these alcohols, hydroxyl group is attached to sp^2 hybridized (double bonded) carbon atom.

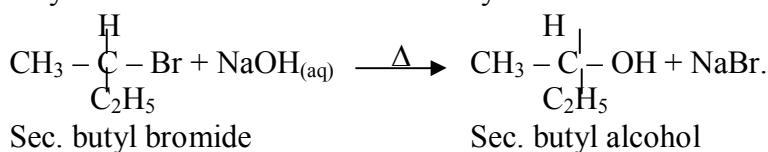
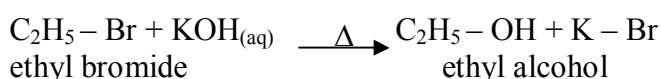
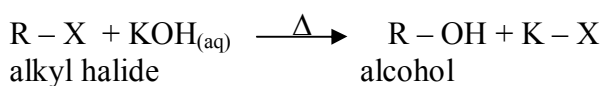
* vinyl alcohol is unsaturated alcohol showing resonance.



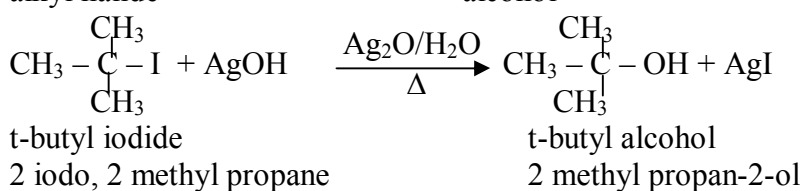
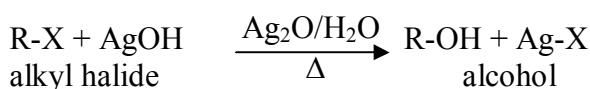
Methods of Preparation of alcohols.

1) By the alkaline hydrolysis of alkyl halides.

When alkyl halide is boiled with either aqueous KOH or aqueous NaOH undergoes alkaline hydrolysis giving alcohols.



Above hydrolysis can also be done by heating alkyl halide with silver oxide suspended in water. First AgOH is formed in situ which brings about hydrolysis.



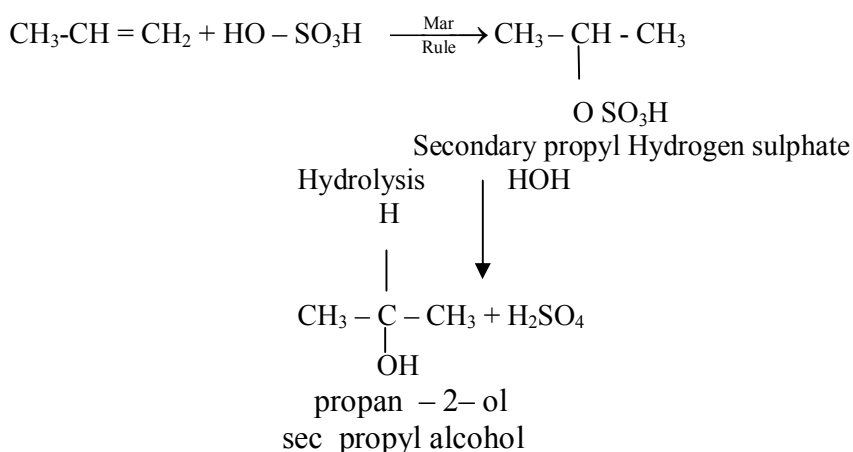
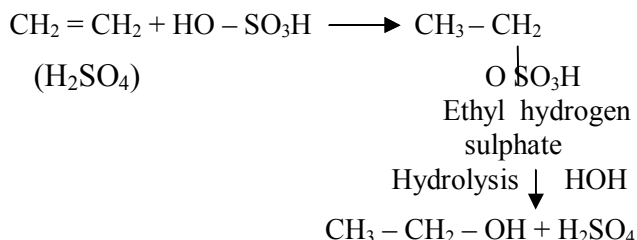
2) By the Hydration of alkenes using concentrated H₂SO₄

Addition of water across double bond of alkenes is called hydration. However, water directly does not react with alkene.

Gaseous alkene is passed through cold and concentrated H₂SO₄. Addition occurs across the double bond giving alkyl hydrogen sulphate. This product is hydrolysed by boiling with water to get corresponding alcohol.

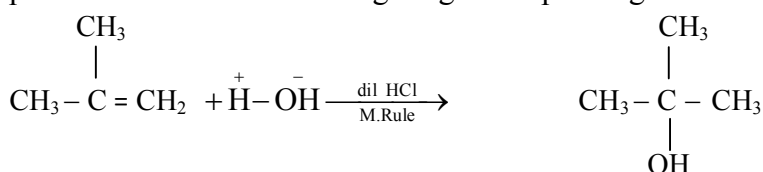
* By this method, methanol cannot be prepared.

* In the case of unsymmetrical alkenes, hydration occurs according to Markownikoff's rule.



* Hydration of branched alkene like isobutylene.

Branched alkenes are highly reactive. For example, isobutylene directly reacts with water in the presence of little dilute HCl giving corresponding alcohol.



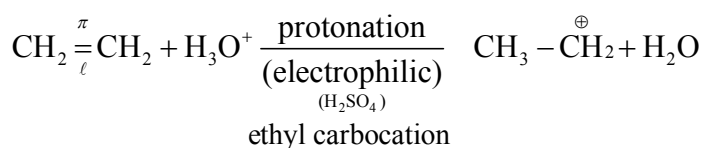
isobutylene / 2- methyl propene

t. butyl alcohol

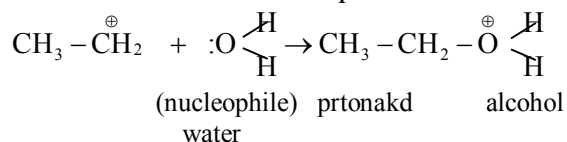
Que. Explain mechanism of hydration of alkenes by H₂SO₄.

Hydration of alkene occurs in three steps:-

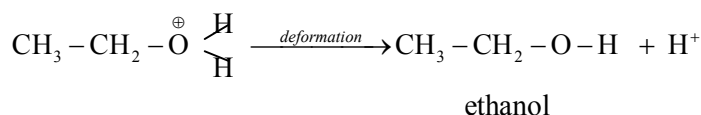
Step (i) : The H⁺ ions from the acid attacks alkene. this electrophilic attack is called **protonation** of alkenes and it results in the formation of carbocation.



Step (ii) : Water behaves as nucleophile and attacks carbocation.



Step (iii) : Finally, deprotonation occurs with the formation of alcohol.

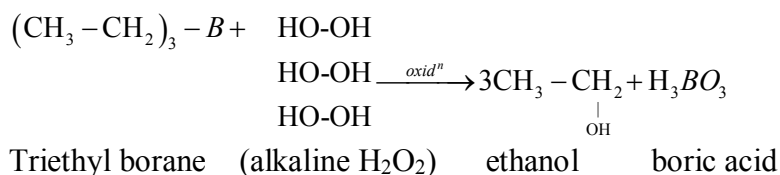
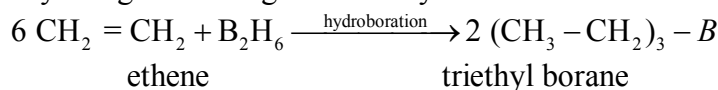


3) By the Hydration of alkenes using diborane (Hydroboration – oxidation process) (B₂H₆)

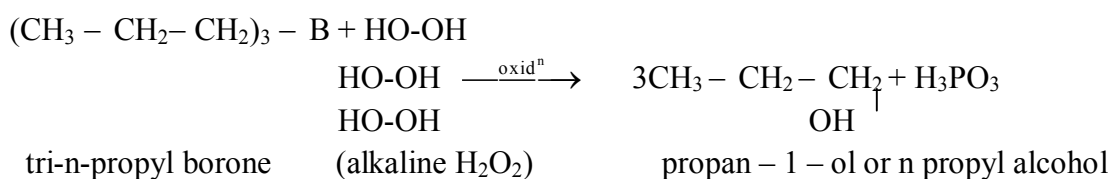
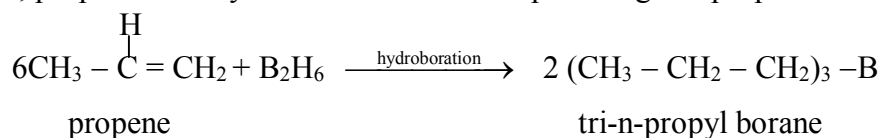
When alkene reacts with diborane, addition occurs across the double bond of alkenes. This gives trialkyl borane. the addition reaction is known as **hydroboration**.

Trialkyl borane is then oxidized by alkaline H₂O₂ giving corresponding alcohol. The complete hydration is called **hydroboration – oxidation process**.

* Hydration by using diborane gives better yield of alcohol than other method.



In the case of **unsymmetrical** alkene hydroboration takes place as per **antimarkownikoff's** rule. Thus, propene after hydroboration oxidation process gives propan – 1 – ol.

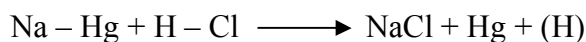
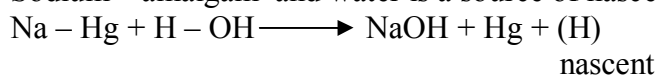


4) By the reduction of carbonyl compounds.

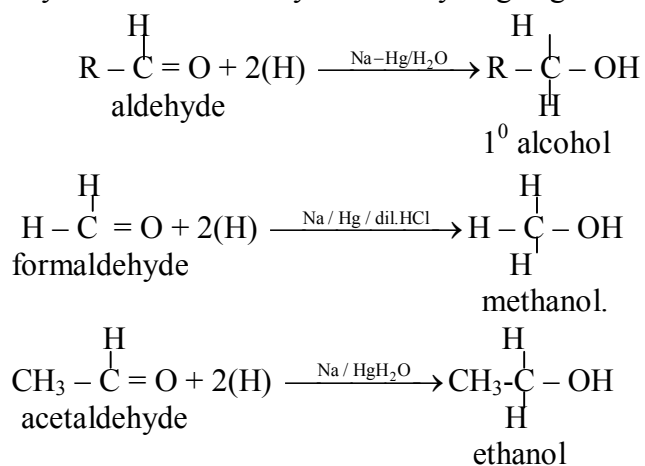
The compounds containing carbonyl group are called **carbonyl compounds**. Ex:- aldehydes, ketones, carboxylic acids and esters are the carbonyl compounds.

A) Reduction of aldehyde/ketones by nascent hydrogen (Reduction by sodium amalgam and water or sodium – amalgam with dil HCl.)

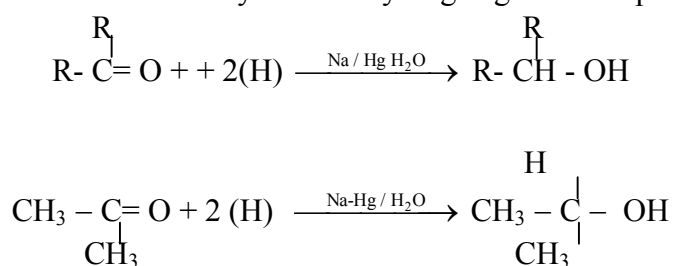
Sodium – amalgam and water is a source of nascent hydrogen.



Aldehydes on reduction by nascent hydrogen give corresponding primary alcohols.



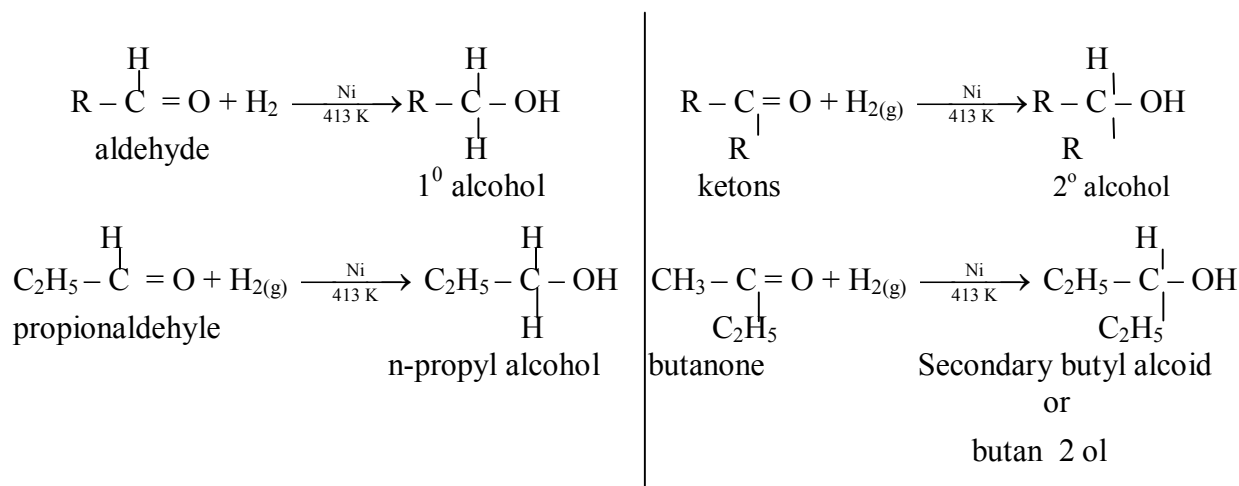
Ketones on reduction by nascent hydrogen give corresponding secondary alcohols.



* By reduction method, tertiary alcohols cannot be prepared.

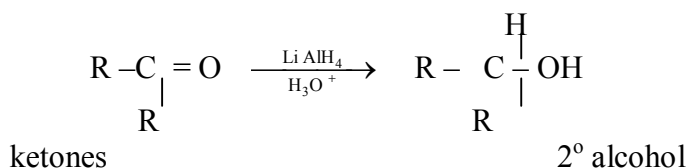
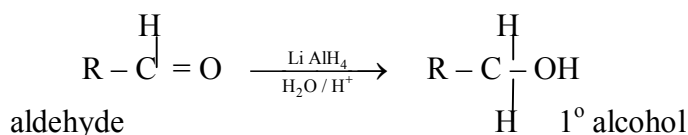
(B) Catalytic reduction of aldehydes and ketones/Catalytic hydrogenation.

Aldehydes and ketones can be reduced by hydrogen gas in the presence of nickel powder at 413 K (platinum or palladium may be used instead of nickel). Aldehydes on catalytic reduction give primary alcohols while ketones give secondary alcohols.

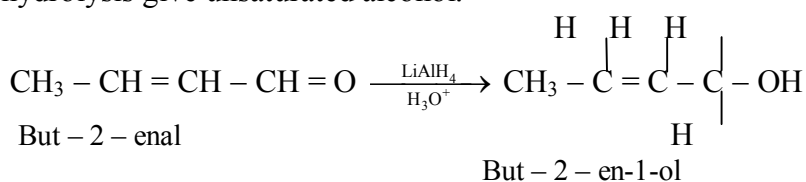


(C) Reduction of aldehydes and ketones by LiAlH₄. (Lithium aluminium hydride) (specific reducing agent)

Aldehydes and ketones can be reduced by LiAlH₄. First the reagent adds on the carbonyl group and the product undergoes acid hydrolysis. Aldehydes give primary and ketones give secondary alcohols.

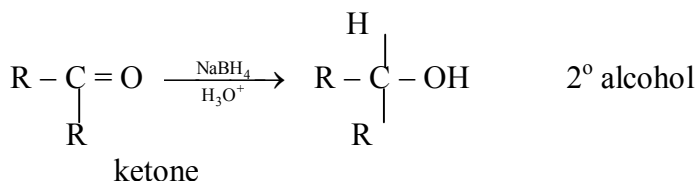
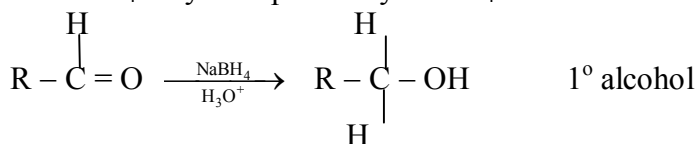


But LiAlH_4 is a specific reducing agent of carbonyl group. It cannot reduce unsaturation of hydrocarbon part. Thus unsaturated aldehyde or ketone on treatment with LiAlH_4 followed by acid hydrolysis give unsaturated alcohol.



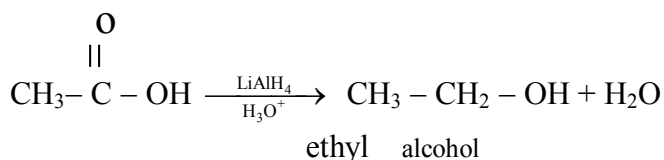
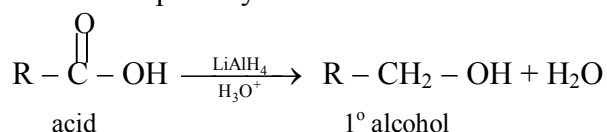
* LiAlH_4 is a very costly reagent and it has explosive reaction with water and alcohol.

* So LiAlH_4 may be replaced by NaBH_4 i.e. sodium boro hydride, which has similar action.



(D) Reduction of carboxylic acids by LiAlH_4

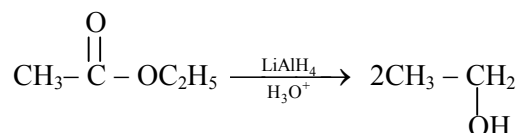
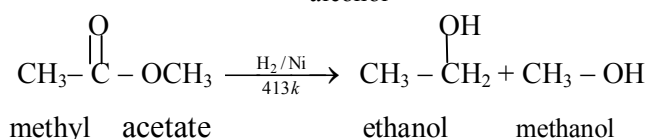
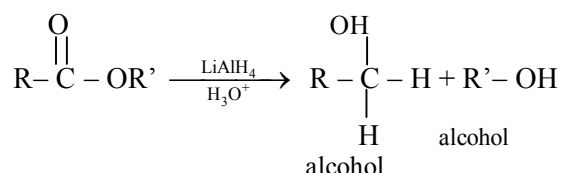
Carboxylic acids are not easily reduced. On reduction by LiAlH_4 , followed by hydrolysis, acids are converted into primary alcohols.



* But LiAlH_4 is very costly. So acids are first converted into esters which are catalytically reduced by Ni/Pt and H_2 gas at 413K.

(E) Reduction of esters

Esters can be reduced catalytically (H_2/Ni) or by LiAlH_4 followed by hydrolysis. On reduction esters may give mixtures of two alcohols or sometimes single alcohol.



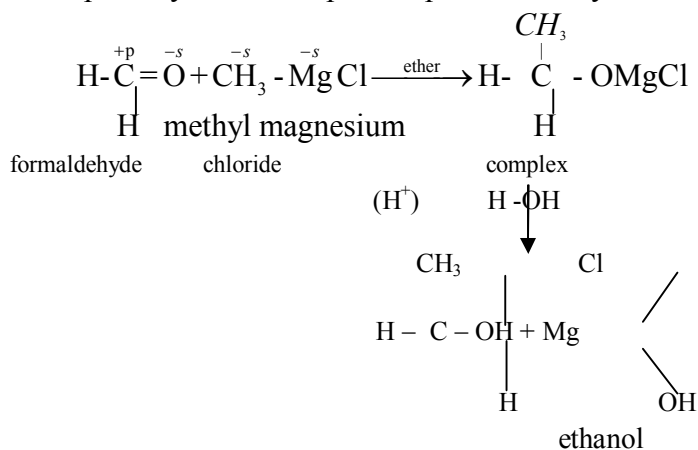
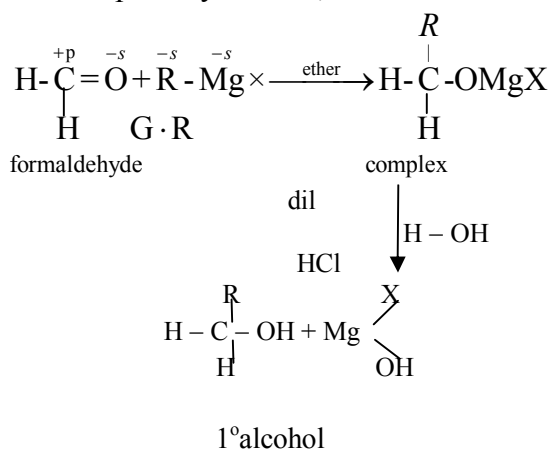
5) Preparation of alcohols from G.R. using carbonyl compounds

a) Preparation of primary alcohols (Formaldehyde+G.R.):

G. R. reacts with formaldehyde in ether medium giving addition product. This addition complex on acid hydrolysis gives corresponding primary alcohols.

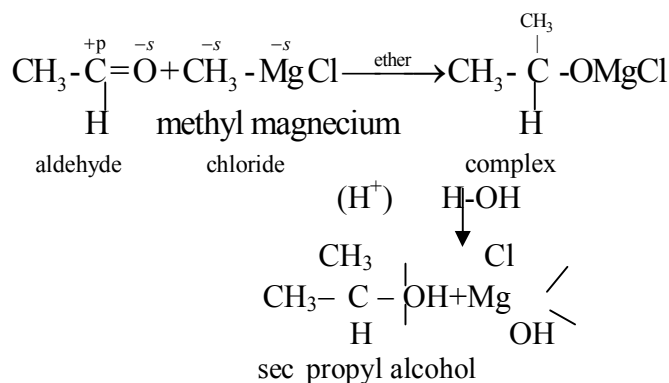
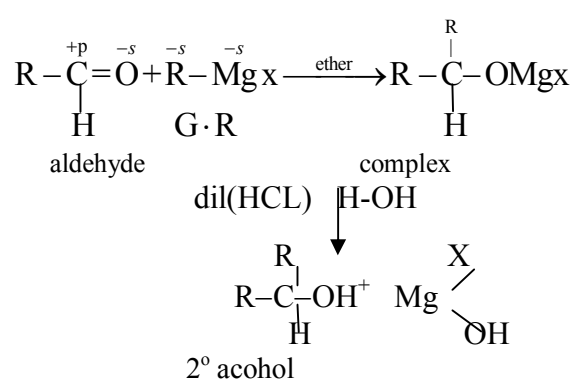
* By using G.R. Methanol cannot be obtained. Formaldehyde on reduction may give methanol.

* In the primary alcohol, 'R' comes from G.R. So the primary alcohol depends upon G.R. only.



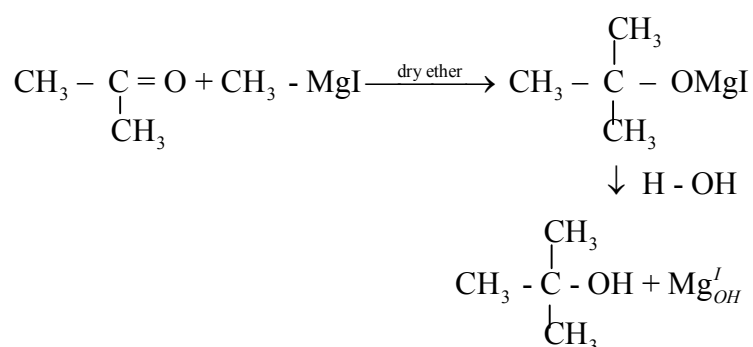
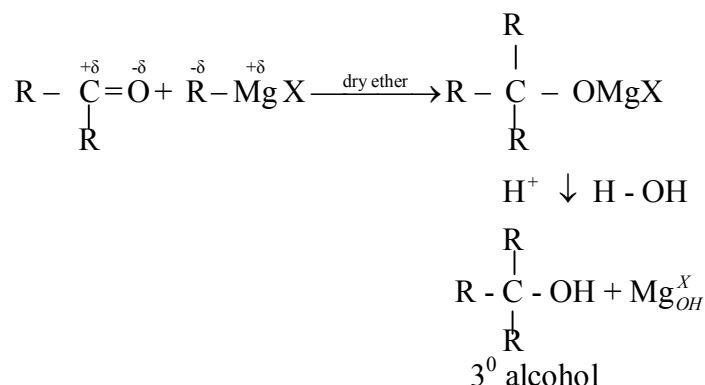
b) Preparation of secondary alcohols (Other aldehydes + G.R.):

G.R. react with aldehydes other than formaldehyde in ether medium giving a complex. This complex on acid hydrolysis gives corresponding secondary alcohol.



c) Preparation of tertiary alcohols (Ketones+G.R.):

G.R. reacts with **ketone** in the ether medium giving addition complex. This complex on hydrolysis gives tertiary alcohols.



Nature of O – H bond in alcohols

In alcohol oxygen is in sp^3 hybridised state. It forms one sigma bond with carbon by $\text{sp}^3 - \text{sp}^3$ overlap. Oxygen forms another sigma bond with hydrogen by $\text{sp}^3 - \text{s}$ overlap. The geometry of alcohol molecule is tetrahedral or angular geometry having a bond angle of 109° . Also oxygen carries two lone pairs of electrons.

Oxygen is more electronegative than hydrogen. It attracts shared electron pair towards itself and gets partial negative charge. Hydrogen gets equivalent partial positive charge. Thus the O – H bond in alcohol becomes polar covalent.

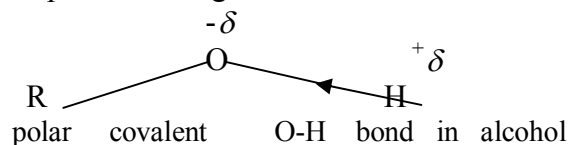
Physical properties of alcohols

1. Alcohols are neutral organic compounds (neither acidic nor basic to litmus).
2. Lower members upto C_{10} are colourless liquid having typical odour. Higher members are solids.
3. Boiling points of alcohols are higher than corresponding other organic compounds. This is due to **intermolecular H – bonding**.
* In the isomeric alcohols, the boiling point becomes less as the branching increases. Because the branching decreases vander Waal's forces. Boiling point $\rightarrow (1^\circ) > (2^\circ) > (3^\circ)$
4. Lower alcohols are highly soluble in water.
5. Methanol is the most toxic (poisonous) alcohol. Ethanol ($\text{C}_2\text{H}_5\text{OH}$) is used in manufacturing of alcoholic drinks (hard drinks)
* Toxicity of alcohols goes on decreasing as the number of carbon atoms are increased.

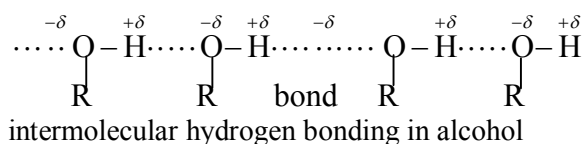
Hydrogen bonding in alcohols:-

Que. why are the boiling points of alcohols higher than other organic compounds?

In alcohols, O – H is polarized. More electronegative oxygen gets partial negative charge while hydrogen gets partial positive charge.



The electronegative oxygen of one molecule & electropositive hydrogen of adjacent molecule develop a force of attraction called as hydrogen bond. Due to the intermolecular H – bonding, alcohol molecules are associated and get liquid state.



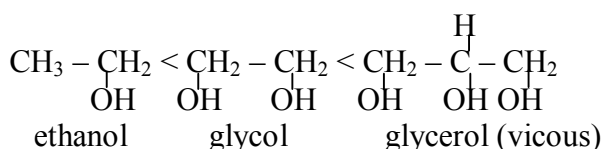
At the time of boiling, some energy is needed for breaking intermolecular hydrogen bonding. Due to this, boiling point of alcohol increases.

Such hydrogen bonding is absent in other organic compounds such as aldehydes, ketones, ethers, etc. So such compounds have low boiling point.

* The boiling point of alcohols are increasing with the increase in molecular weight because Vander Waal's forces are increasing.

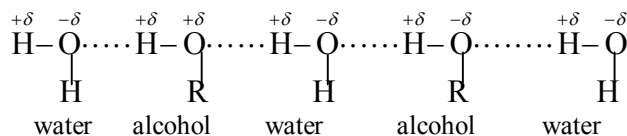
Boiling point order $\rightarrow \text{CH}_3\text{OH} < \text{C}_2\text{H}_5\text{OH} < \text{C}_3\text{H}_7\text{OH} < \text{C}_4\text{H}_9\text{OH}$

* The boiling point and viscosity goes on increasing with the increase in number of hydroxyl group.



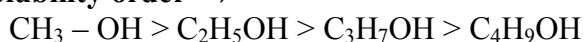
Que. Why are lower alcohols water soluble?

When alcohol is added to water, hydrogen bonds are formed between these two compounds. Thus alcohol molecules get the place in between water molecules. Therefore lower alcohols are water soluble.

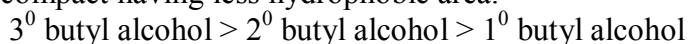


In higher alcohols, size of the alkyl group increases. This hydrocarbon part is water repellent or hydrophobic. Therefore, solubility of alcohol decreases with increasing number of carbon atoms.

Solubility order \rightarrow

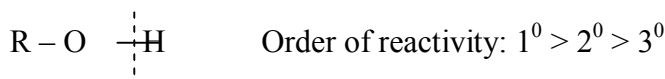


* In isomeric alcohols, the tertiary alcohols are most soluble. Due to branching, the hydrocarbon part is compact having less hydrophobic area.

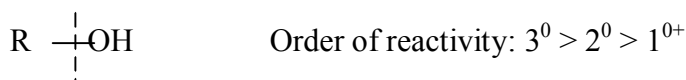


Chemical Properties:

Alcohol can give two types of reaction. The reactions in which only H-atom of alcoholic group is involved, follows S_N^2 path. So primary alcohols are most reactive.

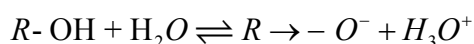


The reactions in which complete $-OH$ group is replaced follows S_N^1 mechanism i.e. carbonium ion formation. So tert. alcohol is most reactive.



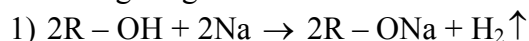
1) Acidic nature of alcohols

Alcohols are practically neutral. In water they have minimum tendency to ionize & liberate H^+ ions because the alkoxide ion is unstable due to +I effect.



Unstable

So above equilibrium is shifted in backward direction. However alcohols react with metals liberating H_2 gas. This indicates their acidic nature.

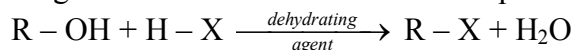


* The order of reactivity in this reaction will be $1^0 > 2^0 > 3^0$.

* This reaction indicates acidic nature of alcohols. But alcohols are less acidic than water.

2) Reaction with halogen acids (HCl, HBr, HI)

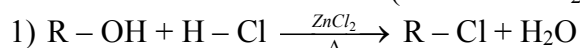
Halogen acids react with alcohol in the presence of dehydrating agent giving alkyl halides.



a) Reaction with concentrated HCl

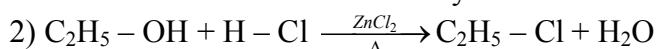
Lucas's Reagent = Concentrated HCl + $ZnCl_2$ (anhydrous)

A Primary or secondary alcohol when heated with Lucas's reagent give corresponding alkyl chlorides. They are insoluble in the medium due to which turbidity appears. A tertiary alcohol directly reacts with concentrated HCl (without $ZnCl_2$) giving t-alkyl halide.



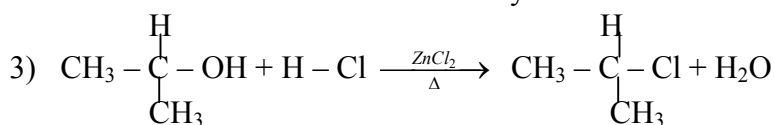
alcohol

alkyl chloride



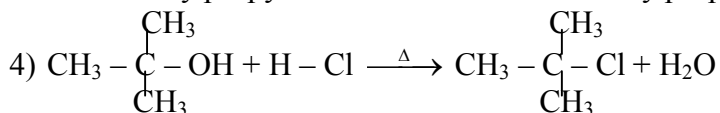
ethanol

ethyl chloride



secondary propyl alcohol

secondary propyl chloride



t-butyl alcohol

t-butyl chloride

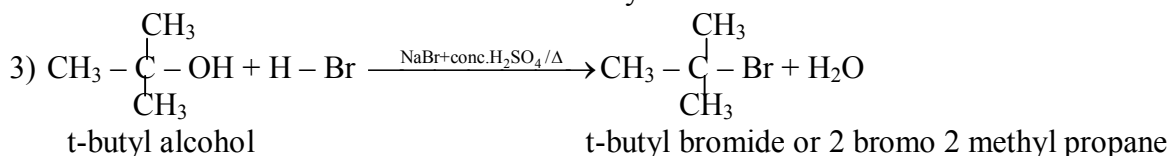
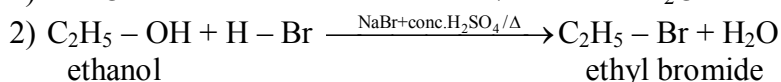
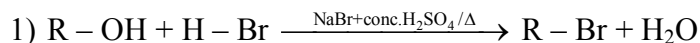
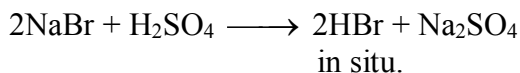
* As complete $-OH$ group is replaced, order of reactivity will be $3^0 > 2^0 > 1^0$.

* Alkyl chlorides are insoluble in the medium producing turbidity. A tert. alcohol gives the turbidity instantly. A secondary alcohol produces turbidity after sometime. But in primary alcohol turbidity

appears after a very long time. Thus **by using time factor**, 1^o, 2^o, 3^o alcohols can be distinguished with the help of Luca's reagent.

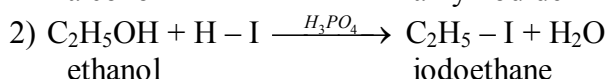
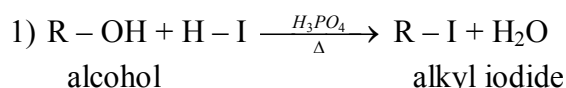
b) Reaction with H-Br or NaBr + concentrated H₂SO₄.

When alcohol is heated with sodium bromide and concentrated H₂SO₄ corresponding alkyl bromides are formed. During the reaction H-Br is formed 'in situ'. Also concentrated H₂SO₄ acts as dehydrating agent.



c) Reaction with H-I

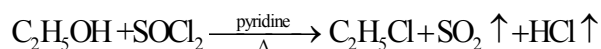
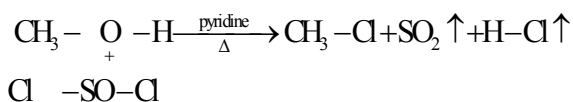
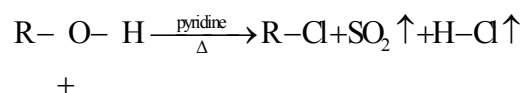
When alcohol is heated with hydrogen iodide in the presence of phosphoric acid (dehydrating agent) corresponding alkyl iodides are formed.



3) Reaction with thionyl chloride

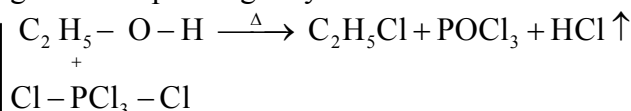
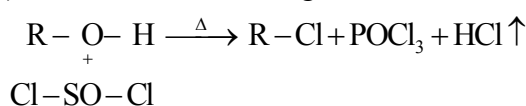
When alcohol is refluxed with thionyl chloride in the presence of pyridine corresponding alkyl chlorides are formed.

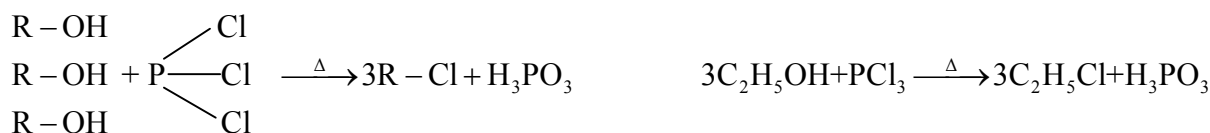
* In this reaction the side products are easily removed. SO₂ gas is evolved. H-Cl combines with pyridine forming a salt.



4) Reaction with Phosphorous Chlorides:

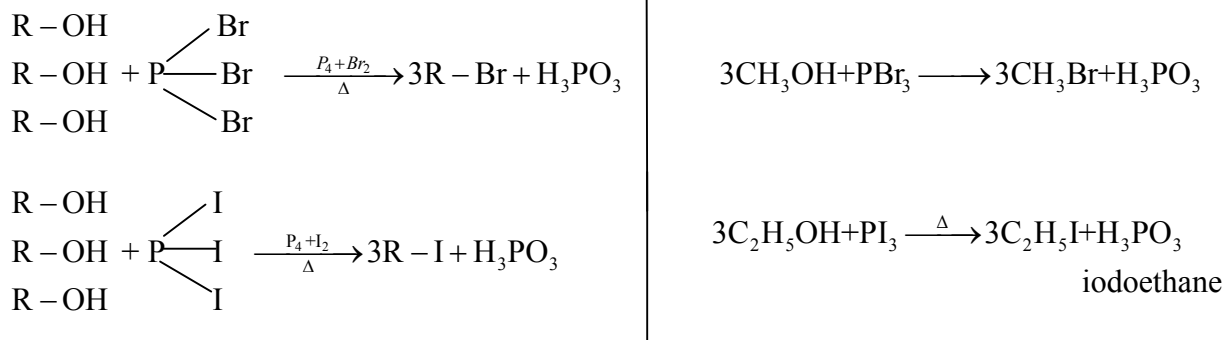
i) Alcohols on refluxing with either PCl₅ or PCl₃ give corresponding alkyl chloride.





5) Reaction with PBr₃ or PI₃

Alcohols react with red phosphorous & Br₂ or red phosphorous and I₂ giving alkyl halide like bromides or iodides respectively.



6) Dehydration of alcohols giving alkenes:

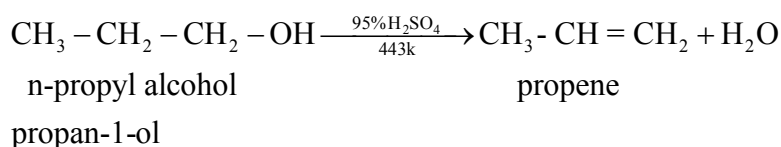
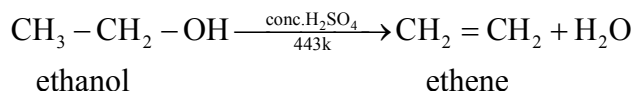
Removal of water molecule from alcohol is called dehydration. When alcohol is heated with a dehydrating agent such as H₂SO₄, Al₂O₃ or P₂O₅, dehydration takes place from the same molecule producing alkene. (H & OH are eliminated from adjacent carbon). This intramolecular dehydration is elimination reaction.

a) Dehydration of primary alcohol:

When a primary alcohol is heated with large **excess of concentrated H₂SO₄**, as dehydrating agent, at 443 K alkenes are formed.

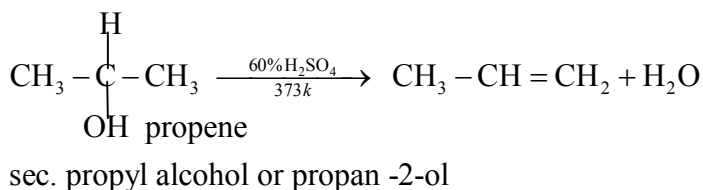
* Concentrated H₂SO₄ = 95% H₂SO₄

* Methanol cannot undergo intramolecular dehydration.



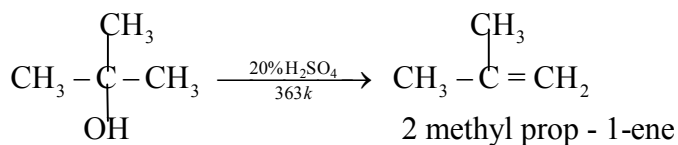
b) Dehydration of secondary alcohol:

When a secondary alcohol is heated with dehydrating agent like 60% H₂SO₄ at 373 K dehydration occurs with the formation of alkene.



c) Dehydration of t-alcohol:

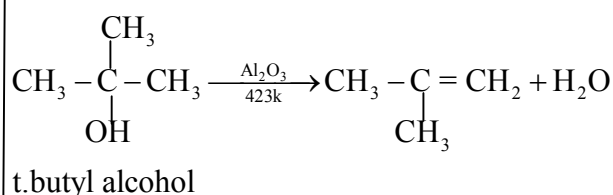
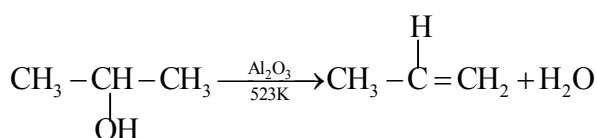
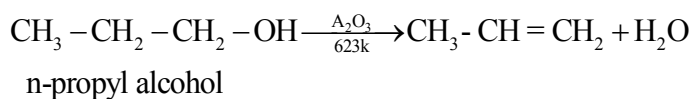
A tertiary alcohol is most easily dehydrated by 20% H₂SO₄ at 363K giving alkene.



t.butyl alcohol or 2. methyl propan 2-ol

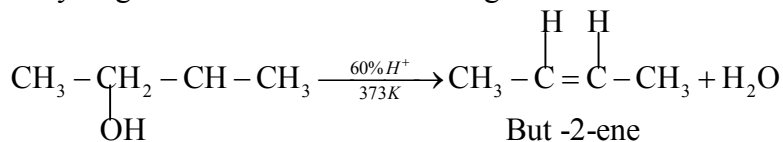
* The **ease of dehydration of alcohols is in the decreasing order of 3° > 2° > 1°**. Because during the reaction complete OH group is involved.

* Dehydration of alcohol can also be done by passing their vapours over red hot alumina (Al₂O₃) with the formation of alkenes.



*** Saytzeff's Rule:**

If an alcohol on dehydration give different alkenes then saytzeff's Rule is applied. The rule states that during elimination reaction more alkylated alkenes are formed. In other words the ease of removal of hydrogen atoms is in the decreasing order of 3°H > 2°H > 1°H.



Butan-2ol

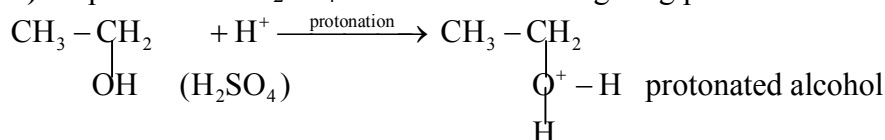
major

Sec-butyl alcohol

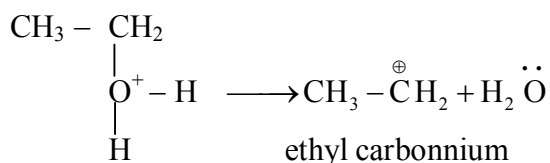
Que. Explain mechanism of dehydration of alcohols in acidic medium.

Dehydration of alcohol occurs in three steps.

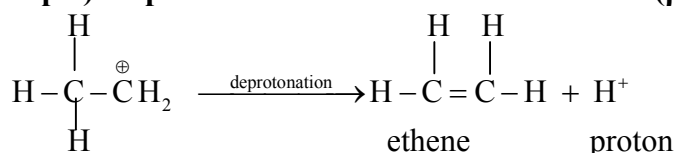
Step 1) A proton from H₂SO₄ reacts with alcohol giving protonated alcohol.



Step 2) Protonated alcohol loses water molecule with the formation of carbonium ion.



Step 3) A proton is lost from beta carbon atom (β -carbon) with the formation of alkene.



- * During the reaction carbonium ion is formed, therefore tertiary alcohols are most easily dehydrated.
- * Alkenes formed during dehydration should be removed from the reaction vessel to prevent backward reaction. (hydration of alkene).

7) Oxidation of alcohol:

Distinguishing reaction of 1^o, 2^o, 3^o alcohol.

Alcohols on oxidation give different products therefore oxidation is a distinguishing reaction of 1^o, 2^o, 3^o alcohols. Oxidation is carried out by using oxidizing agents which can supply nascent oxygen. Following are the oxidizing agents (O.A) in the increasing order of their strength.

1) P.C.C. (Pyridinium chloro chromate)

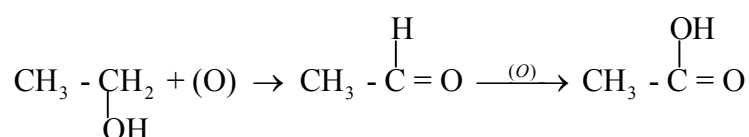
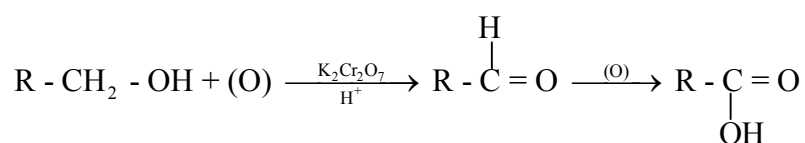
OR

P.D.C. (Pyridinium dichromate)

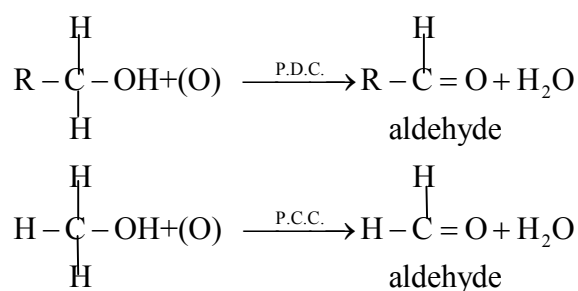
- 2) Alkaline potassium permanganate $\text{KMnO}_4/\text{NaOH}$
- 3) Acidified potassium dichromate $\text{K}_2\text{Cr}_2\text{O}_7/\text{dil H}_2\text{SO}_4$.
- 4) Acidified potassium permanganate $\text{KMnO}_4/\text{dil H}_2\text{SO}_4$.
- 5) Chromic oxide CrO_3 .
- 6) Concentrated nitric acid HNO_3 .

a) Oxidation of 1^o alcohol:

Primary alcohols are **most easily oxidized**. On oxidation a primary alcohol first gives **aldehyde** which on further oxidation give corresponding carboxylic acid.

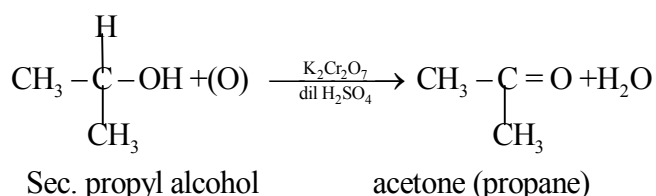
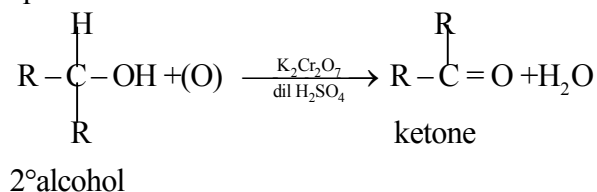


* If a primary alcohol is oxidized by mild oxidizing agent such as P.C.C. or P.D.C. then oxidation stops in the first step giving aldehyde as the final product.



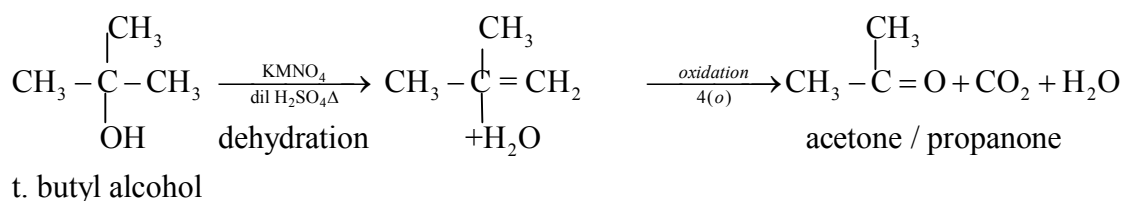
b) Oxidation of 2^o alcohol:

When a secondary alcohol is oxidized by acidified potassium dichromate it gives ketone containing **same number of carbon atom**, as that of alcohol. Further oxidation of ketone does not occur as it requires drastic conditions.

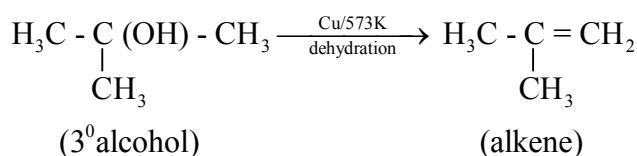
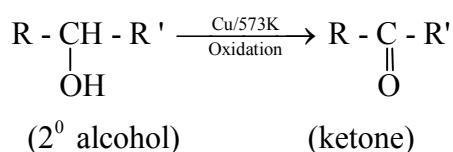
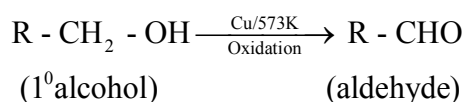


c) Oxidation of 3^o alcohols:

A tertiary alcohol is highly resistant to oxidation. It can be oxidized by stronger oxidizing agent such as acidified KMnO₄ or CrO₃. A tertiary alcohol first undergoes dehydration giving an alkene. This alkene is then oxidized giving **ketone containing less number of carbon atoms**.

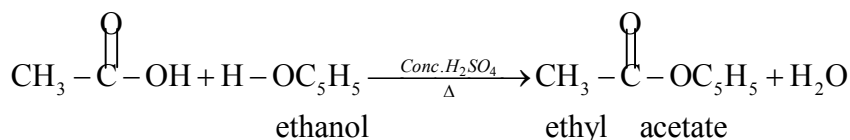
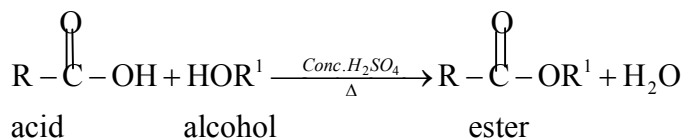


*** Alcohols are oxidized by dehydrogenation by passing their vapours over red hot copper metal at 573 K.**



8) Esterification: (Formation of esters from carboxylic acid & alcohol)

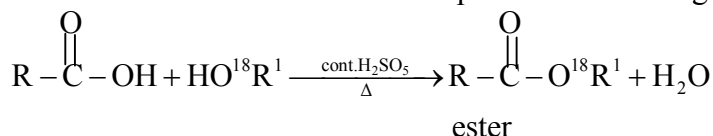
A carboxylic acid when heated with alcohol in the presence of dehydrating agent such as concentrated H_2SO_4 esters are formed. This reaction is called esterification.



* Tracer Technique:

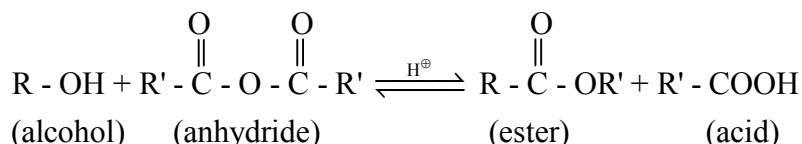
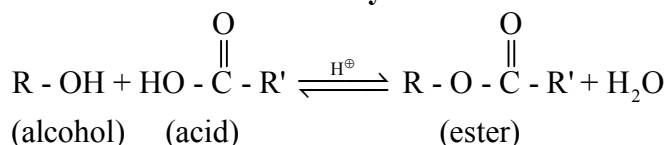
By using radioactive isotope of oxygen (O^{18}) mechanism of esterification is confirmed. It is called Tracer Technique. Because radioactive isotopes can be traced.

* During esterification, H from alcohol and OH from carboxylic acid are removed in the form of water molecule. Because radioactive O^{18} present in alcohol goes in ester molecule.



* Acylation (acetylation of alcohols)

Alcohols react with either acid anhydrides or acid chlorides giving corresponding esters



Uses of Methanol:

1. Being liquid, methanol is used as a solvent for organic solutes like fats, oils, cellulose, gum, resin.
2. It is used in dry cleaning of clothes.
3. Methanol is used in denaturing of spirit.

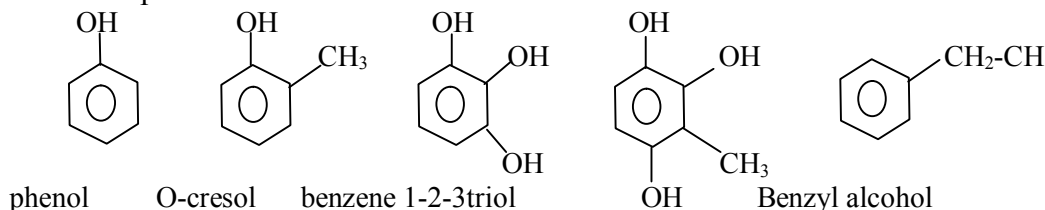
Uses of Ethanol:

1. Ethanol is a liquid and used as solvent for organic compounds such as oils, fats, dyes.
2. Mixture of petrol and ethanol is called **gasohol**. It is used as fuel for automobiles.
3. Ethanol is used as an antiseptic in mouthwash.
4. Spirit is mixture of ethanol (96%) and water (4%) which is then denatured by methanol, to make it unfit for drinking purpose.
5. Ethanol is used in the preparation of chloroform, Iodoform, Acetaldehyde, acetic acid, ether etc.
6. Ethanol is the constituent of alcoholic or hard drinks.
7. Ethanol may be used as antifreeze agent, in car engines as its freezing point is very low.

Phenols

Phen = benzene (Greek) **ol** = hydroxyl group

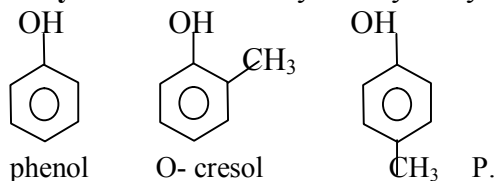
Aromatic hydroxy derivatives in which the hydroxyl group is directly attached to the benzene ring are called phenol.



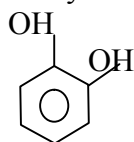
Classification:

Phenols are classified on the basis of hydroxyl group directly attached to the benzene nucleus.

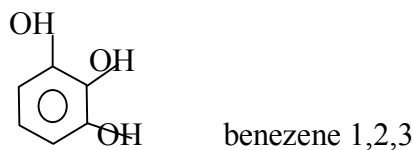
1) Monohydric Phenol: Only one hydroxyl group is directly attached to benzene.



2) Dihydric Phenol: Two hydroxyl groups directly attached to benzene.



3) Trihydric Phenol:



PHENOL or Carboic acid C_6H_5OH or $Ar - OH$

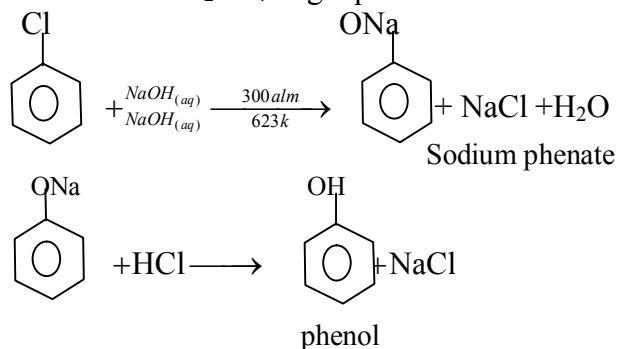
* Phenol also occurs is Black oil.

Methods of Preparation of Phenol:

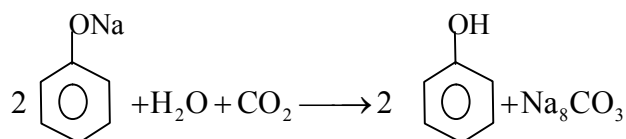
1) From Chlorobenzene :

Dow's Process:

In the Dow's process, gaseous chlorobenzene is hydrolyzed by caustic soda solution at 623K under 300 atm pressures. Sodium phenate is formed. This compound is decomposed by using dilute mineral acid like H-Cl or H_2SO_4 to get phenol. But due to **drastic conditions**, Dow's process is not in use.



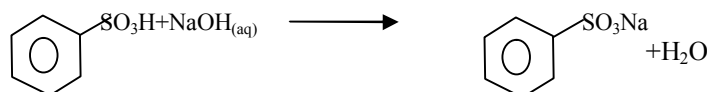
* Sodium phenate can also be decomposed by passing $\text{CO}_{2(g)}$ in its aqueous solution.



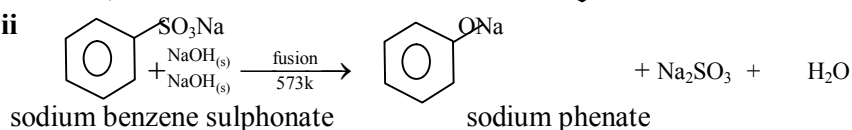
2) From benzene sulphonic acid:

By this method phenol is obtained in three steps. In the first step, benzene sulphonic acid is neutralized by aqueous caustic soda solution to get a salt called sodium benzene sulphonate. In the second step, sodium benzene sulphonate is **fused** with solid caustic soda at 573K. This gives sodium phenate. Finally in the third step, sodium phenate is decomposed by dilute H_2SO_4 or dil HCl or CO_2 .

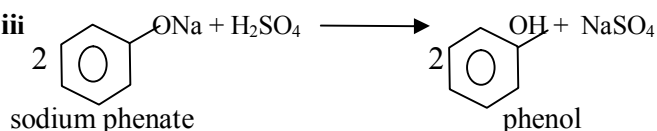
step i



step ii



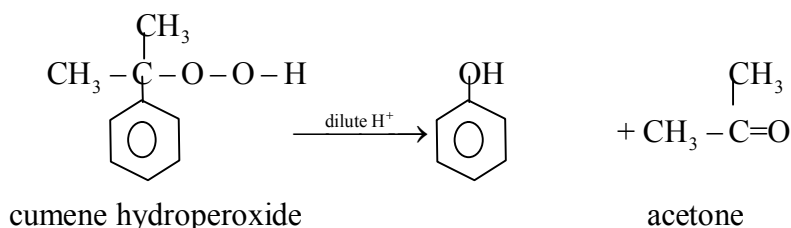
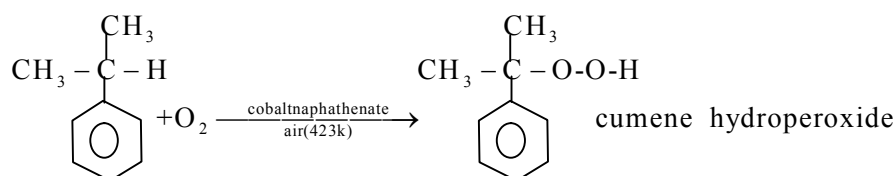
step iii



3) By auto-oxidation of Cumene (isopropyl/benzene)

In this method cumene is suspended in sodium carbonate solution. A catalyst called cobalt naphthenate is added in the solution. Then air is bubbled through this solution at 423K. Cumene undergoes oxidation giving cumene hydroperoxide. In the second step, this cumene hydroperoxide is decomposed in the presence of any dilute mineral acid to get phenol. Acetone is obtained as a side product. This is industrial preparation of phenol.

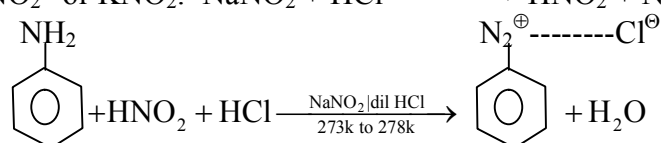
step i



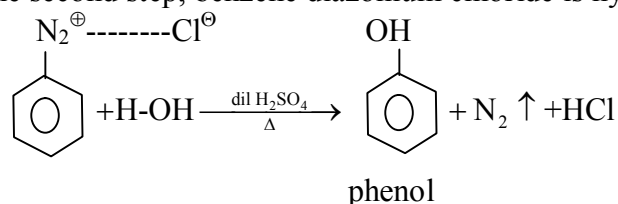
4) Preparation of phenol from aniline (Diazotization of aniline):

Aniline reacts with nitrous acid in the presence of dil HCl giving benzene diazonium chloride at **273K to 278K (cold)**. The process is called **diazotization**.

❖ Nitrous acid is not stored in laboratory. It is obtained in situ by the action of dil HCl on either NaNO_2 or KNO_2 . $\text{NaNO}_2 + \text{HCl} \longrightarrow \text{HNO}_2 + \text{NaCl}$

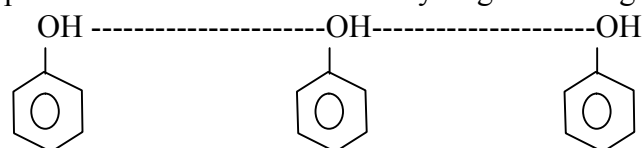


In the second step, benzene diazonium chloride is hydrolysed by using dil H_2SO_4 to get phenol.



Physical Properties:

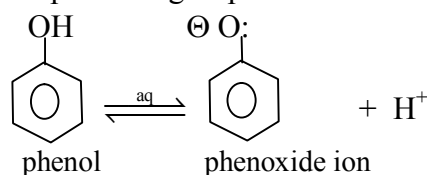
1. Phenol is a low melting solid with M.P of 315K. It boils at 455K. The higher boiling point of phenol is due to intermolecular hydrogen bonding.



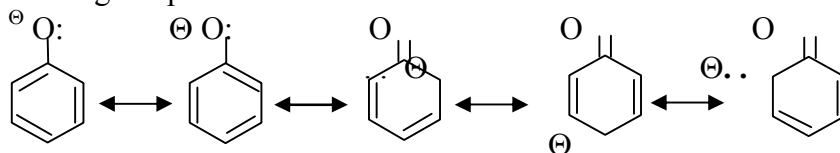
2. Phenol is a crystalline solid and highly corrosive.
3. Phenol has typical phenolic odour.
4. Phenol is sparingly soluble in water. Its aqueous solution turns blue litmus red. However, phenol is highly soluble in the organic solvent such as ethers, alcohols, CCl_4 etc.
5. When exposed to air phenol turns pink. Due to its oxidation, forming quinone.

Acidic nature of phenolic group:

The phenolic group is acidic and can liberate H^+ ions giving a phenoxide ion.

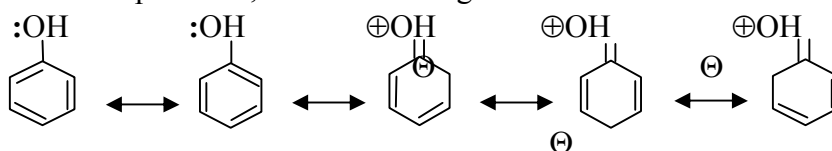


The phenoxide ion is highly stabilized due to five resonating structures. In these structures unit negative charge of phenoxide ion is delocalized.



Highly stable resonance structure of phenoxide ion

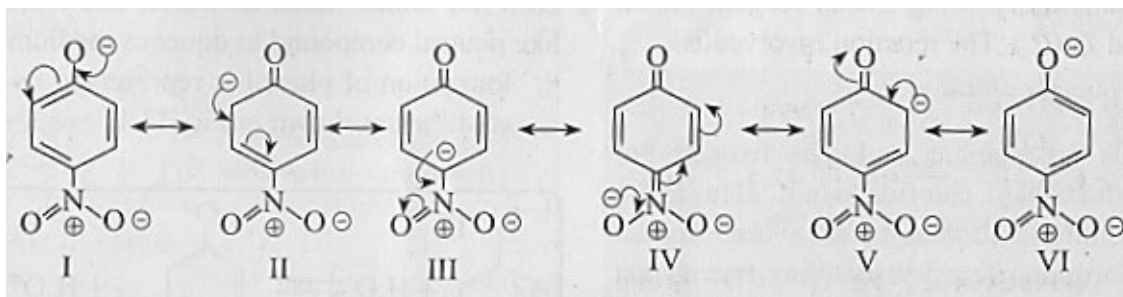
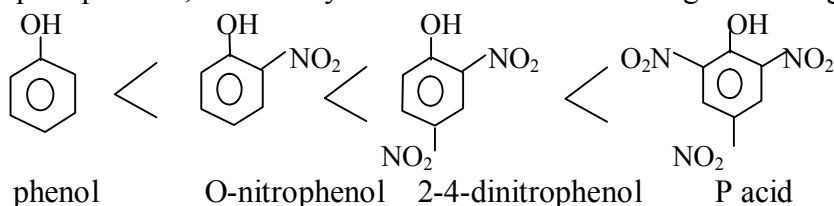
Resonance is also shown by neutral phenol molecule. It also has five resonating structures. But due to presence of bipolar ion, these resonating structures are less stable than those of phenoxide ion.



Resonating Structures of phenol

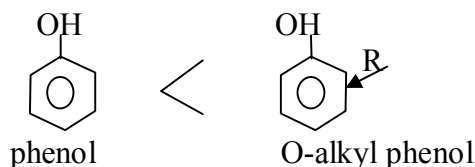
In alcohols, alkyl radical is electron releasing i.e. $\text{R} \rightarrow \text{O}-\text{H}$. Also there is no resonance. So alcohols cannot liberate H^+ ions and behave as neutral compounds.

* If electron withdrawing group such as nitro group (NO_2) or cyanide group (CN^-) are present on ortho or para position, the acidity increases. Because the negative charge is further stabilized by this groups.

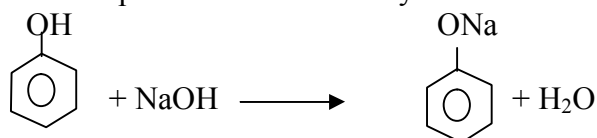


* If the nitro group is at meta position, acidity is not affected.

* If the electron releasing groups such as R , $\ddot{\text{N}}\text{H}_2$, Cl , etc are at ortho or para position acidity decreases.



* Acidic nature of phenol is confirmed by neutralization reaction with alkly.



Chemical Properties of Phenol:

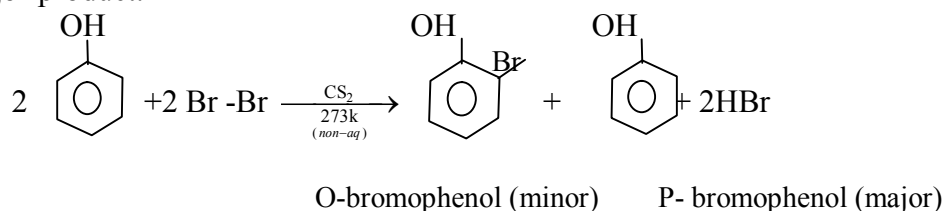
Being aromatic, phenol undergoes electrophilic substitution reactions. The phenolic group is ortho-para directing. So electrophilic substitution take place at ortho or para position only.

1) Bromination of Phenol:

Bromination is a electrophilic substitution in which hydrogen atom of the benzene nucleus in phenol is replaced by bromine. Phenol undergoes bromination under two conditions.

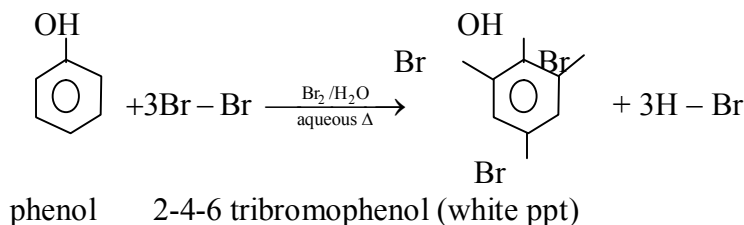
a) Bromination in non-aqueous medium like CS_2 or CCl_4 .

Carbolic acid reacts with bromine in the presence of non-aqueous solvent such as CS_2 or CCl_4 at 273 K. Bromination takes place either at ortho position or at para-position. But p-bromophenol is a major product.



b) Bromination in aqueous medium (Reaction of phenol with Bromine water)

Bromine water is a strong brominating agent. Reaction occurs at three position simultaneously (both ortho and para). This gives a white ppt of 2,4,6 tribromophenol. During the reaction, reddish brown coloured bromine water is decolourised. So this reaction may be used as laboratory test for phenol.

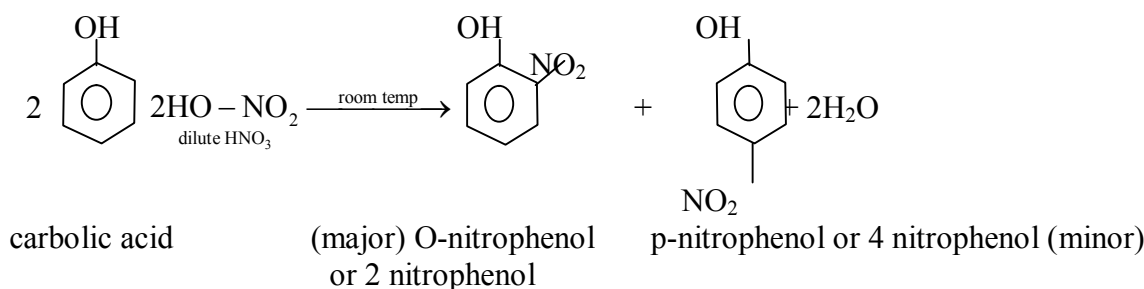


2) Nitration of Phenol:

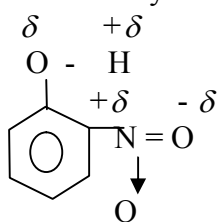
Electrophilic substitution in which hydrogen atom of the benzene nucleus in phenol are replaced by nitro group is called nitration. Phenol undergoes nitration under two conditions.

a) Nitration by dil HNO_3 :

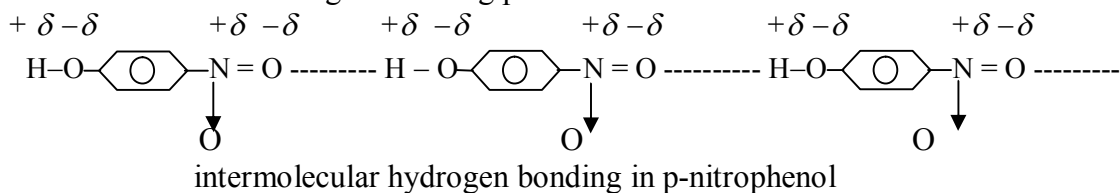
Phenol reacts with dil HNO_3 at room temperature. Nitration takes place only at single position. This give mixture of O-nitrophenol and p-nitrophenol. But O-nitrophenol is a **major product**.



* O-nitrophenol has intramolecular hydrogen bonding. This gives extrastability to the molecule. Therefore O-nitrophenol is major product. But the melting point and the boiling point of such compounds are very less. They become volatile.



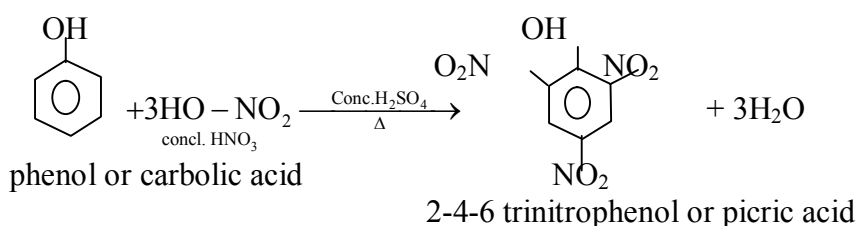
* In p-nitrophenol, there is intermolecular hydrogen bonding. It does not give stability to the molecule. But the melting and boiling points are increased.



* Due to large difference in boiling point, O-nitrophenol & p-nitrophenol are easily separated by distillation.

b) Nitration of phenol by nitrating mixture (Concentrated HNO₃ + Concentrated H₂SO₄)

When phenol is heated with nitrating mixture (Concentrated HNO₃ + Concentrated H₂SO₄), nitration occurs at three positions simultaneously. This gives 2,4,6 trinitrophenol or picric acid. It is **yellow coloured solid** and used as an explosive.



* During nitration the electrophile is nitronium ion i.e. NO_2^+

3) Sulphonation of phenol:

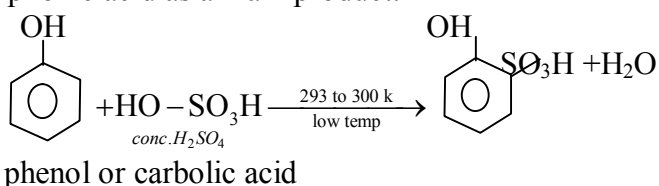
* During suphonation the electrophile is suphonium ion i.e. SO_3H^+

Electrophilic substitution in which hydrogen atoms of the benzene nucleus in phenol are replaced by sulphonic group (-SO₃H) is called sulphonation.

Phenol undergoes sulphonation on treatment with concentrated sulphuric acid. But temperature is the controlling factor.

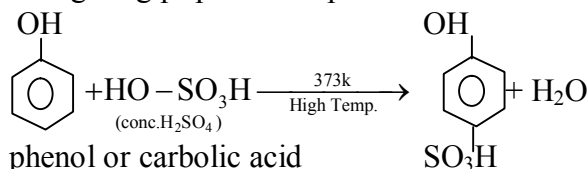
Low Temperature:

Phenol reacts with concentrated H₂SO₄ at low temperature i.e. 298 to 300K giving o-phenol sulphonic acid as a main product.



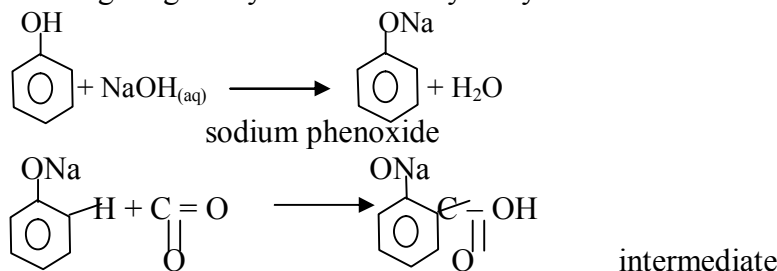
High Temperature:

When phenol is heated with concentrated H₂SO₄ at 373K, sulphonation occurs mainly at para position giving p-phenol sulphonic acid as a main product. (Little O isomer is also formed).



4) Kolbe's Reaction (Formation of salicylic acid from phenol)

In this reaction, Salicylic acid is formed in three steps. In the first step, phenol is neutralized by caustic soda to get sodium phenoxide. It is more reactive than phenol. In the second step, sodium phenoxide reacts with CO₂, forming an intermediate. In the third step, the intermediate is decomposed by dilute HCl giving salicylic acid or O hydroxyl benzoic acid as a major product.



$$\text{C}_6\text{H}_4(\text{ONa})\text{COOH} + \text{HCl} \xrightarrow{\text{(dilute)}} \text{C}_6\text{H}_4(\text{OH})\text{COOH} + \text{NaCl}$$

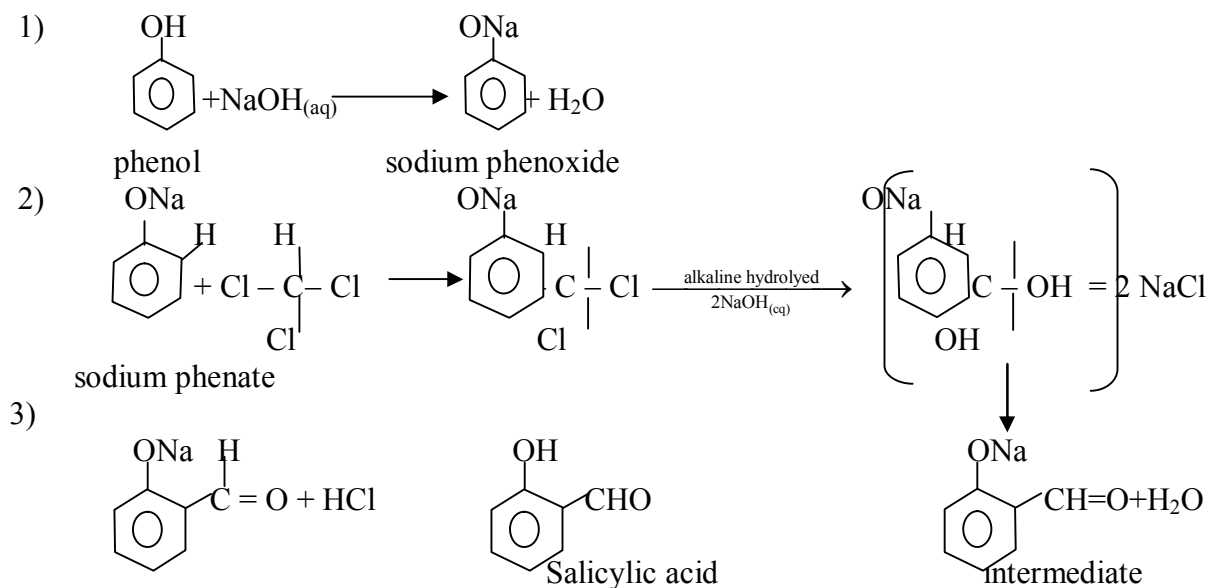
Salicylic acid

Formation of salicylaldehyde from phenol.

Phenol is converted into sodium phenoxide in the first step. This sodium phenate reacts with chloroform (CHCl_3). The product is hydrolysed and finally decomposed by dilute HCl to get salicylaldehyde or O hydroxy benzaldehyde.

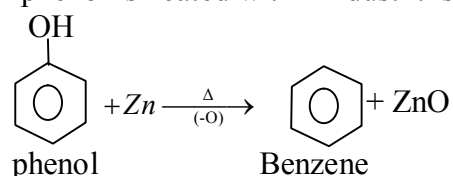
* Due to intramolecular H-bonding, ortho is a major product.

* During Reimer – Tiemann reaction dichlorocarbene (CCl_2) acts as electrophile.



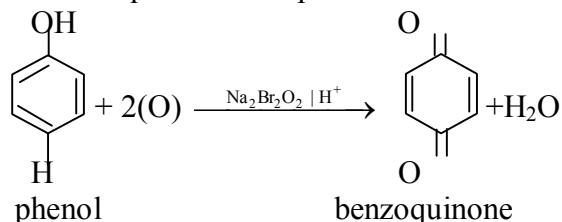
6) Reduction of phenol by Zn dust.

When phenol is heated with Zn dust it is reduced giving benzene.



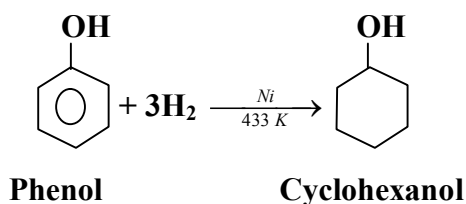
7) Oxidation of Phenol:

Phenol is oxidized by acidified dichromate or by chromic anhydride giving a conjugated diketone called as benzoquinone. It is pink coloured.



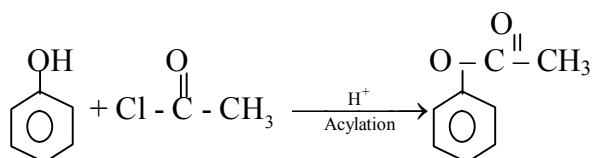
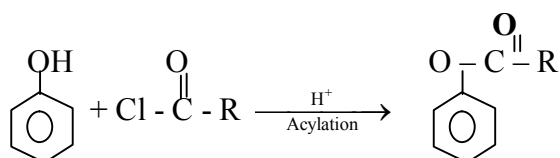
8) Catalytic hydrogenation of phenol:

Phenol is catalytic reduce by nickel and H_2 at 443 K giving cyclohexanol.

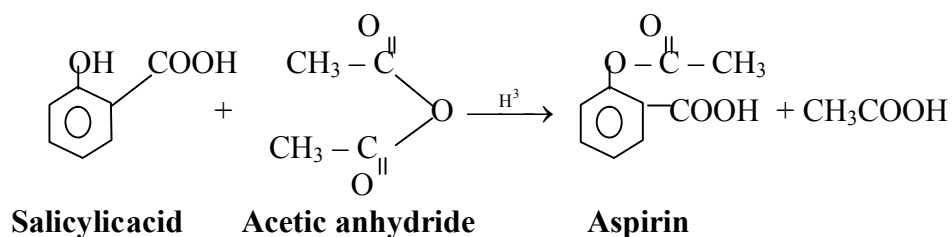
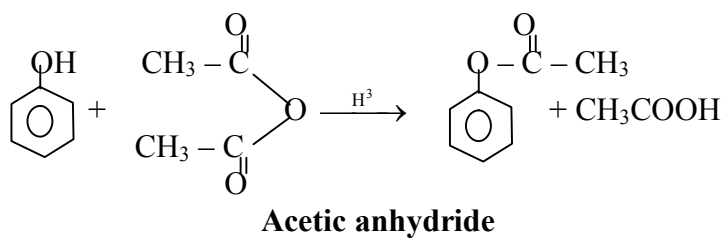


9) Acylation/Acetylation of phenol

Phenol reacts with acyl chloride ($\text{R} - \text{CO} - \text{Cl}$) or acetyl chloride ($\text{CH}_3 - \text{CO} - \text{Cl}$) giving corresponding aromatic esters.



The reaction can be done by acid anhydride also.

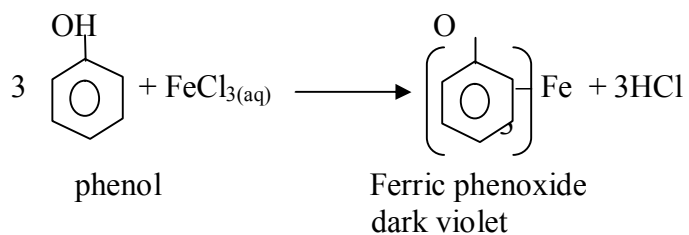


*Aspirin is acetyl derivative of salicylic acid formed by acetylation. It is used as general analgesic medicine (mostly for headache).

Distinguishing Test of Phenol from alcohol:

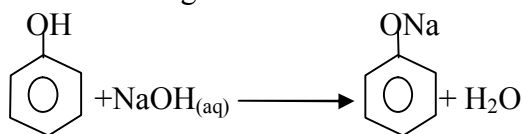
1) Alcohol is neutral and has no action with litmus. But phenol is acidic. So aqueous phenol turns blue litmus into red.

2) **FeCl₃ Test:** When phenol is added to the aqueous solution of ferric chloride, dark violet colour appears due to formation of Ferric phenoxide. (alcohol does not react with FeCl₃)



3) Neutralization

Phenol is a weak acid so neutralized by strong base like NaOH. However it is not neutralized by weak base like baking soda.



Phenol + NaHCO₃ → No Reaction

Uses of Phenol:

- 1) Phenol and formaldehyde form a polymer called **Backelite** which is used as plastic.
- 2) Phenol is antiseptic in common products like air fresheners, Deodronts, mouth wash, calamine lotion, floor cleaners.
- 3) Phenol is used in the preparation of salicylic acid, salicylaldehyde, Dettol, aspirin etc.
- 4) It is used in making picric acid which is explosive.