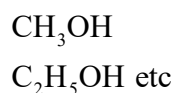


CHAPTER - 08

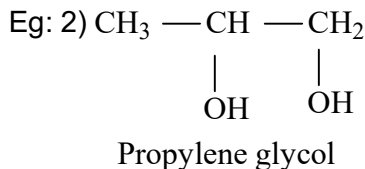
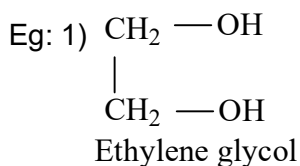
ALCOHOLS PHENOLS AND ETHERS

Alcohols are hydroxy derivatives of hydrocarbons. Monohydric alcohols contain one –OH group per molecules. Dihydric, trihydric and polyhydric alcohols are also there.

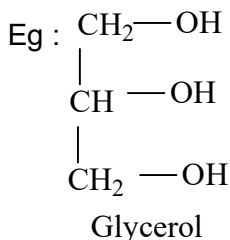
Monohydric



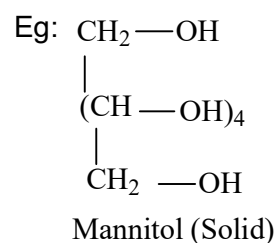
Dihydric



Trihydric



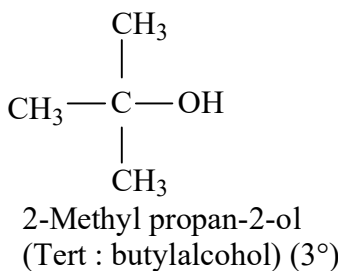
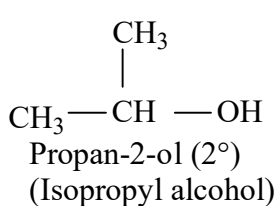
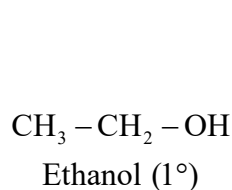
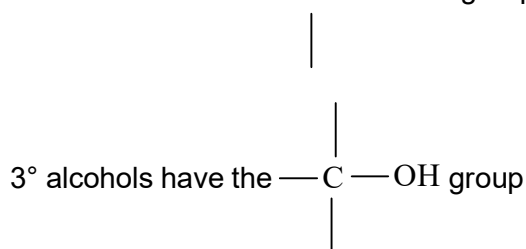
Polyhydric



Aliphatic saturated monohydric alcohols and ethers have the G.F. C_nH_(2n+2)O.

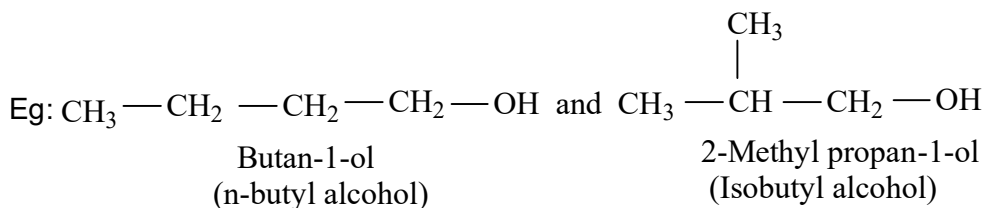
1° alcohols contain –CH₂–OH grouping

2° alcohols contain —CH—OH group

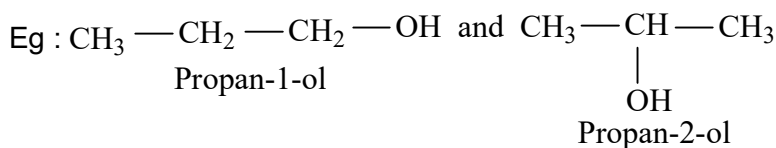


Alcohols exhibit different types of structural isomerism.

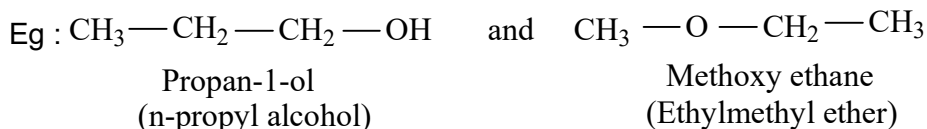
1. Chain isomerism



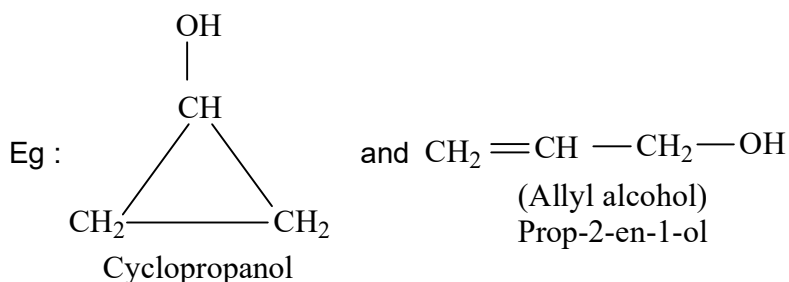
2. Position isomerism



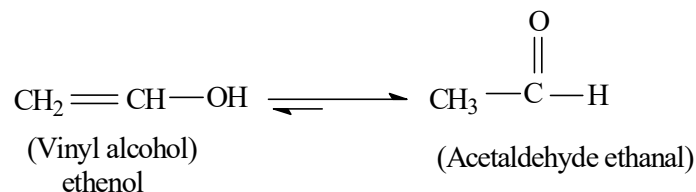
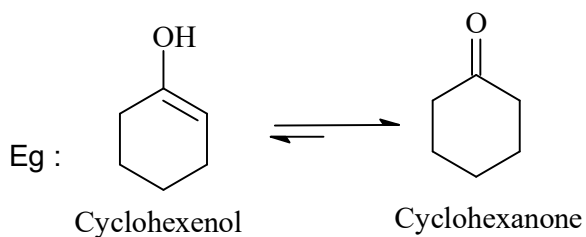
3. Functional isomerism



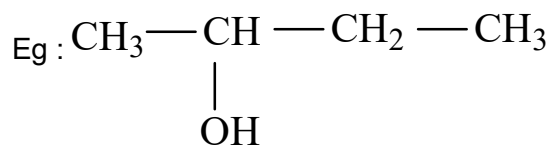
4. Ring chain isomerism



5. Vinylic alcohols are tautomeric forms of aldehydes or ketones



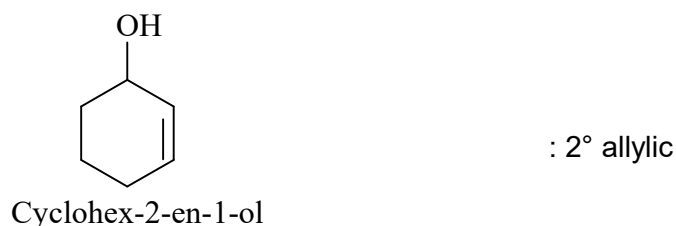
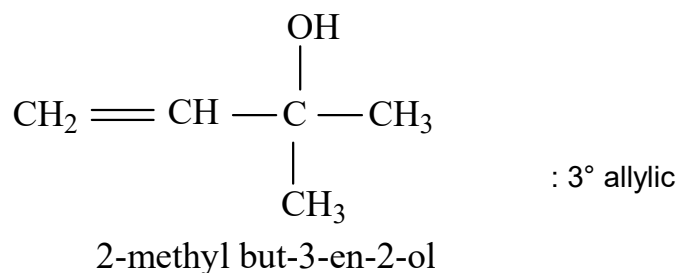
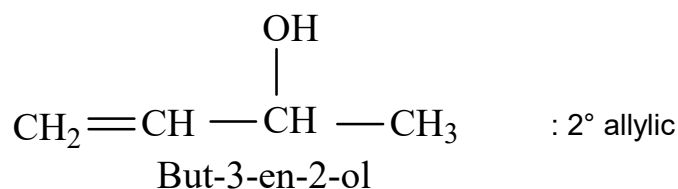
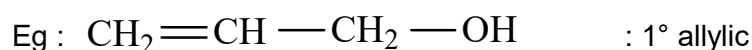
Alcohols containing asymmetric carbon can exhibit optical isomerism.



Butan-2-ol

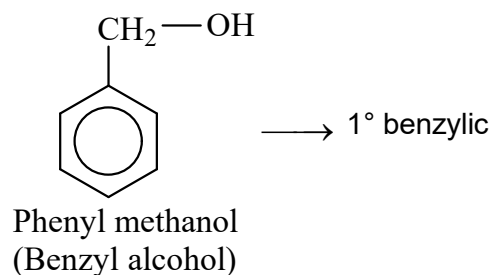
ALLYLIC ALCOHOLS :

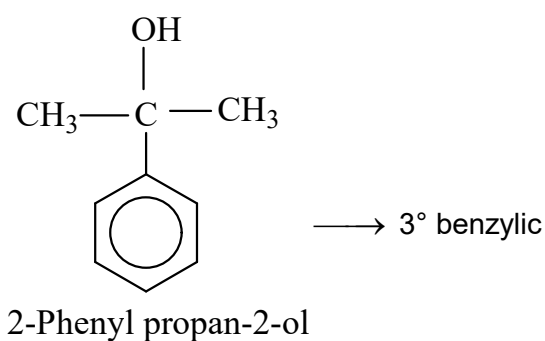
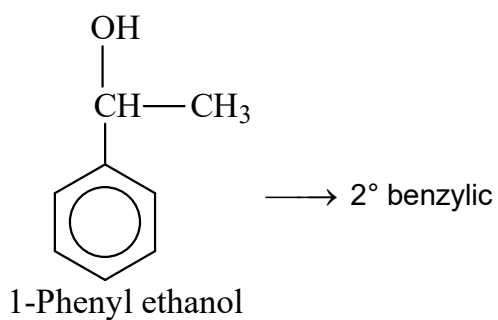
Here –OH group is connected to allylic carbon. i.e. sp^3 carbon which is directly connected to olefinic carbon. If the allylic carbon is 1° , the alcohol is 1° allylic. In 2° allylic alcohol, the allylic carbon is 2° and so on.



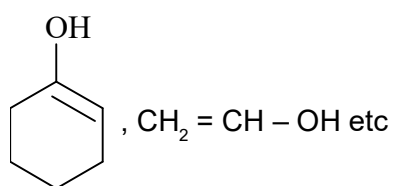
BENZYLIC ALCOHOLS

–OH group is connected to benzylic carbon ie sp^3 carbon directly connected to benzene ring.



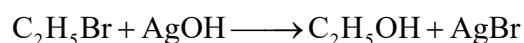
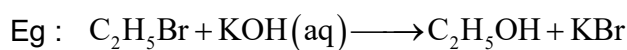


VINYLIC ALCOHOLS (ENOLS)

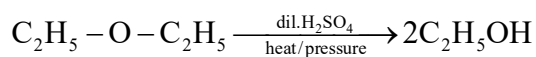


General methods of preparation

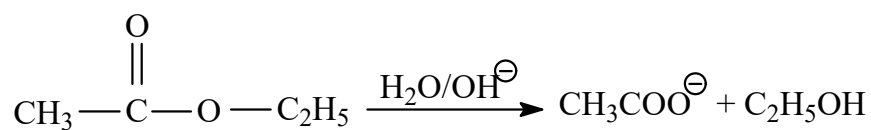
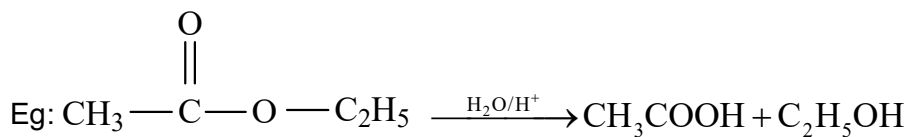
1. **Hydrolysis of alkyl halides with aqueous alkali or moist Ag_2O .**



2. **Hydrolysis of ethers**

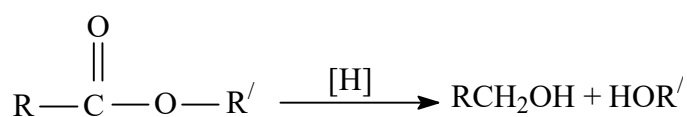
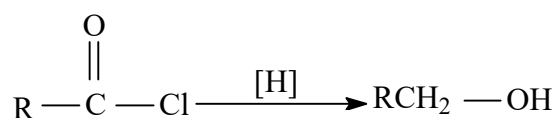
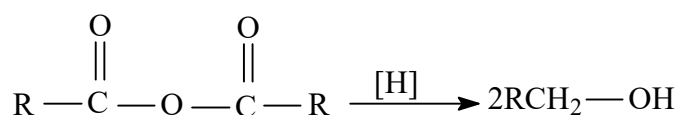
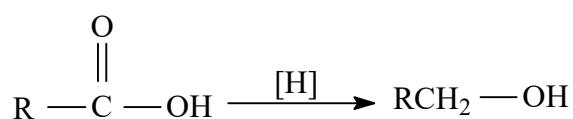
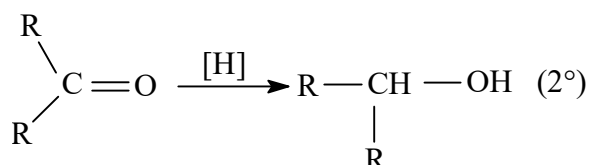
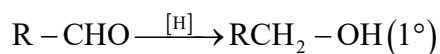


3. **Hydrolysis of esters**



4. Reduction of carbonyl compounds

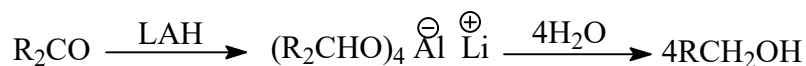
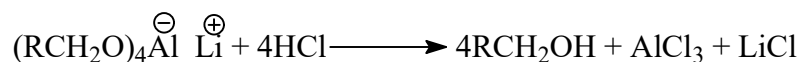
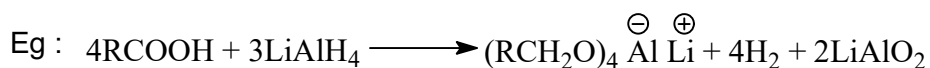
Aldehydes, ketones, carboxylic acids and acid derivatives like acid chlorides, anhydrides and esters can be reduced to alcohols.



The commonly used reducing agents are

1) $LiAlH_4$ (LAH) (2) B_2H_6 in THF (3) $NaBH_4$ (4) H_2 /catalyst (5) Na in ethanol

LAH can reduce all the above six carbonyl compounds. Tetra alkoxy lithium aluminate is formed, which is then hydrolysed with dil. acid to generate the alcohol.

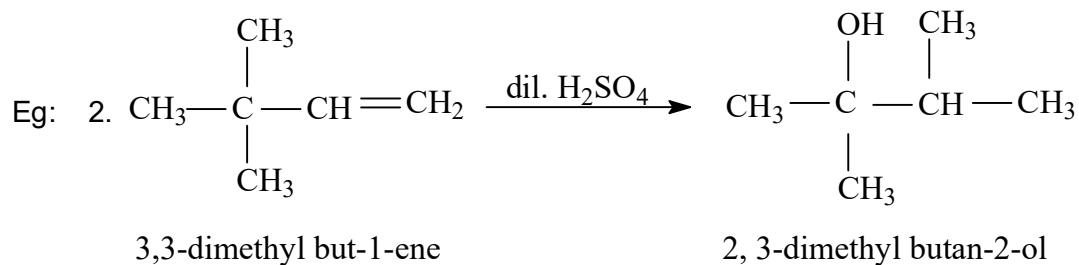
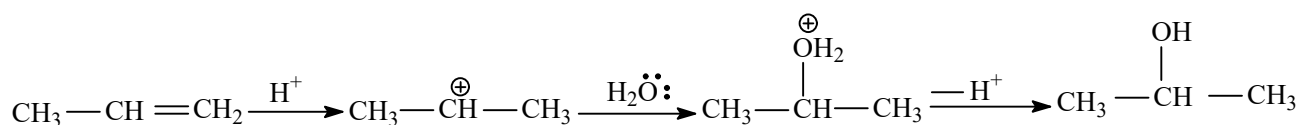
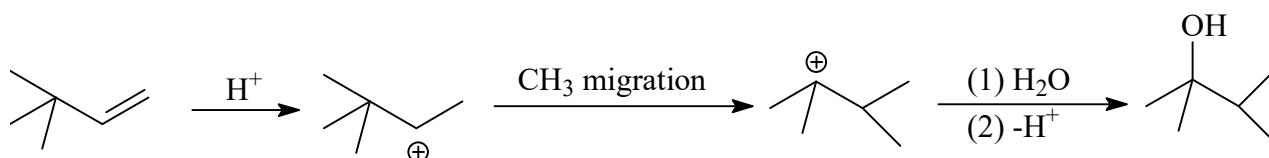


B_2H_6 reduces all except $RCOCl$

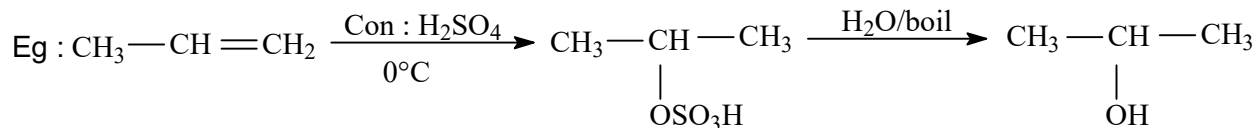
H_2/Ni reduces all except $RCOOH$

$NaBH_4$ reduces, Aldehyde, ketone and acid chloride

Na/ethanol reduces, Aldehyde, ketone and ester

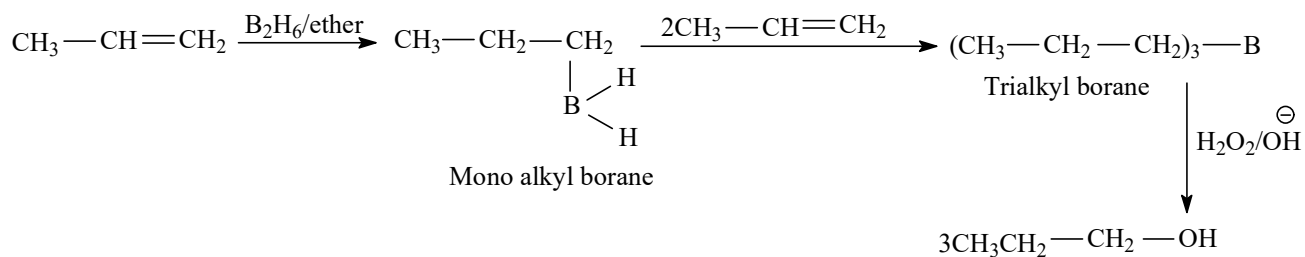
**Mechanism:**

Alkenes can be absorbed in con: H_2SO_4 at 0°C and the alkyl hydrogen sulphate formed on boiling with water, alcohol is obtained.



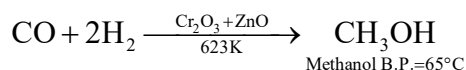
Isopropyl hydrogen sulphate

(Con: H_2SO_4 adds in Markownikoff's direction)

8. Hydroboration oxidation of alkene

The net result is anti Markownikoff addition of H and OH

9. Commercial production of methanol (Carbinol or wood spirit)



Physical properties

Lower members are colourless liquids. Higher members having more than 12 carbon atoms are wax like solids.

Eg : Lauryl alcohol $\text{C}_{12}\text{H}_{25} - \text{OH}$ M.P = 24.5°C

Cetyl alcohol $\text{C}_{16}\text{H}_{33} - \text{OH}$ M.P. = 49°C

First three members, methanol, ethanol and propanol are completely miscible with water in all proportions. i.e. their solubility in water is infinity (∞). But from butanol onwards, solubility in water decreases with molecular mass. Among isomeric alcohols, the solubility in water is in the order $3^\circ > 2^\circ > 1^\circ$. Boiling point increases with increase in molecular weight.

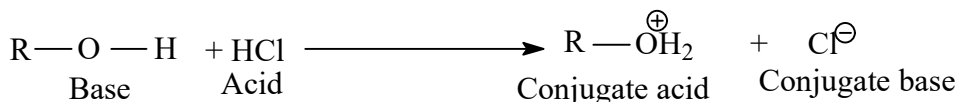
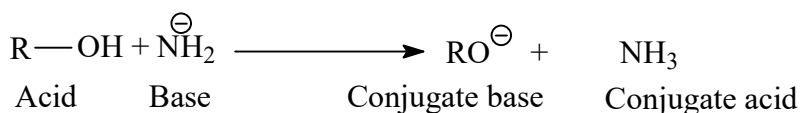
For isomeric alcohol the boiling point order is $1^\circ > 2^\circ > 3^\circ$.

Eg : Butan-1-ol (B.P. = 118°C), Isobutanol (B.P. = 108°C), Sec:Butyl alcohol (B.P. = 100°C)

Tert:butyl alcohol (B.P. = 83°C)

Chemical properties

Alcohols can behave as Bronsted acids as well as Bronsted bases.

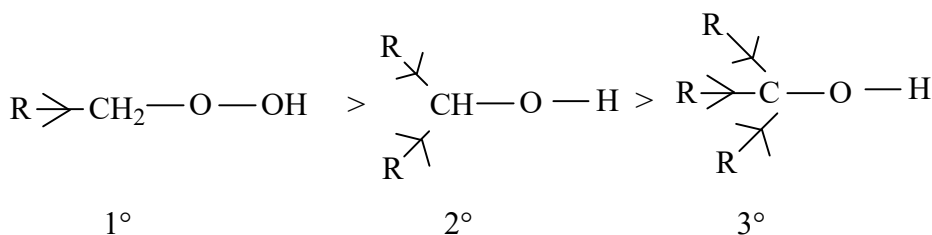


Alcohols are neutral to litmus, but they are extremely weak acids, weaker than water pK_a of H_2O is 15.74, while that of ethanol is ≈ 16

CH_3OH	H_2O	$\text{C}_2\text{H}_5\text{OH}$	2° alcohol	3° alcohol
$\text{PK}_a = 15.54$	$\text{PK}_a = 15.74$	$\text{PK}_a = 16$	$\text{PK}_a \approx 17$	$\text{PK}_a = 18$

Lower the PK_a stronger the acid.

The slight acidic character of alcohols is due to the polar nature of O-H bond. An electron releasing group like $-\text{CH}_3$, $-\text{C}_2\text{H}_5$ etc increases the electron density on oxygen and thereby decrease the polarity of the O-H bond. This decreases the acid strength. So the acidic strength of alcohols follow the order $1^\circ > 2^\circ > 3^\circ$.



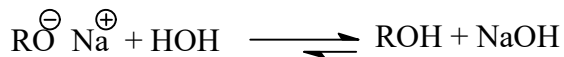
Strong acids $\text{pK}_a < 1$

Moderately strong acid, $pK_a = (1 \rightarrow 5)$

Weak acids $pK_a = (5 \rightarrow 15)$

Extremely weak acids, $pK_a > 15$

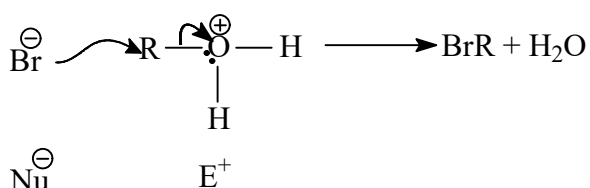
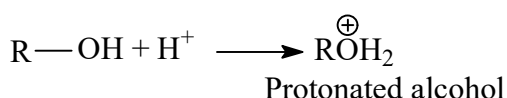
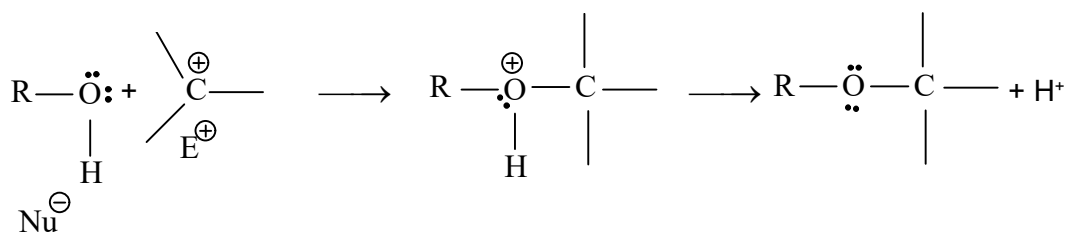
The following equilibrium also shows that alcohols are weaker acids than water.



i.e. HOH is a better proton donor than R-OH

See the equilibrium lies mainly to the r.h.s. The position of equilibrium also shows that RONA is a stronger base than NaOH (or RO^- is a stronger base than OH^-)

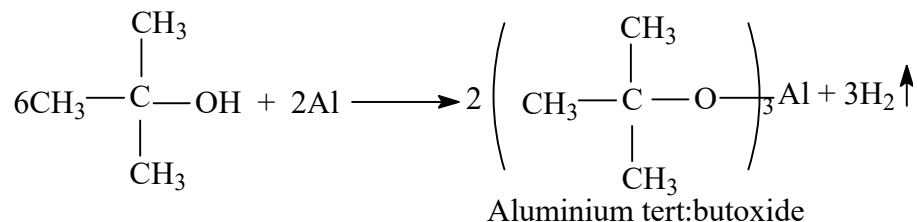
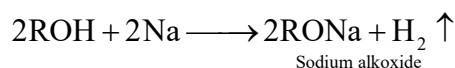
Unprotonated alcohol is a nucleophile, while protonated alcohol behaves as an electrophile.



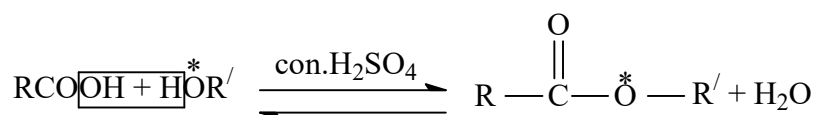
REACTIONS OF ALCOHOLS

I. Reactions involving the cleavage of only $O-H$ bond

1. With active metals they form alcoholates or alkoxides with the liberation of hydrogen. The order of reactivity is same as acidic strength order. i.e. $1^\circ > 2^\circ > 3^\circ$.

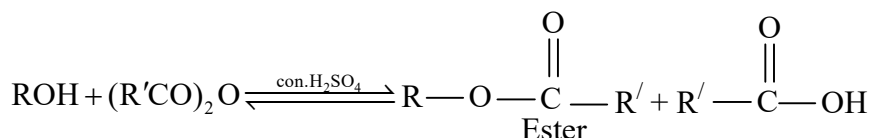
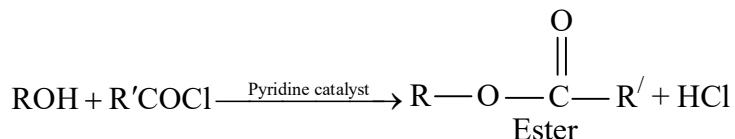


2. With carboxylic acids, they give esters.



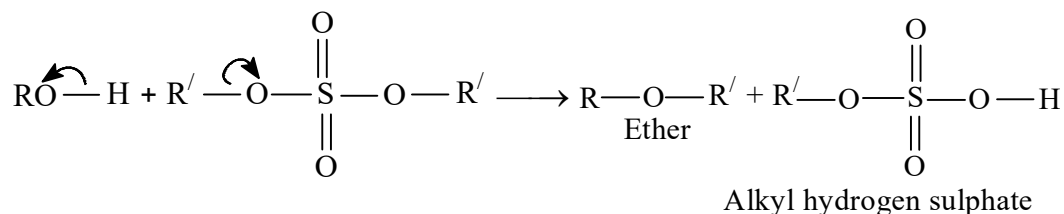
Acyl oxygen of the ester is from the acid and alkoxy oxygen is from the alcohol

3. With acid chlorides and acid anhydrides they form esters.

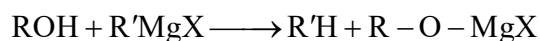


Note that acyl portion is from acid chloride or anhydride. Alkoxy portion is from the alcohol.

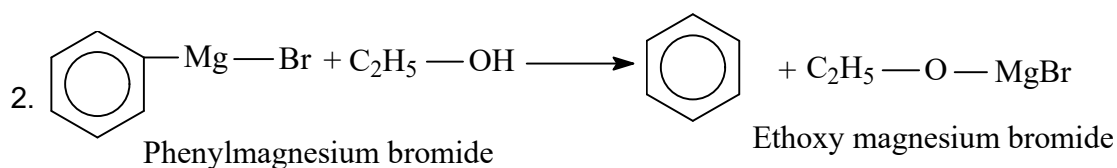
4. With dialkyl sulphates, they form ethers.



5. With Grignard reagent they form hydrocarbon



Eg : 1. $\text{CH}_3\text{OH} + \text{C}_2\text{H}_5\text{MgBr} \longrightarrow \text{C}_2\text{H}_6 + \text{CH}_3-\text{O}-\text{MgBr}$ -(Methoxymagnesium bromide)



II. Reactions involving the cleavage of $\text{R}-\text{OH}$ bond

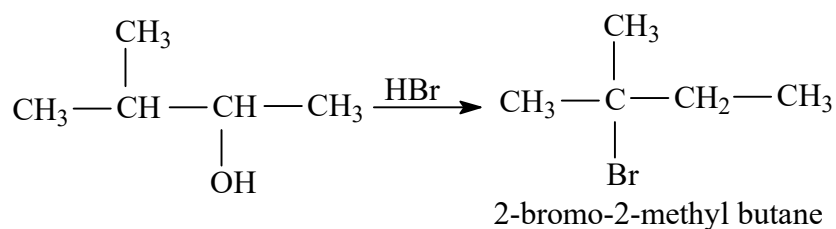
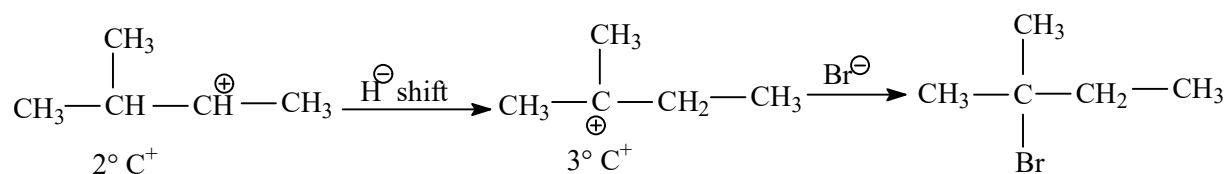
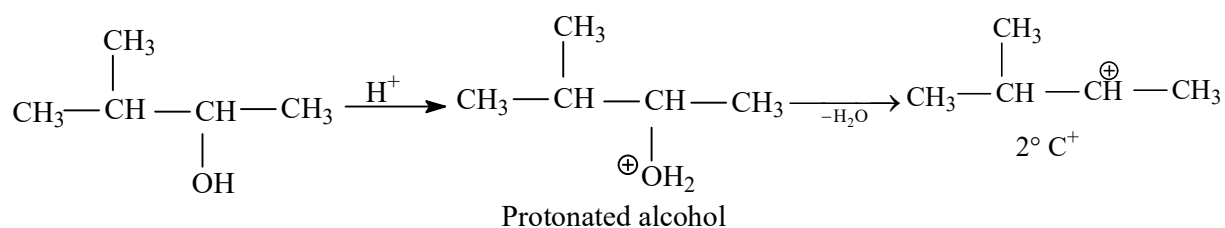
1. Reaction with halogen acids (HX)

The reactivity order of HX is $\text{HI} > \text{HBr} > \text{HCl}$, while the reactivity order of alcohols towards HX is $3^\circ > 2^\circ > 1^\circ < \text{CH}_3\text{OH}$. Allylic and benzylic alcohols are as reactive as 3° .

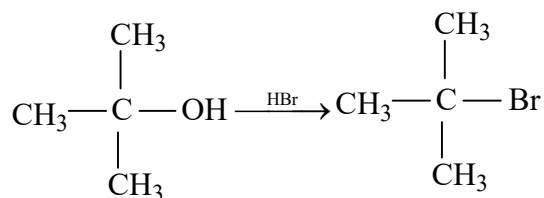
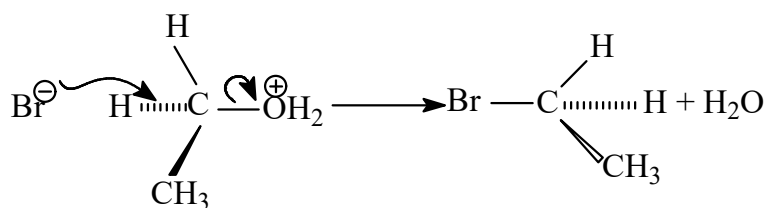
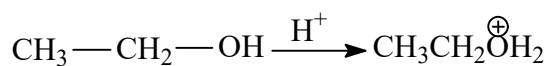
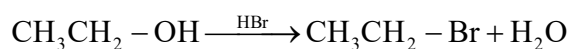
Here 3° and 2° alcohols react with HX by $\text{S}_{\text{N}}1$ pathway while most of the 1° alcohols react by $\text{S}_{\text{N}}2$ mechanism. So among 1° alcohols, methanol show greater reactivity because, no steric effect is present with methyl group.

When $\text{S}_{\text{N}}1$ mechanism operates in suitable cases, there is a possibility of rearrangement.

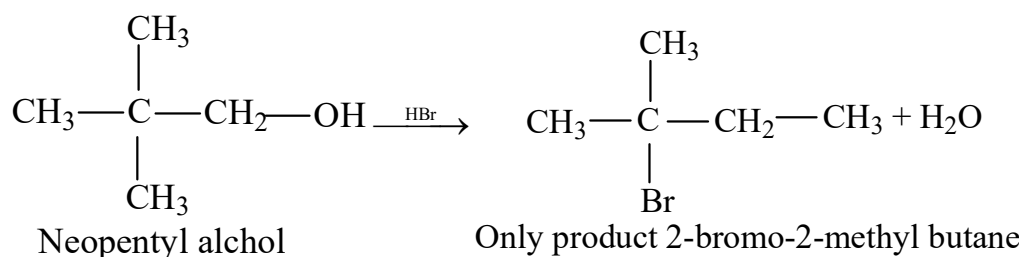
Eg :

**Mechanism:**

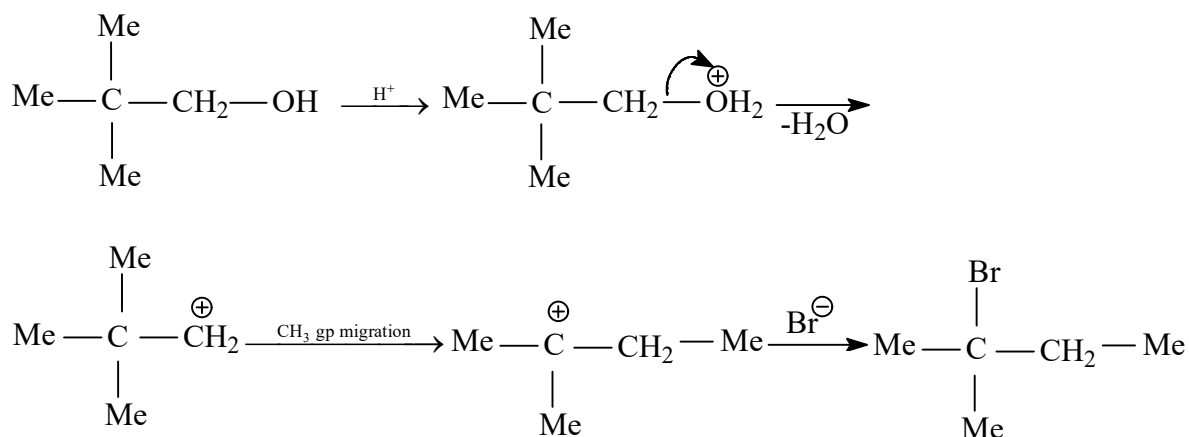
But in the following $\text{S}_{\text{N}}1$ reaction, there is no rearrangement.

 **$\text{S}_{\text{N}}2$ mechanism**

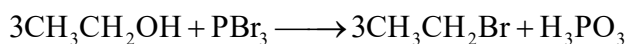
Neopentyl alcohol though 1° , it cannot react by $\text{S}_{\text{N}}2$ path so it reacts by $\text{S}_{\text{N}}1$ path.



Mechanism



2. **With PBr₃** alcohols give alkyl bromide by S_N2 mechanism



For the reaction between a 1° alcohol and HCl, anhydrous ZnCl₂ is used as a catalyst (it is a must otherwise, the reaction will be too slow). But for HBr and HI, ZnCl₂ catalyst is not necessary, because Br[−] and I[−] are stronger nucleophiles than Cl[−].

Alcohols react with thionylchloride SOCl₂ producing alkyl chloride by S_Ni mechanism (Darzen's procedure). But if this reaction is carried out in presence of pyridine, the reaction proceeds by S_N2 mechanism. When S_Ni mechanism operates, there is retention of configuration but when S_N2 operates, there is inversion of configuration.

3. **With NH₃**



III. Reactions involving cleavage of alkyl and -OH group

1. **Dehydration** : Relative ease of dehydration is 3° > 2° > 1°

For dehydration of 1° alcohols, conc:H₂SO₄ AND 170°C is required.

For 2° alcohols 60% H₂SO₄ or H₃PO₄ and 100°C is enough

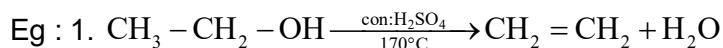
For 3° alcohols 20% H₂SO₄ at 80°C, is sufficient for dehydration.

Dehydration is also effected by heating with Al₂O₃ (Alumina)

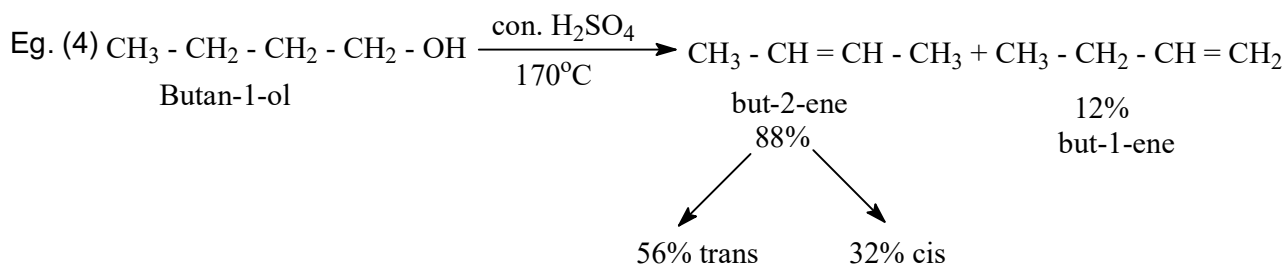
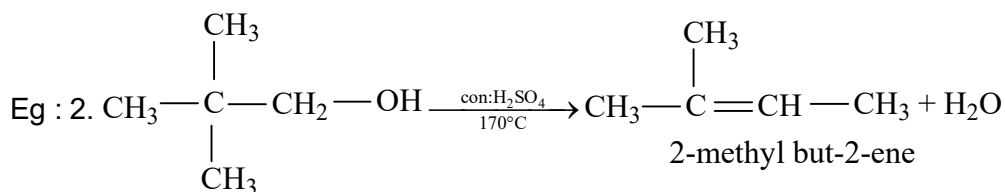
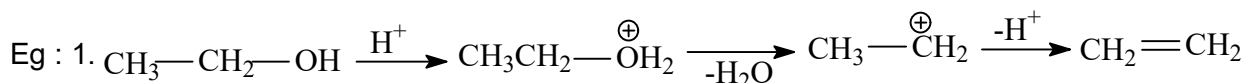
For 1° alcohols Al₂O₃ at 350°C is required

For 2° alcohols Al₂O₃ at 250°C is enough

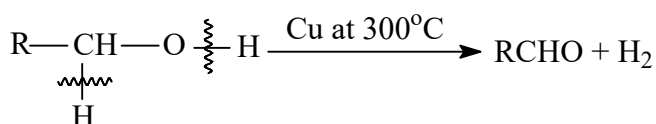
For 3° alcohols, Al_2O_3 at 150°C is sufficient.



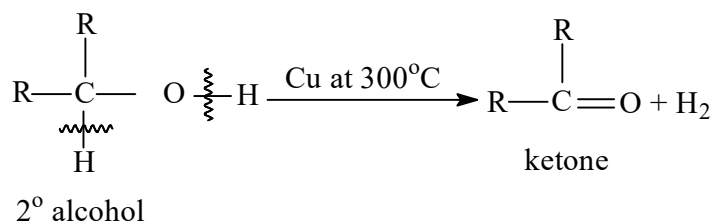
For acid catalysed dehydration, the most widely accepted mechanism involves the formation of carbocation intermediate.



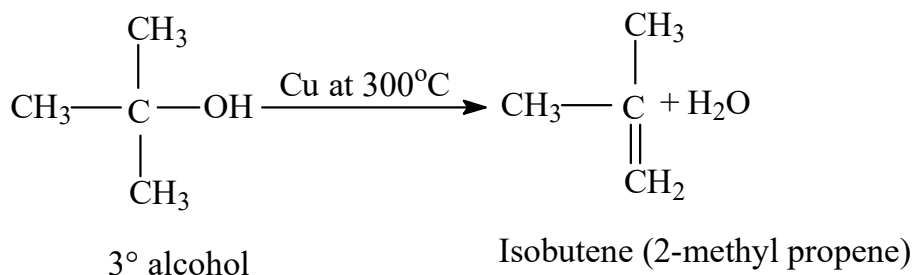
2) **Dehydrogenation** : When vapors of alcohols are passed over heated copper at 300°C , 1° alcohols yield aldehyde, 2° gives ketone and 3° alcohols produce alkene. (Here 3° undergo dehydration)



Here a $\text{C} - \text{H}_\sigma$ bond and $\text{O} - \text{H}_\sigma$ bond undergo cleavage and a carbon-oxygen π bond is formed.



Here also $\text{C} - \text{H}$ and $\text{O} - \text{H}$ σ bonds undergo cleavage and a carbon-oxygen π bond is formed.

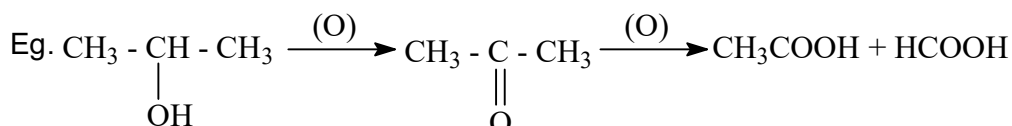


3) Oxidation of alcohols :

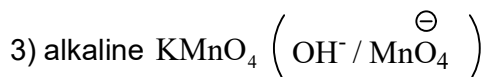
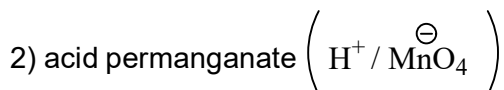
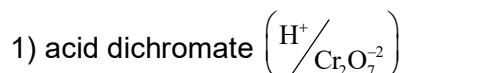
Primary alcohol on oxidation, first forms an aldehyde which further undergo oxidation giving a carboxylic acid, both containing the same number of carbon atoms as in the alcohol.



2° alcohols on oxidation, ketone is formed first. Ketones require vigorous conditions for oxidation and forms a mixture of two carboxylic acids.

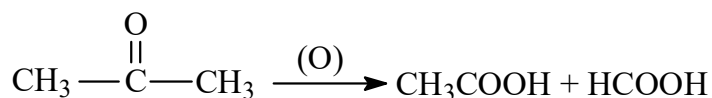
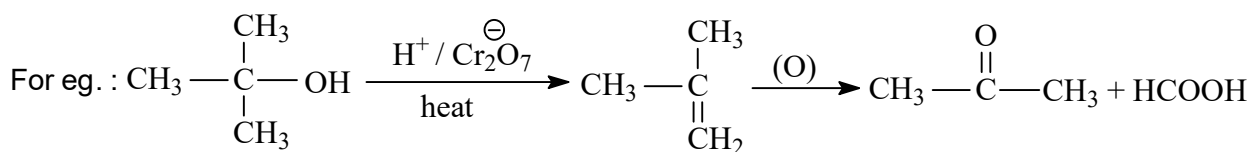


The oxidising agents used for oxidation of alcohols are



4) dil. HNO_3

Tertiary alcohols cannot be oxidised in alkaline or in neutral media. But they can be oxidised in acid medium on prolonged heating with oxidising agent.



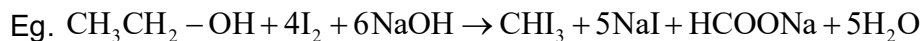
Halogen in aqueous solution will oxidise 1° alcohol to aldehyde and 2° alcohol to ketone

4) Haloform reaction by alcohols

Alcohols which possess $\text{CH}_3 - \underset{\text{OH}}{\underset{|}{\text{CH}}} -$ group connected to carbon or hydrogen, on heating with halogen and alkali, will produce, the corresponding haloform CHCl_3 (If Cl_2 and alkali are used) CHBr_3 (If Br_2

and alkali) or CHI_3 (iodoform, if I_2 and alkali are used)

CHCl_3 and CHBr_3 are colourless liquids, but CHI_3 is a yellow solid. So iodoform test is conducted.



Yellow ppt.

About iodoform reactions of alcohols

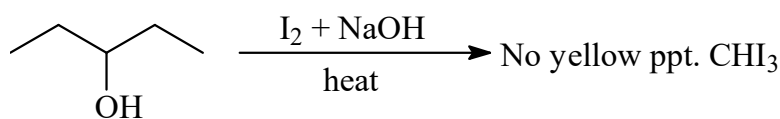
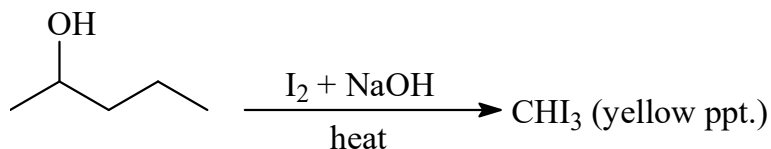
1) Ethanol is the only 1° alcohol that answers iodoform test

2) No tertiary alcohol will answer this test

3) Only those secondary alcohols having $\text{CH}_3 - \overset{\text{OH}}{\underset{|}{\text{CH}}} -$ group will answer this test.

NB : Haloform reaction is given by compounds having either $\text{CH}_3 - \overset{\text{O}}{\parallel}{\text{C}} -$ group or $\text{CH}_3 - \overset{\text{OH}}{\underset{|}{\text{CH}}} -$ group connected to carbon or hydrogen.

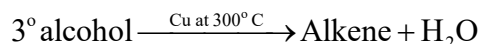
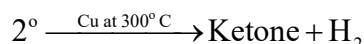
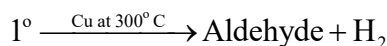
Pentan-2-ol and pentan-3-ol can be distinguished by iodoform test



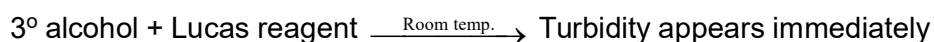
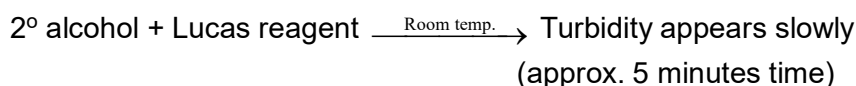
NB : $\text{C}_5\text{H}_{12}\text{O}$ has 8 structurally isomeric alcohols and 6 structurally isomeric ethers. Out of these fourteen structural isomers only two will answer iodoform test.

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

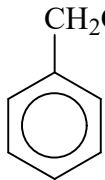
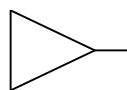
1) Dehydrogenation test



2) Lucas test (Lucas reagent is con. HCl + anhy. ZnCl_2)



(NB : If heated with Lucas reagent 1° will also give turbidity)

Exceptional cases $\text{CH}_2 - \text{CH} - \text{CH}_2 - \text{OH}$ and  as well as  will
(cyclo propyl methanol)

give a turbidity even at room temperature .

3) Acid dichromate test

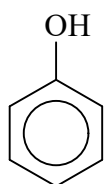
1° alcohol + acid dichromate soln. $\xrightarrow{\text{Room temp.}}$ Green colour (Cr^{+3})
(orange colour)

2° alcohol + acid dichromate soln. $\xrightarrow{\text{Room temp.}}$ Green colour (Cr^{+3})
(orange colour)

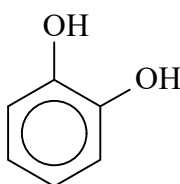
3° alcohol + acid dichromate soln. $\xrightarrow{\text{Room temp.}}$ No colour change
(orange colour) (orange colour persists)

PHENOLS

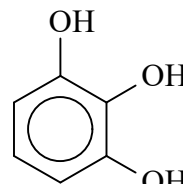
Phenols are hydroxy derivatives of aromatic hydrocarbons in which the $-\text{OH}$ group is directly attached to the carbon atom of the aromatic ring. The natural source of phenol is the middle oil fraction during the fractional distillation of coal tar.



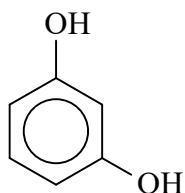
Phenol or carbolic acid
(monohydric phenol)



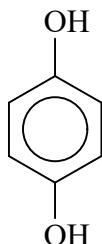
Catechol
Benzene-1,2-diol
(Dihydric phenol)



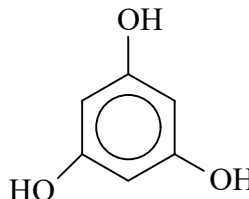
Pyrogallol
Benzene 1,2,3-triol
(Trihydric phenol)



Resorcinol

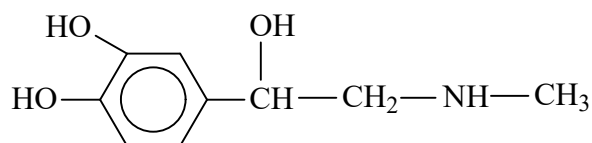


quinol or hydroquinone

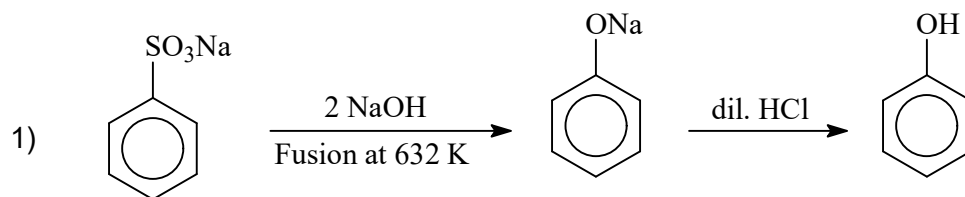


Phloroglucinol

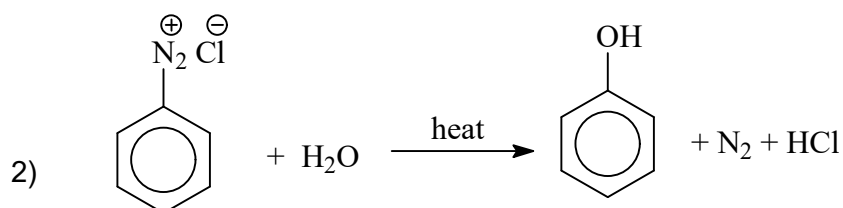
The hormone adrenaline contains catechol unit



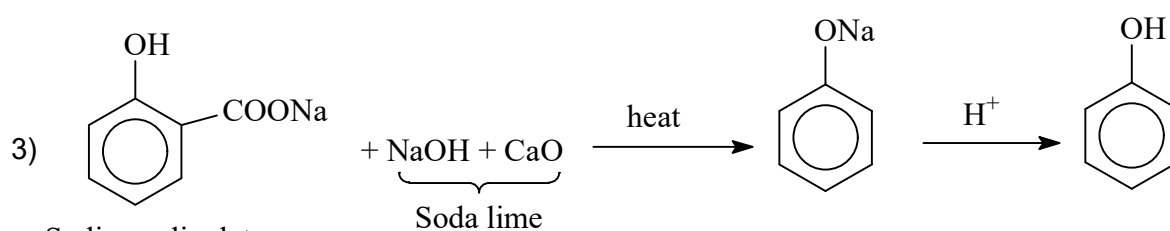
Adrenaline

Laboratory method of preparation of phenol

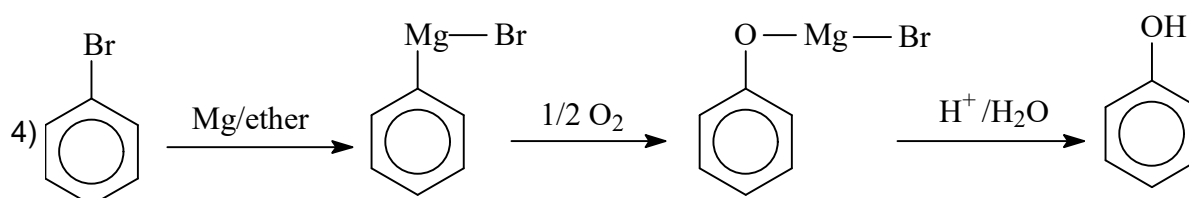
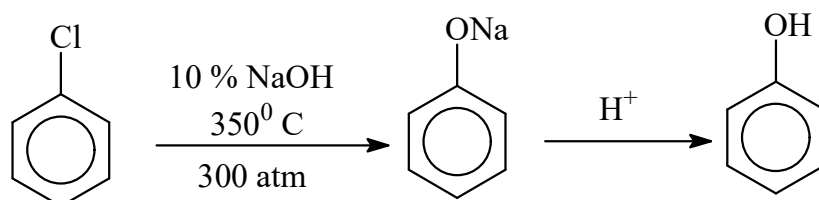
Sodium benzene sulphonate



Benzenediazoniumchloride

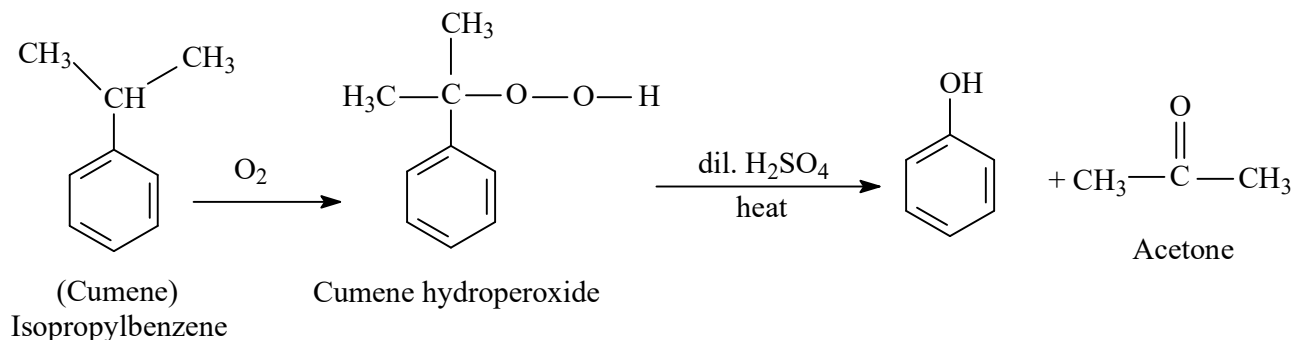


Sodiumsalicylate

**Manufacture of phenol****1) Dow process**

This reaction is an aromatic nucleophilic substitution that occurs by the elimination-addition mechanism and involves the formation of a benzyne intermediate (also called benzyne mechanism).

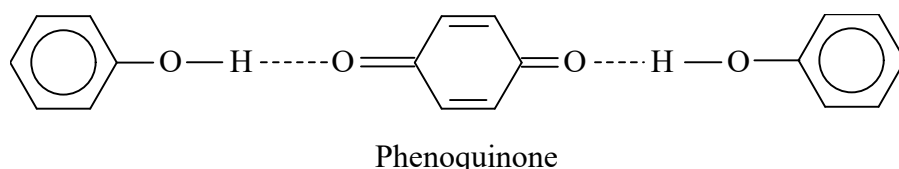
2) Cumene hydroperoxide process (Most widely used method)



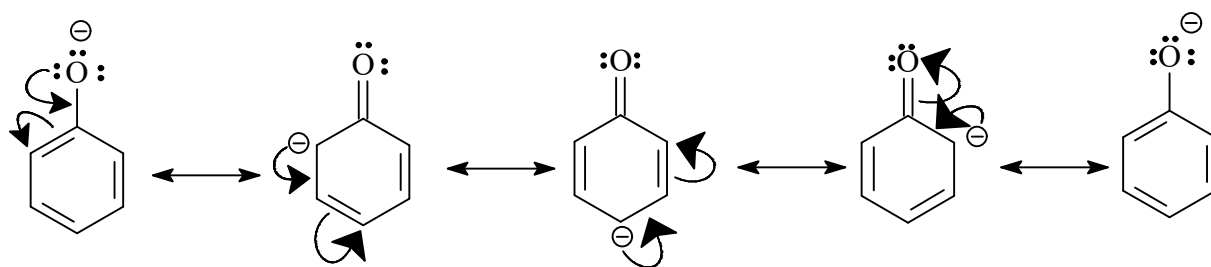
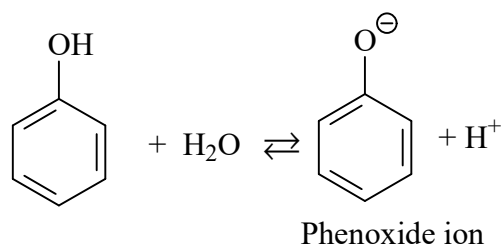
Here acetone is a valuable by product.

Physical properties of phenol

Pure phenol is a colourless crystalline solid. M.P. = 43° C. But due to atmospheric oxidation. Phenol turns slightly coloured pink and finally the colour turns brown. The colour is due to the formation of phenoquinone.



Phenol is moderately soluble in cold water. Phenol is a weak acid, when phenol ionises, the resulting phenoxide ion is more resonance stabilized than unionised phenol.

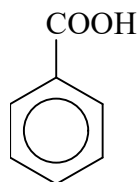


Phenol is more acidic than alcohols, but much less acidic than carboxylic acids. Carboxylic acids are much less acidic than mineral acids like HCl acid. Consider the following compounds and their pKa values.

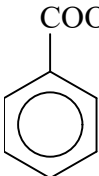
Presence of electron withdrawing groups like —NO₂, —CN, halogens (X) etc. increases the acidic

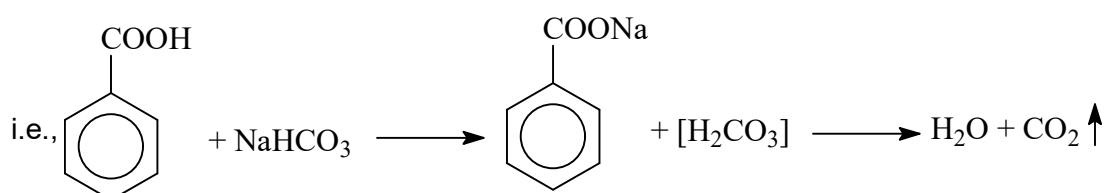
strength of phenol where as electron donating groups like —CH_3 , —OCH_3 etc decreases the acidic strength of phenol.

2,4,6 trinitrophenol called picric acid is a strong acid.



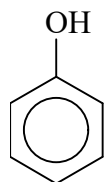
will dissolve in NaHCO_3 solution, but phenol will not. Why ?

Benzoic acid is a stronger acid than H_2CO_3 . Therefore  can displace H_2CO_3 from the salt NaHCO_3 .



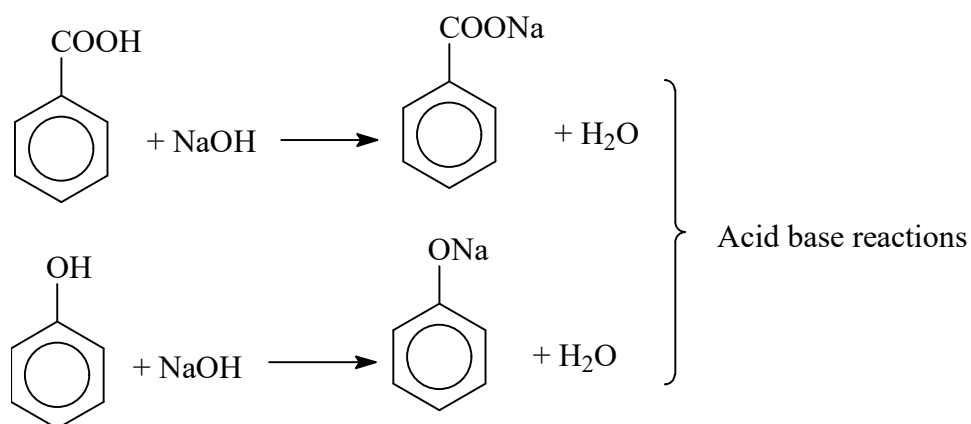
So we observe brisk effervescence.

But phenol is a weaker acid than H_2CO_3 . So it cannot displace H_2CO_3 from NaHCO_3 .



+ NaHCO_3 solution \longrightarrow No reaction

So phenol and benzoic acid can be distinguished by NaHCO_3 solution. But NaOH cannot distinguish these two. Both will dissolve in NaOH solution.

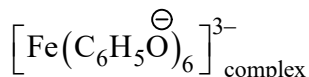


When NaHCO_3 solution is added to benzoic acid and phenol separately they behave differently. Benzoic acid will dissolve in NaHCO_3 solution. So the visible change is evolution of CO_2 , when benzoic acid is added to NaHCO_3 solution and due to the formation of sodium benzoate, benzoic acid dissolves in NaHCO_3 solution. But phenol will not dissolve in NaHCO_3 solution. Picric acid 2,4,6 trinitrophenol is a strong acid and it will dissolve in NaHCO_3 solution. pK_a of picric acid is 0.38.

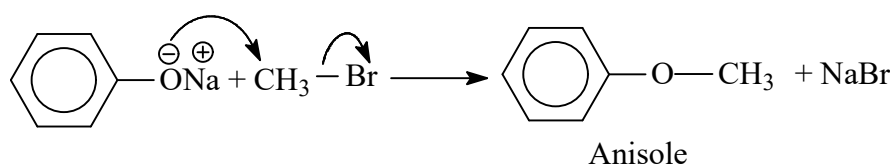
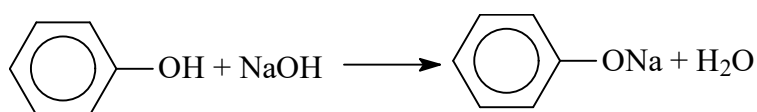
Reactions of phenol

A. Reactions due to the $-\text{OH}$ group

1) with FeCl_3 solution a violet colour is produced

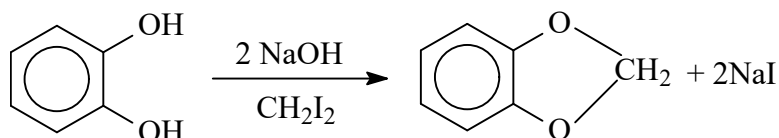
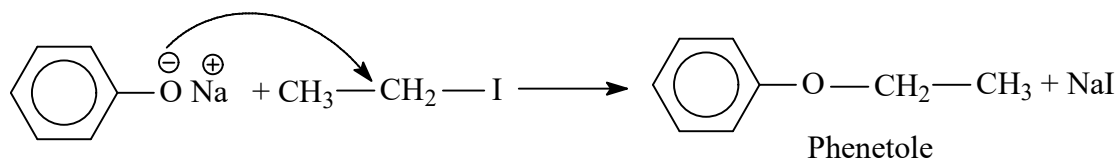


2) Phenol reacts with alkyl halide in presence of alkali to form alkyl aryl ether (Williamson's reaction)

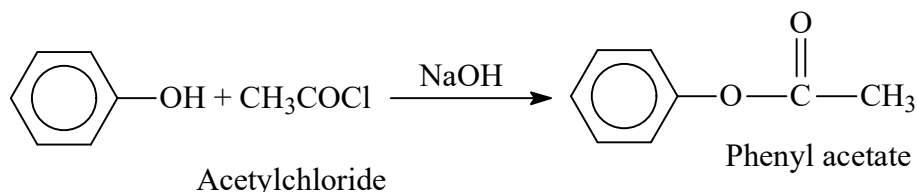


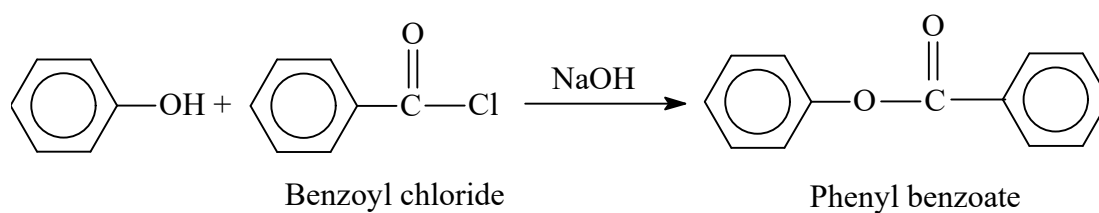
This is a nucleophilic substitution reaction.

Phenoxide ion displaces Br^-



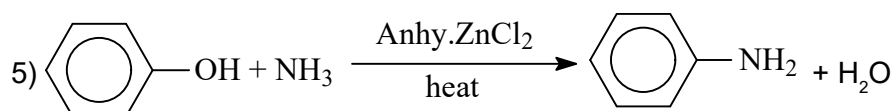
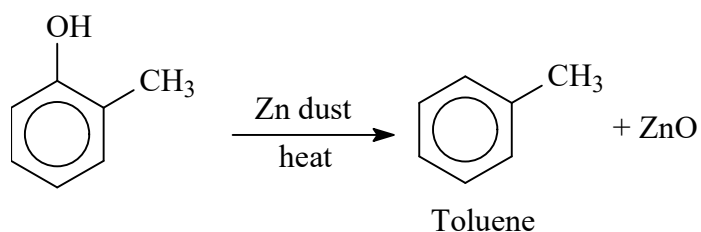
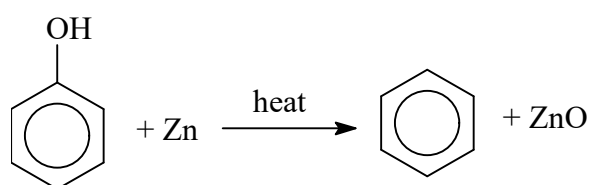
3) Ester formation : Phenol reacts with acid chlorides or acid anhydrides in presence of alkali to form phenyl esters.





This benzoylation of phenol is Schotten Baumann reaction.

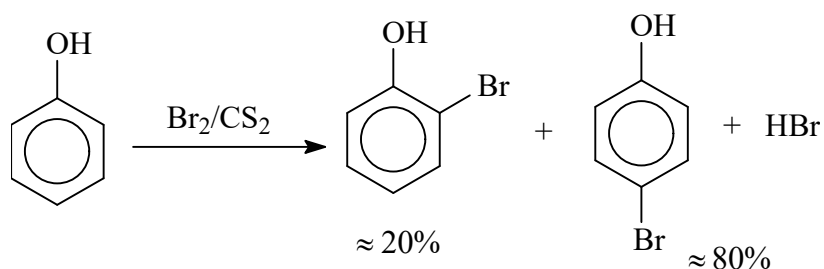
4) When distilled with Zn dust phenol gives benzene



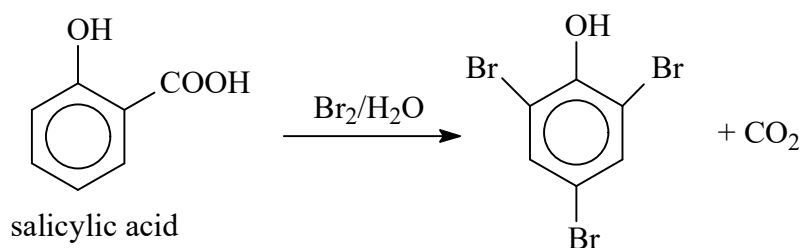
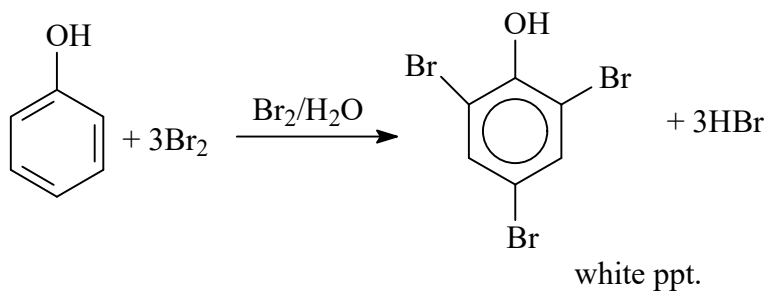
B. Reactions of benzene nucleus

Electrophilic substitutions

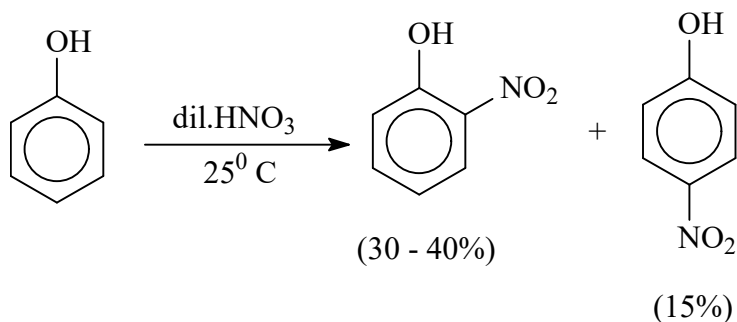
1) Bromination of phenol with Br₂/CS₂ gives a mixture of ortho and para bromo phenols.



2) With Br₂ water, 2,4,6 tribromophenol is formed

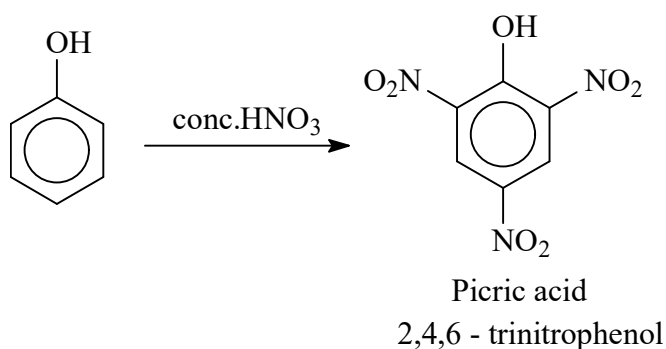


3) Nitration with dil.HNO_3 gives ortho and para - nitrophenols

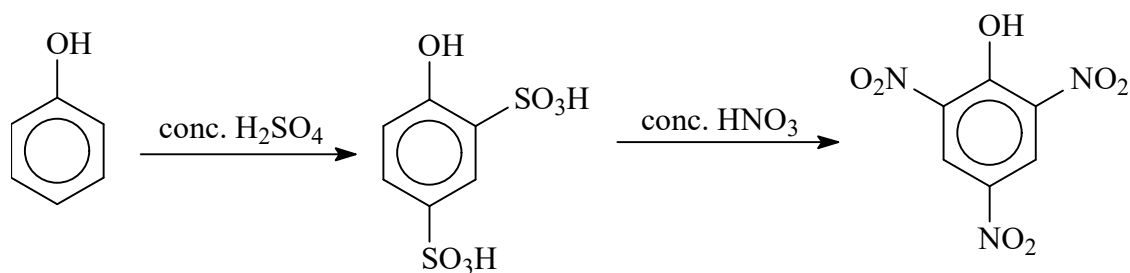


Ortho and para isomers can be separated by steam distillation, since ortho isomer is steam volatile.

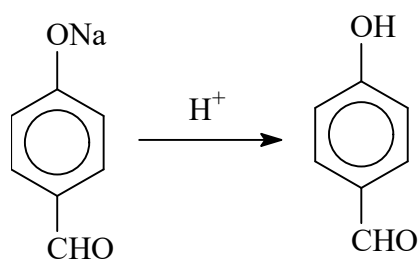
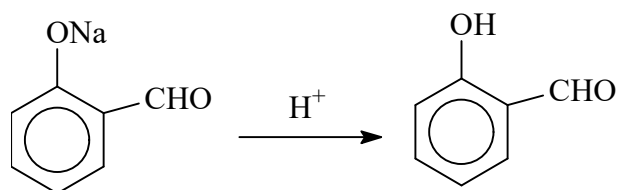
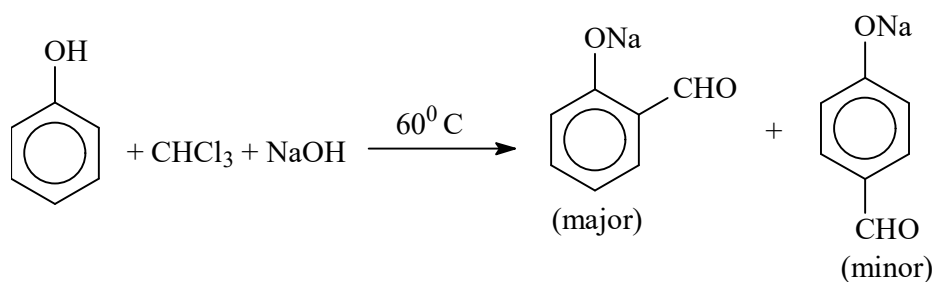
4) With **conc. HNO_3** picric acid is produced



But the yield is low, due to oxidation of phenol, so, picric acid is prepared as follows.



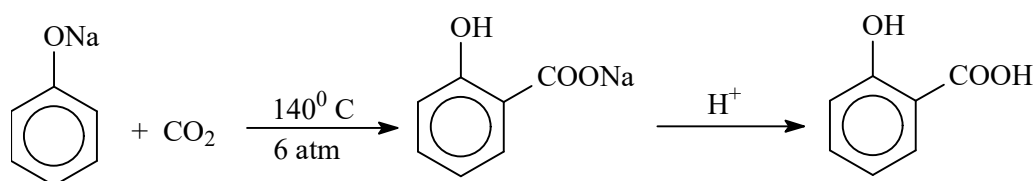
5) Reimer-Tiemann reaction



When phenol is heated with CCl_4 and NaOH at 70°C salicylic acid is obtained. This is also Reimer-Tiemann reaction. But here mechanism is different. No carbene intermediate is formed here.

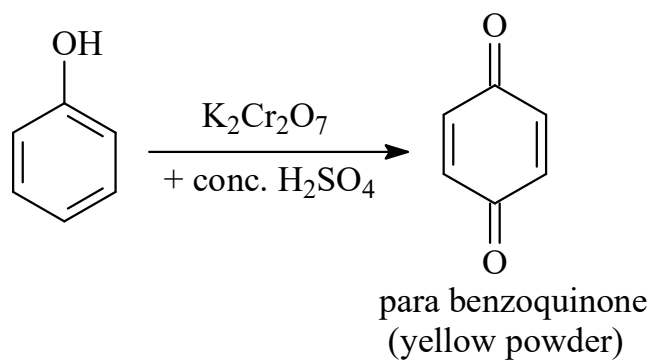
6) Kolbe-Schmidt reaction

Sodium phenoxide on heating with CO_2 at $130 - 140^\circ\text{C}$ and a pressure of 6 atm. Salicylic acid is produced.



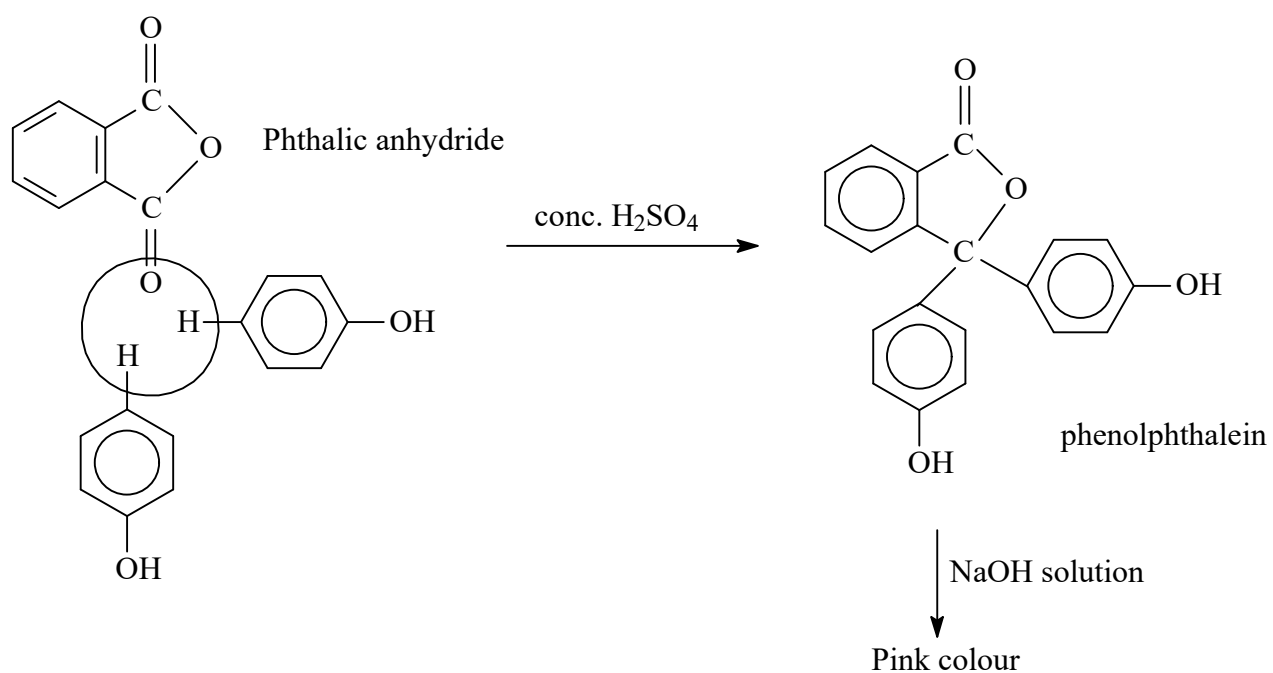
Here the attacking electrophile is CO_2

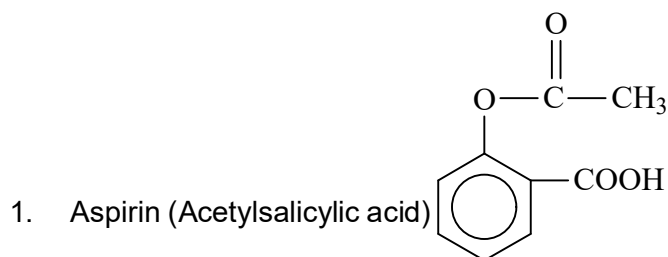
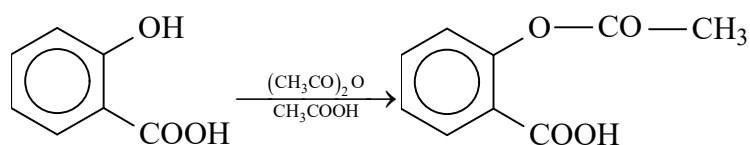
7) Oxidation of phenol



Phenolphthalein formation

Phenol + Phthalic anhydride + few drops of conc. $\text{H}_2\text{SO}_4 \xrightarrow{\text{heat}}$ colourless solution
 $\xrightarrow{\text{NaOH solution}}$ pink colour.

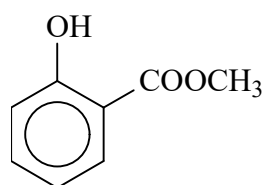
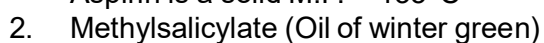


SOME IMPORTANT DERIVATIVES OF SALICYLIC ACID**Preparation**

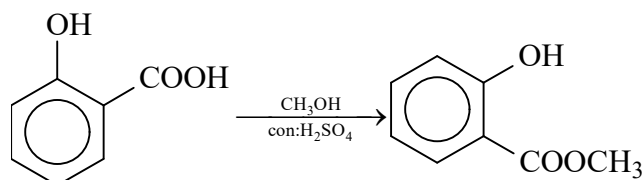
Salicylic acid is acetylated with a mixture of acetic anhydride and acetic acid.

Aspirin has analgesic, antipyretic and antiblood clotting properties

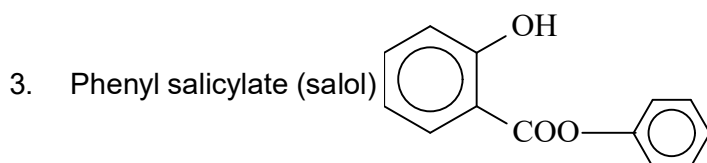
Aspirin is a solid M.P. = 135°C



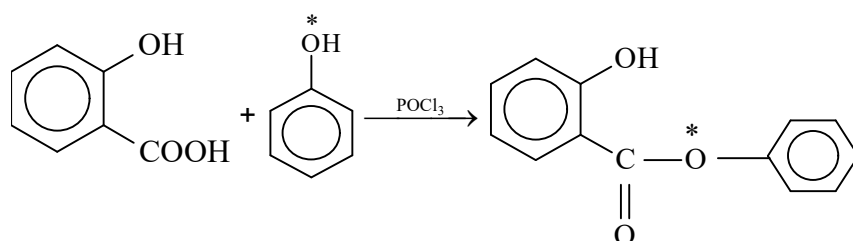
It is prepared by esterification of salicylic acid with methanol.



It is a pleasant smelling liquid. b.p. = 224°C. It is used in rubbing liniments (used in Rheumatic pains)



Prepared by heating salicylic acid with phenol in presence of phosphoryl chloride POCl₃.



It is a white solid. m.p. = 42°C. It is used as intestinal antiseptic.

ETHERS

Ethers are named, in substitutive IUPAC nomenclature as alkoxy derivatives of alkanes. Functional class IUPAC names of ethers are derived by listing the two alkyl groups in the general structure ROR' in alphabetical order as separate words, and then adding the word 'ether' at the end. When both the alkyl groups are the same, the prefix di- precedes the name of the alkyl group.

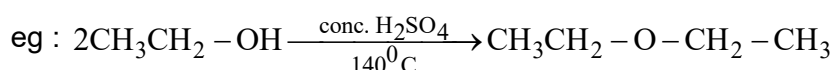
Substitutive IUPAC name	$\text{CH}_3 - \text{CH}_2 - \text{O} - \text{CH}_2 - \text{CH}_3$ Ethoxy ethane	$\text{CH}_3 - \text{CH}_2 - \text{O} - \text{CH}_3$ Methoxy ethane
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Functional class IUPAC name	diethyl ether	Ethyl methyl ether
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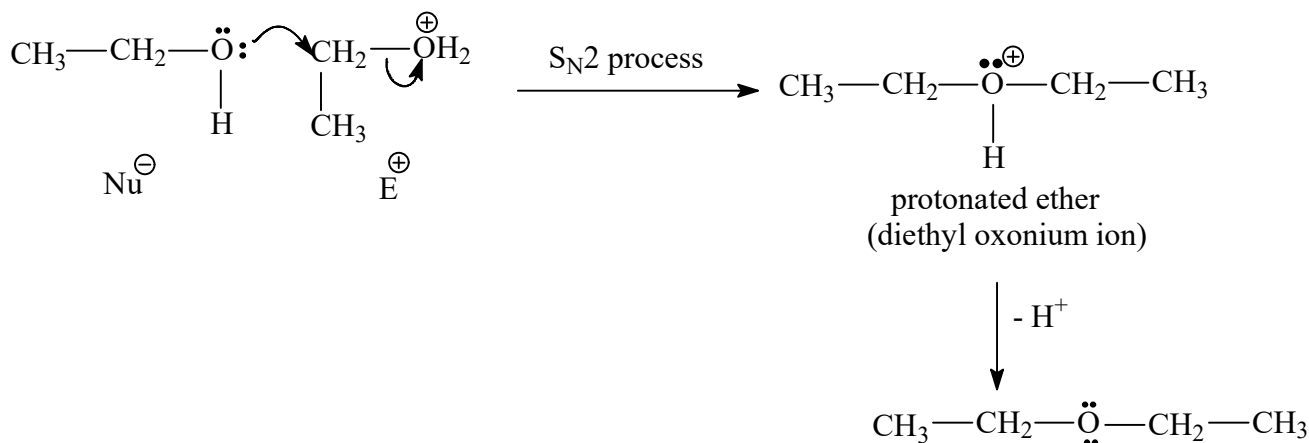
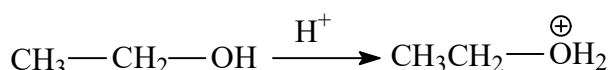
Ethers are described as symmetrical or unsymmetrical depending on whether the two groups bonded to oxygen are the same or different. Symmetrical ethers are also called simple ethers and unsymmetrical ethers are called mixed ethers.

Preparation

- Dehydration of primary alcohols by heating with conc. H_2SO_4 at 140°C .

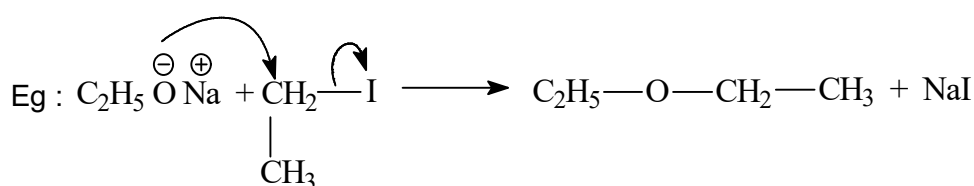


Mechanism



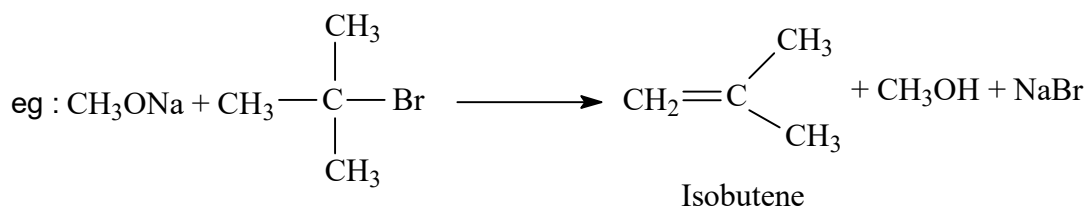
2. Williamson's method

Alkoxide + Alkyl halide \rightarrow ether

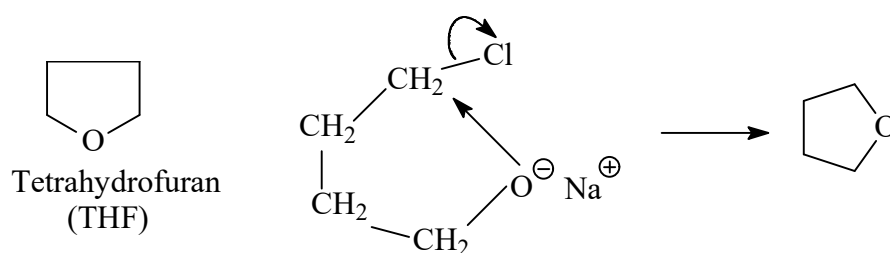
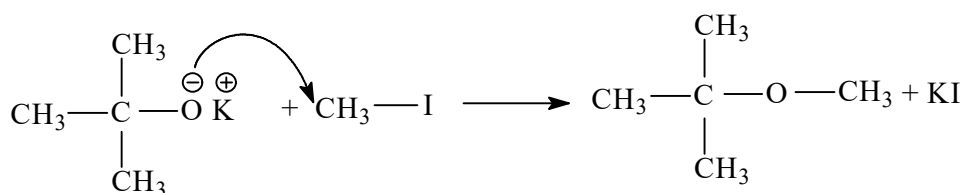
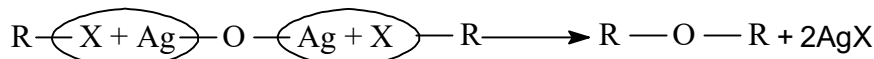


Limitation of this method

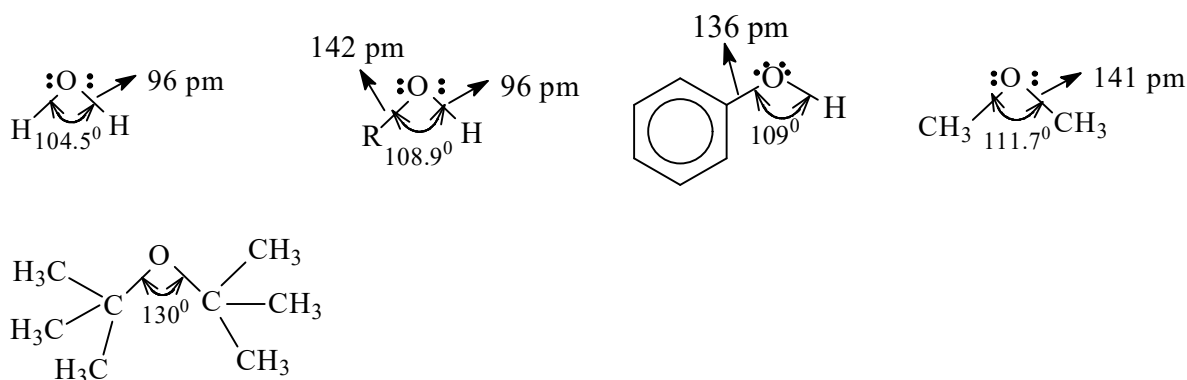
This method fails with tert. alkyl halides, because they undergo elimination.

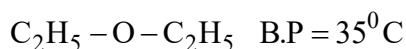
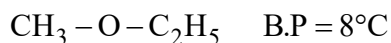
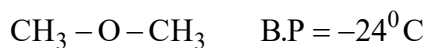


So to prepare tert. butyl methyl ether, tert. butoxide and methyl iodide are allowed to react

**3) Action of dry Ag_2O on alkyl halide****General properties of ethers**

The lower members are gases or volatile liquids and their vapours are highly inflammable. Their boiling points are much lower than those of the alcohols containing the same number of carbon atoms, and this is due to the fact that ethers cannot associate through hydrogen bonding. All the ethers are less dense than water in which they are not much soluble. Just as in alcohols and phenols oxygen is sp^3 hybridised in ethers also.

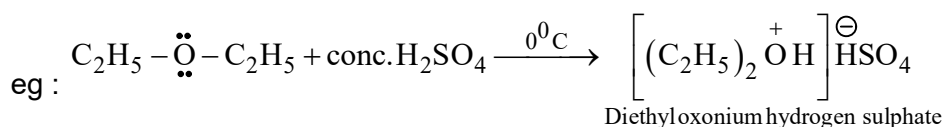
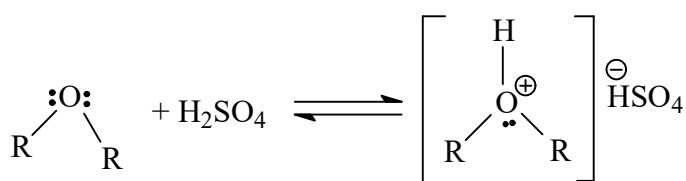




Chemical properties of ethers

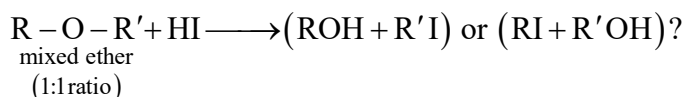
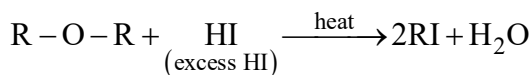
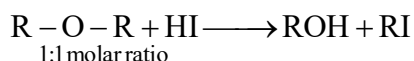
1) Oxonium salt formation

Ethers dissolve in conc. solutions of strong inorganic acids to form oxonium salts. So ethers behave as Bronsted base.



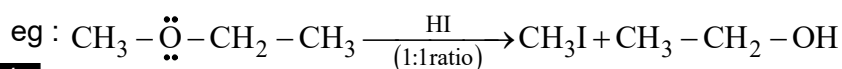
2) Cleavage of C–O bond in ether

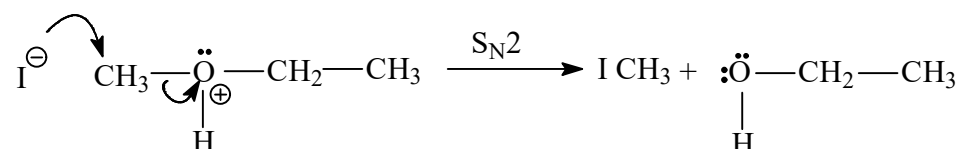
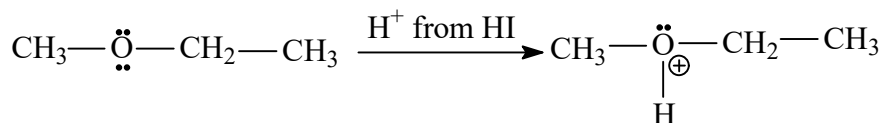
Ethers are the least reactive of the various functional groups. The cleavage of C–O bond in ethers takes place under drastic conditions with excess of halogen acids. Among the halogen acids HI is most effective. Usually conc. HI or HBr is used at high temperature.



To answer this question, the following rules are helpful.

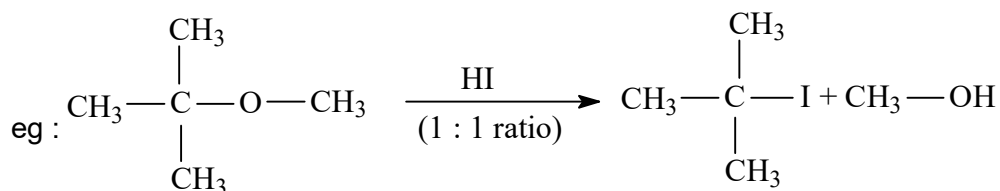
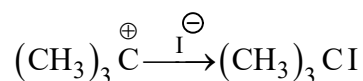
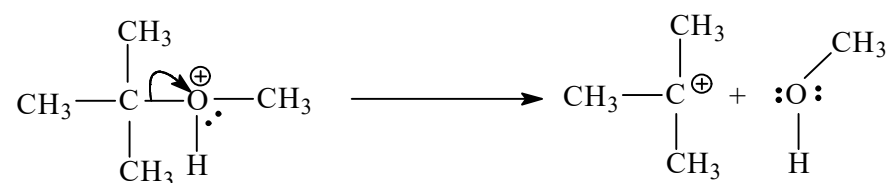
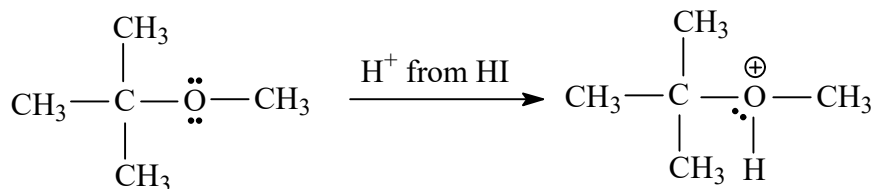
1) If both the alkyl groups are 1° or 2°, then smaller alkyl iodide is formed by an S_N2 mechanism.



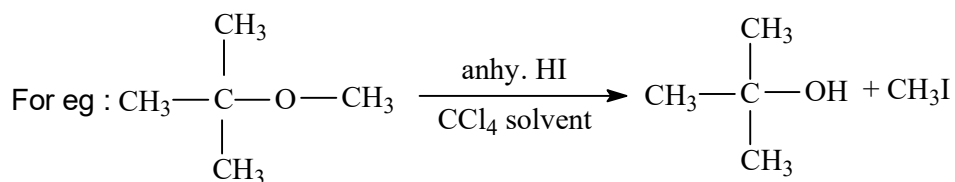
Mechanism

i.e. ether gets protonated first and then I^- will attack the protonated ether from the back side of the smaller alkyl group.

2) If one alkyl group is tertiary then tertiary alkyl iodide is formed and mechanism is $\text{S}_{\text{N}}1$.

**Mechanism**

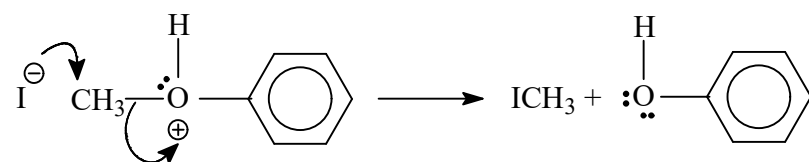
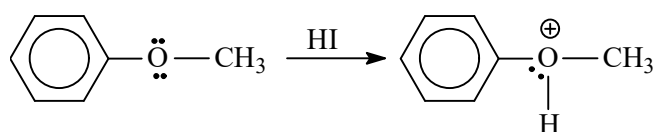
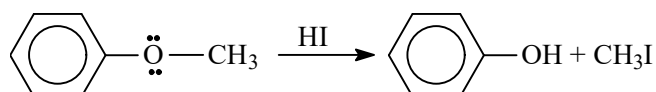
NB: Even if one alkyl group is tertiary, $\text{S}_{\text{N}}1$ cannot operate, if the solvent is non polar.



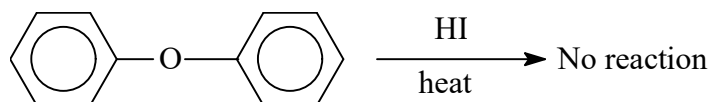
Using anhydrous HI in non polar solvent, S_N1 cannot operate, and cleavage is by S_N2 path, so smaller alkyl iodide is formed.

Rule 3

Aryl alkyl ether always gives phenol and alkyl iodide not phenyl iodide, because bond between benzene ring and oxygen is very strong. Irrespective of the mechanism, i.e, whether S_N1 or S_N2 , phenol and alkyl iodide are formed.

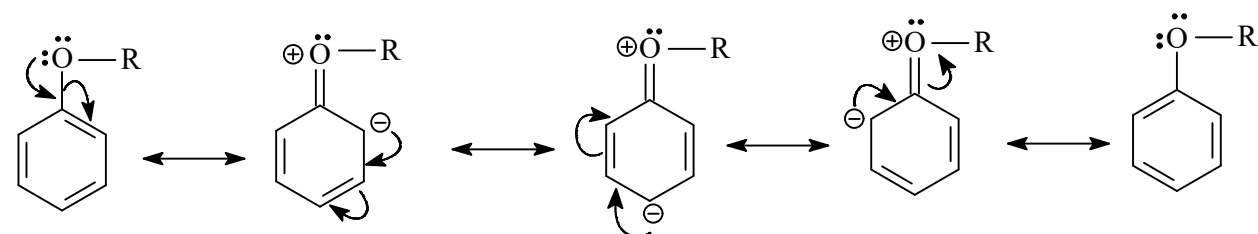


Rule 4 : Diaryl ethers cannot be cleaved by halogen acid

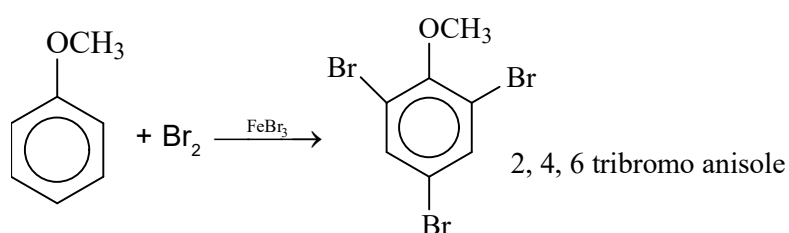
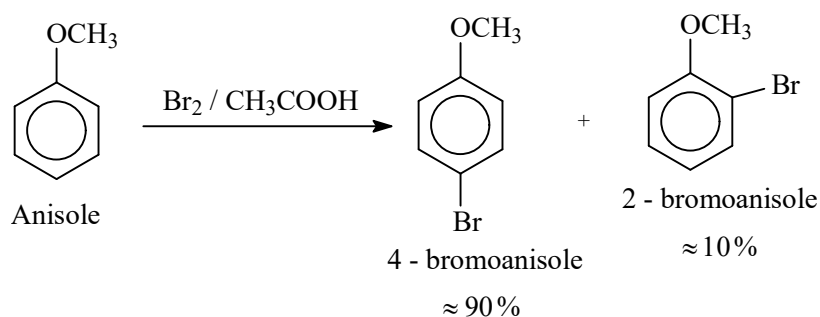


Electrophilic substitution in aromatic ethers

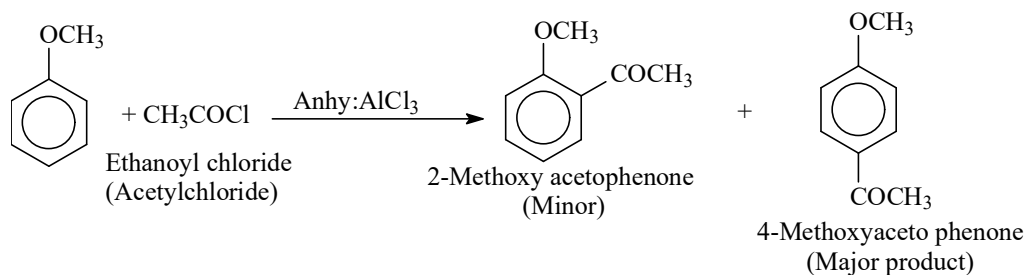
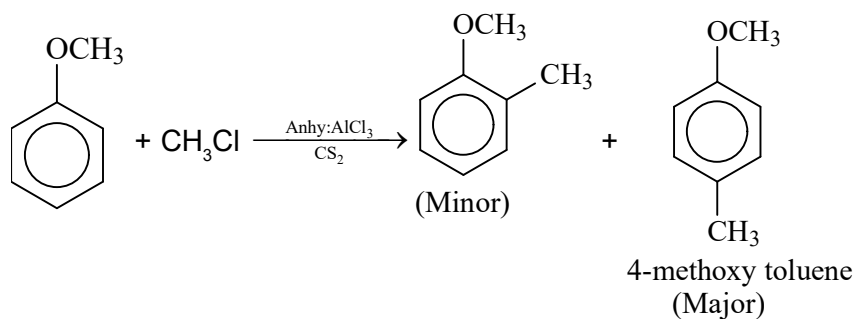
The alkoxy group ($-\text{OR}$) is ortho, para directing and activates the aromatic ring towards electrophilic substitution.



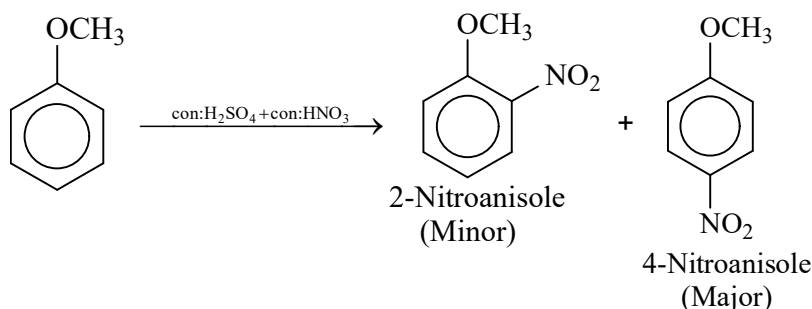
1. Halogenation



2. Friedel-Crafts Alkylation and acylation



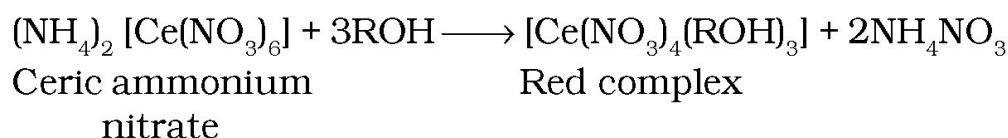
3. Nitration



Test for Alcoholic [R-OH] Group

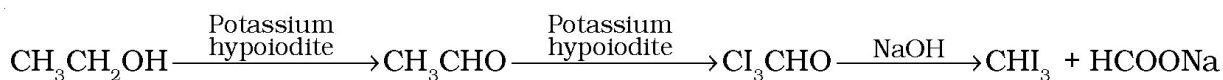
Theory

Alcoholic compounds on reaction with ceric ammonium nitrate give a red colouration due to the formation of a complex.



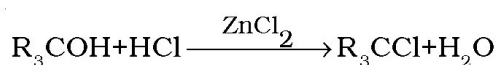
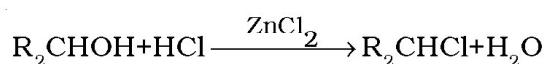
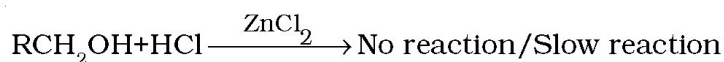
Distinction between primary, secondary and tertiary alcohols can be done on the basis of iodoform test and Lucas test.

Ethanol and secondary alcohols which contain $\text{CH}_3\text{—CH(OH)R}$ group (iodoform reaction) give positive iodoform test. To carry out reaction, potassium iodide and sodium hypochlorite solution are added to the compound in the presence of sodium hydroxide solution. Probably sodium hypochlorite first oxidises potassium iodide into potassium hypoiodite, which oxidises $\text{CH}_3\text{—CH(OH)R}$ group to CH_3COR group and then iodinate it in the alkaline medium of the reaction mixture by replacing the α -hydrogen attached to the carbon atom adjacent to carbonyl group by iodine. Iodoform is formed after cleavage of C—C bond.



Lucas Test

Lucas reagent contains zinc chloride and concentrated hydrochloric acid. This reagent reacts with primary, secondary and tertiary alcohols at different rates. Tertiary alcohols react almost instantaneously, secondary alcohols react in about 1-5 minutes and primary alcohols react very slowly. The reaction may take 10 minutes to several days.



Alcohols are soluble in Lucas reagent but the formed alkyl halides are not soluble. Therefore, formation of two layers in the reaction medium indicate the occurrence of the reaction.

- Primary alcohols – Layers do not separate
- Secondary alcohols – Layers separate within 1-5 minutes
- Tertiary alcohols – Layers separate immediately

Material Required



- Test tube holder : One
- Test tubes : As per need



- Ceric ammonium nitrate solution : As per need
- Sodium hydroxide : As per need
- Iodine solution : As per need
- Lucas reagent : As per need
- Dioxan : As per need

Procedure

A. Ceric ammonium nitrate test

Take 1 mL solution of organic compound dissolved in a suitable solvent. Add a few drops of ceric ammonium nitrate solution. Appearance of red colour shows the presence of alcoholic – OH group.

Note : The red colour disappears after keeping the reaction mixture for sometime. The colour also disappears if excess of ceric ammonium nitrate solution is added. Therefore, use of excess of ceric ammonium nitrate solution should be avoided.

Sodium hydroxide



Iodine



B. Iodoform Test

First method

Take 0.2 mL of the compound in a test tube, add 10 mL of 10% aqueous KI solution and 10 mL of freshly prepared NaOCl solution. Warm gently; yellow crystals of iodoform separate.

Second method

Dissolve 0.1 g or 4 to 5 drops of compound in 2 mL of water. If it does not dissolve, add dioxane drop by drop to get a homogeneous solution. Add 2 mL of 5% sodium hydroxide solution followed by potassium iodide-iodine reagent* dropwise with continuous shaking till a definite dark colour of iodine persists. Allow the reactants to remain at room temperature for 2-3 minutes. If no iodoform separates, warm the reaction mixture in a water bath at 60°C. Add more drops of potassium iodide-iodine reagent. If colour of iodine disappears continue addition of reagent till the colour of iodine persists even after two minutes of heating at 60°C. Remove excess iodine by adding a few drops of sodium hydroxide solution with shaking. Dilute the mixture with equal volume of water and keep it at room temperature for 10-15 minutes. A yellow precipitate of iodoform is obtained if test is positive.

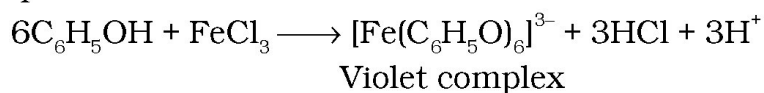
C. Lucas test

Take 1 mL of compound in a test tube. Add 10 mL of Lucas reagent. Shake well and note the time for the separation of two distinct layers.

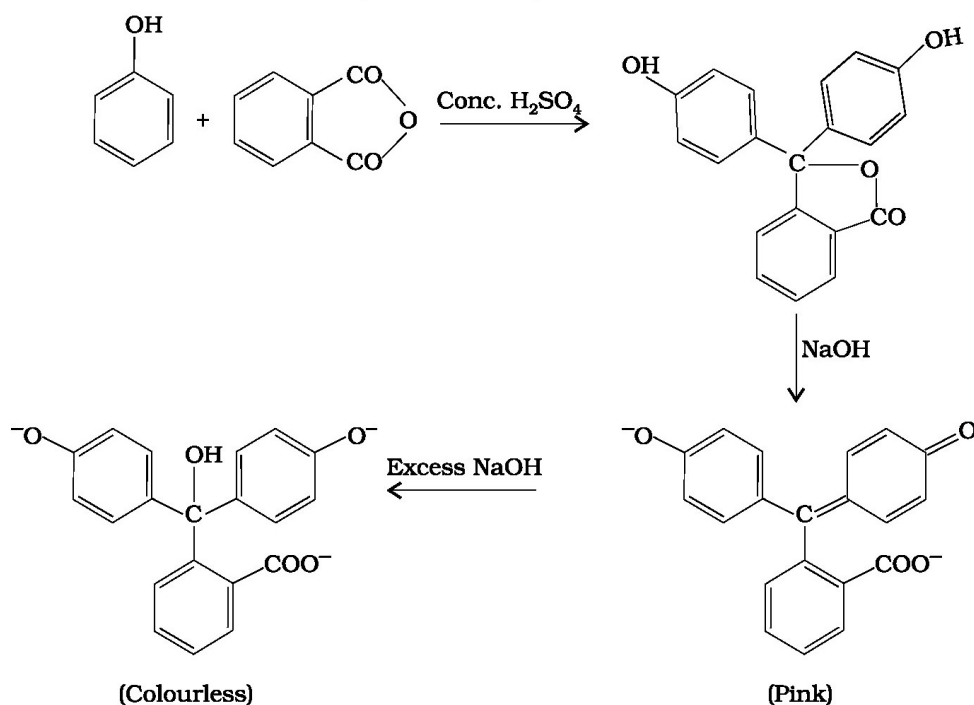
Note : *Lucas test is applicable to only those alcohols which are soluble in the reagent because the test is based on separation of alkyl halides as separate layer.*

III. PHENOLIC [AR - OH] Group

The -OH group attached directly to the ring carbon of an aromatic ring is called phenolic -OH group. Phenols are weakly acidic, therefore they are soluble in NaOH solution but at the same time they are not sufficiently acidic to be soluble in sodium hydrogencarbonate solution. Phenols give coloured complex with neutral ferric chloride solution. For example, phenol gives a complex of violet colour as follows :



Resorcinol, *o*-, *m*- and *p*-cresol give violet or blue colouration, catechol gives green colour which rapidly darkens. 1 and 2-Naphthol do not give characteristics colours. Phenols condense with phthalic anhydride in the presence of concentrated H_2SO_4 , Phenol condenses to give phenolphthalein which gives a dark pink colour with NaOH solution. This is called phthalein dye test.



Colours produced by some other phenolic compounds in phthalein dye test

Compound	Colour	Compound	Colour
<i>o</i> -Cresol	red	Catechol	Usually blue takes longer time to appear
<i>m</i> -Cresol	bluish-purple	Resorcinol	Green fluorescent colour of fluorescein
<i>p</i> -Cresol	No colour		

Material required

- Test tube holder : One
- Test tubes : As per need

- Blue litmus paper
- Ferric chloride solution
- Conc. sulphuric acid
- Sodium hydroxide
- Phthalic anhydride
- Organic compound containing phenolic -OH group

}

According to requirement

Procedure

A. Ferric chloride test

Take 2 mL of aqueous or alcoholic solution of the organic compound in a test tube, add neutral ferric chloride solution dropwise and note the colour change. Appearance of a blue, green, violet or red colour indicates the presence of phenolic –OH group.

*Sulphuric
acid*



*Sodium
hydroxide*



B. Phthalein dye test

Take 0.1 g of organic compound and 0.1 g of phthalic anhydride in a clean dry test tube and add 1-2 drops of conc. H_2SO_4 . Heat the test tube for about 1 minute in an oil bath. Cool and pour the reaction mixture carefully into a beaker containing 15 mL of dilute sodium hydroxide solution. Appearance of pink, blue, green, red etc. colours indicates the presence of phenolic –OH group in the compound. However, the colour disappears on addition of large excess of sodium hydroxide solution.

*Phthalic
anhydride*

