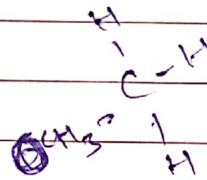
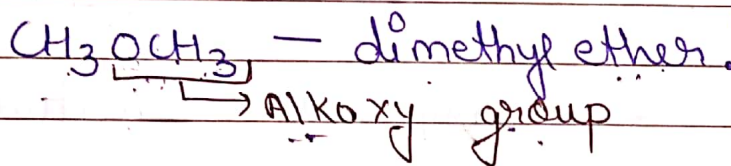
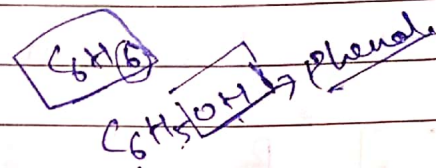
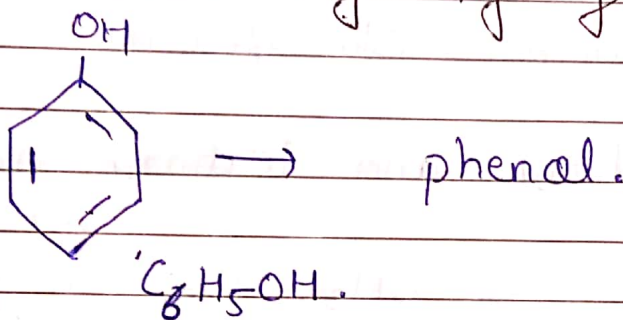
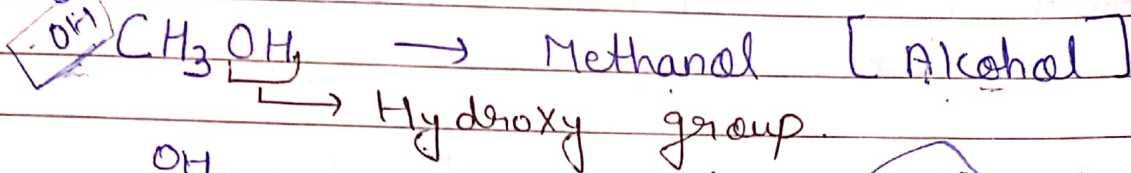
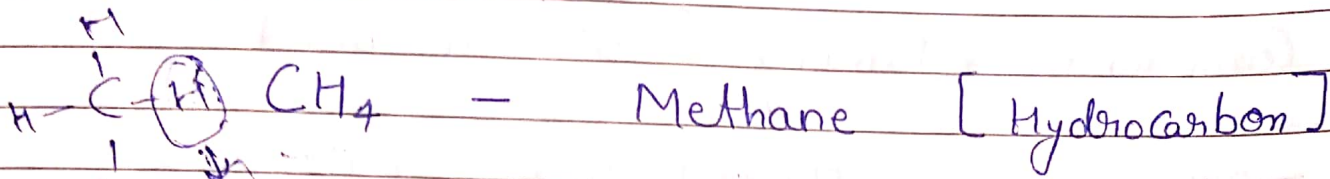


Unit - II  
Alcohols, phenol, and Ethers.

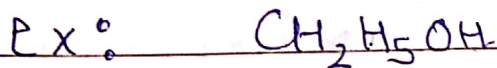
Introduction.



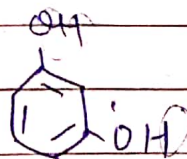
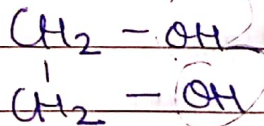
# Classification :

[a] Alcohol and phenols

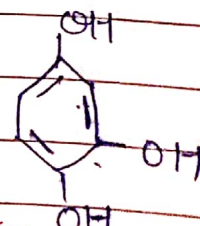
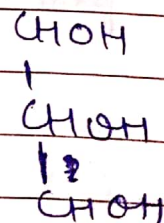
→ They are classified as, Mono, Di, Tri or polyhydric



~~Mono~~ Monohydric



Dihydric



Trihydric

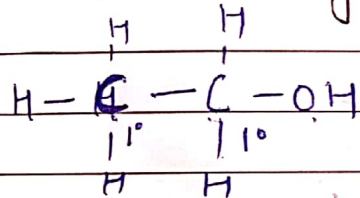
→ Monohydric alcohol further classified to hybridisation of Carbon atom to which hydroxy group is attached.

(i) Compound containing  $sp^3 - OH$  bond.

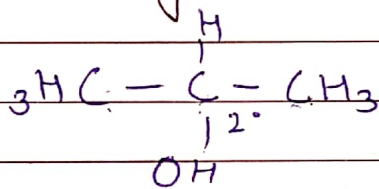
→  $-OH$  group is attached to  $sp^3$  hybridised Carbon.

→ They are further classified as.

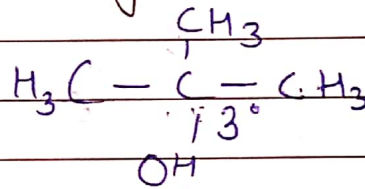
[a] Primary, Secondary and Tertiary alcohol.



primary ( $1^\circ$ )

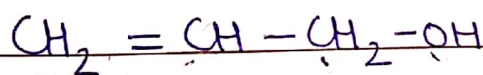


Secondary ( $2^\circ$ )

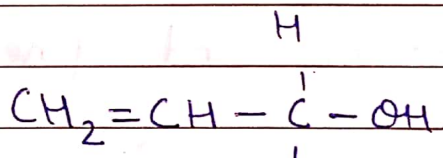


Tertiary ( $3^\circ$ )

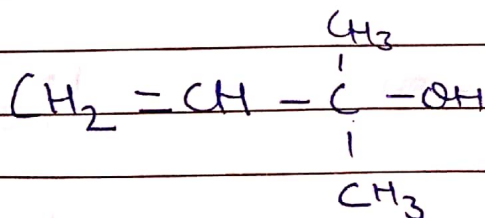
[b] Allylic alcohol.



primary



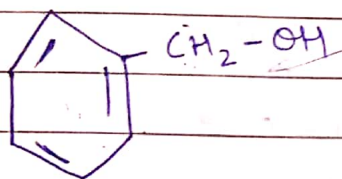
Secondary



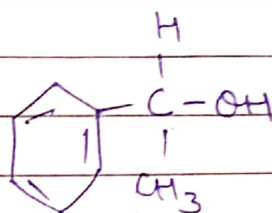
Tertiary.



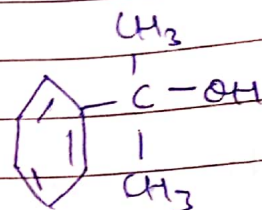
[c] Benzylic alcohol.



1°

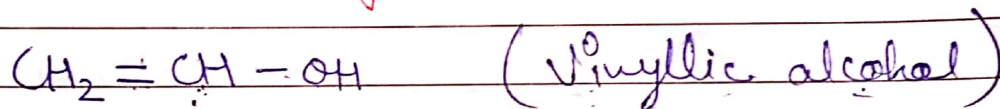


2°



3°

[ii] Compound containing  $C_{sp^2} - OH$  bond:



[B] Ethers

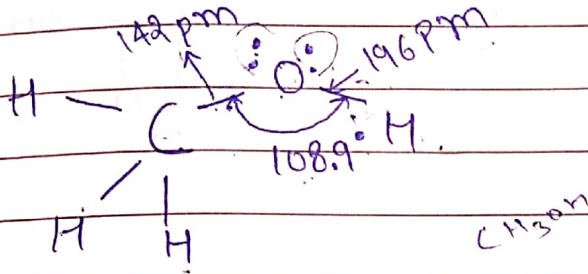
→ They are classified as Simple/Symmetrical and Mixed/Unsymmetrical.

For ex: (i)  $C_2H_5 - O - C_2H_5$  → Symmetrical ether

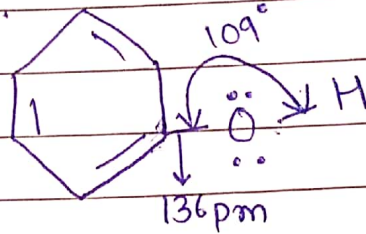
(ii)  $C_2H_5 - O - CH_3$  → Unsymmetrical.



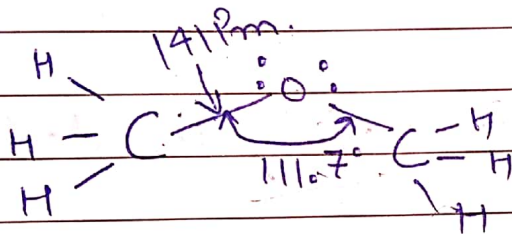
## # Structure of functional group.



Methanol.



phenol.

→ Methoxy methane.  
(ether)

Q. The bond angle in alcohol is slightly less than tetrahedral angle ( $109^\circ - 28'$ ). why?

Ans Due to the repulsion b/w the unshared pairs of electron of oxygen.

Q. Carbon-oxygen bond length in phenol is less than that in methanol. why?

Ans (i) due to partial double bond character  
(ii)  $sp^2$  hybridised state of carbon to which oxygen is attached. [50% s-character]

Q. The bond angle in Methoxymethane [ether] is slightly greater than tetrahedral angle. why?

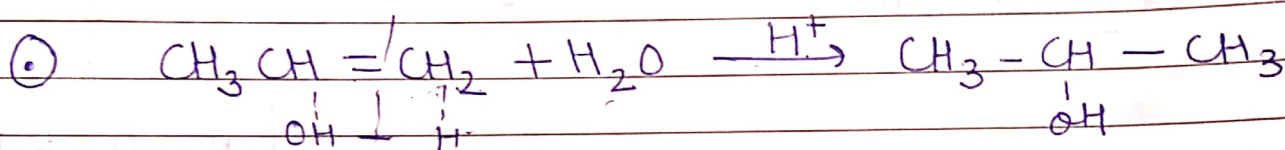
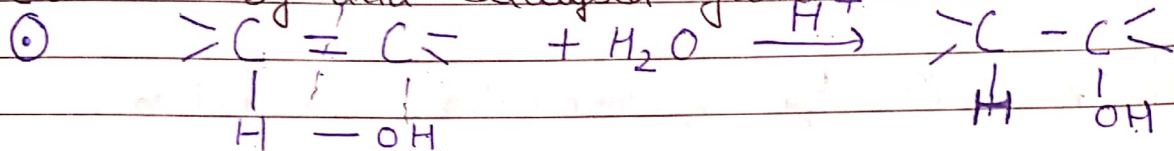
Ans due to bulky alkyl groups.

# # Alcohols and phenols.

## ⊙ Preparation of Alcohols.

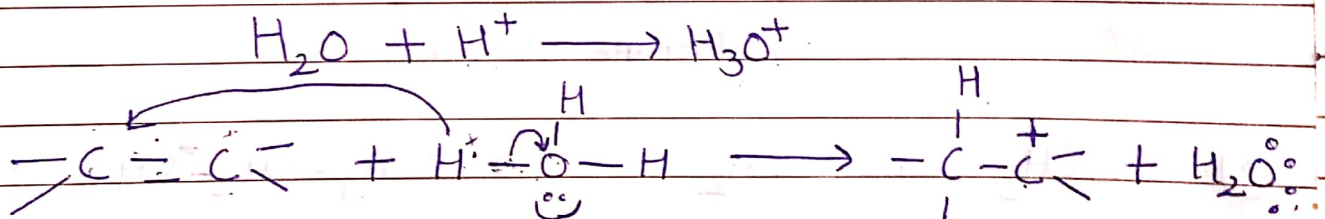
1. from alkenes

[i) By acid Catalysed hydration.

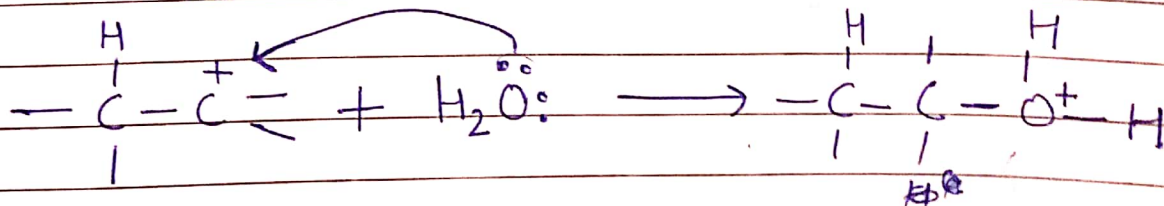


→ Mechanism

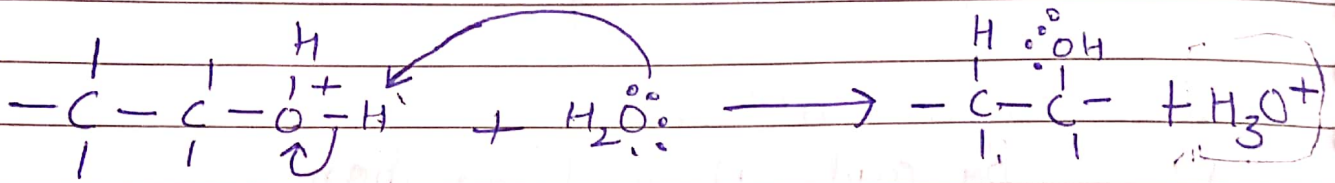
STEP-1 Protonation of alkene to form Carbocation  
by electrophilic attack of  $\text{H}_3\text{O}^+$ .



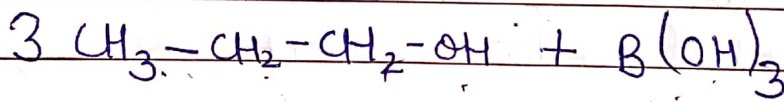
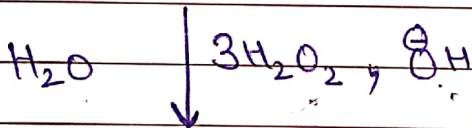
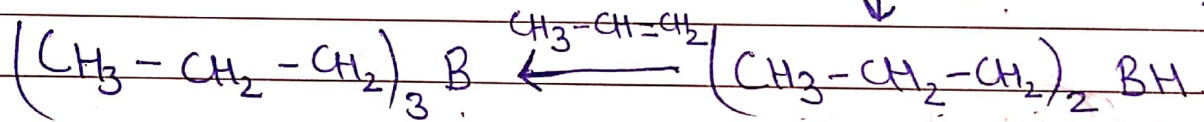
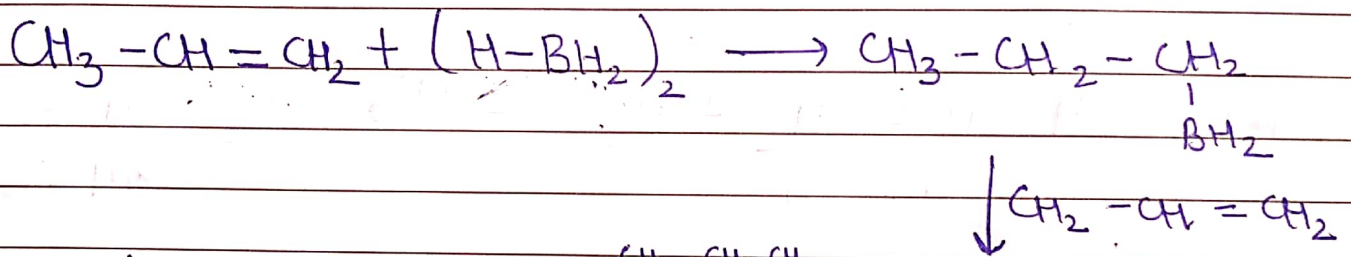
STEP-2: Nucleophilic attack of water on Carbocation.



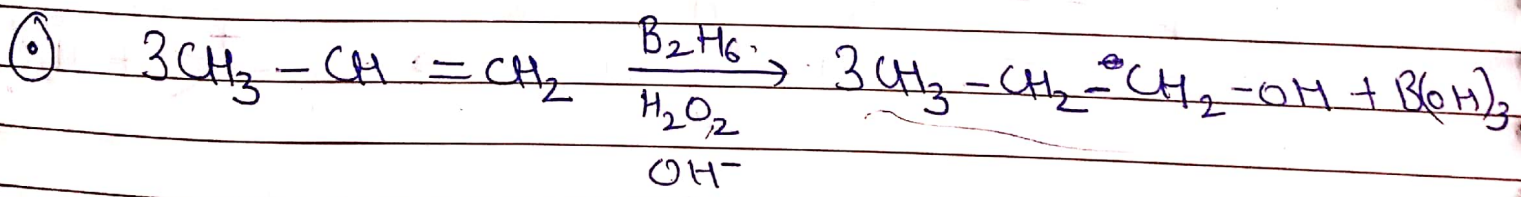
STEP-3 Deprotonation to form an alcohol.



(ii) Formed by hydroboration Oxidation.

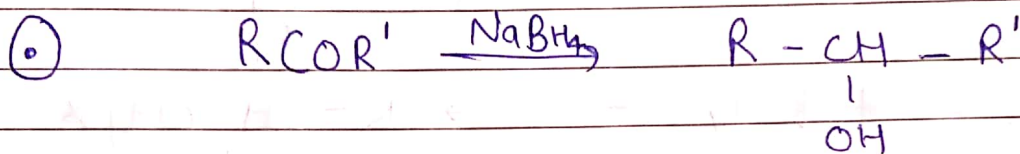
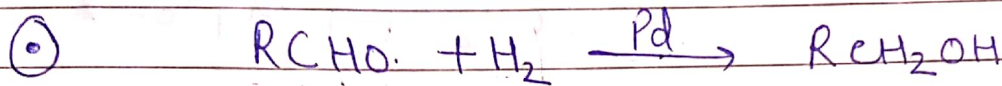


Propane-1-ol.



## 2. from Carbonyl Compounds.

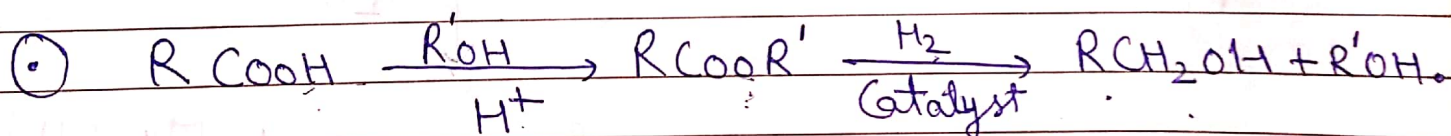
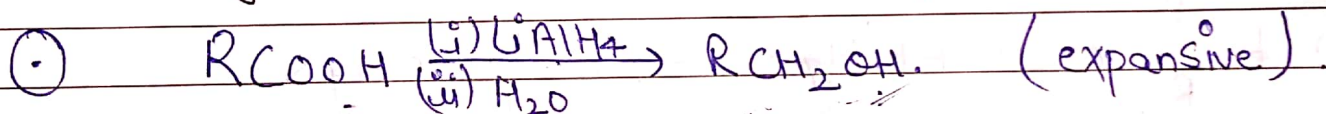
[i] Reduction of aldehyde and ketone.



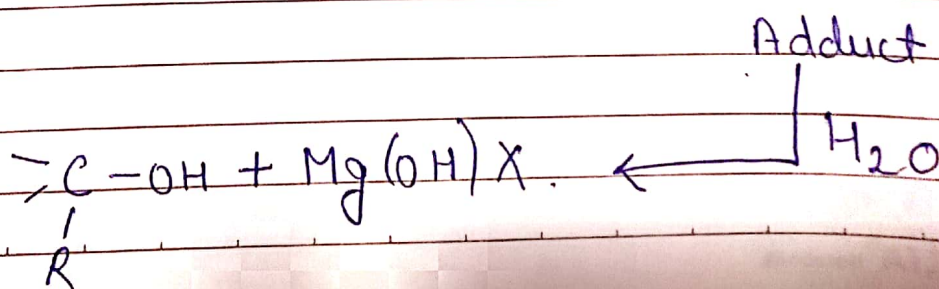
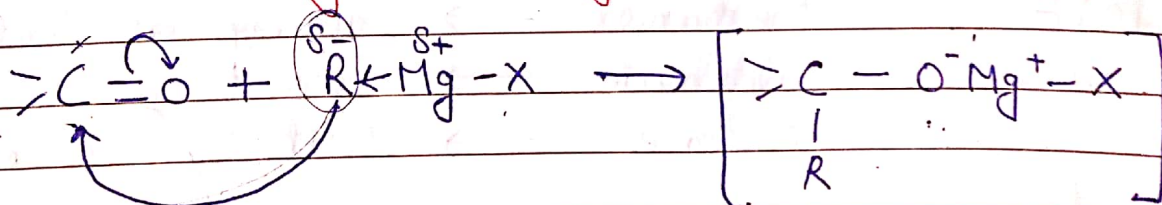
NOTE

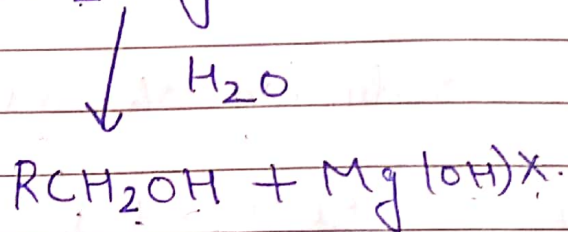
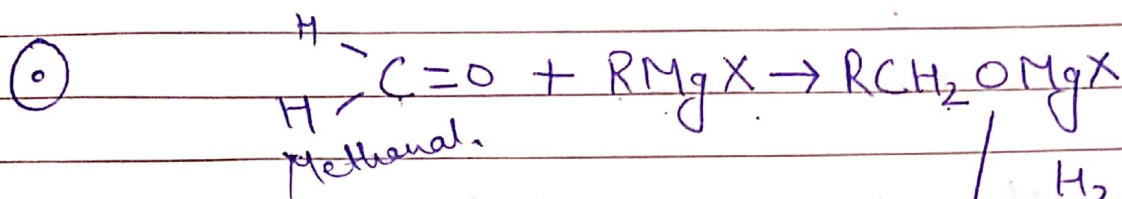
Aldehyde  $\longrightarrow$  primary alcohols  
ketone  $\longrightarrow$  secondary alcohols

[ii] By reduction of carboxylic acid and ester.

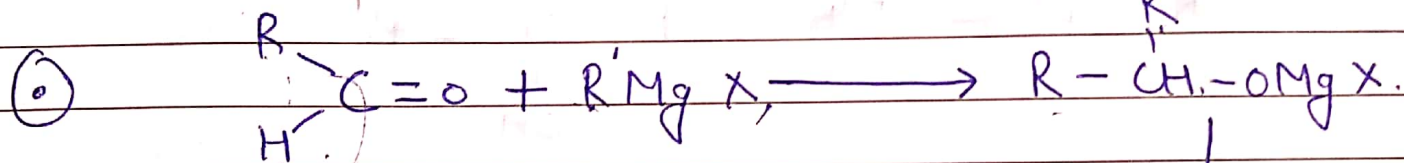


## 3. From Grignard reagent.

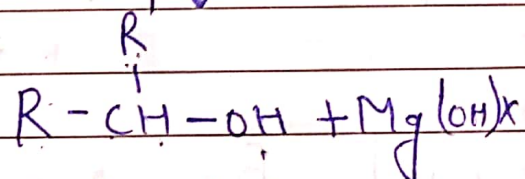




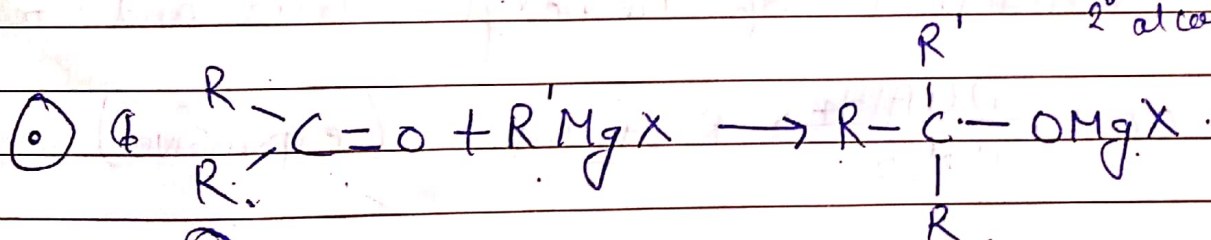
1° alcohol.



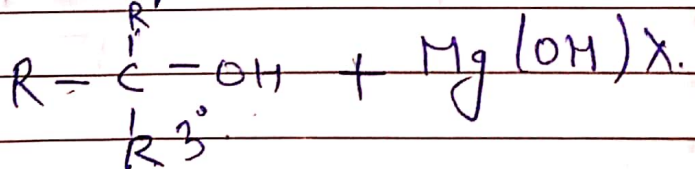
↓ H<sub>2</sub>O



2° alcohol.



↓ H<sub>2</sub>O



**NOTE**

Methanal

→ primary alcohol.

aldehyde

→ Secondary alcohol.

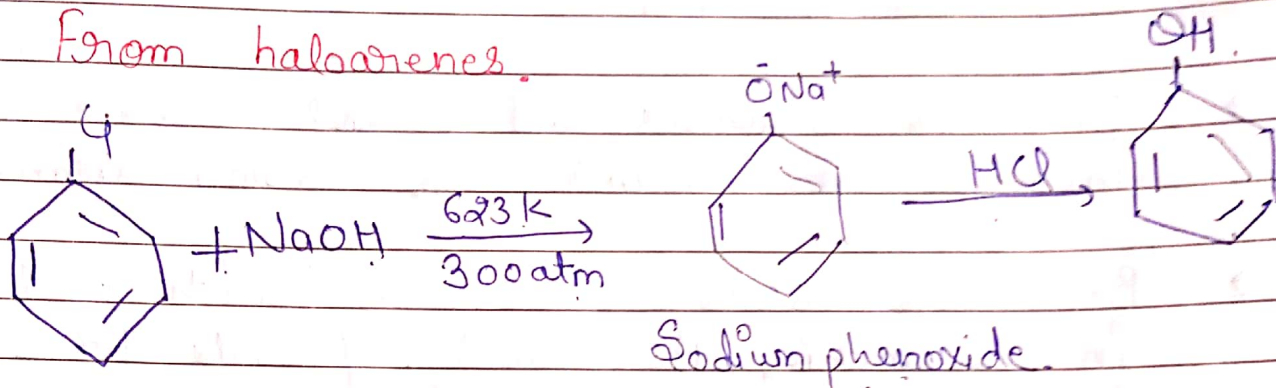
Ketone

→ tertiary alcohol.

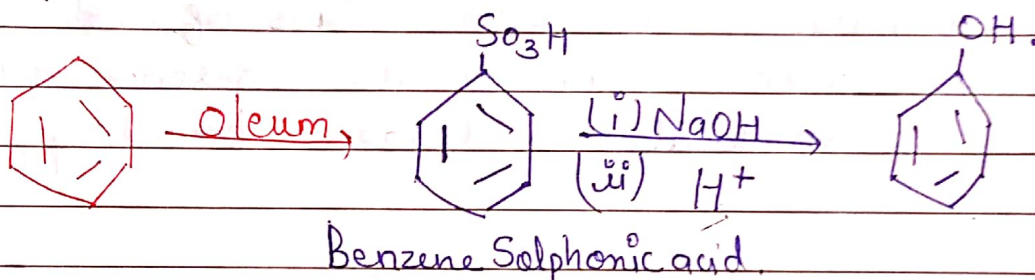


# # Preparation of phenol.

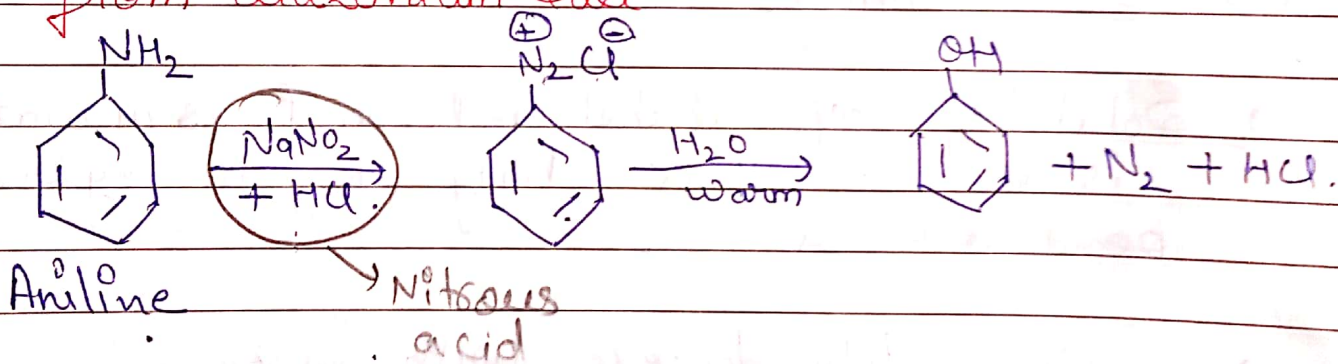
## 1. From haloarenes.



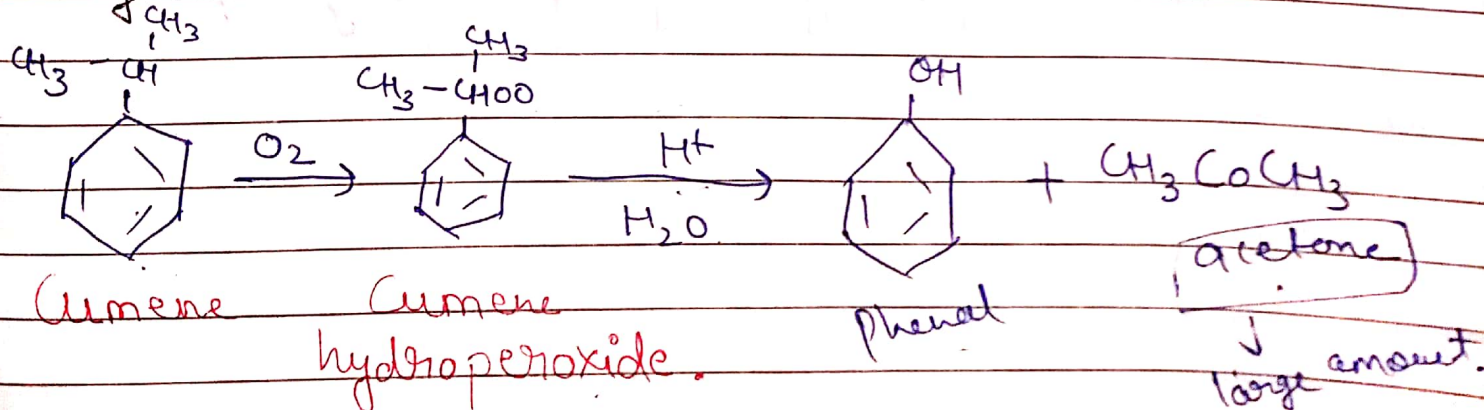
## 2. From benzenesulphonic acid.



## 3. From diazonium salt



## 4. From Cumene.



##

## Physical properties.

### ① Boiling point.

→ B.P of alcohols and phenol increase with increase in number of carbon atoms.

→ B.P of alcohols decrease with increasing in branching. As Vander Waals force decrease with decrease in surface area.

**Note:** B.P of alcohols and phenol higher in comparison to other class of compound (Hydrocarbon). due to the presence of intermolecular hydrogen bonding.

### ① Solubility.

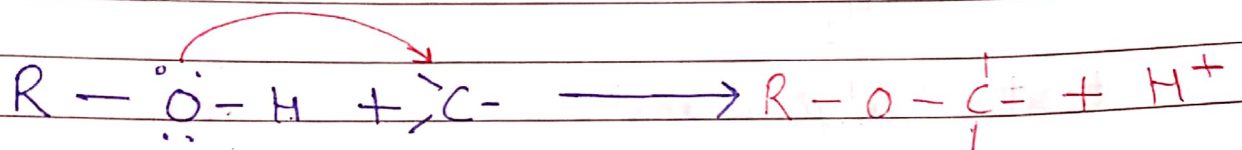
→ Solubility of alcohol and phenol in water is due to their ability to form hydrogen bond with water.

→ Solubility decrease with increase in size of alkyl/aryl (hydrophobic) group.

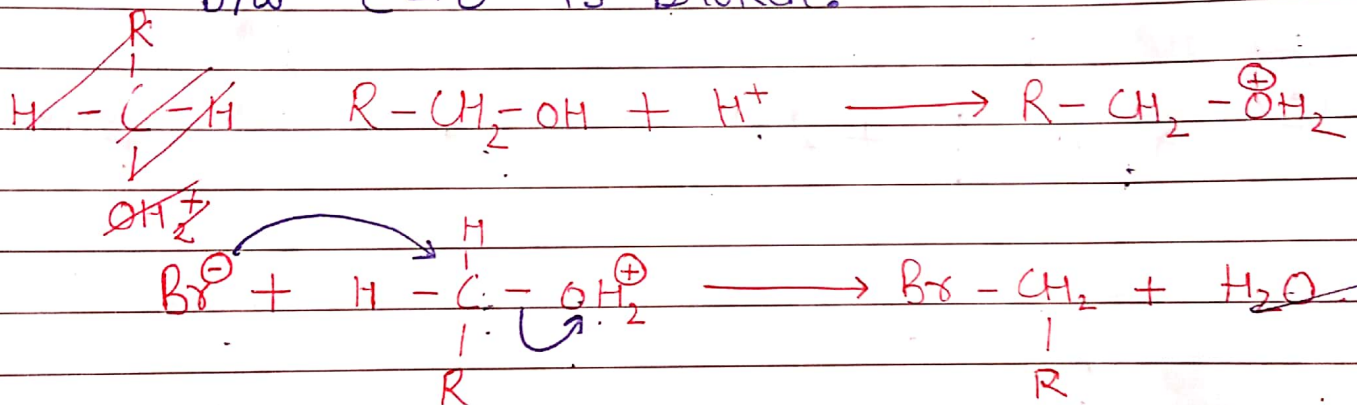
# # CHEMICAL REACTIONS.

- Alcohols are versatile compounds. They react as nucleophiles as well as electrophiles.

NOTE: when alcohol react with as nucleophiles bond b/w O-H is broken.



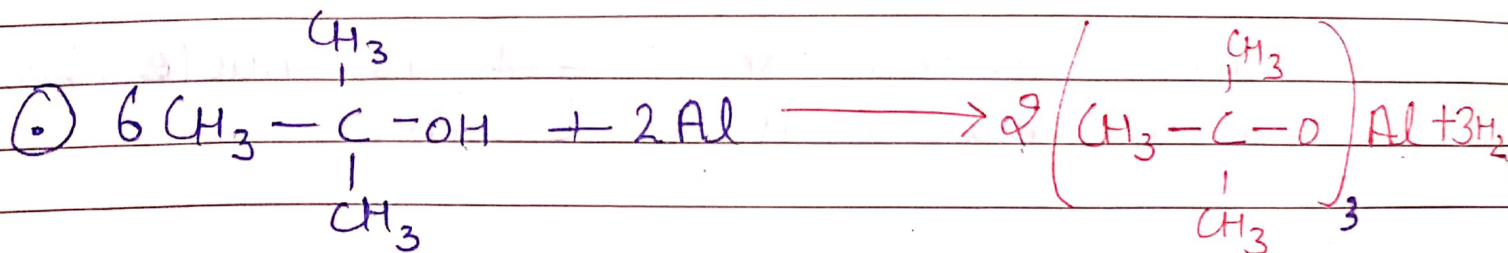
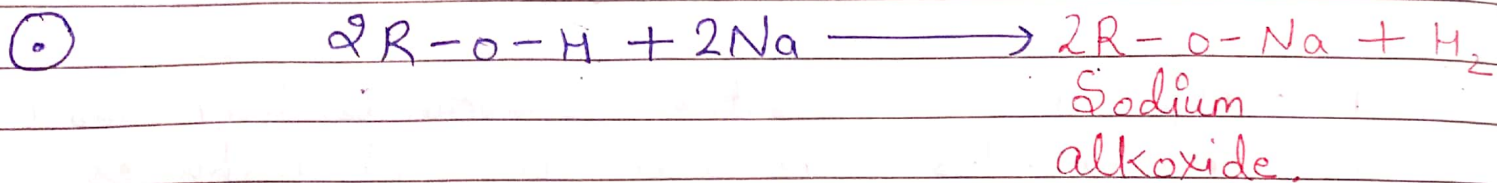
- (ii) when alcohol react as electrophiles. bond b/w C-O is broken.



[a] Reaction involving cleavage of O-H bond.

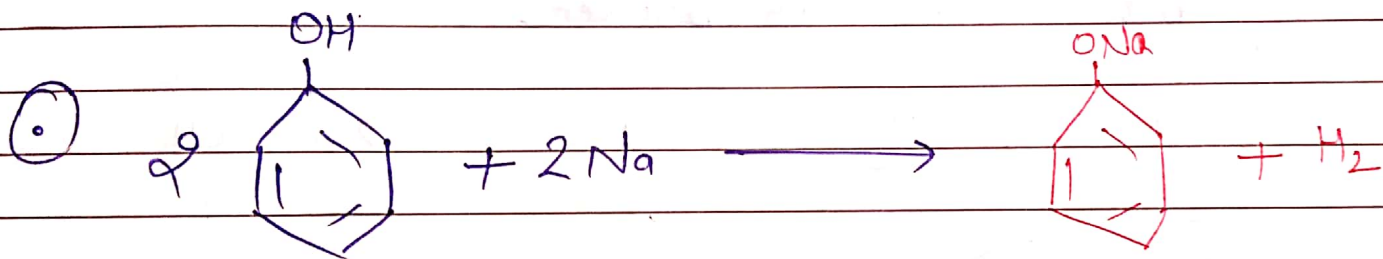
## 1. Acidity of alcohols and phenols.

→ Alcohol and phenol react with Metal Such as Sodium, potassium and aluminium to yield alkoxide/phenoxide.

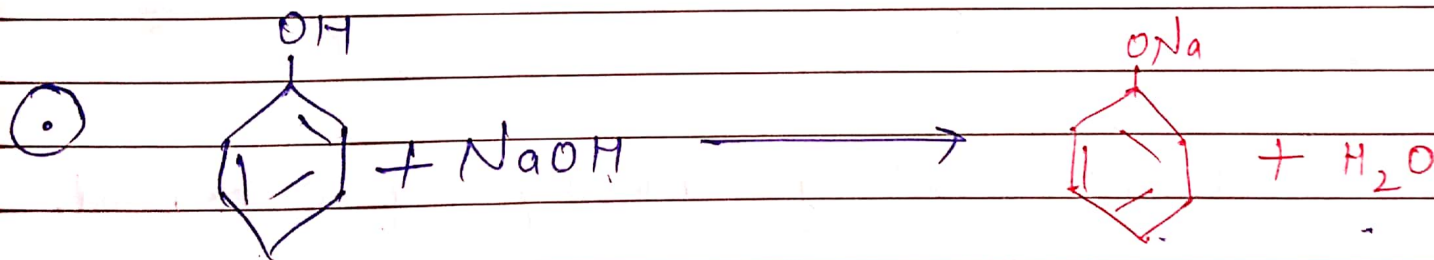


tert-Butyl alcohol.

Aluminium tert-butoxide

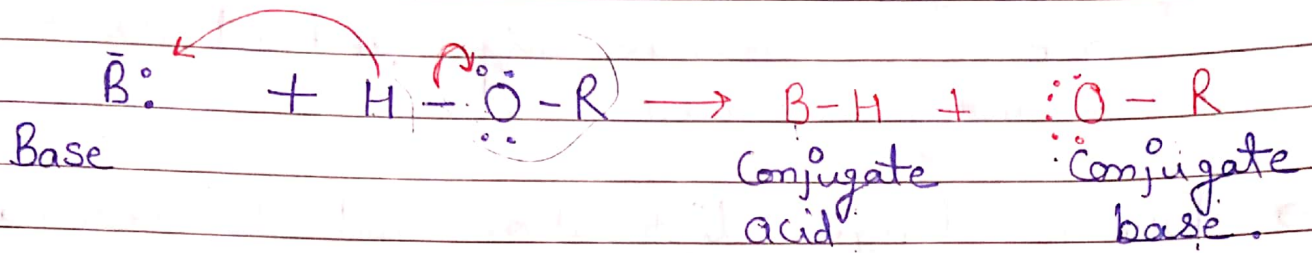


Sodium phenoxide

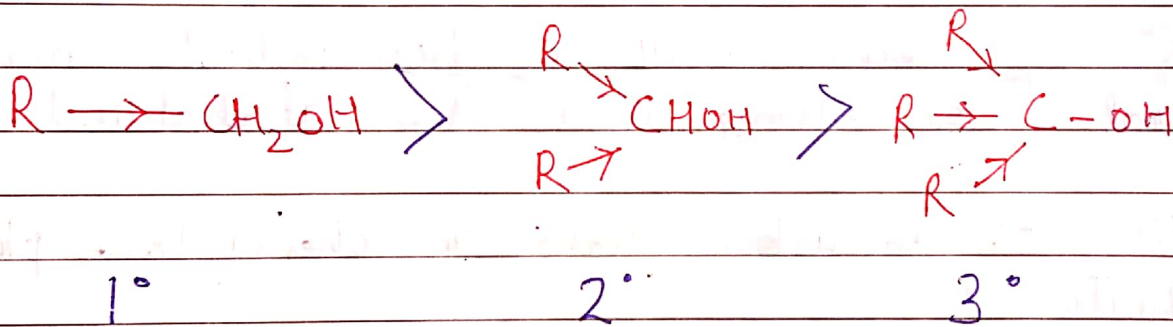


→ The above reaction show that alcohol and phenol are acidic in nature.

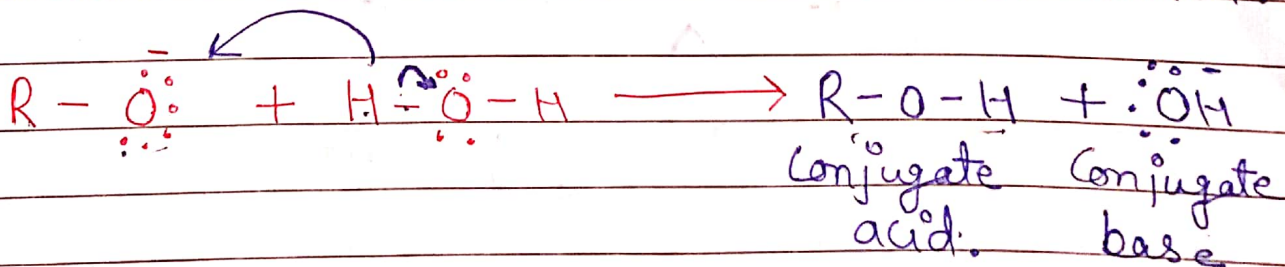
⊙ Alcohol and phenol are Bronsted acid. i.e. they can donate a proton to a strong base.



[ii] Acidity of phenol & alcohol: It is due to the polar nature of O-H bond. Presence of e<sup>-</sup> donating group (-CH<sub>3</sub>, -C<sub>2</sub>H<sub>5</sub>) increase e<sup>-</sup> density on oxygen. Result in decreasing the polarity of OH bond. Hence, decrease the acid strength.



→ Alcohols are weaker acid than water.

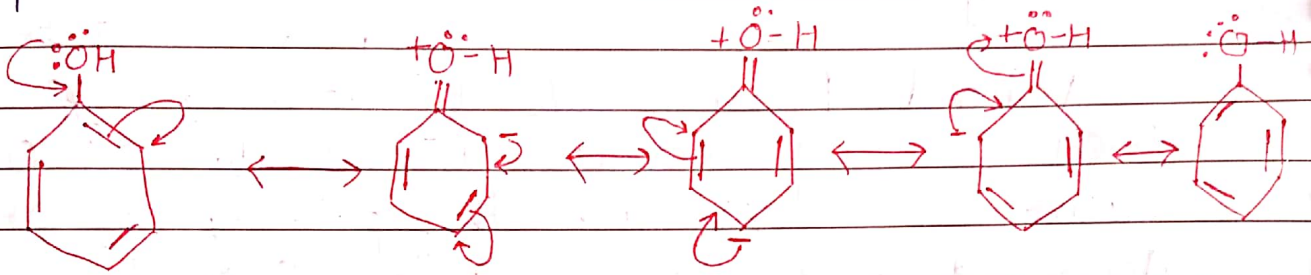


⊙ Alcohol act as Bronsted base as well due to the presence of unshared paired e<sup>-</sup> on oxygen which make them proton acceptor.

### (iii) Acidity of phenols:

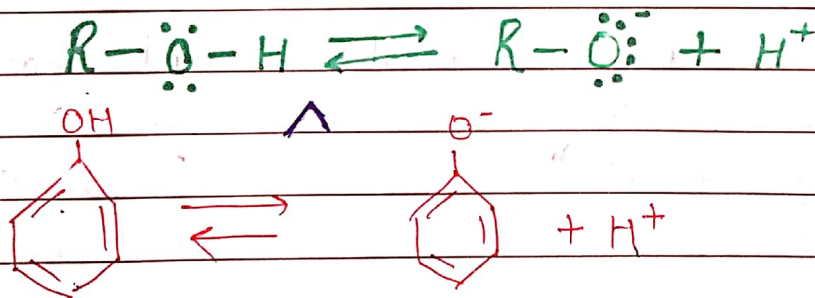
○ Hydroxy group is directly attached to  $sp^2$  hybridised carbon of benzene ring and act as  $e^-$  withdrawing group.

→ Due to charge distribution and its resonance structure cause oxygen of OH group to be positive.



→ The  $R^H$  of phenol with aq. NaOH indicate that phenol are strong acid than alcohol and water.

○ Ionisation of an alcohol and phenol take place as follow:



Due to higher electronegativity of  $sp^2$  hybridised carbon of phenol to which  $-OH$  is attached, electron density decr. on oxygen and incr. the polarity of  $O-H$  bond and increase ionisation in phenol that of alcohol.

alcohol.

→ The presence of  $e^-$  withdrawing group such as Nitro group increase the acidic strength of phenol. This effect is more pronounced when such a group is present at Ortho and para positions.

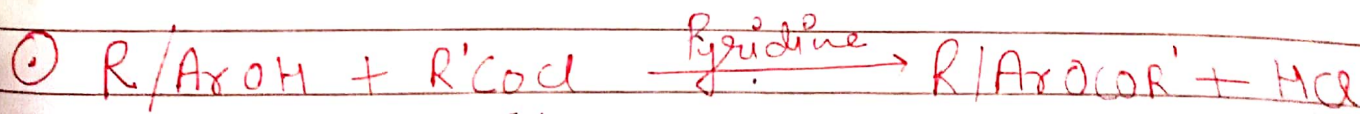
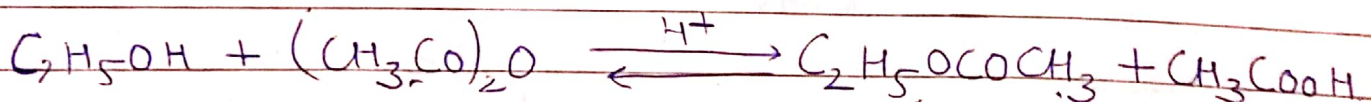
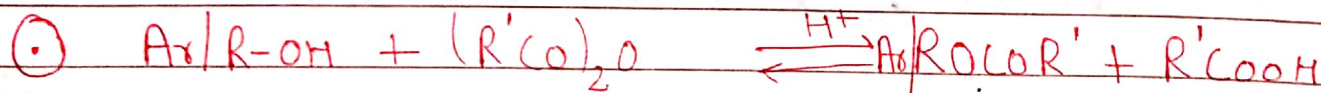
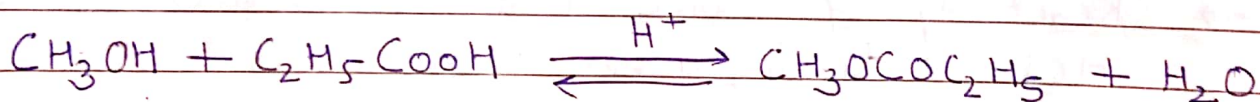
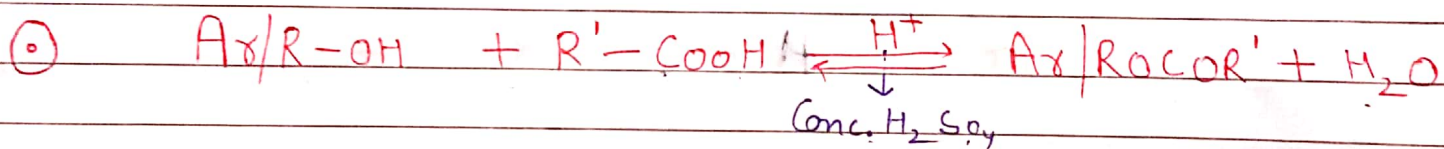
(1,2)

(1,4)

→ Presence of  $e^-$  donating group such as alkyl group decrease the acidic strength of phenol.

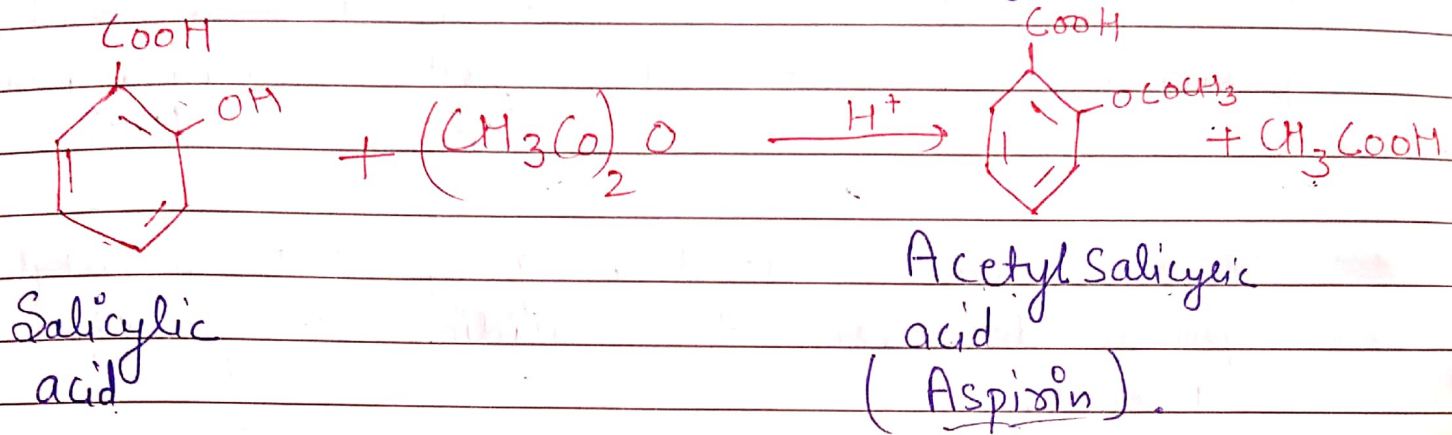
## # Esterification.

Alcohol and phenol react with Carboxylic acid, acid chloride and acid anhydrides to form ester.



## ① Acetylation of Salicylic acid.

→ Introduction of acetyl ( $\text{CH}_3\text{CO}$ ) group in alcohol and phenol is known as acetylation.



[b] Reaction involving cleavage of C-O bond in alcohols.

[i] Reaction with hydrogen halides:



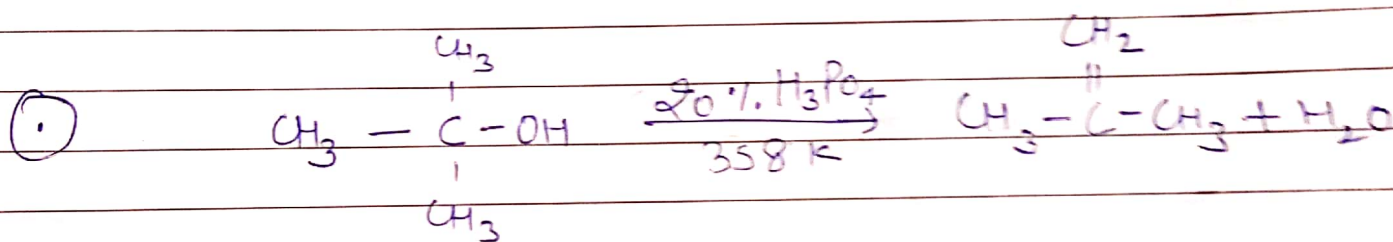
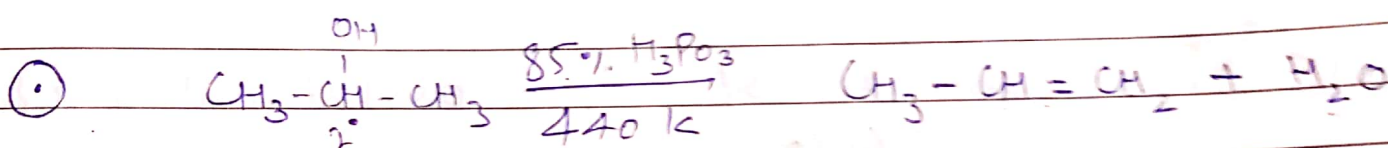
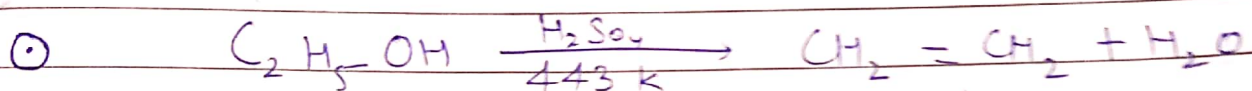
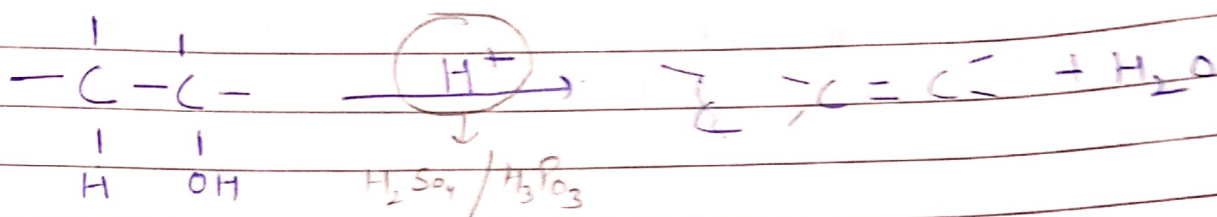
→ Reactivity of three class of alcohol with HCl distinguishes from Lucas test

Lucas Reagent (Conc. HCl and  $\text{ZnCl}_2$ )

- $3^\circ$  alcohol → turbidity produce immediately
- $2^\circ$  alcohol → Take some time.
- $1^\circ$  alcohol → do not produce turbidity.



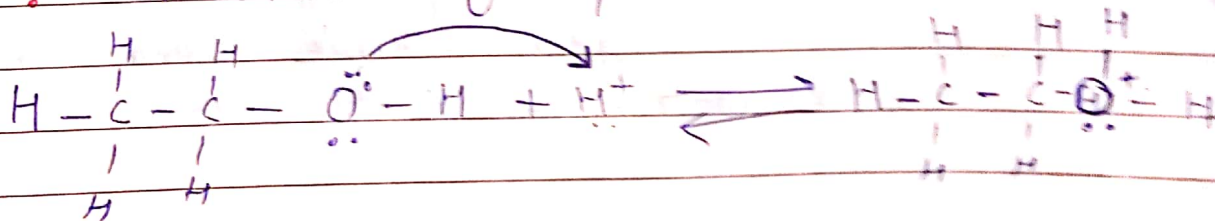
## → Dehydration [Loss of water]



Tertiary > Secondary > Primary

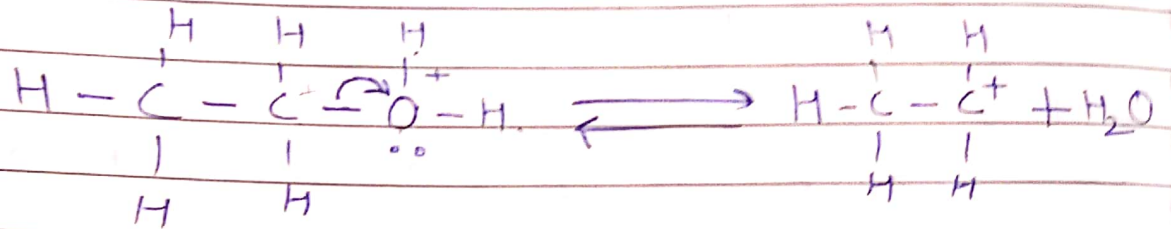
## → Mechanism

① STEP 1: Formation of protonated alcohol.

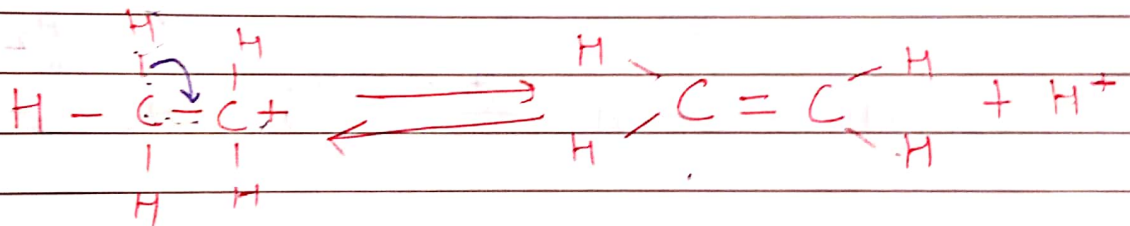


Protonated alcohol  
(Ethyl Oxonium ion)

STEP 2: Formation of Carbocation: It is Slowest Step and hence, the rate determining Step of Reaction.



STEP 3: Formation of ethene by elimination of a proton.

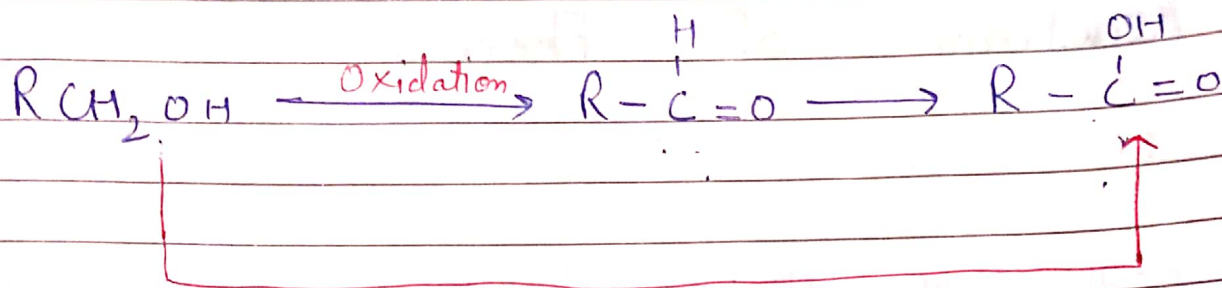


① The acid used in Step 1 released & in Step 3.

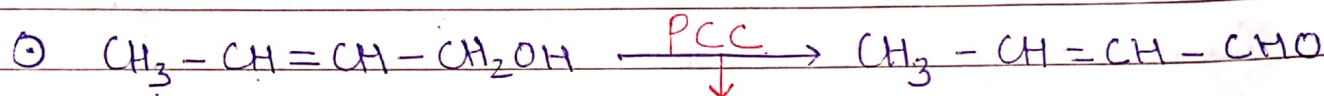
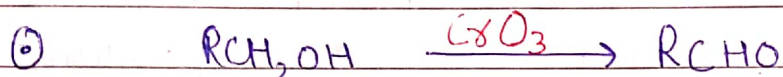
② Oxidation: involve the formation of Carbon Oxygen double bond with cleavage of an O-H and C-H bond.



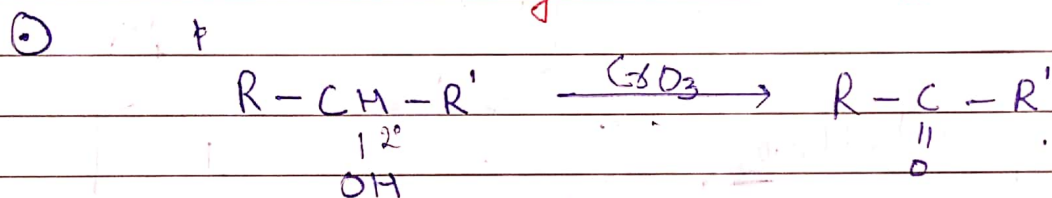
also known as dehydrogenation reaction as loss of dihydrogen from an alcohol.



acidic KMnO<sub>4</sub>

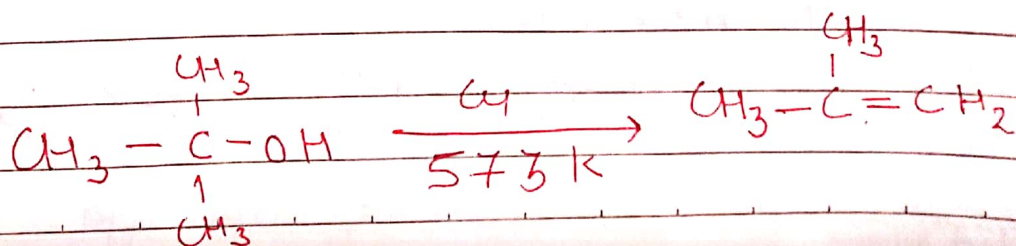
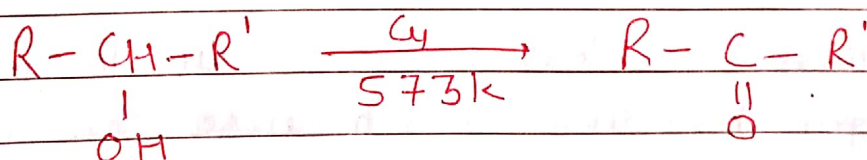
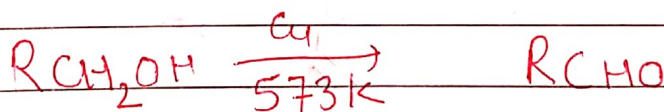


Pyridinium chlorochromate



**NOTE:** 3° Alcohol do not Undergo Oxidation.

① When Vapour of 1° or a 2° alcohol are passed over heated Cu at 573K. then.

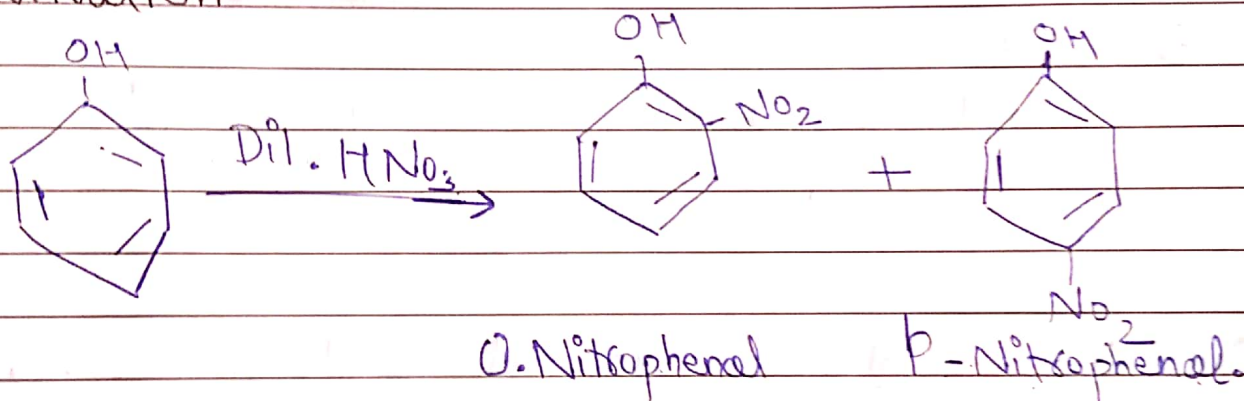


# # Reactions of Phenols

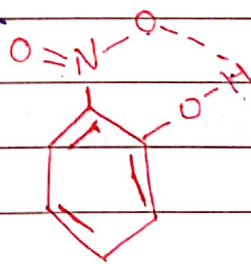
## 1. Electrophilic aromatic Substitution.

- The -OH group attached to benzene ring activates it toward electrophilic Substitution.
- Also it direct the incoming group to ortho and para position in ring as these position become electric rich due to resonance effect caused by -OH group

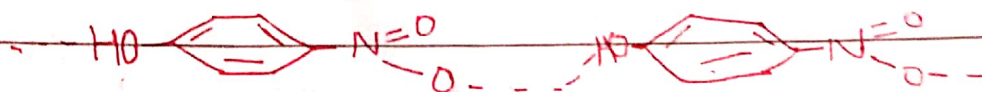
### [i] Nitration

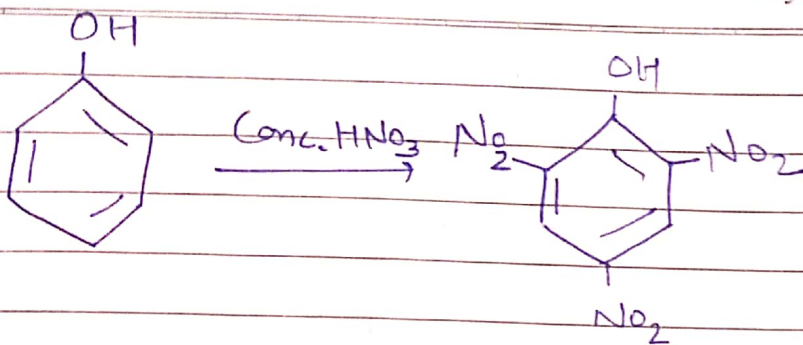


→ o-nitrophenol is steam volatile due to intramolecular hydrogen bonding.



→ p-nitrophenol is less volatile due to intermolecular hydrogen bonding which cause the association of molecule

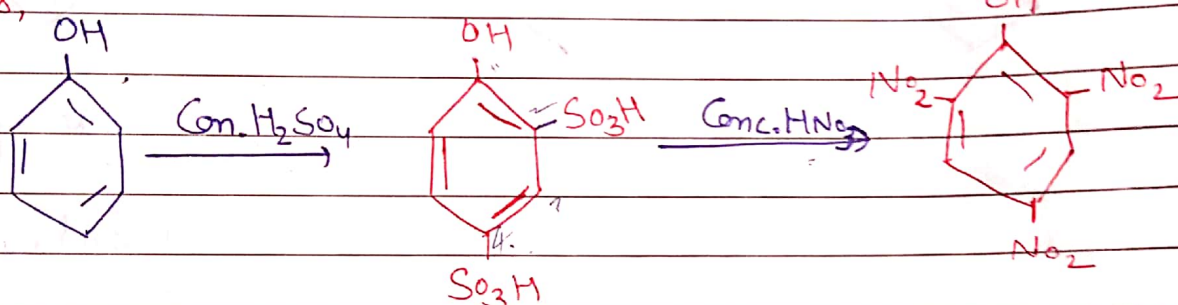




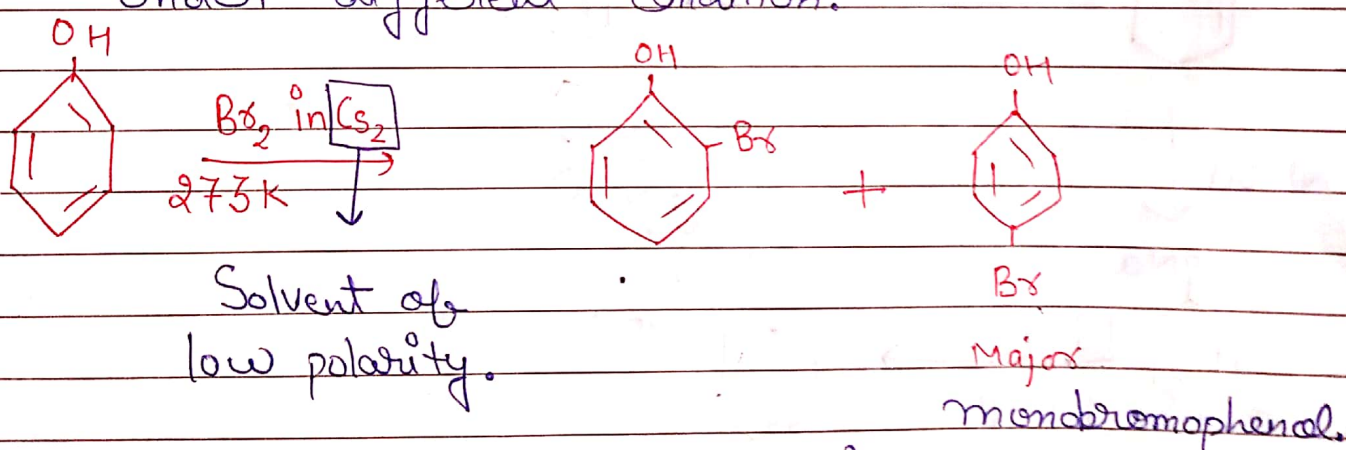
2,4,6-Trinitrophenol.  
(picric acid)

The yield of reaction product is poor.

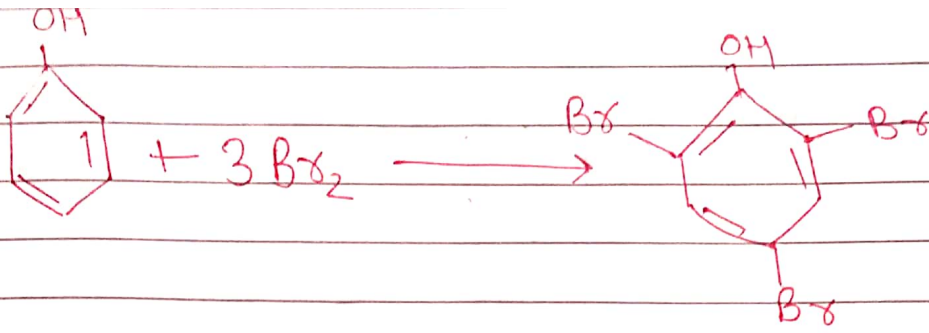
New days,



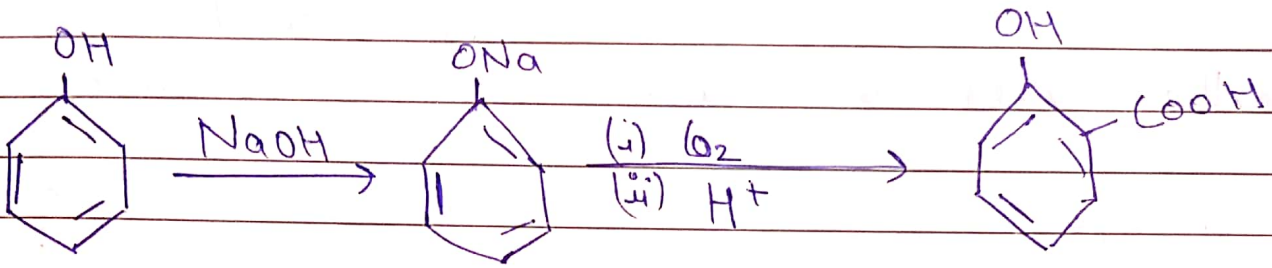
(ii) Halogenations: Treating phenol with bromine different product are formed under different condition.



⊙ Halogenation of benzene take place in presence of Lewis acid such as  $\text{FeBr}_3$ , which polarise halogen molecule. In case of phenol polarisation of bromine molecule take place in absence of Lewis acid. due to highly activating effect of  $-\text{OH}$  group.



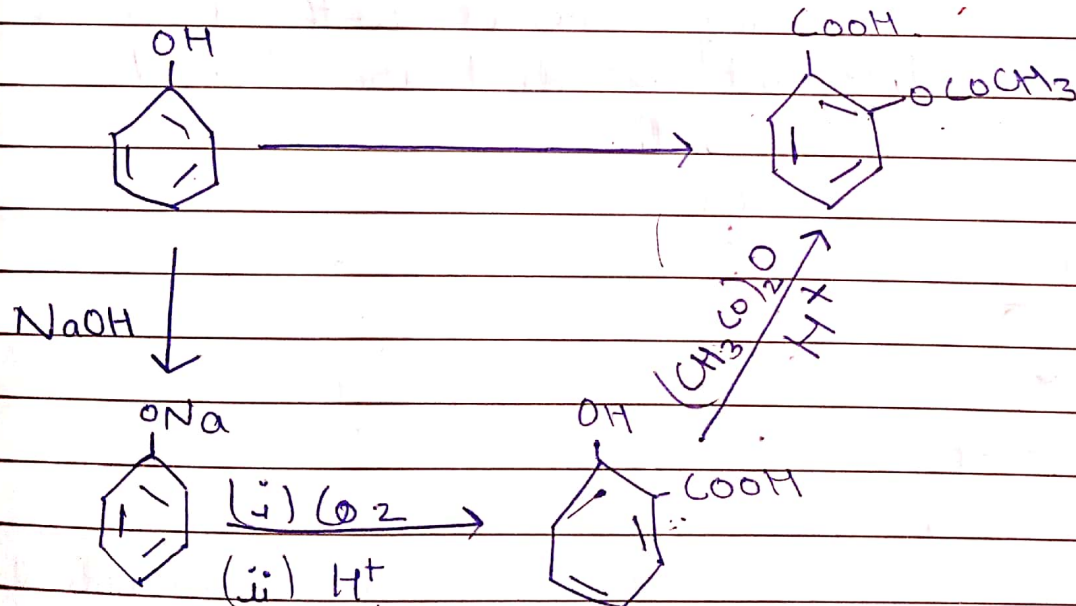
2. Kolbe's reaction



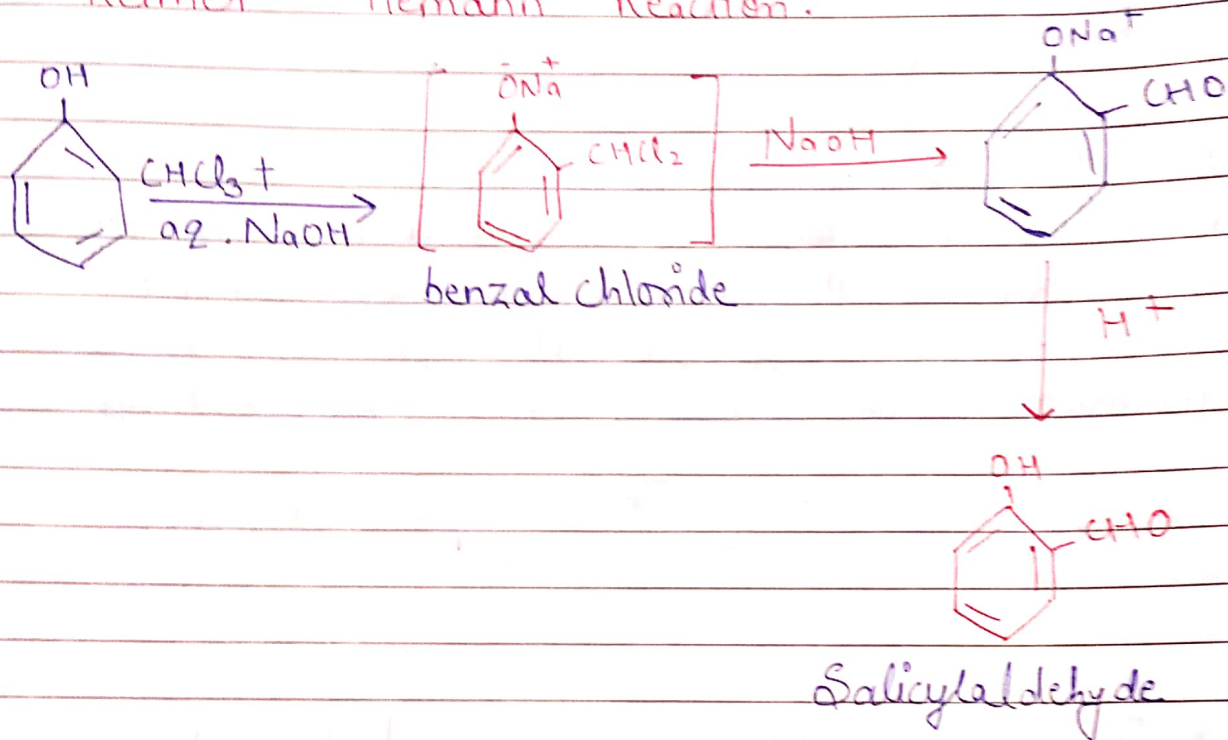
2-Hydroxybenzoic acid

(Salicylic acid)

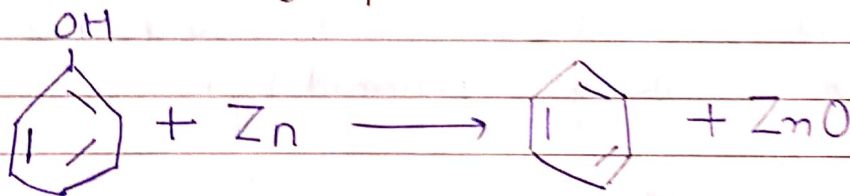
Q. Convert phenol into Aspirin.



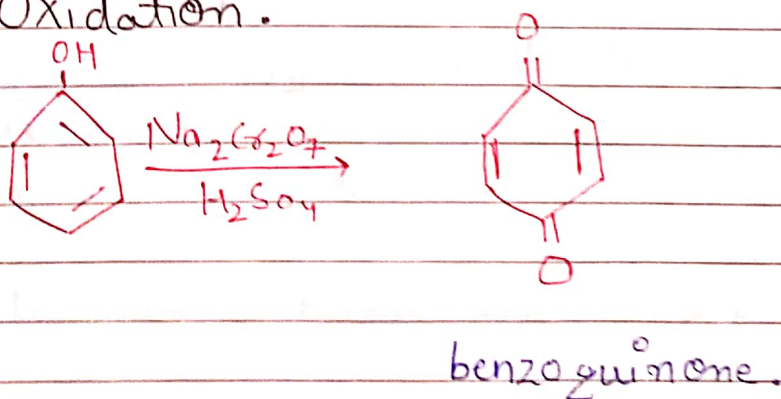
### 3. Reimer - Tiemann Reaction.



### 4. Reaction of phenol with Zinc dust.



### 5. Oxidation.



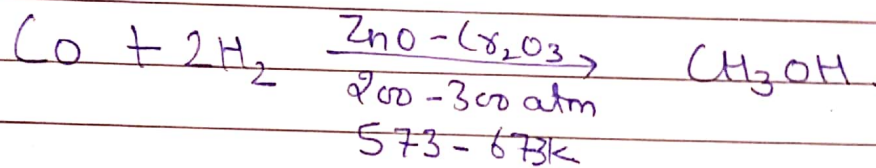
# # COMMERCIALLY IMPORTANT ALCOHOLS.

## 1. Methanol.

→ Formula =  $\text{CH}_3\text{OH}$

→ produce by destructive distillation of wood.

Today, Methanol is produce by Catalytic hydrogenation of CO at high pressure and temperature in presence  $\text{ZnO}-\text{Cr}_2\text{O}_3$  catalyst



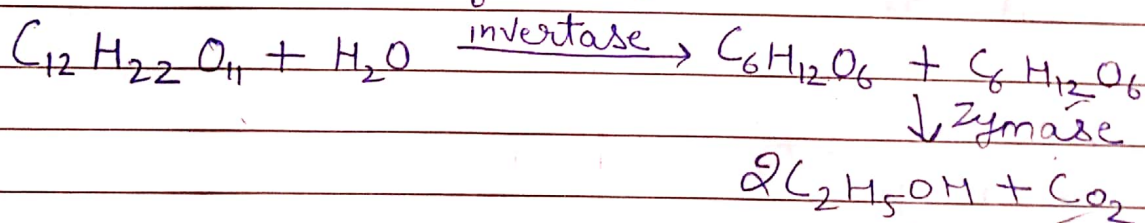
→ It is a Colourless liquid and boil at 337K.

→ poisonous in nature

→ Used as Solvent in paints, Varnishes and for making Formaldehyde.

## 2. Ethanol. [ $\text{C}_2\text{H}_5\text{OH}$ ]

→ Commercially produce by Fermentation of Sugar.



→ Action of Zymase inhibit once the % of alcohol exceed 14%.

→ It is a Colourless and boil at 351K. Used as Solvent in paint industry. Commercially alcohol made Unfit for drinking by adding  $\text{CuSO}_4$  and pyridine. It is known as **denaturation of alcohol.**





#

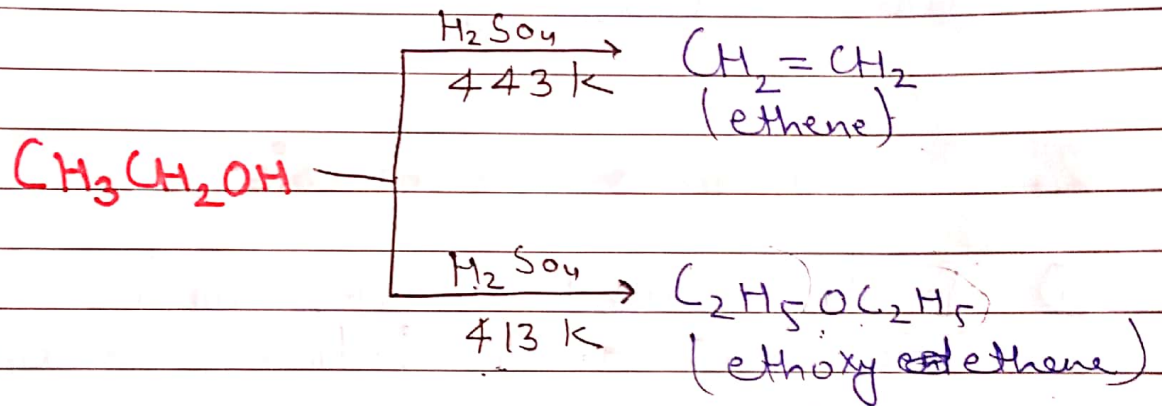
# ETHERS

#

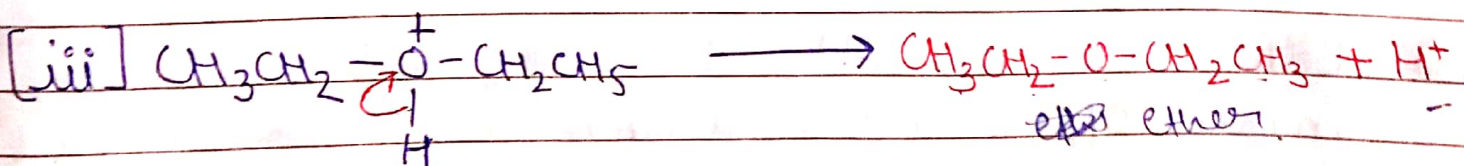
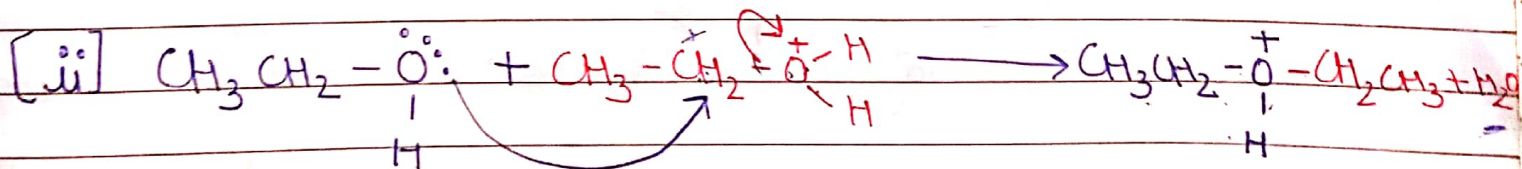
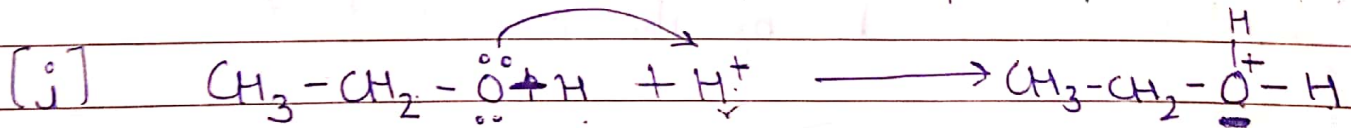
## Preparation of ether.

1. by dehydration of alcohol.

→ Alcohol undergoes dehydration in presence of protic acid ( $H_2SO_4$ ,  $H_3PO_4$ ). Reaction product depend on reaction condition.



○ Formation of ether is ( $S_N2$ ) reaction involving the attack of alcohol on a protonated alcohol.



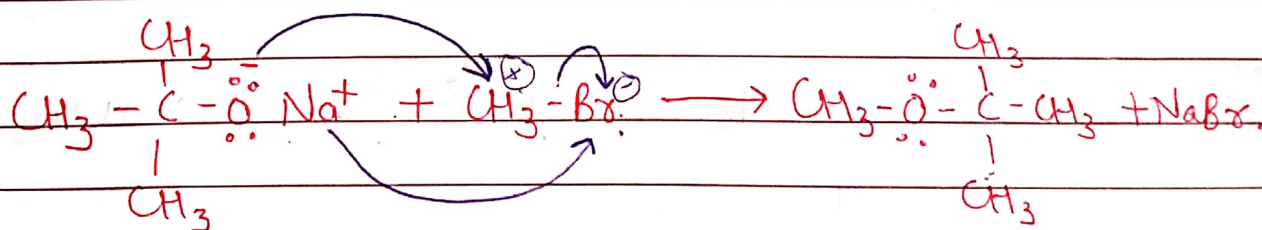
- ① The method is suitable for preparation of ethers having primary alkyl groups only.
- ② The reaction follows  $S_N1$  pathway when the alcohol is  $2^\circ$  or  $3^\circ$ .
- ③ Dehydration of secondary and tertiary alcohols to give ethers is unsuccessful and alkenes are easily formed.

## 2. Williamson Synthesis

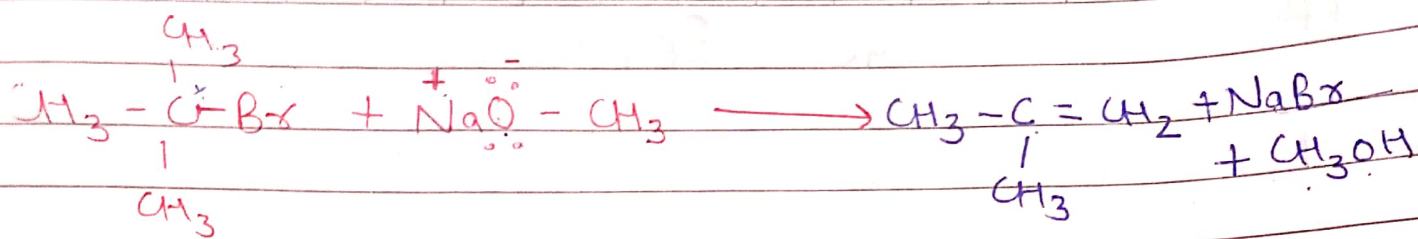
- ① In this method an alkyl halide is allowed to react with sodium alkoxide.



- ② Ethers containing substituted alkyl group ( $3^\circ$  or  $2^\circ$ ) also prepared by this method.

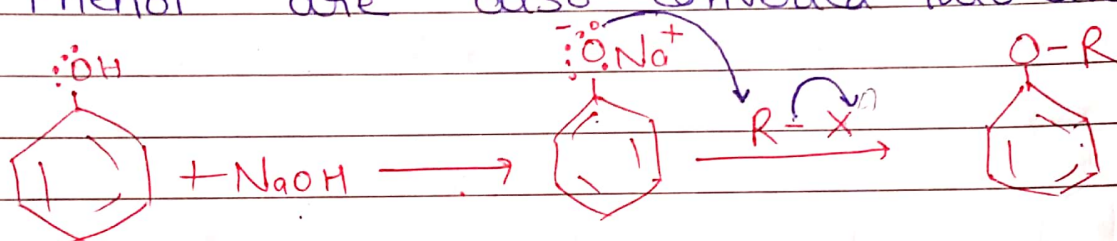


- ③ Better results are obtained if alkyl halide is primary. In case of  $2^\circ$  or  $3^\circ$  alkyl halide elimination competes over substitution.



→ It is because alkoxide are also strong base as well. They react with alkyl halide leading to elimination  $\text{R}^n$ .

① Phenol are also converted into ether.



## # Physical properties

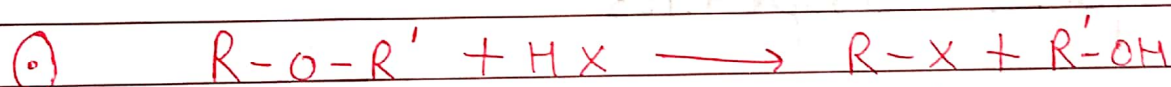
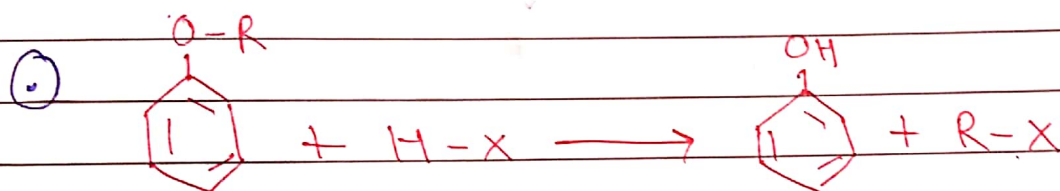
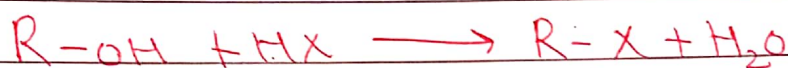
① B.P of ethers are comparable of alkene having comparable molecular mass. but less than that of alcohol.

② The miscibility of ether with water resembles those of alcohol of same molecular mass. due to the presence of oxygen in ether which can also form hydrogen bonding with water.

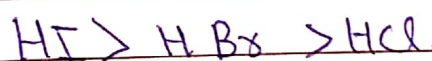
# # CHEMICAL REACTION.

## 1. Cleavage of C-O bond in ethers.

Reaction of dialkyl ether give two molecules alkyl halide when react with excess of hydrogen halide.

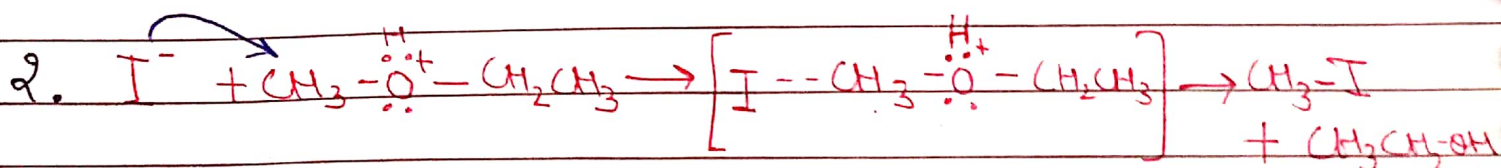
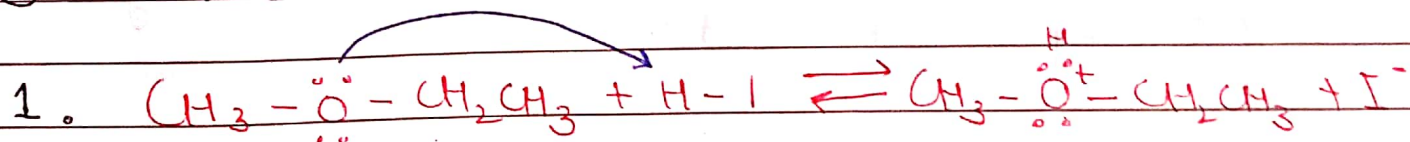


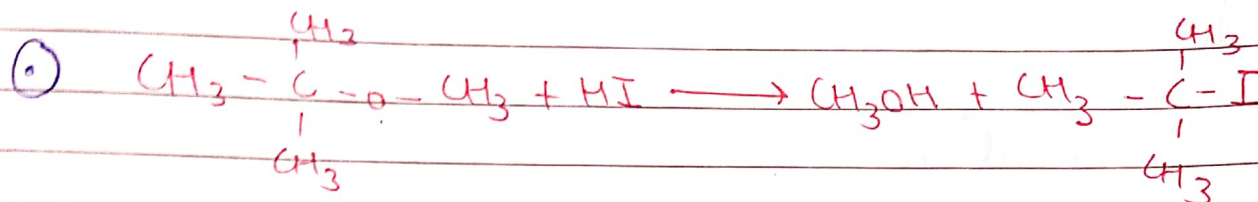
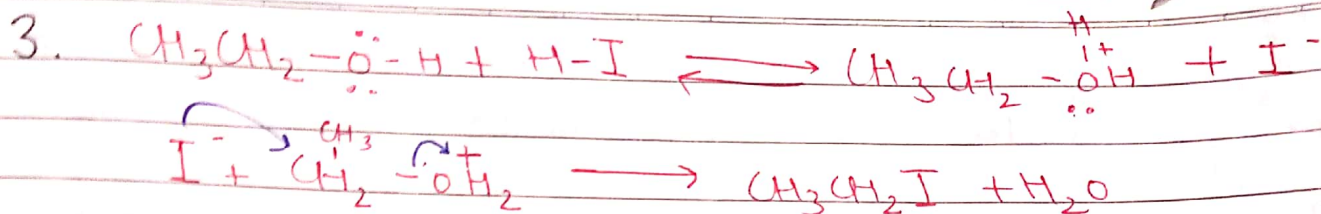
③ order of reactivity of hydrogen halide.



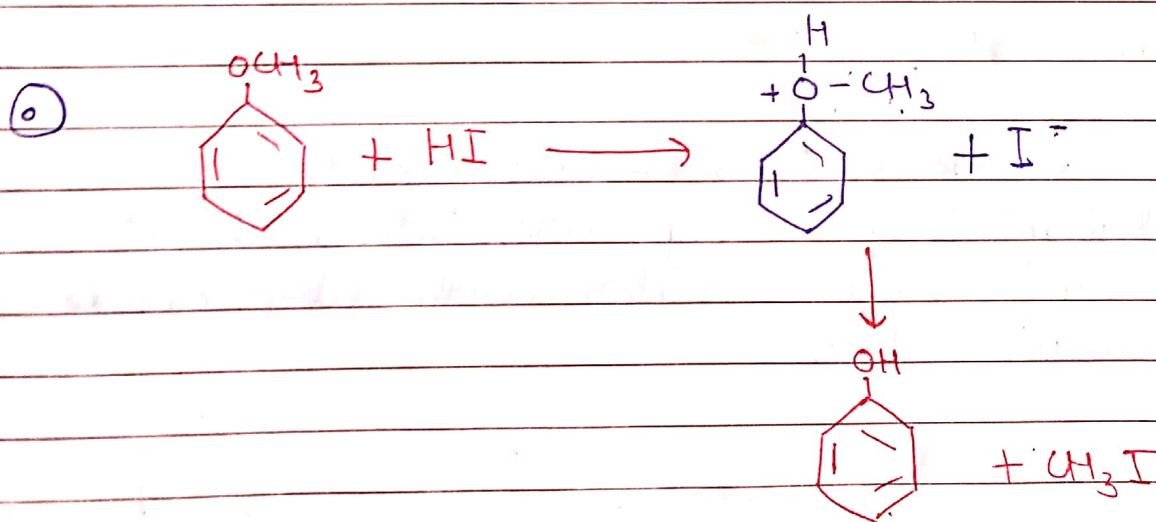
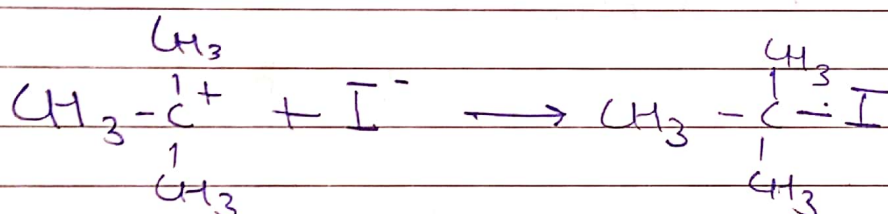
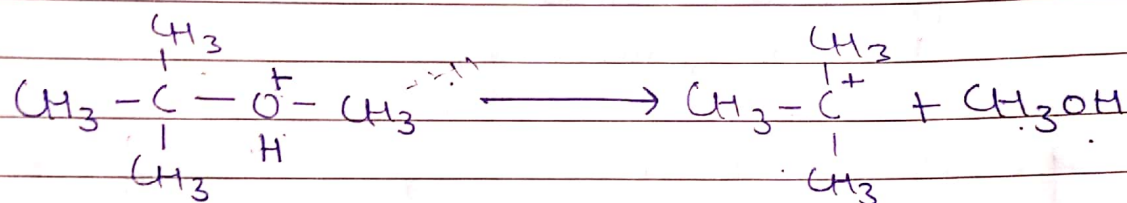
→ Cleavage of ether take place with conc. HI or HBr at high temperature.

④ Mechanism





Mechanism.



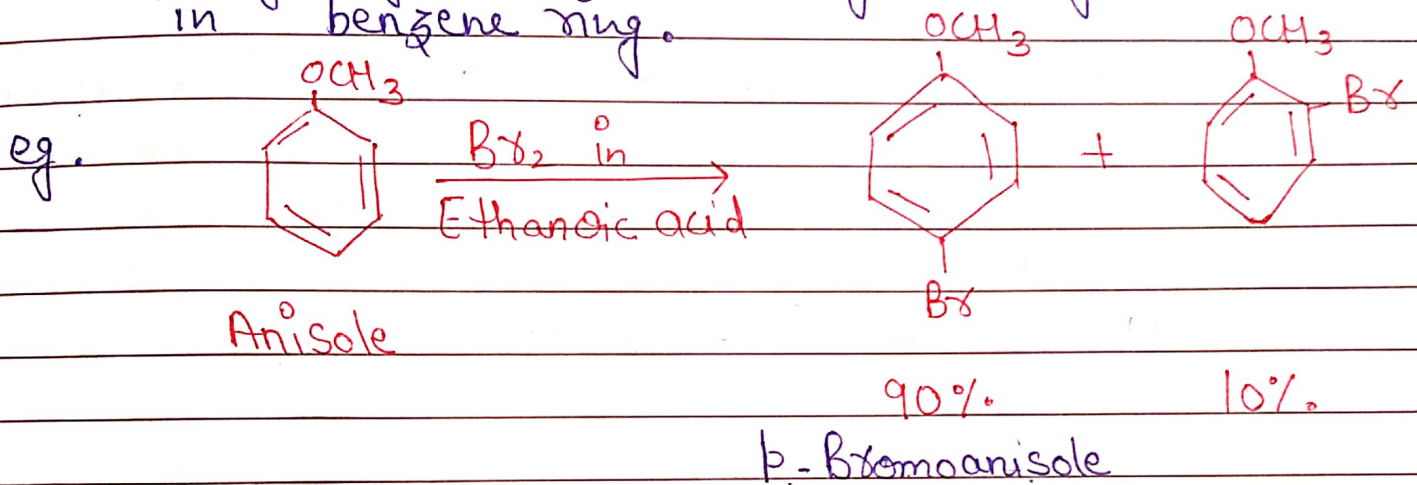
→ The bond b/w O-CH<sub>3</sub> is weaker than the bond b/w O-C<sub>6</sub>H<sub>5</sub> because carbon of phenyl group is sp<sup>2</sup> hybridised and there is a partial double bond character.

## 2. Electrophilic Substitution.

⊙ The alkoxy group (-OR) is Ortho and para directing.

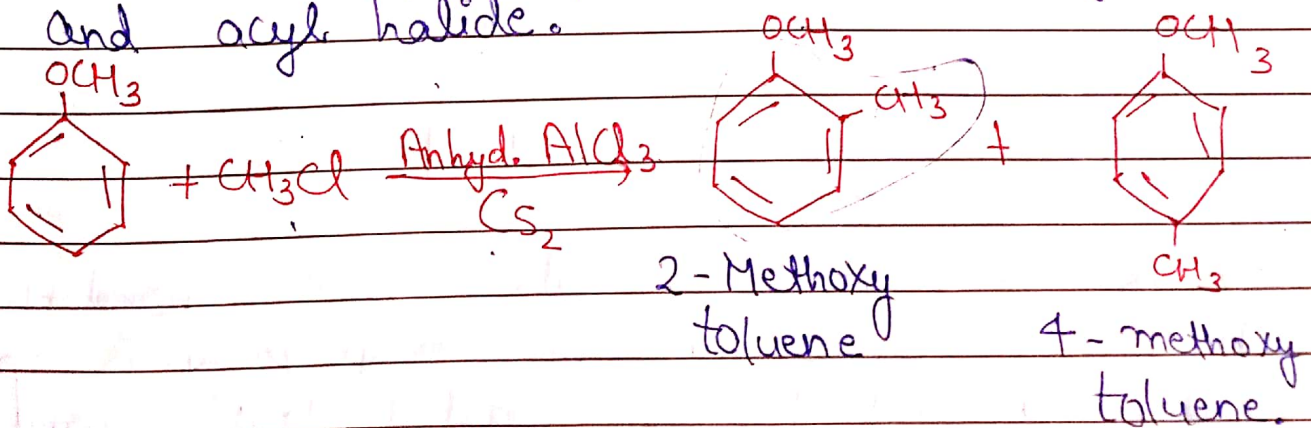
### (i) Halogenation :

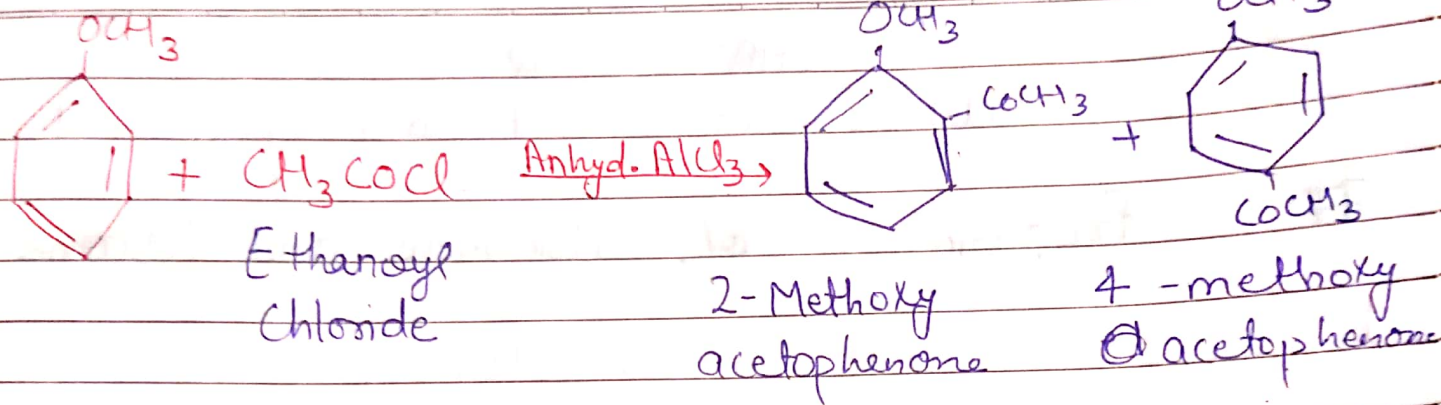
⊙ Phenylalkyl ethers undergo halogenation in benzene ring.



### (ii) Friedel-Craft reaction.

⊙ Anisole undergoes Friedel-Craft reaction i.e. alkyl and acyl group are introduced at Ortho and para position with alkyl halide and acyl halide.





(iii) Nitration:

