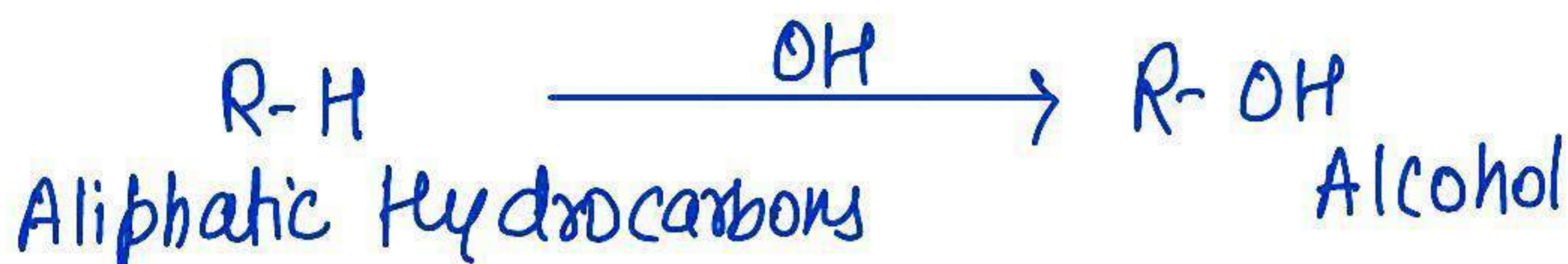


Alcohol, Phenol & Ethers

Alcohols and Phenols:-

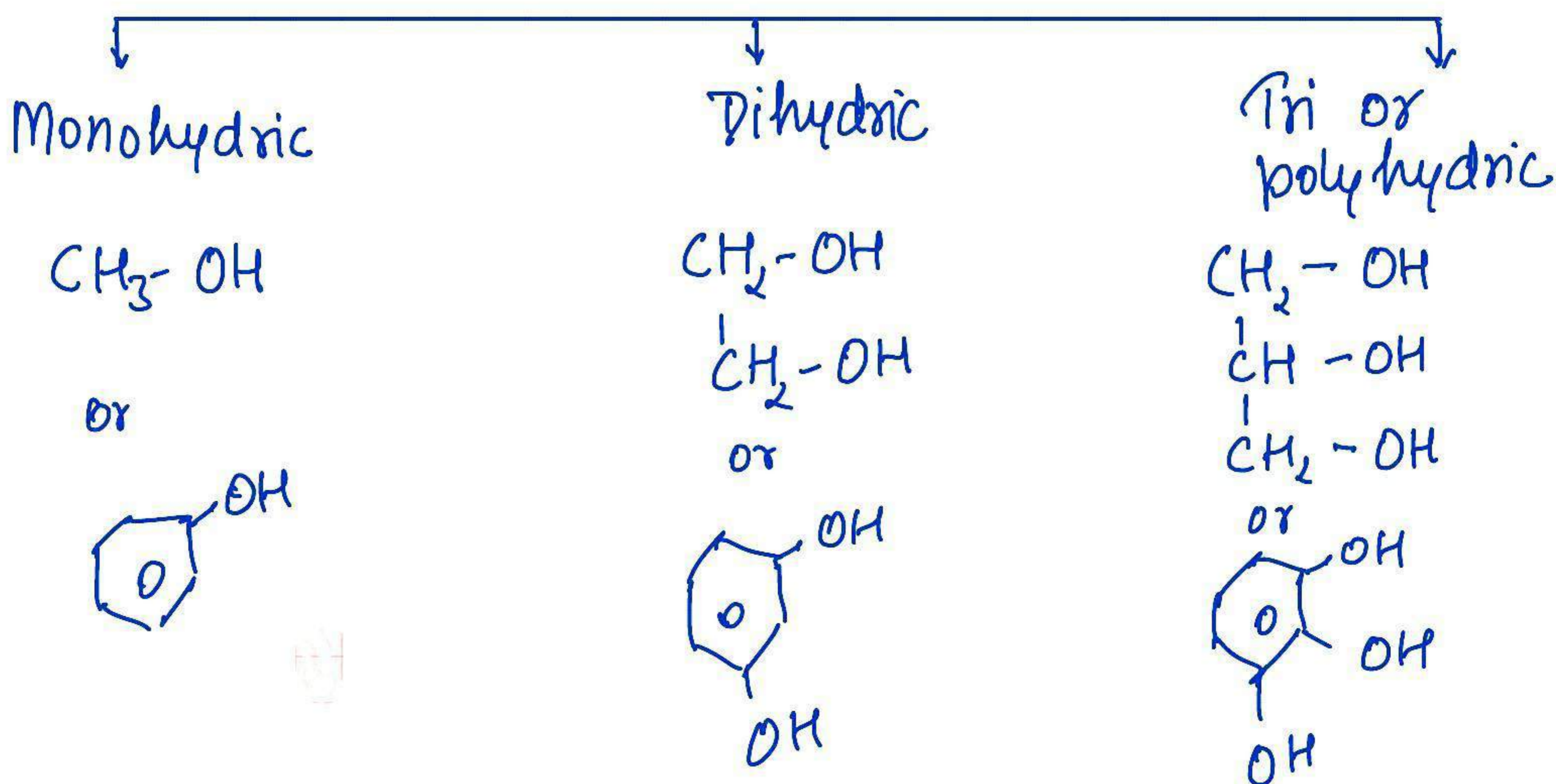
When a hydrogen of aliphatic or aromatic hydrocarbons is replaced by (-OH) group then the compounds which are obtained are called alcohols and phenols.

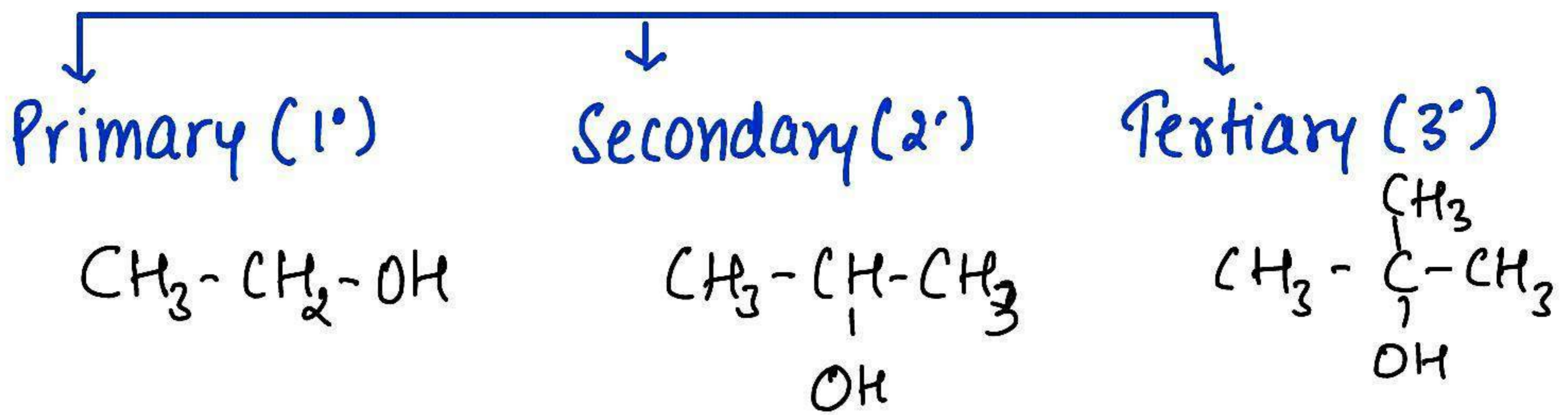


↳ Also called hydroxy derivatives of hydrocarbons.

Classification of Alcohol and Phenols

• On the basis of no. of -OH groups-





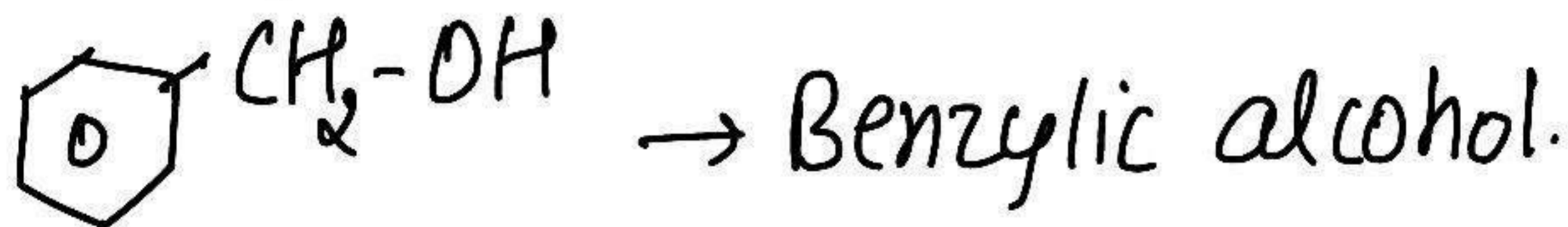
• Allylic Alcohols

In this type of alcohols, -OH group is attached to the sp^3 hybridised carbon which itself attached to a double bonded carbon atom



• Benzylic Alcohols:

In this type of alcohol the -OH group is attached to the sp^3 hybridized carbon which itself attached to a benzene ring.

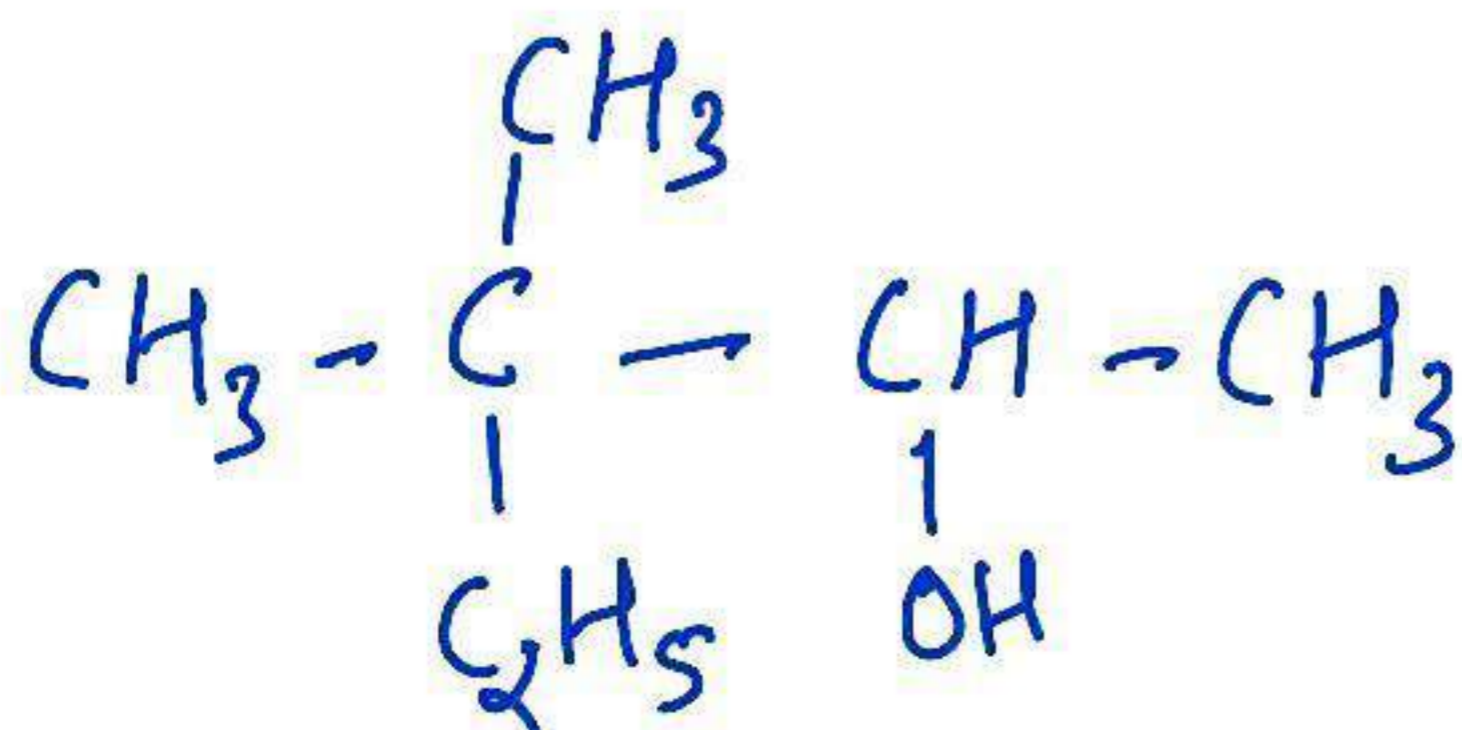


• Vinylic alcohol:

In this type of alcohols -OH group is attached to a double bonded carbon atom.

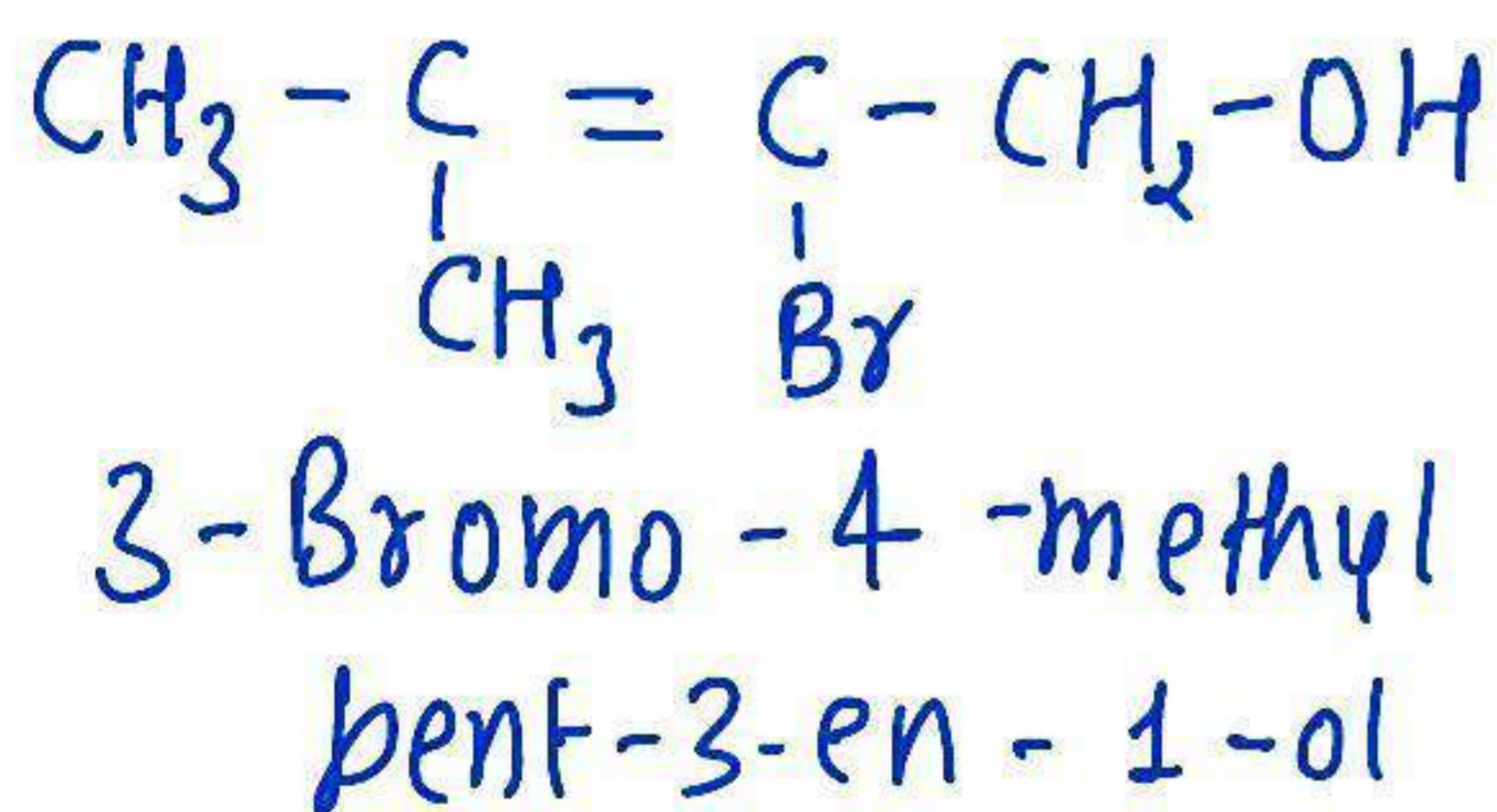


NOMENCLATURE :

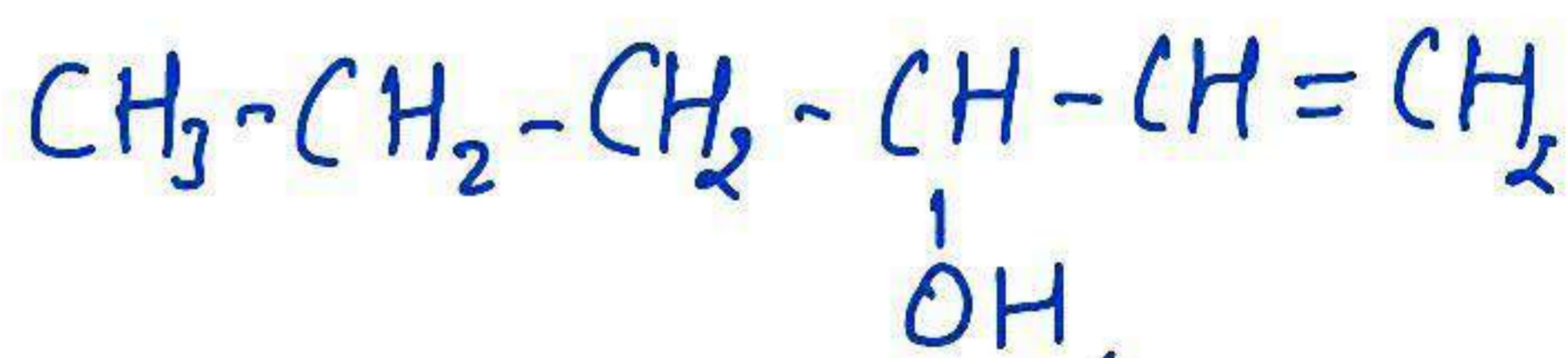


3,3-Dimethylpentan-2-ol

Compound	Common name	IUPAC name
$\text{CH}_3 - \text{OH}$	Methyl alcohol	Methanol
$\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{OH}$	<i>n</i> -Propyl alcohol	Propan-1-ol
$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_3 \\ \\ \text{OH} \end{array}$	Isopropyl alcohol	Propan-2-ol
$\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{OH}$	<i>n</i> -Butyl alcohol	Butan-1-ol
$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CH}_3 \\ \\ \text{OH} \end{array}$	<i>sec</i> -Butyl alcohol	Butan-2-ol
$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CH}_3 \\ \\ \text{OH} \end{array}$	Isobutyl alcohol	2-Methylpropan-1-ol
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{C} - \text{OH} \\ \\ \text{CH}_3 \end{array}$	<i>tert</i> -Butyl alcohol	2-Methylpropan-2-ol
$\begin{array}{c} \text{CH}_2 - \text{CH} - \text{CH}_2 \\ \quad \quad \\ \text{OH} \quad \text{OH} \quad \text{OH} \end{array}$	Glycerol	Propane -1, 2, 3-triol



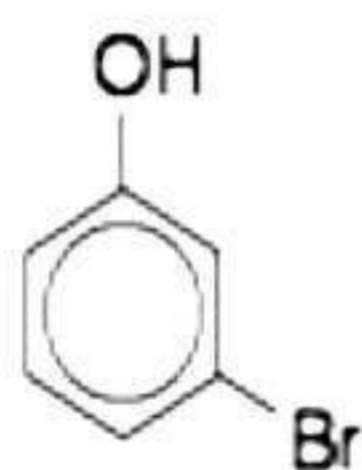
• Draw the str. of
Hex-1-en-3-ol



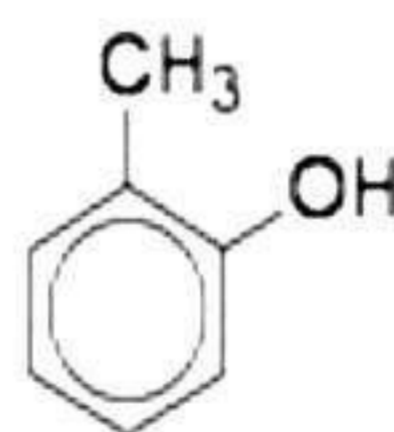
NOMENCLATURE OF PHENOL



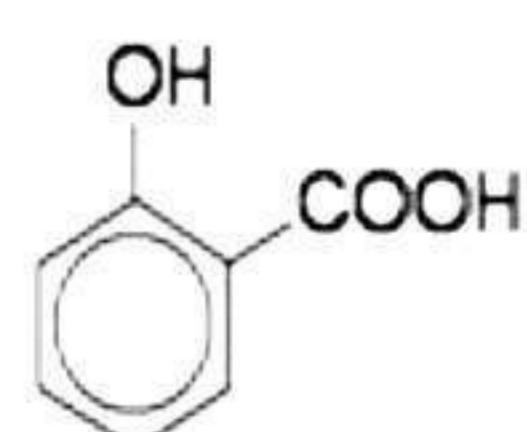
phenol



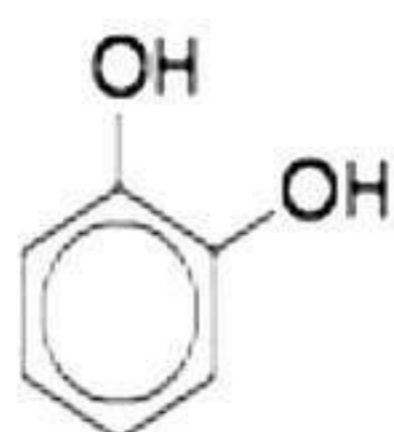
m-bromophenol



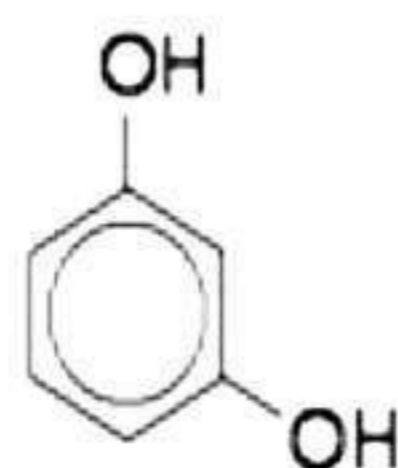
o-cresol



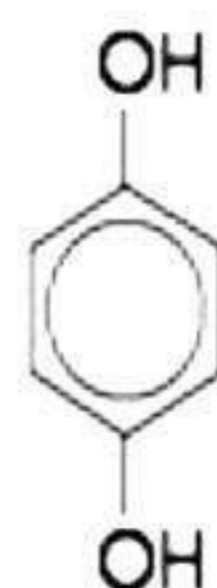
salicylic acid



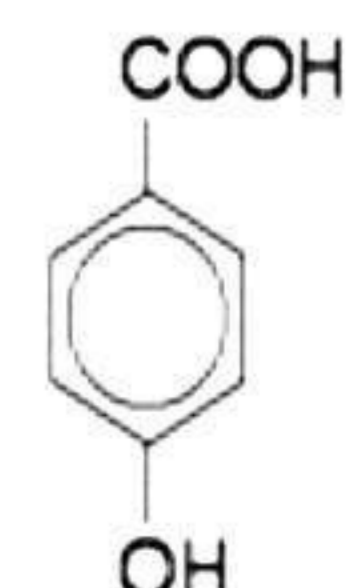
catechol



resorcinol

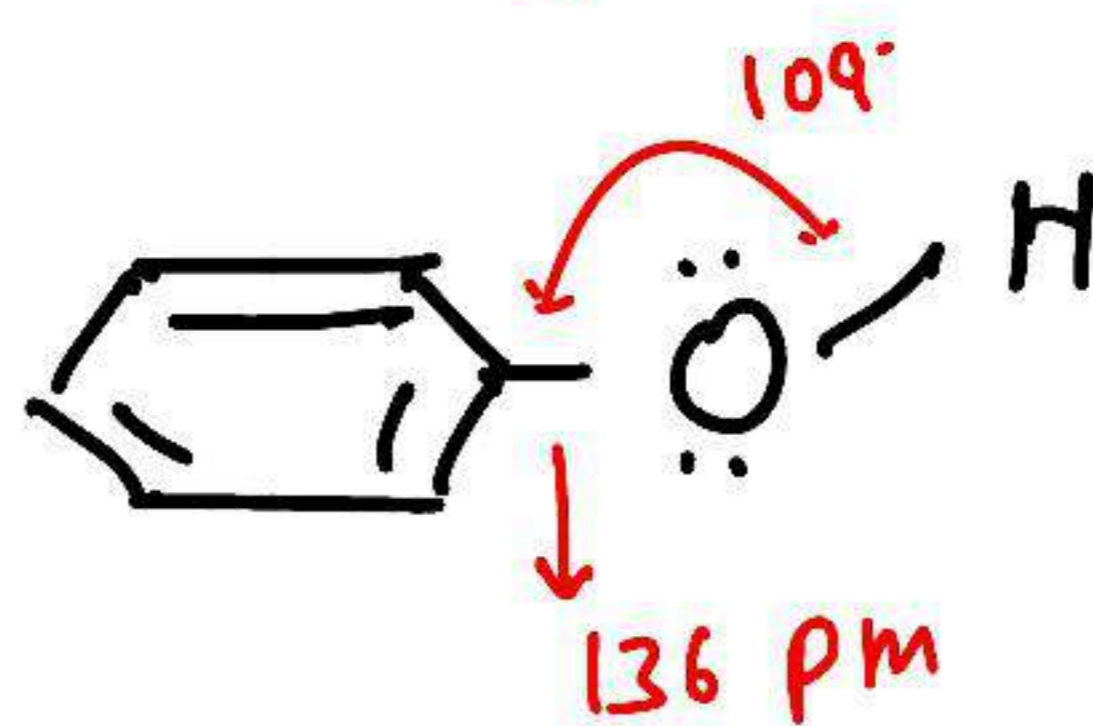
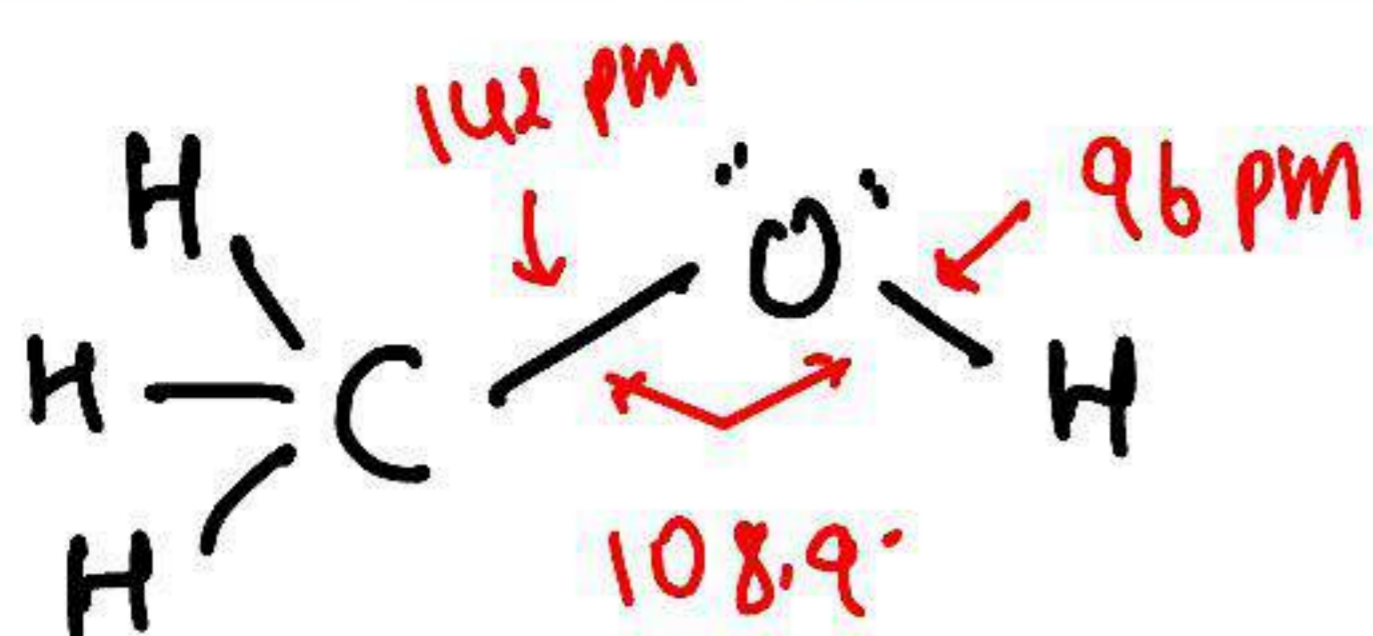


hydroquinone



p-hydroxybenzoic acid

Structure of Alcohol and Phenol group:

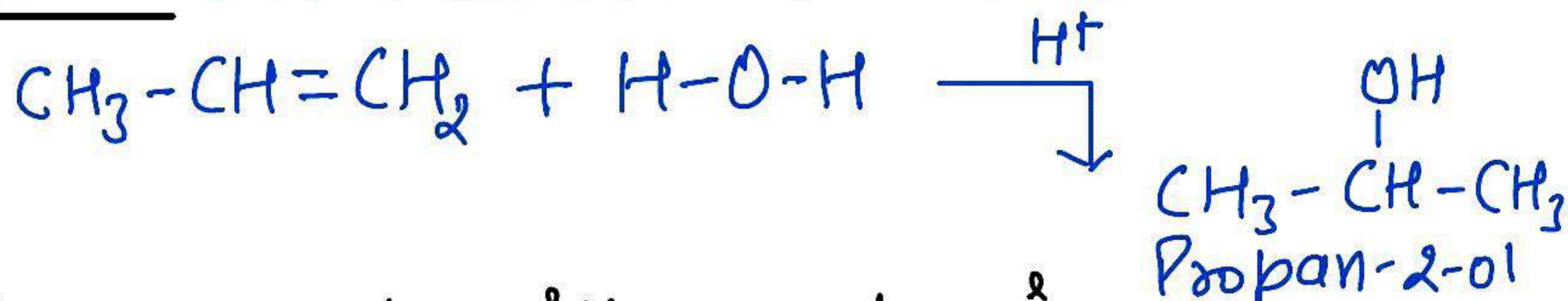


Note

- The C-O bond length in phenol is 136 pm which is less than alcohol due to
- (i) In phenol, lone pair of oxygen is conjugation with π bond of aromatic ring and acquire partial double bond character.
 - (ii) In phenol, oxygen atom is attached to sp^2 hybridised carbon.

Preparation of Alcohols:

From Alkenes: (By Hydration of Alkene)



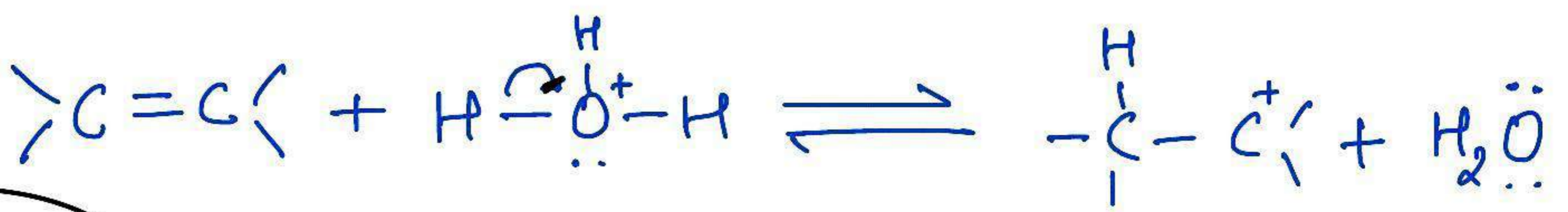
When alkene reacts with water in the presence of acid catalysed, then alcohol is formed.

On an unsymmetrical alkene, when water molecule is added, then product is formed according to Markovnikov's Rule.

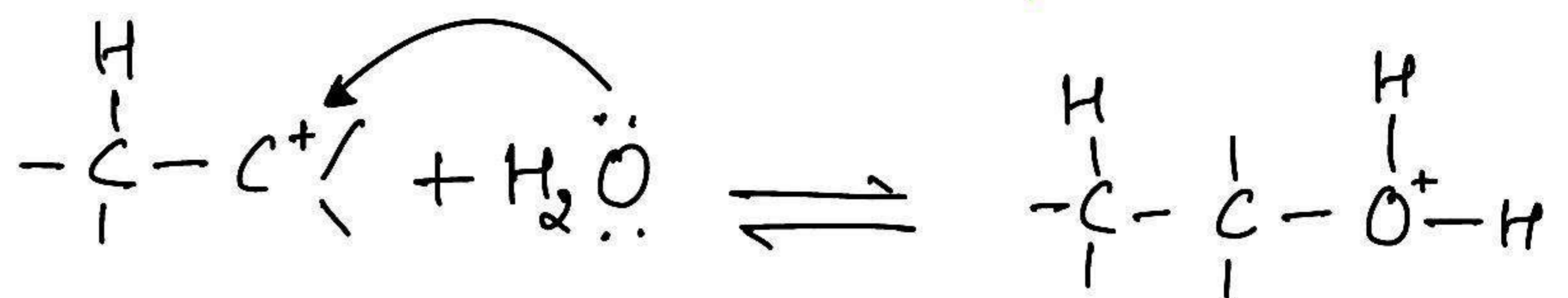
★ Mechanism:

Step-1

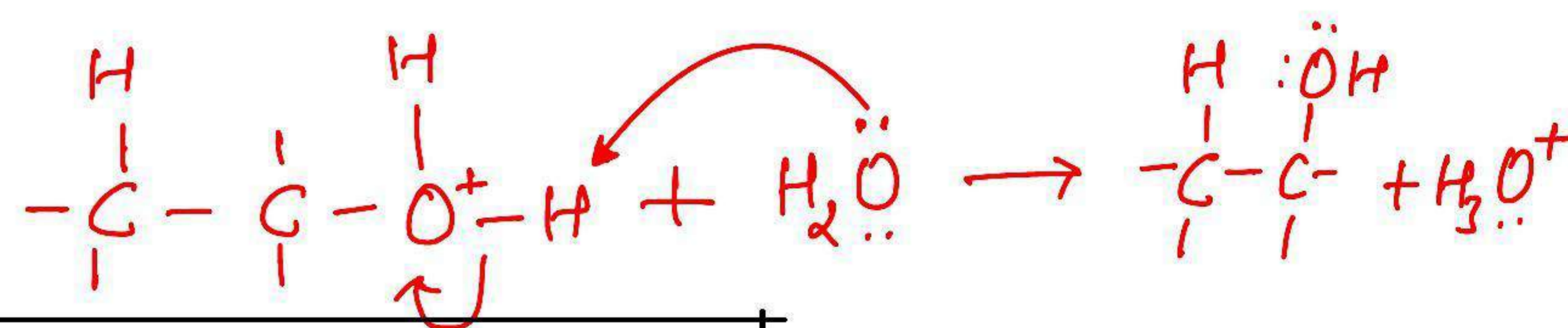




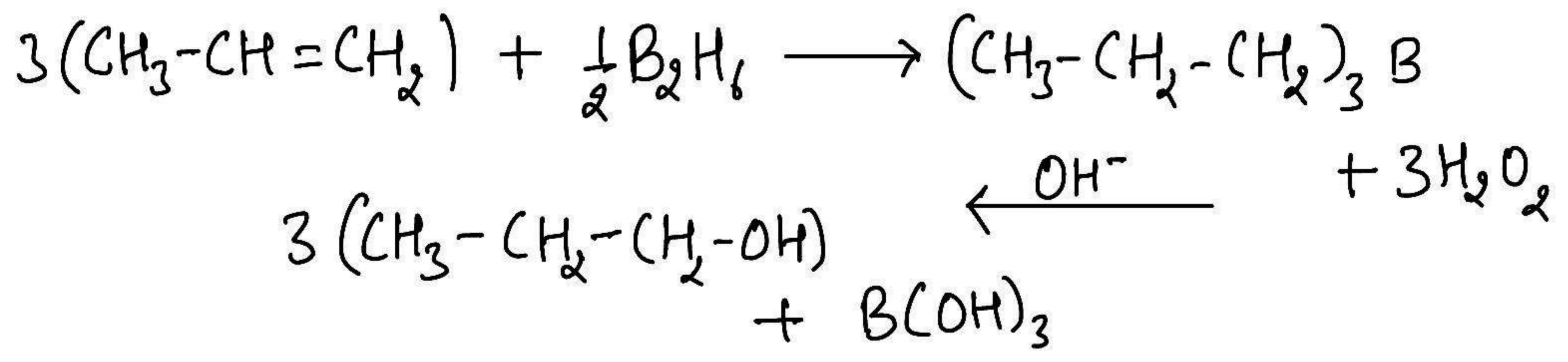
Step 2:



Step 3:



By Hydroboration-Oxidation:



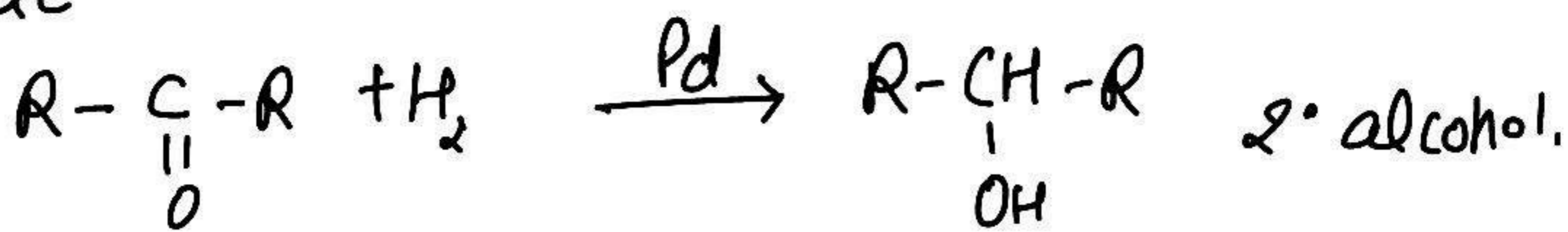
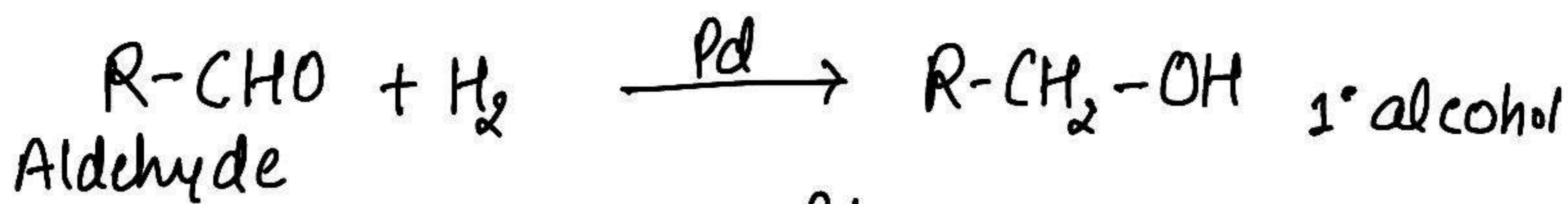
When alkene react with diborane (B₂H₆), then trialkyl borane is formed which gives alcohol by the oxidation of H₂O₂ in the presence of sodium hydroxide.

From Carbonyl Compound:

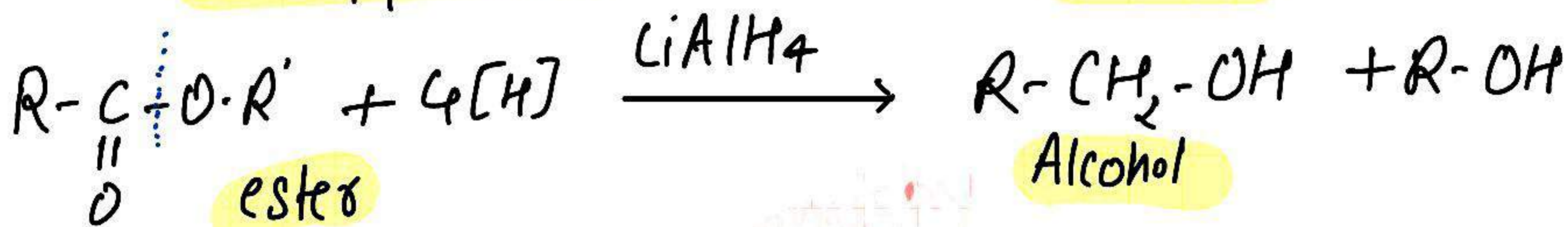
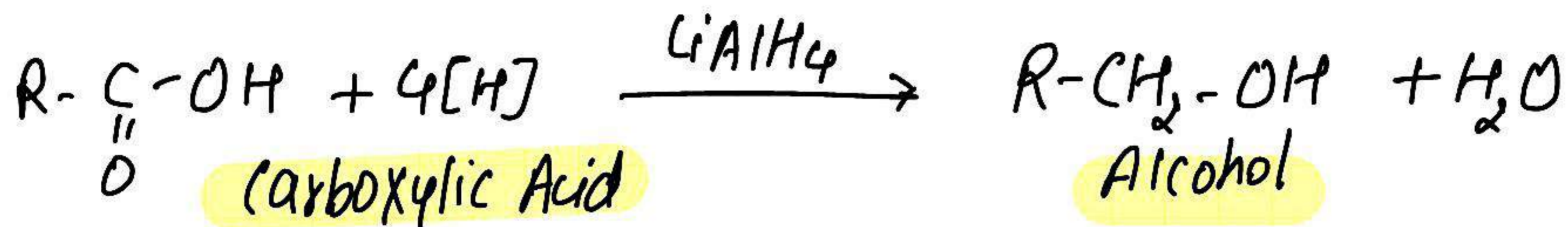
• By the reduction of aldehyde and ketones

Aldehydes and Ketones are reduced to the corresponding alcohols by hydrogen in the presence of reagent like Pt, Pd, Ni, LiAlH₄, NaBH₄ etc.

{ In the presence of Pt/Pd we take H₂ & rest of these take 2H }

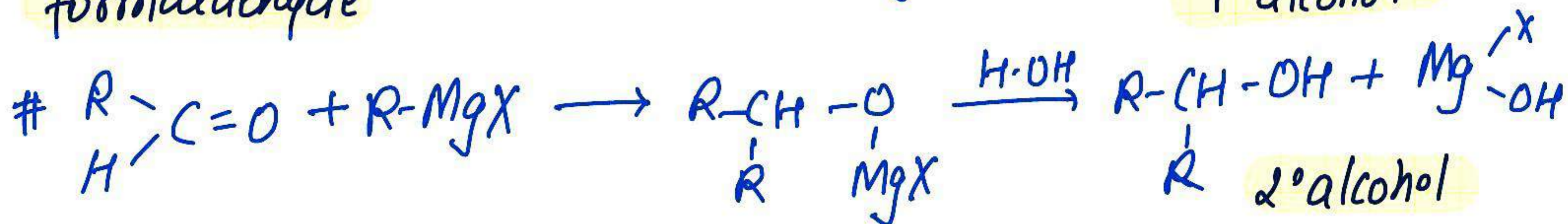
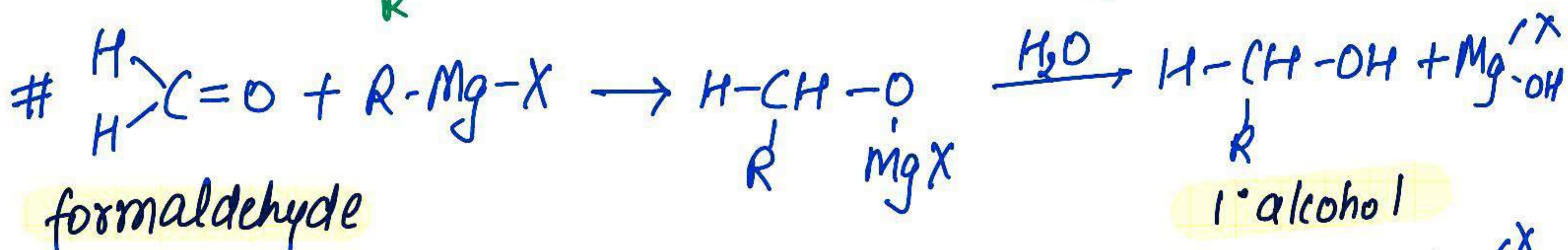
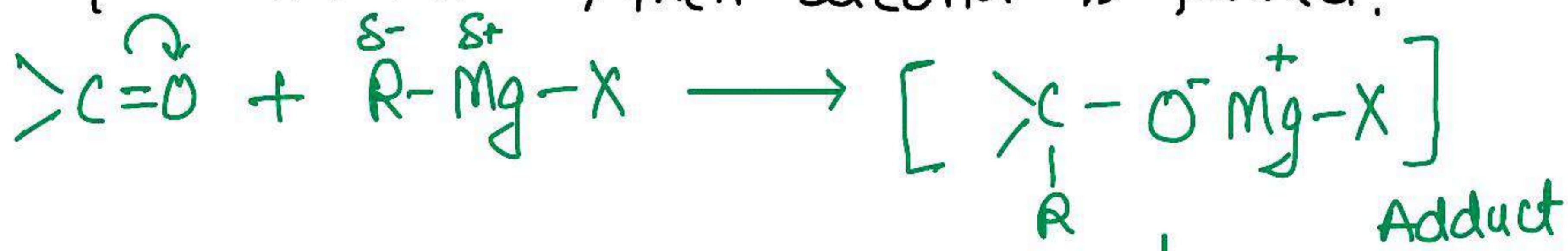


• From the reduction of carboxylic acid & ester \Rightarrow

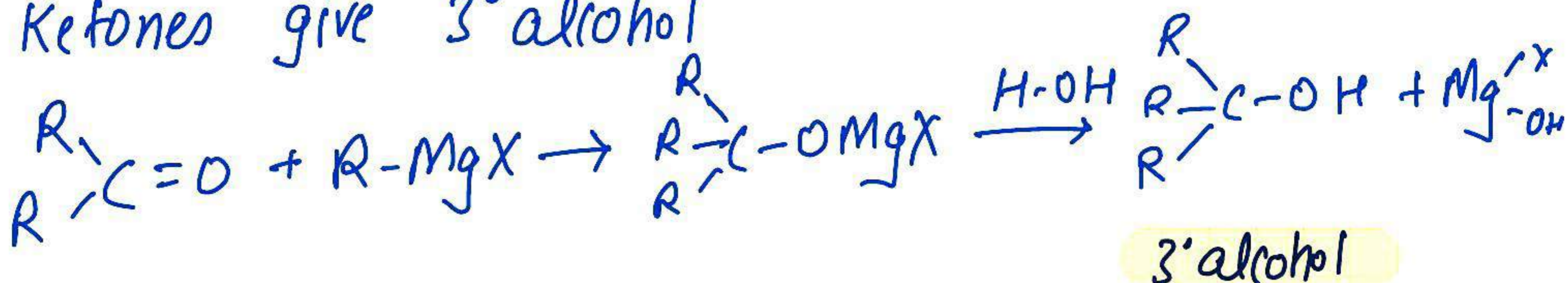


• From Grignard Reagent:

when grignard reagent react with aldehyde and ketone, then alcohol is formed.



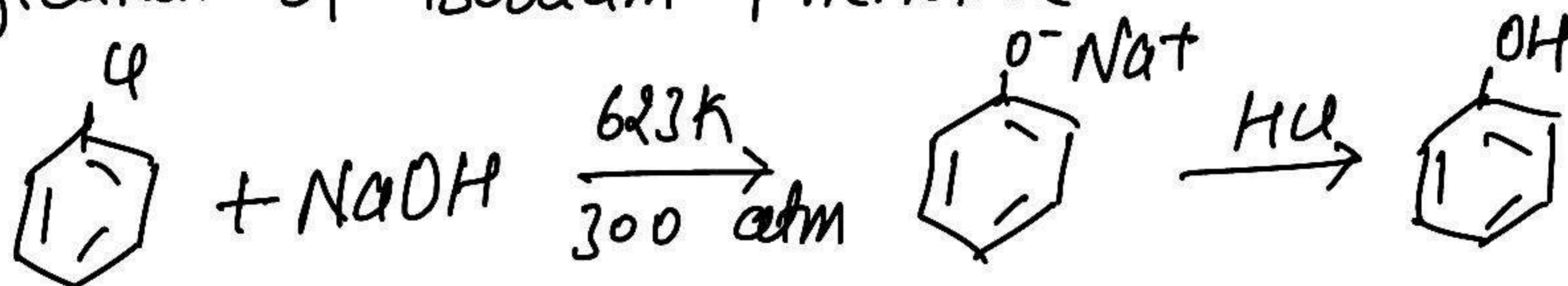
Ketones give 3° alcohol



Preparation of Phenol

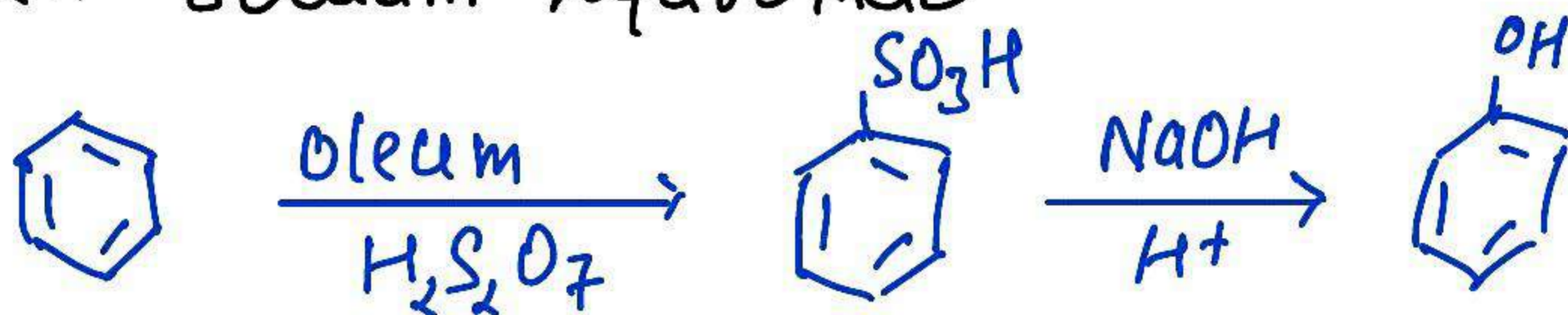
From Haloarenes

Chlorobenzene is fused with NaOH at 623K and 300 atm pressure. Phenol is obtained by acidification of sodium phenoxide.



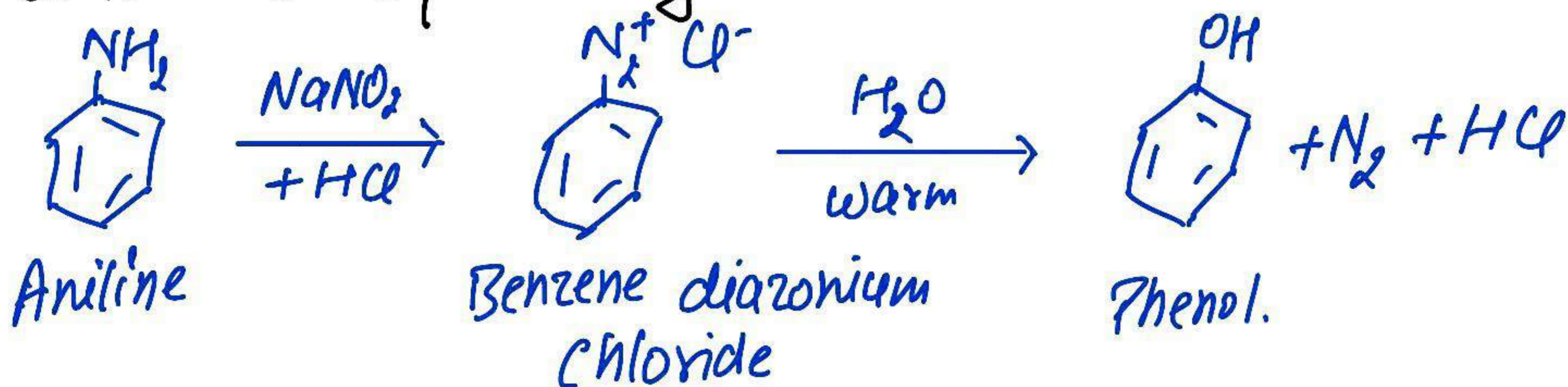
From Benzene Sulphonic acid:

Benzene is sulphonated with oleum and benzene sulphonic acid so formed is converted to sodium phenoxide on heating with molten sodium hydroxide.



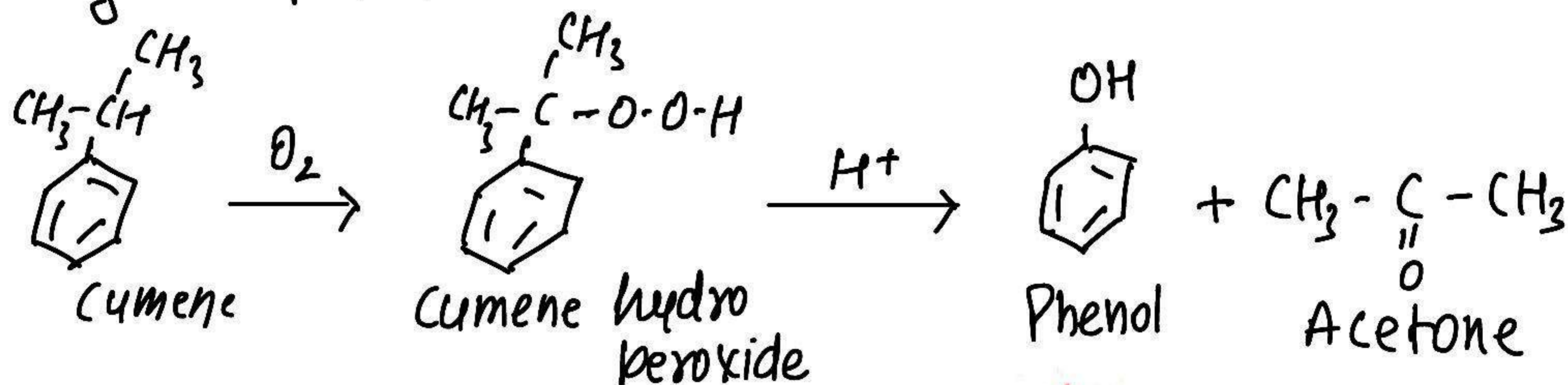
From Diazonium Salts:

A diazonium salt is formed by treating an aromatic 1° amine with nitrous acid ($\text{NaNO}_2 + \text{HCl}$) at 273K-278K. Diazonium salts are hydrolysed to phenols by warming with water or by treating with dilute acids.



• From Cumene

In this method cumene is oxidised in the presence of air then cumene hydroperoxide is obtained. Now it reacts with dilute acid, gives phenol and acetone.



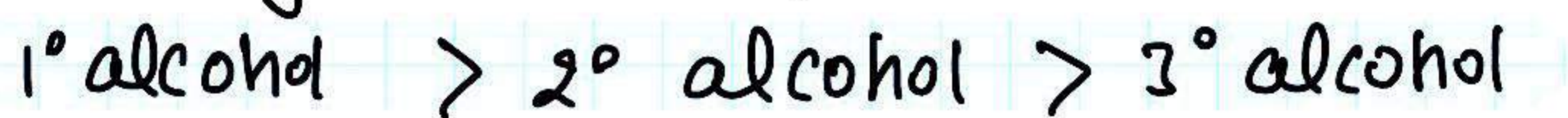
• Physical Properties

Boiling Point:

The b.pt of alcohols and phenols increase with increase in no. of carbon atoms (increase in van der Waals forces)

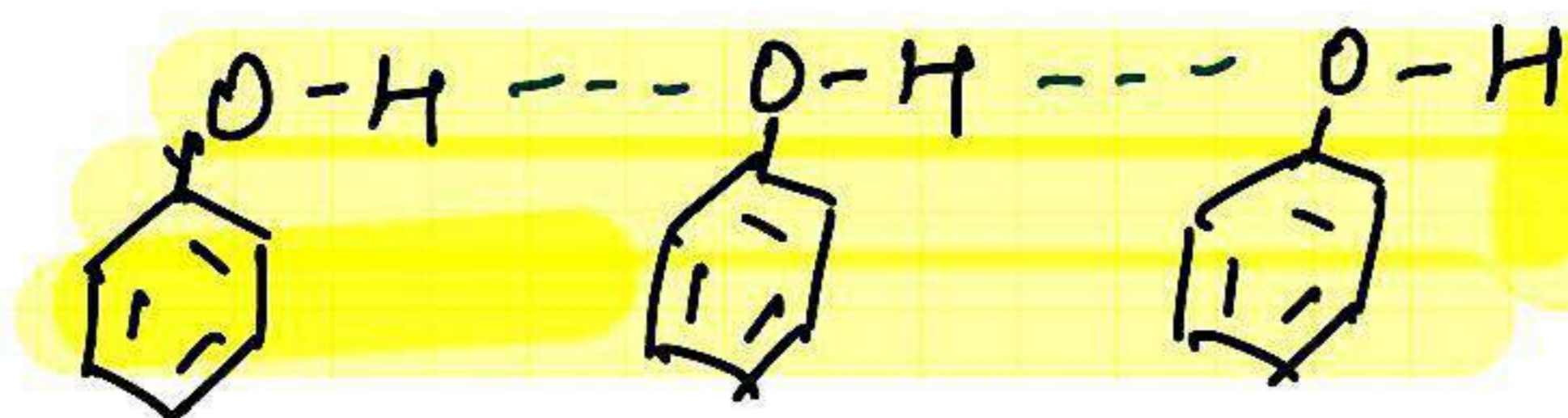
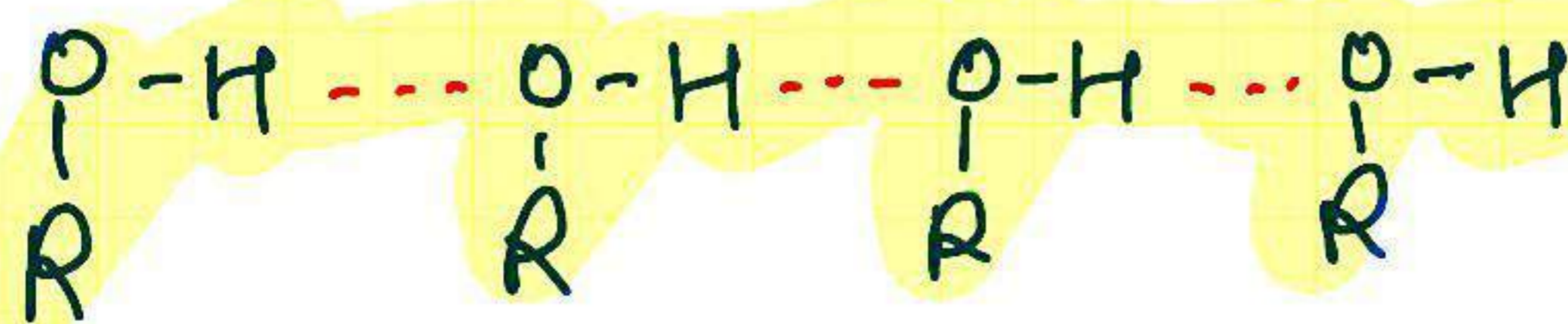
e.g. Boiling Point of butanol is more than ethanol.

→ In isomeric alcohol, the B.Pt decreases with increase in branching. i.e. B.Pt follows the order



[Because of decrease in van der Waals forces with decrease in surface area]

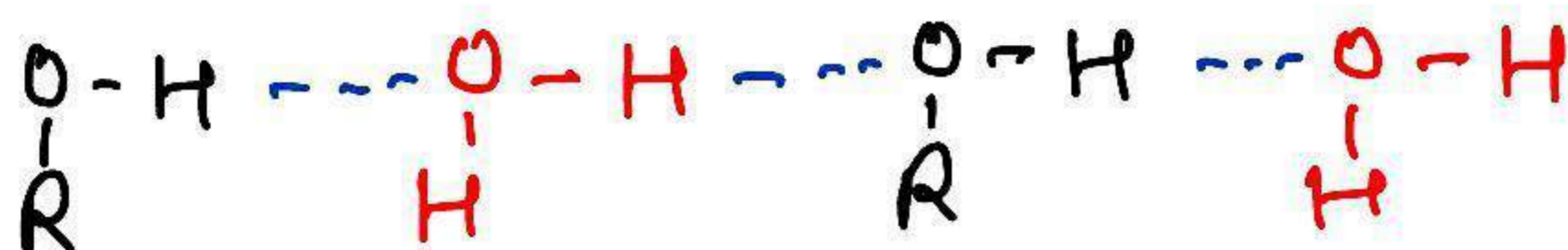
→ The $-OH$ group in Alcohols and phenols is involved in intermolecular Hydrogen Bonding.



► Solubility:

→ Solubility of alcohols and phenols in water is due to their ability to form hydrogen bonds with water molecules.

→ The solubility decreases with increase in size of alkyl / aryl (hydrophobic) groups.



→ Chemical Properties of Alcohols:

1. Rxn in which cleavage of $-\text{O}\ddot{\text{O}}\text{H}$ bond takes place
2. Rxn in which cleavage of $-\text{C}\ddot{\text{O}}\text{H}$ bond takes place

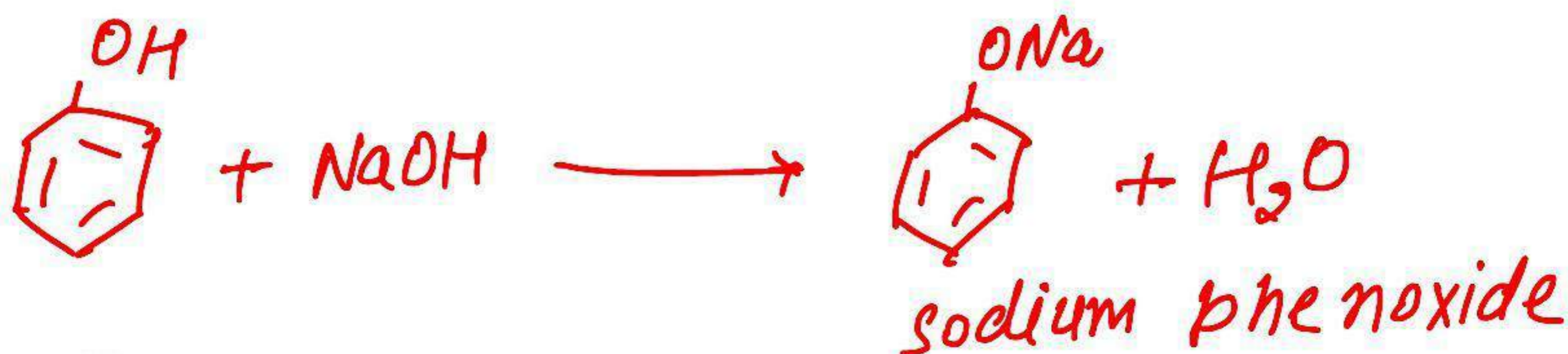
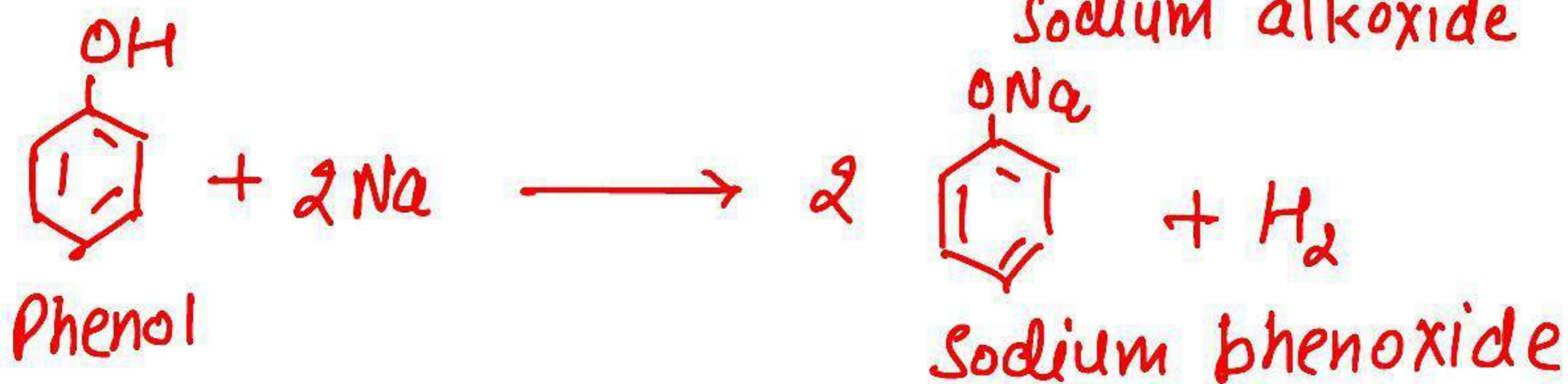
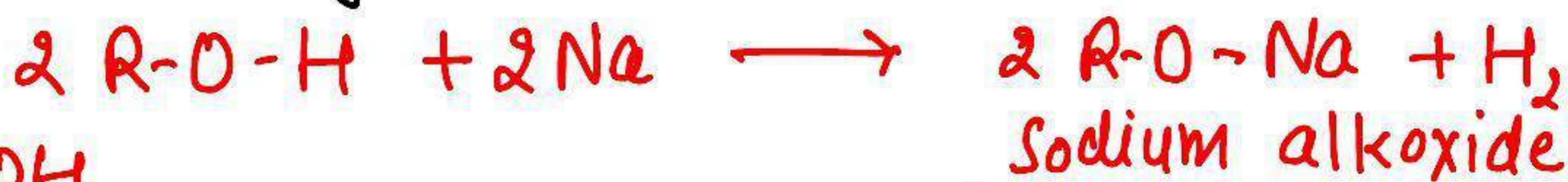
Rxn in which cleavage of $-\text{O}-\text{H}$ bond takes place

1° alcohol $>$ 2° alcohol $>$ 3° alcohol

i) Acidic Nature of Alcohol and Phenol

a) Rxn with Metal

Alcohols and phenols react with active metals such as sodium, potassium and aluminium to yield corresponding alkoxides / phenoxides and hydrogen.

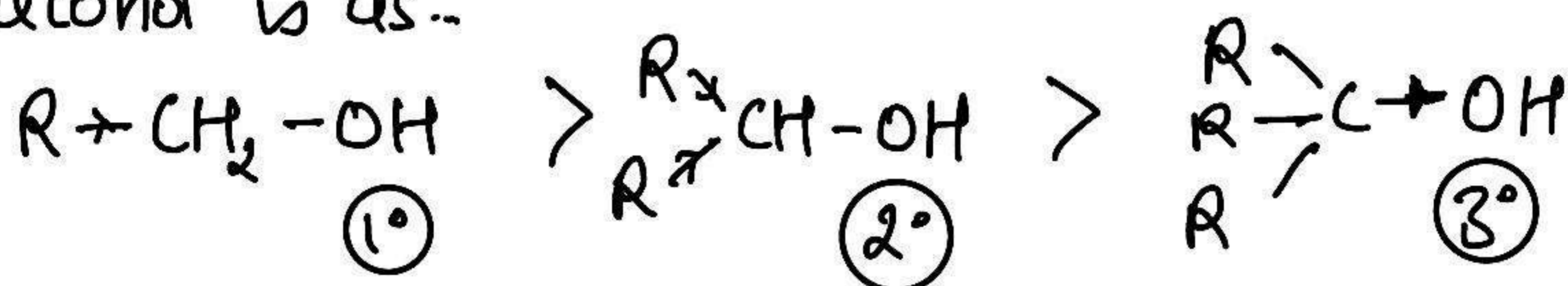


b.) Acidity of Alcohol -

The acidic nature of alcohol is due to the polar nature of $-OH$ bond.

➤ In alcohol an e^- releasing group ($-CH_3$, $-C_2H_5$) increase the e^- density on oxygen atom and decrease the polarity of $-OH$ bond. Due to this the acidic strength of alcohol also decreases.

Therefore the order of acidity of different alcohol is as..



Q. why alcohols are weak acid than compare to water?

Ans: In alcohol, alkoxide ion is formed after removing H^+ ion and in water hydroxide ion is formed after removing H^+ ion.

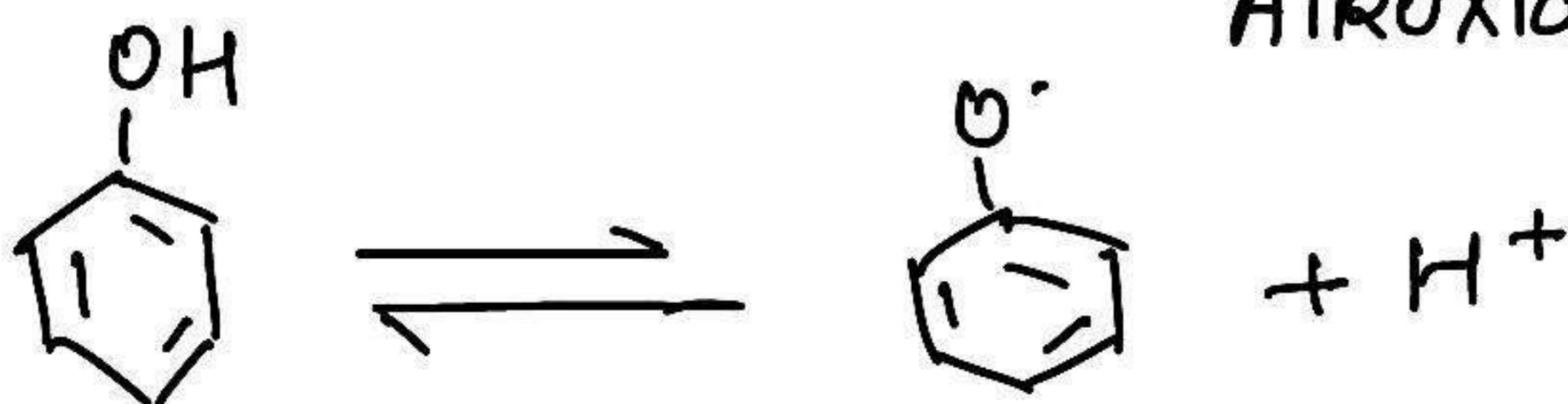
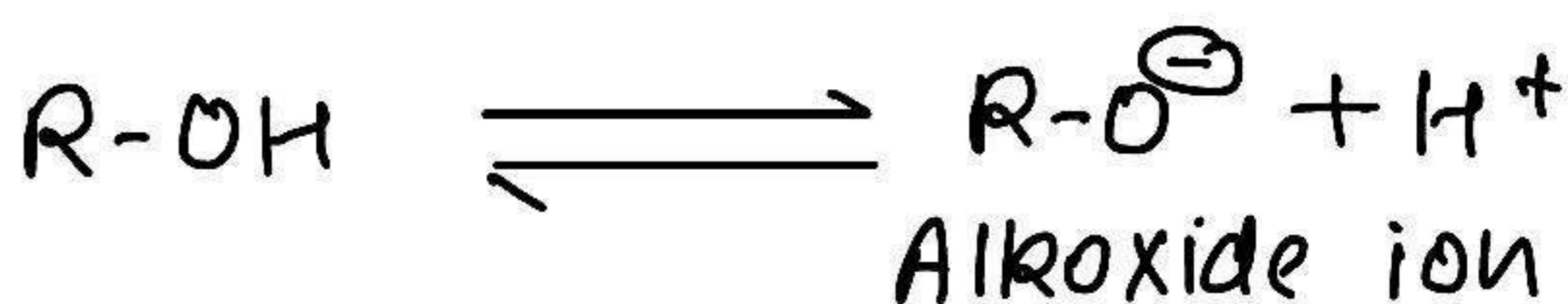
But alkoxide ion is less stable than compare to OH^- ion due to the presence of more e^- density on oxygen atom. Therefore, alcohol act as weak acid than compare to water.



c.) Acidity of Phenol:

Phenol is more acidic in nature than compare to alcohol.

Reason: The ionisation of alcohol and phenol takes place as -



Due to the higher electronegativity of sp^3 hybridised

carbon of phenol to which $-OH$ is attached, e^- density decreases on oxygen. This increase the polarity of OH bond and result in an increase in ionisation of phenols that that of alcohols.

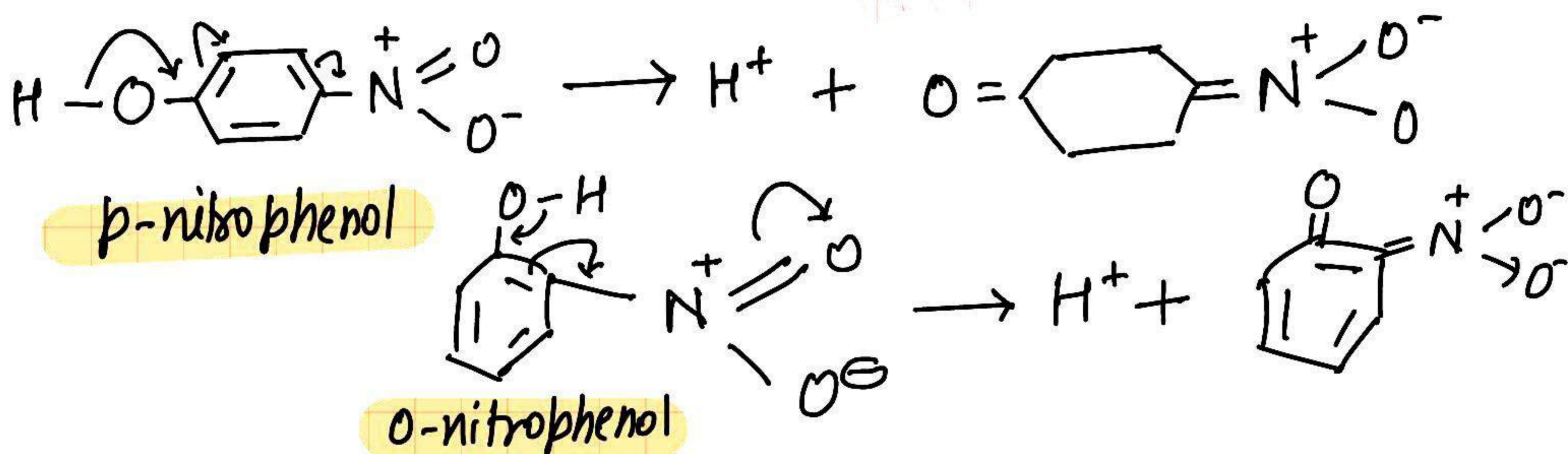
In alcohol, alkoxide ion is formed and in phenol, phenoxide ion after removing H^+ ion. Phenoxide ion is more stable due to resonance than compare to alkoxide ion.

Therefore phenol is more acidic than alcohol.

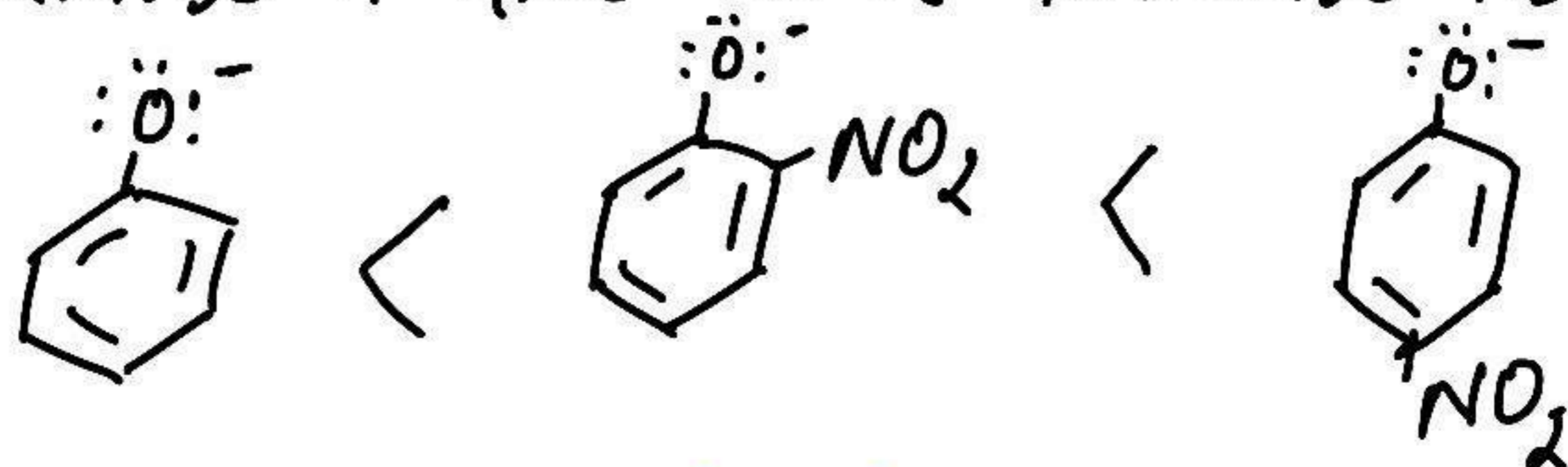
Q Explain the following observation -

***o*- and *p*-nitrophenols are more acidic than phenol.**

Ans. NO_2 being an electron withdrawing group when present at ortho and para-positions withdraws e^- density from benzene ring thereby decreasing the e^- density of OH bond and thus make the release of proton easier.



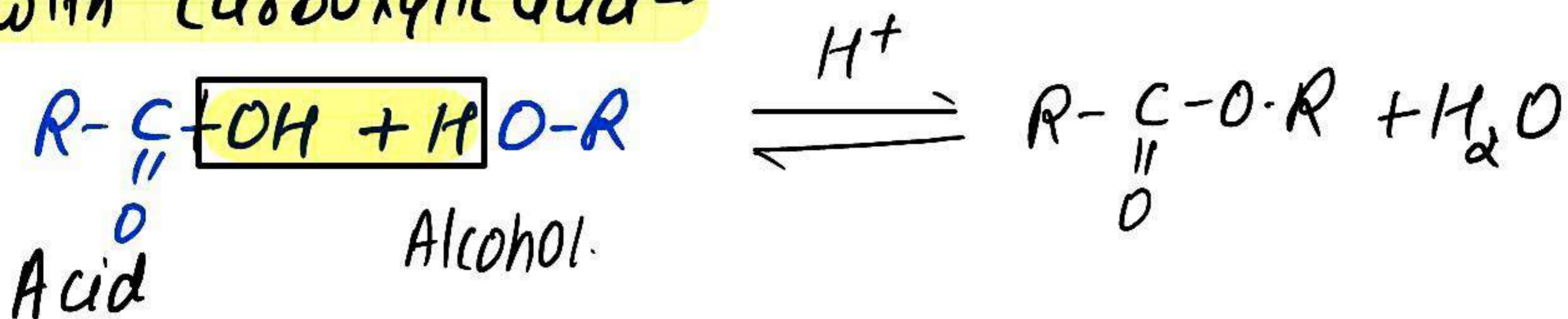
Also, the $-NO_2$ group intensifies the e^- charge of phenoxide ion and thus, stabilise it and hence increase its acidic strength as..



Hence *ortho* and *para* nitrophenol are more acidic than phenol.

Esterification of Alcohol -

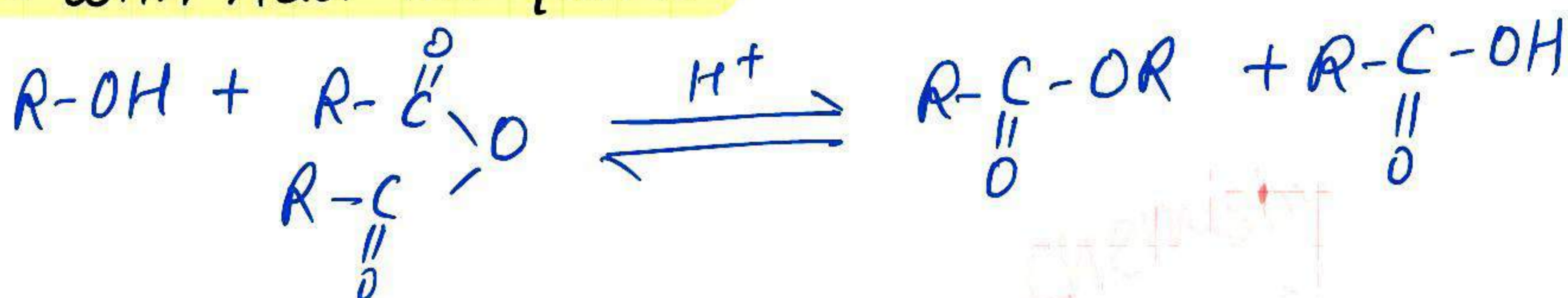
Rxn with Carboxylic acid -



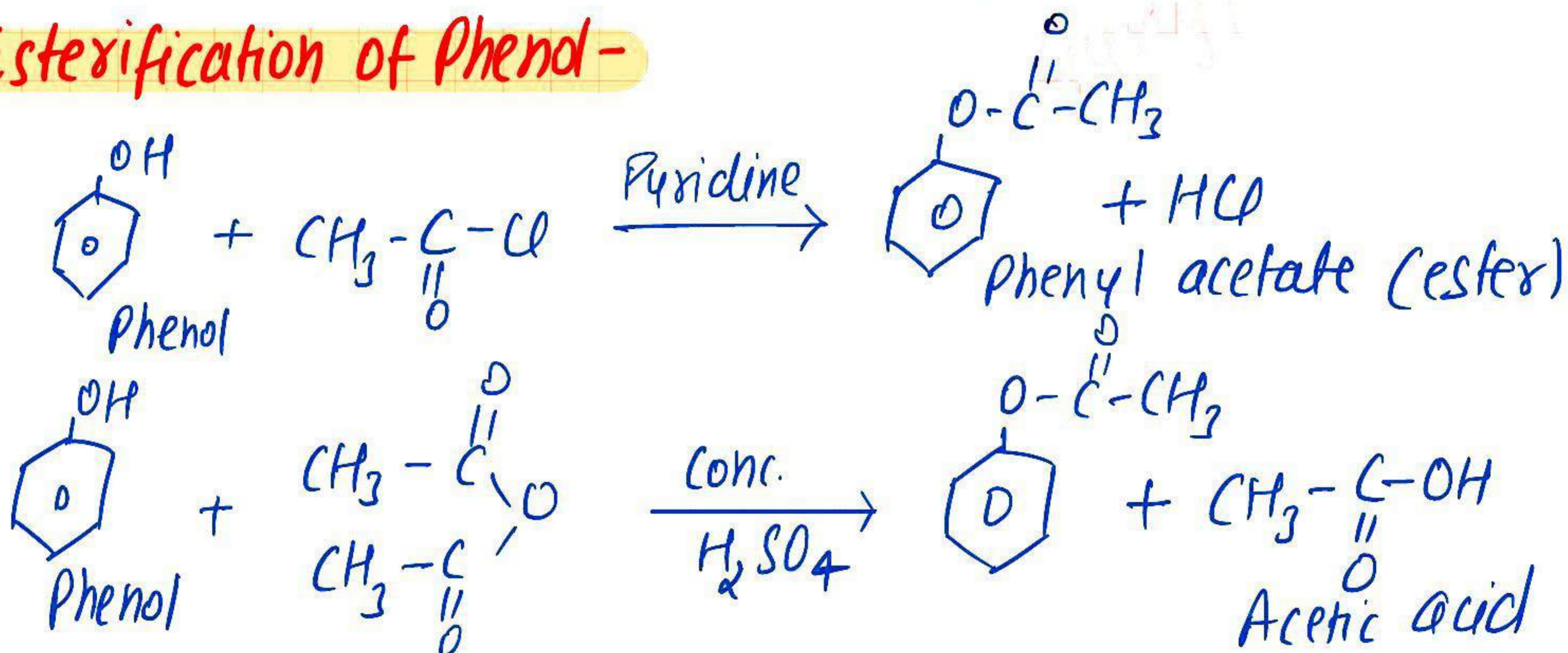
Rxn with Acid Chloride -



Rxn with Acid Anhydride -



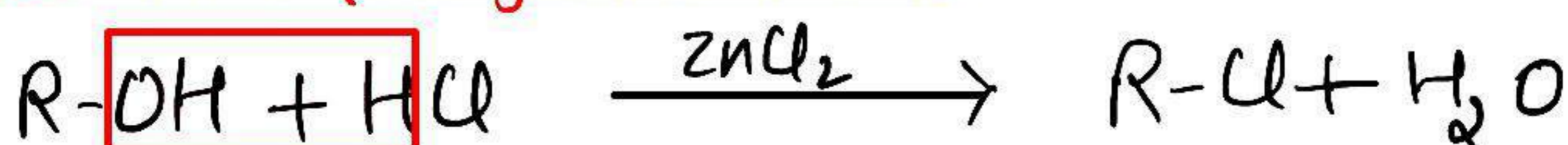
Esterification of Phenol -



Reaction in which cleavage $\text{C}-\text{OH}$ bond takes place:

In this type of reaction, alcohol behaves as an electrophile

Rxn with Hydrogen Halide

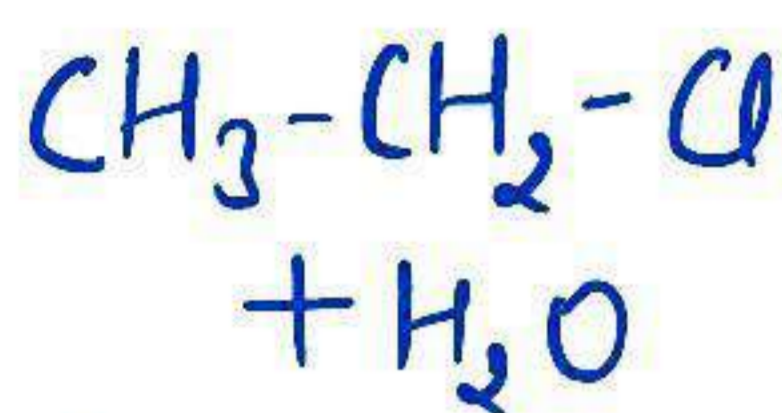
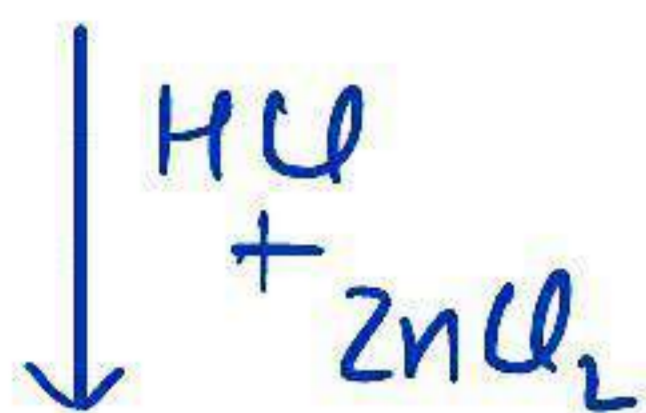


mixture of $\text{HCl} + \text{ZnCl}_2 \longrightarrow$ Lucas Reagent



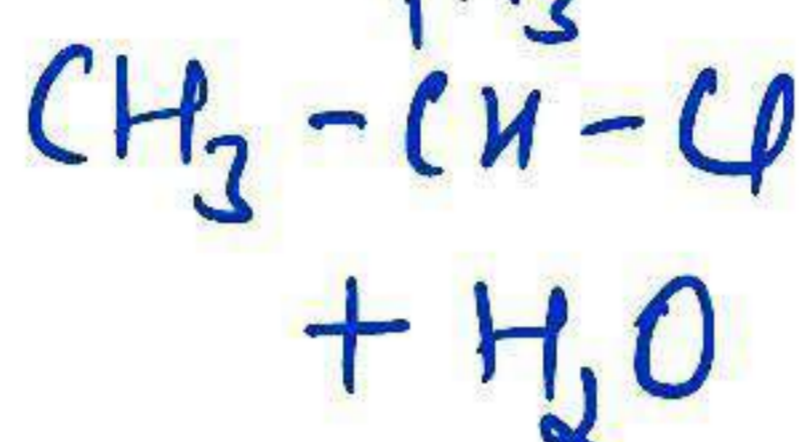
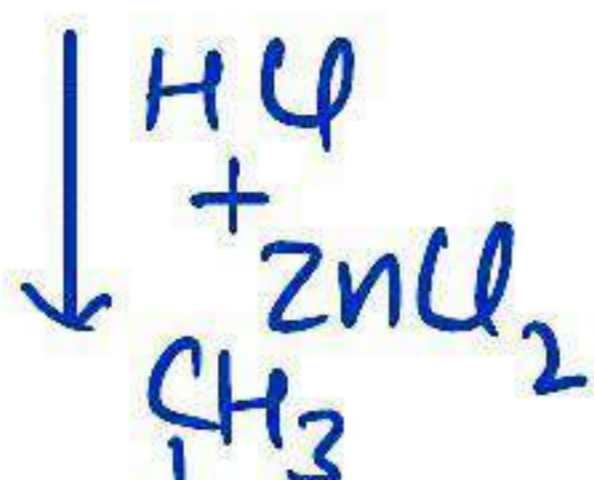
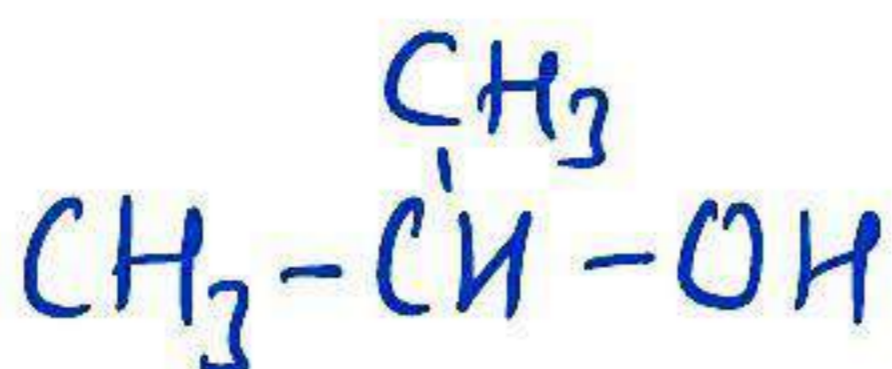
Lucas Test:

1° alcohol



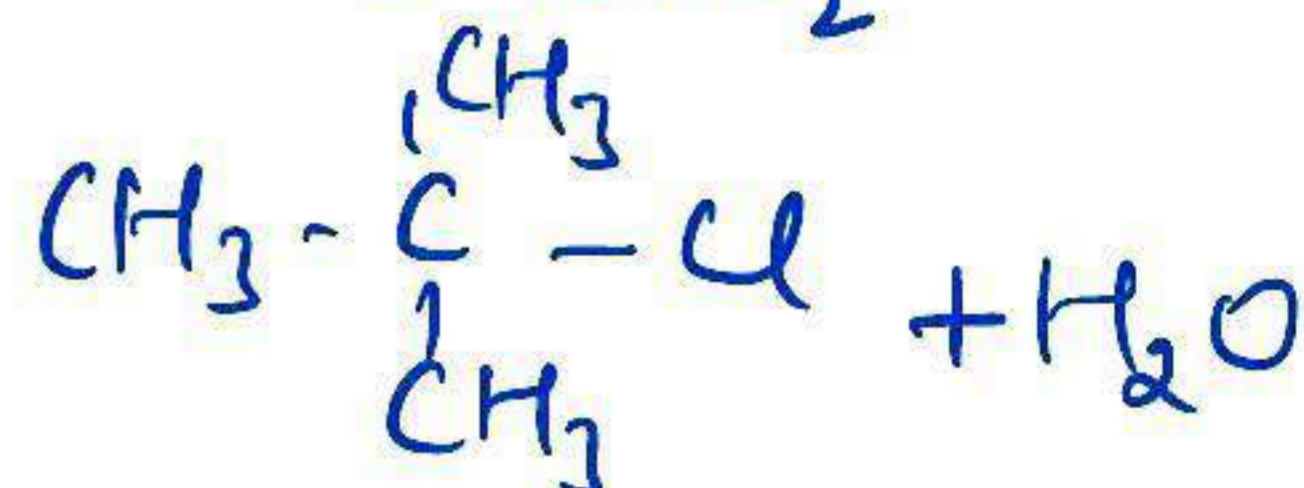
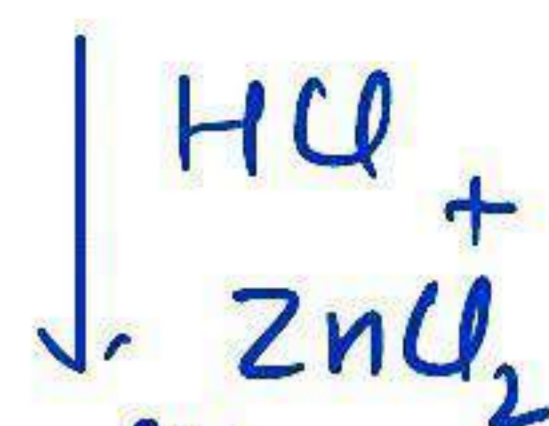
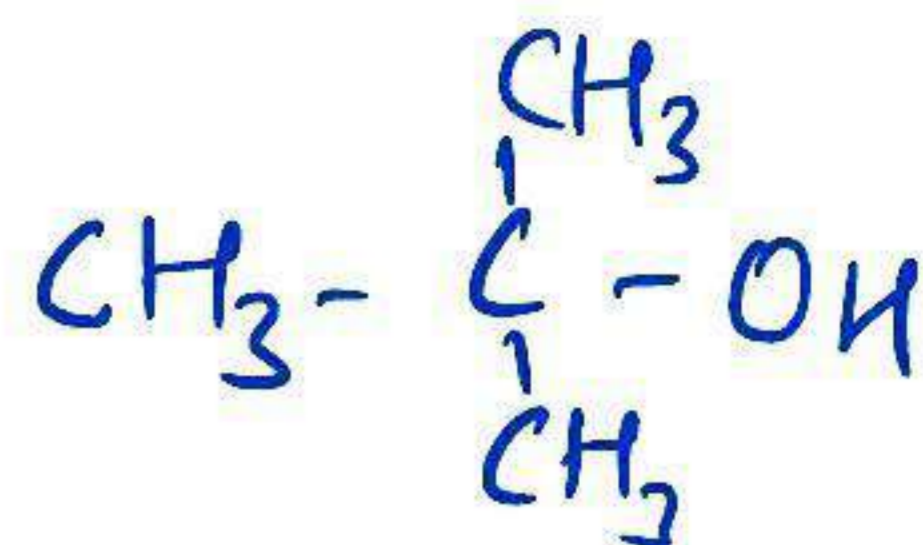
Turbidity appears after heating

2° alcohol



Turbidity appears after 5 min.

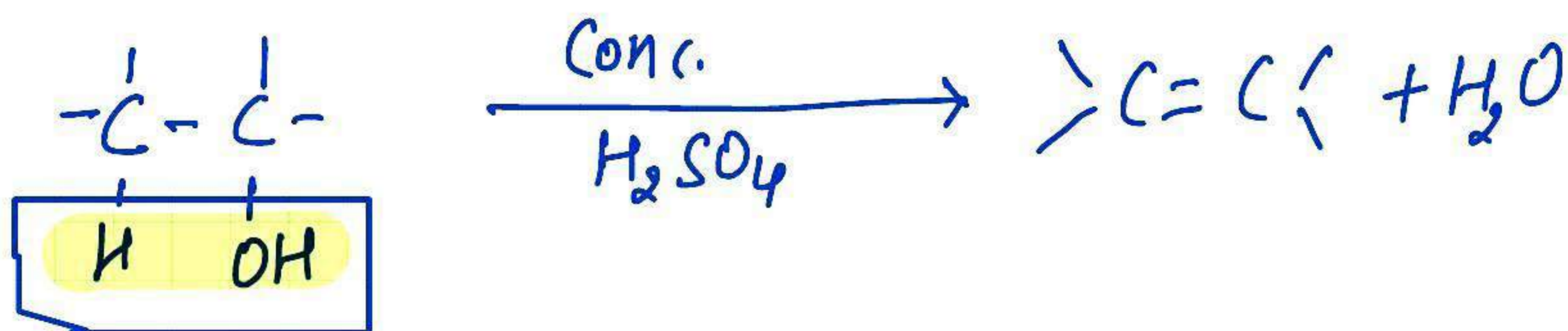
3° alcohol



Turbidity appears immediately

Dehydration

Removing of water molecule from alcohol is called dehydration of alcohol. It is an elimination reaction in which conc. H_2SO_4 , Phosphorous Pentoxide (P_2O_5), Alumina (Al_2O_3) is used for dehydration and alkene is formed as product.



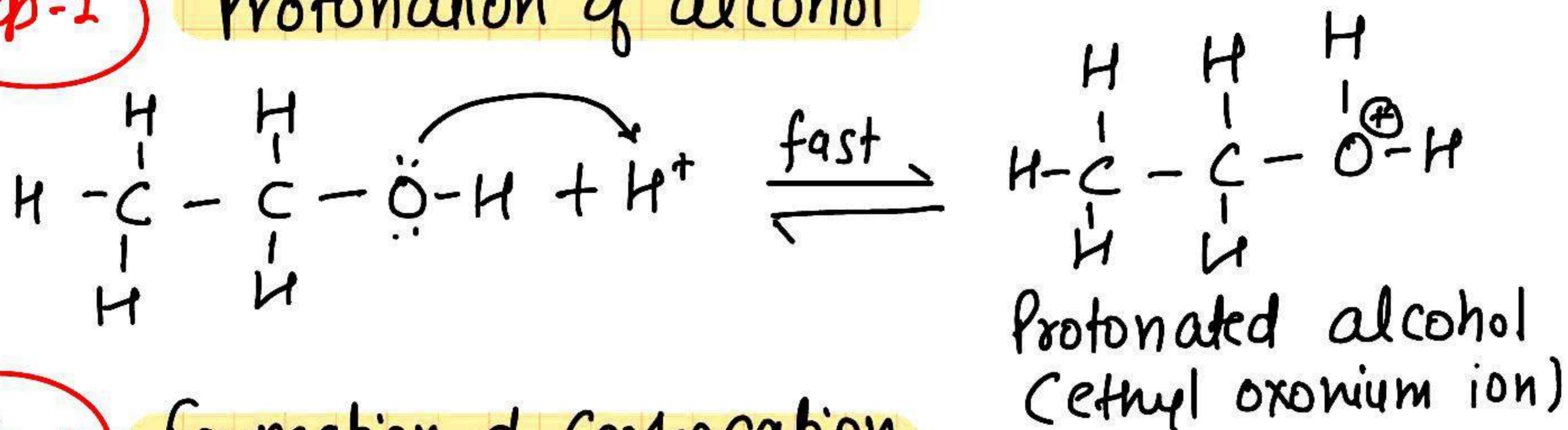
The order of reactivity of different alcohols



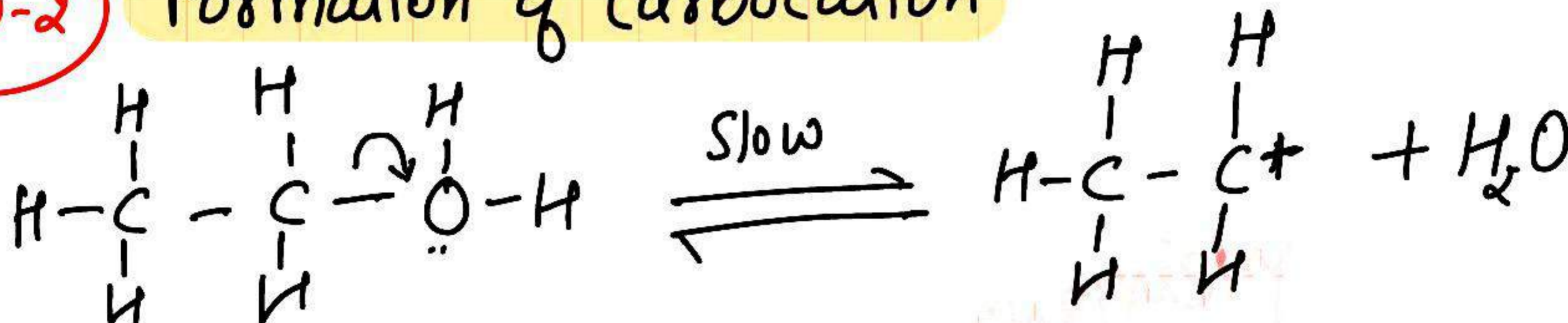
Mechanism of Dehydration of Ethanol:

Dehydration of ethanol in the presence of conc H_2SO_4 involve the following steps:

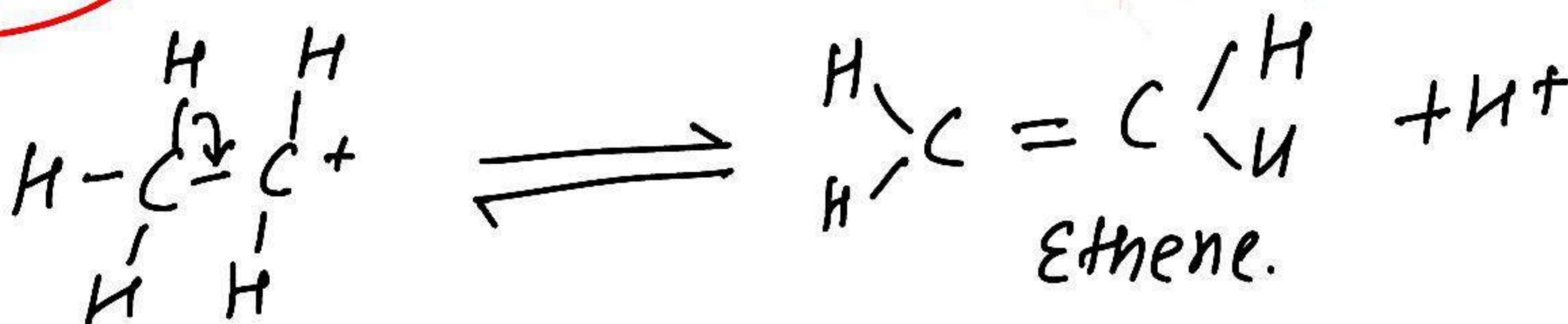
Step-1 Protonation of alcohol



Step-2 Formation of Carbocation



Step-3 Elimination of Proton



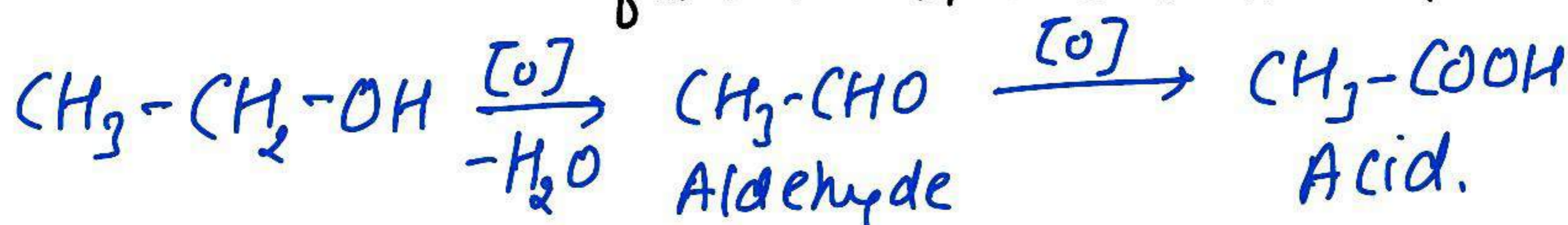
Oxidation-

oxidation of alcohol involve the formation of carbon-oxygen bond with cleavage of an 'O-H' bond and 'C-H' bond.



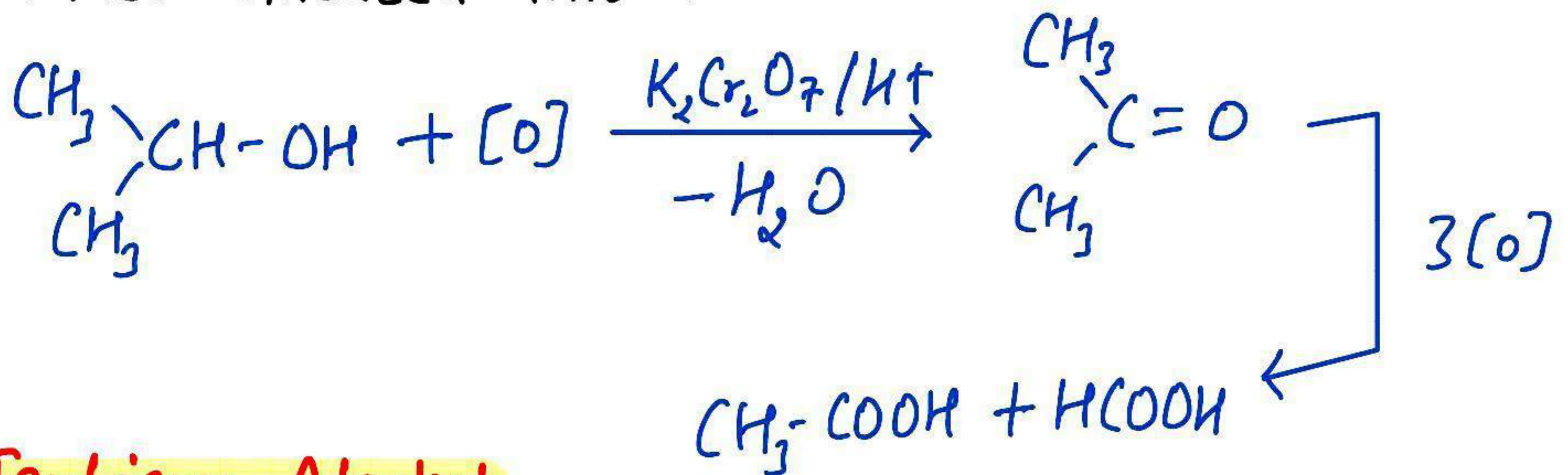
➤ This process is also known as **dehydrogenation**

Primary Alcohol \Rightarrow It is oxidised into aldehyde which is further oxidised into an acid.



Secondary Alcohol

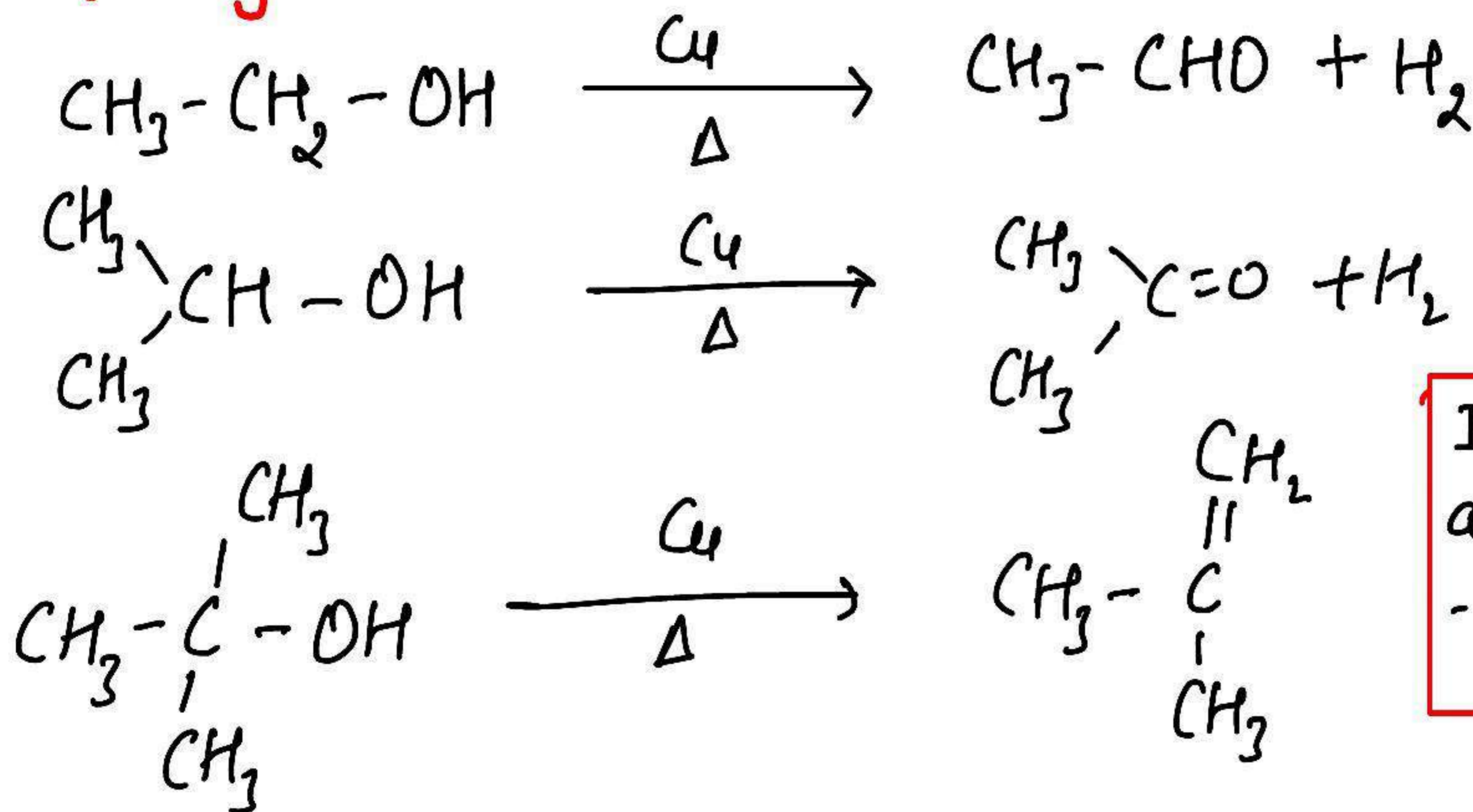
It is oxidised into ketone which is further oxidised into acid



Tertiary Alcohol

It is not oxidised in ordinary condition but in the presence of strong oxidising agent, a mixture of carboxylic acid is formed.

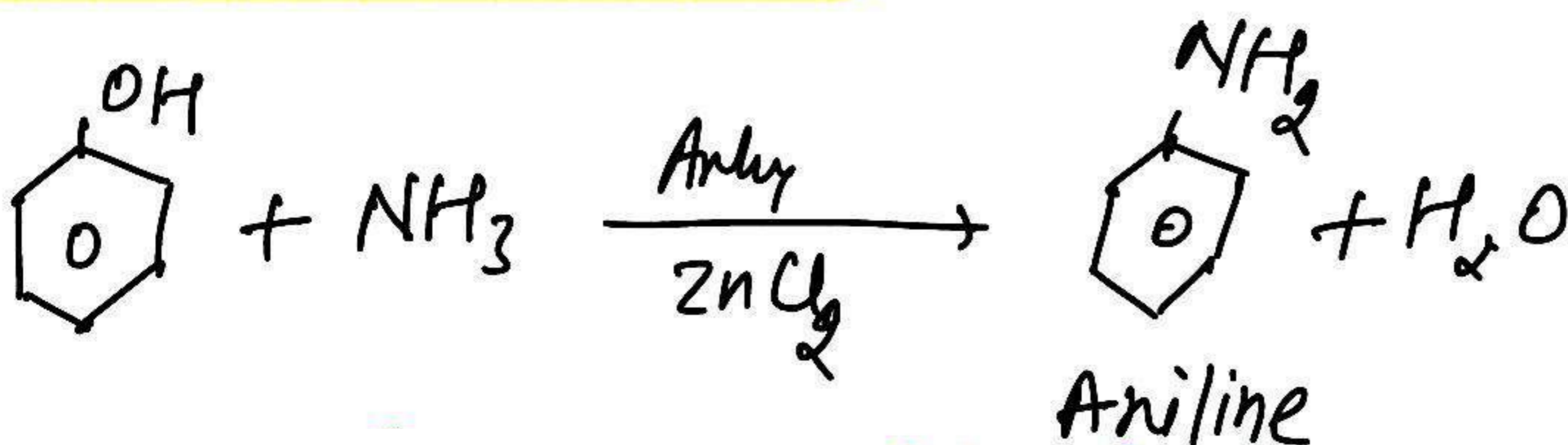
Dehydrogenation:



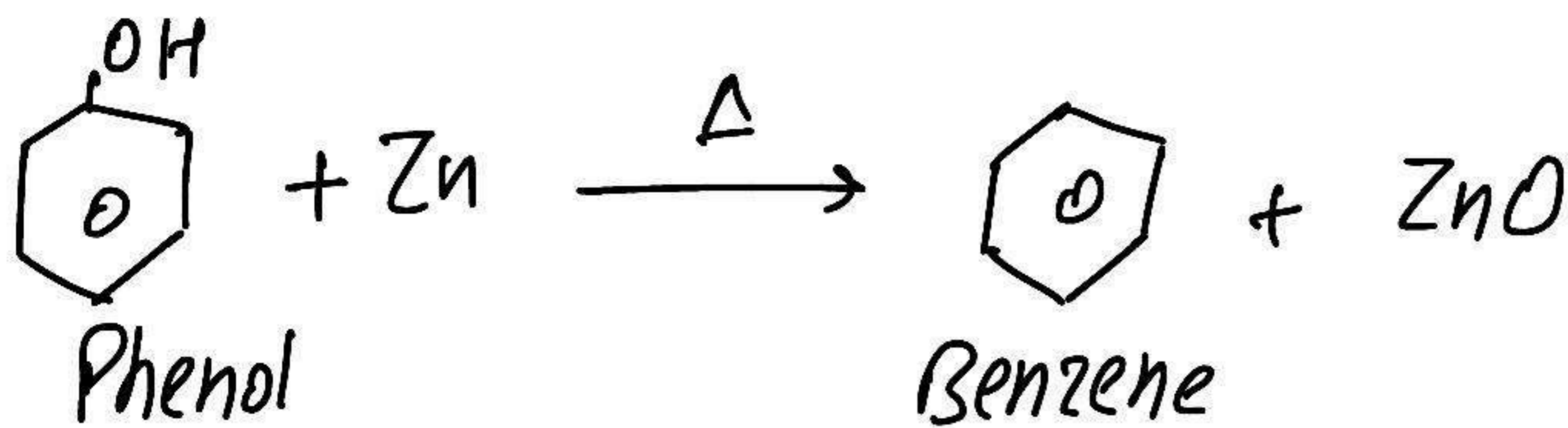
In case of 3° alcohol, dehydration takes place.

Rxn due to -OH group of phenol

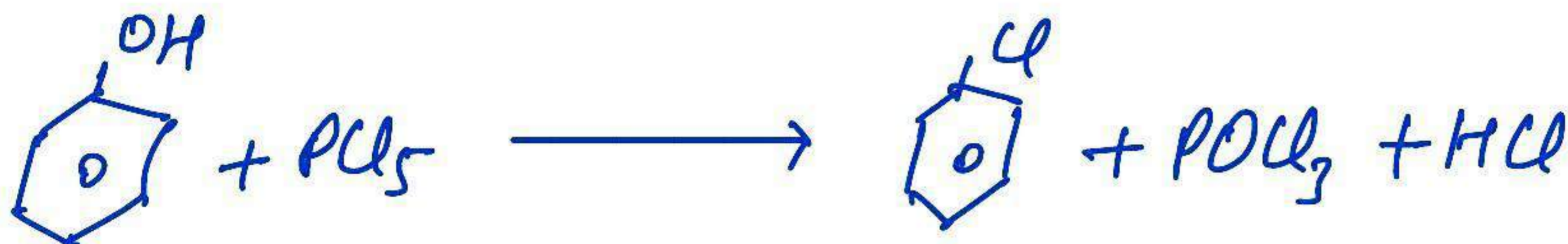
Rxn with Ammonia



Rxn with Zinc Powder -

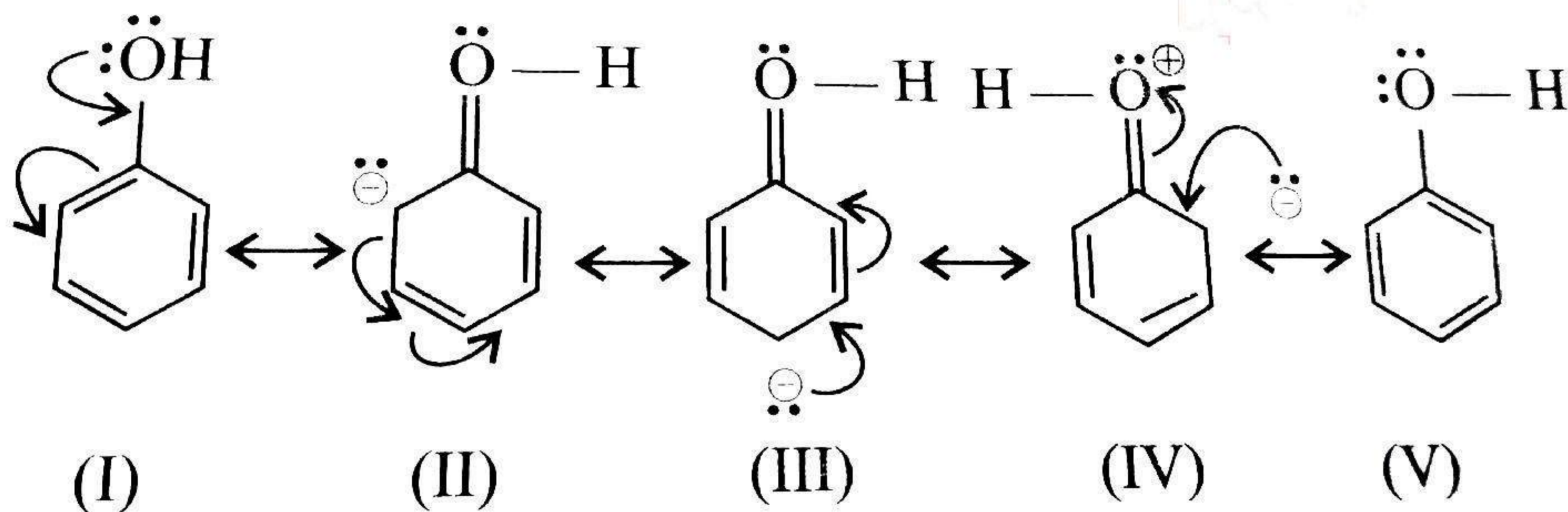


Rxn with Phosphorous Pentachloride (PCl₅)



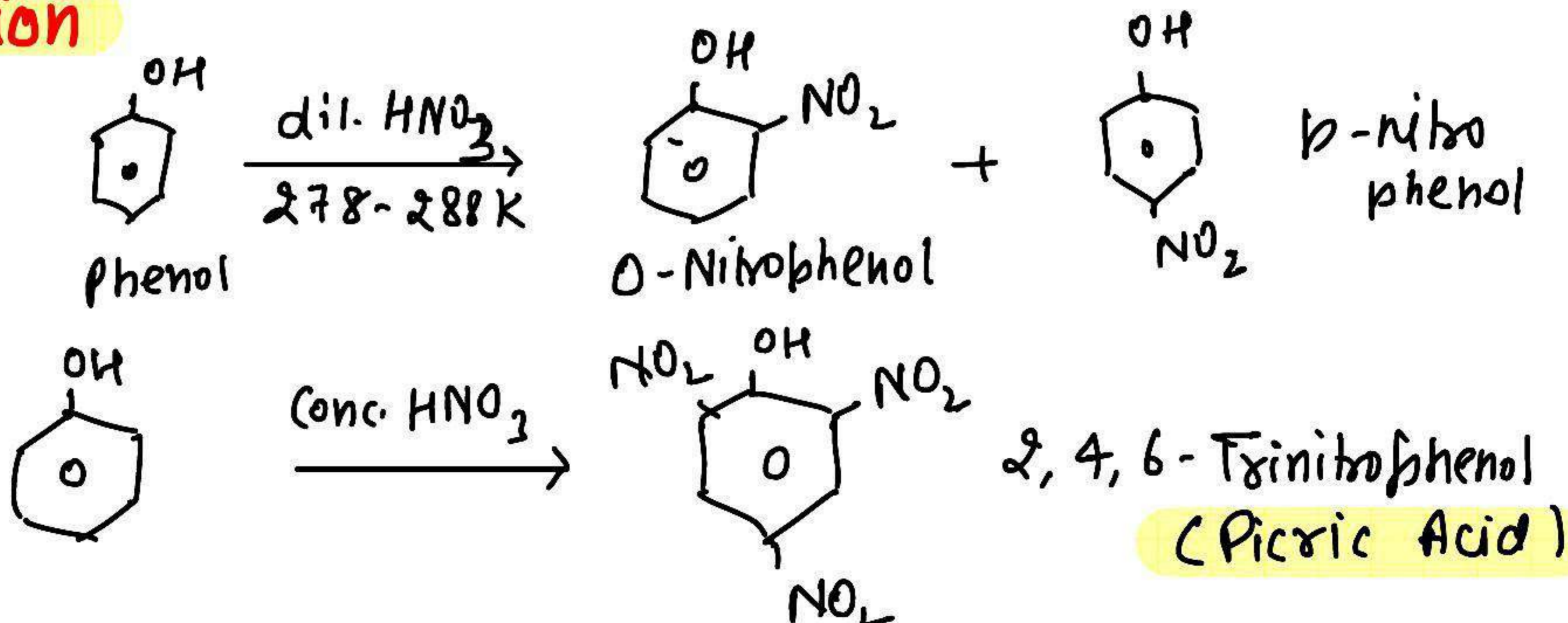
Rxn due to benzene ring of phenol

Resonance in phenol

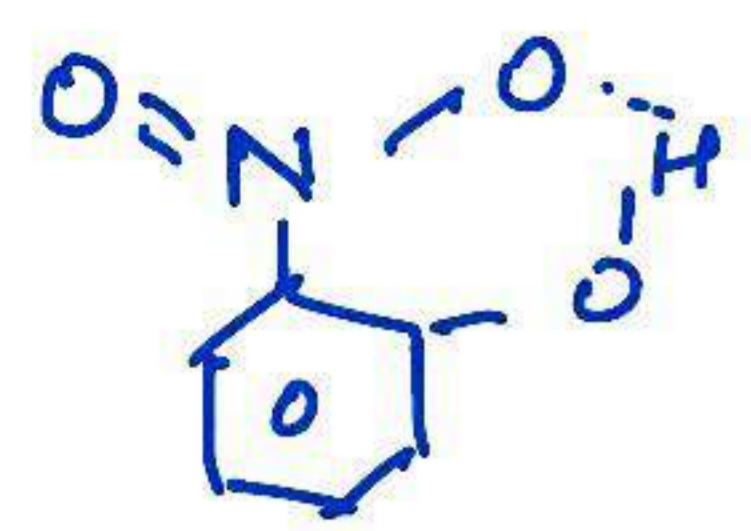


As a result of resonance, electrophilic substitution rxn takes place at ortho and para position.

Nitration

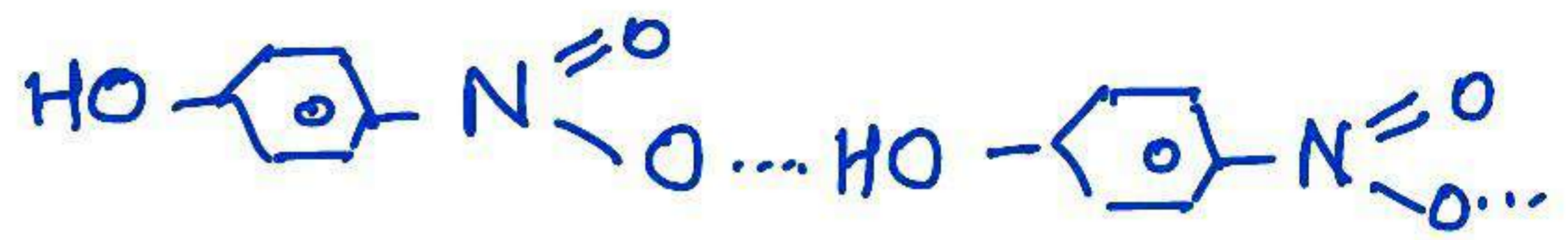


Note The ortho and para isomers can be separated by steam distillation. *o*-Nitrophenol is steam volatile due to intramolecular H-Bonding, while *p*-nitrophenol is less volatile due to intermolecular H-Bonding which causes the association of molecules



o-Nitrophenol

(intramolecular H-Bonding)

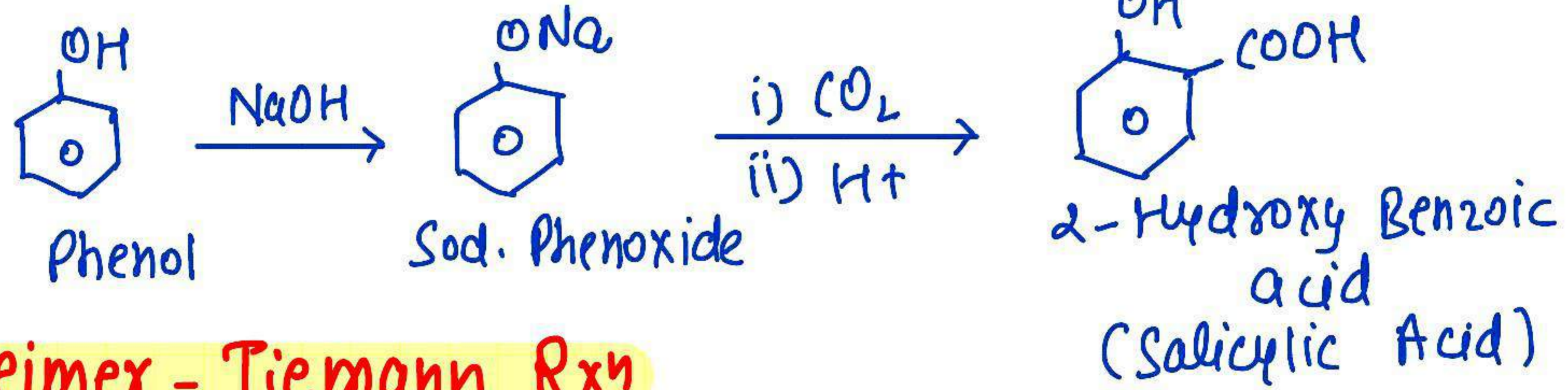


p-Nitrophenol

(intermolecular H-Bonding)

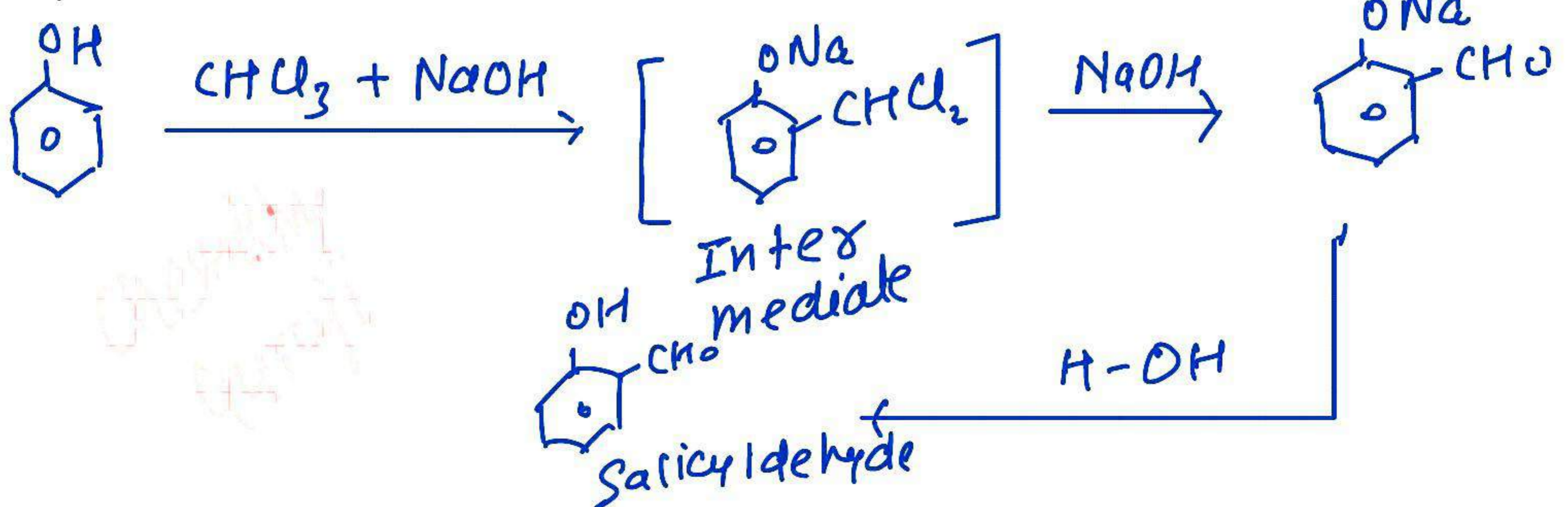
Kolbe's Reaction

Phenoxide ion is more reactive than phenol towards electrophilic sub. reaction. Therefore when phenoxide ion react with CO_2 , then salicylic acid is formed as a product. This reaction is called Kolbe's Reaction



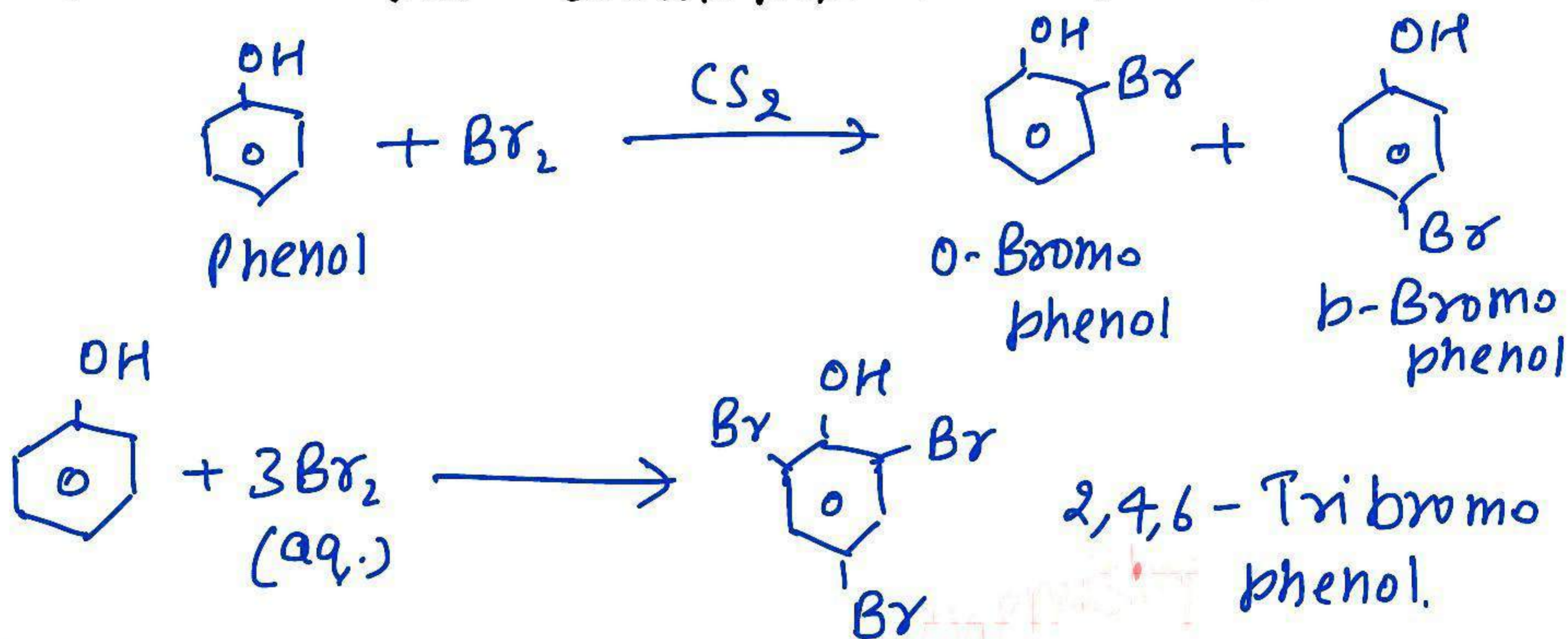
Reimer - Tiemann Rxn

when phenol react with chloroform in the presence of sodium hydroxide then salicylaldehyde is formed as a product. This is called Reimer - Tiemann Rxn.



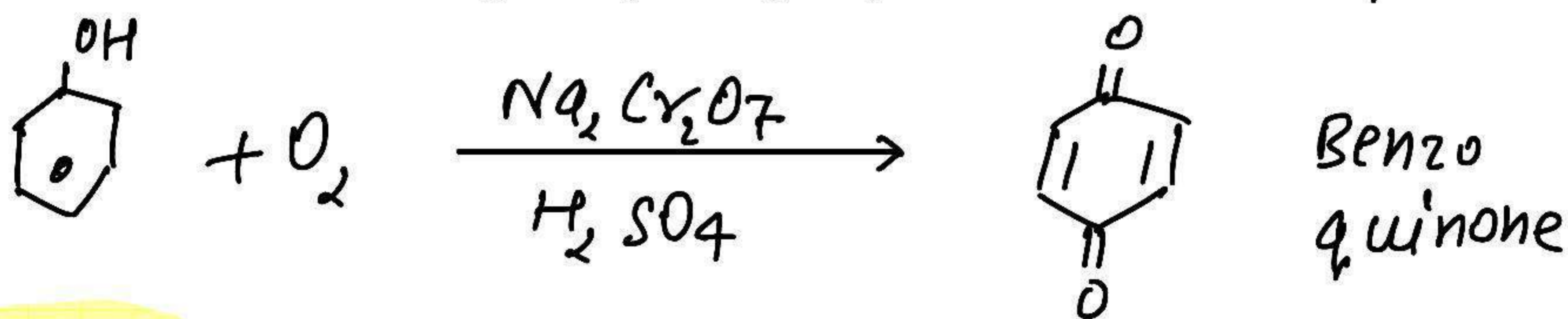
Halogenation

When phenol reacts with bromine in the presence of CS_2 , $CHCl_3$ or CCl_4 at low temp, then ortho and para bromophenol is formed.



Oxidation:

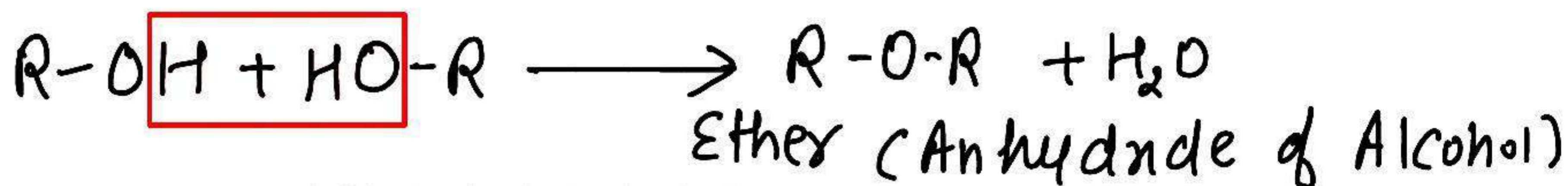
Oxidation of phenol in the presence of air with chromic acid ($Na_2Cr_2O_7 + H_2SO_4$) form benzoquinone



Ethers (R-O-R)

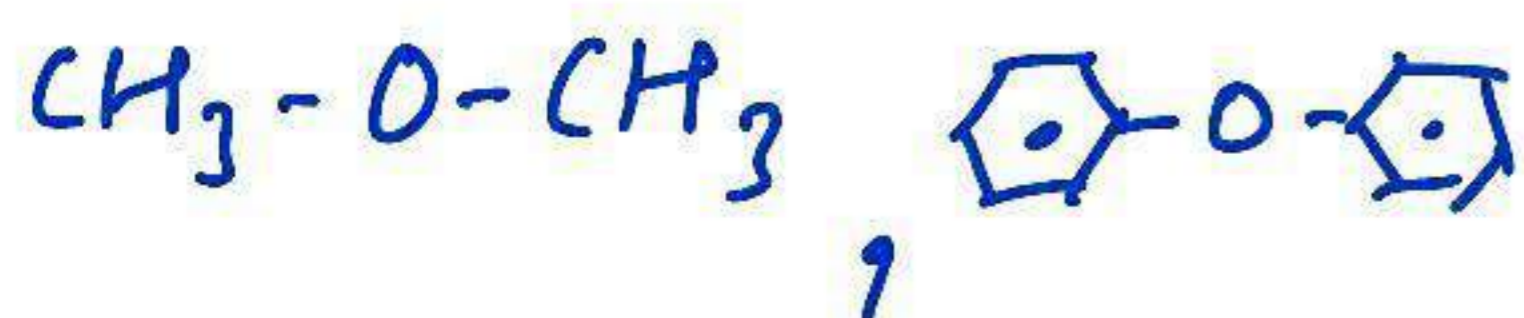
The general formula of ether is $C_nH_{2n+2}O$

- In ether two alkyl group are attached with the both side of oxygen atom R-O-R
- Ether is also known as Anhydride of Alcohol.



Types of Ethers

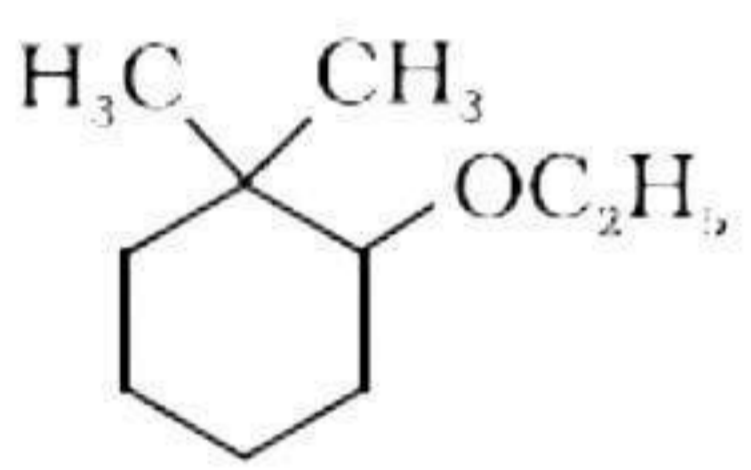
Simple ethers



Mixed Ethers



Common & IUPAC Name of Ethers

Compound	Common name	IUPAC name
CH_3OCH_3	Dimethyl ether	Methoxymethane
$\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$	Diethyl ether	Ethoxyethane
$\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_3$	Methyl n-propyl ether	1-Methoxypropane
$\text{C}_6\text{H}_5\text{OCH}_3$	Methyl phenyl ether (Anisole)	Methoxybenzene (Anisole)
$\text{C}_6\text{H}_5\text{OCH}_2\text{CH}_3$	Ethyl phenyl ether (Phenetole)	Ethoxybenzene
$\text{C}_6\text{H}_5\text{O}(\text{CH}_2)_6-\text{CH}_3$	Heptyl phenyl ether	1-Phenoxyheptane
$\text{CH}_3\text{O}-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_3$	Methyl isopropyl ether	2-Methoxypropane
$\text{C}_6\text{H}_5-\text{O}-\text{CH}_2-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_3$	Phenyl isopentyl ether	3-Methylbutoxybenzene
$\text{CH}_3-\text{O}-\text{CH}_2-\text{CH}_2-\text{OCH}_3$	—	1,2-Dimethoxyethane
	—	2-Ethoxy- -1,1-dimethylcyclohexane

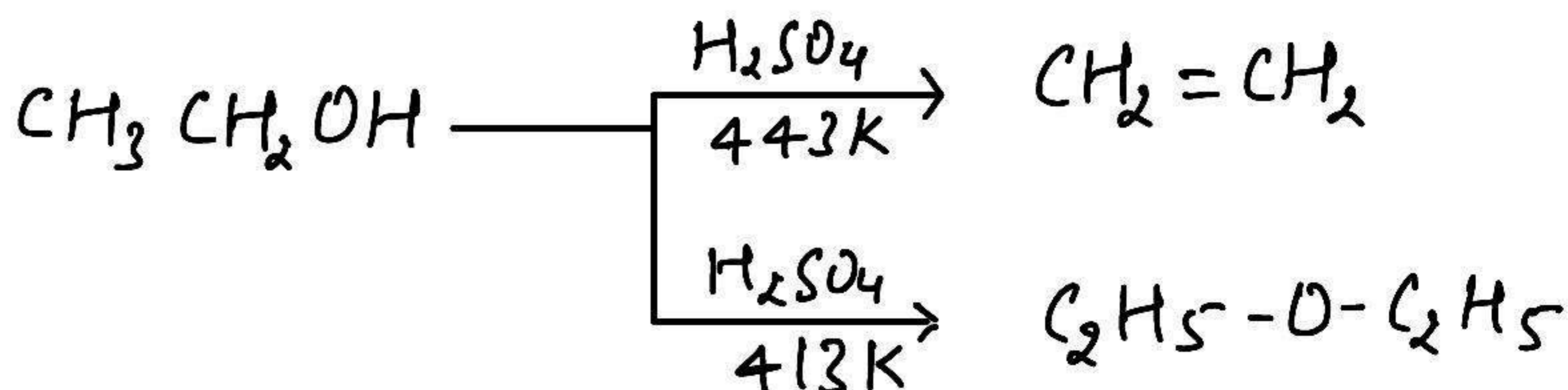
Structure of Ethers:

The bond angle b/w ($\text{C}-\text{O}-\text{C}$) is 111° due to repulsion between alkyl groups, which are attached to oxygen atom



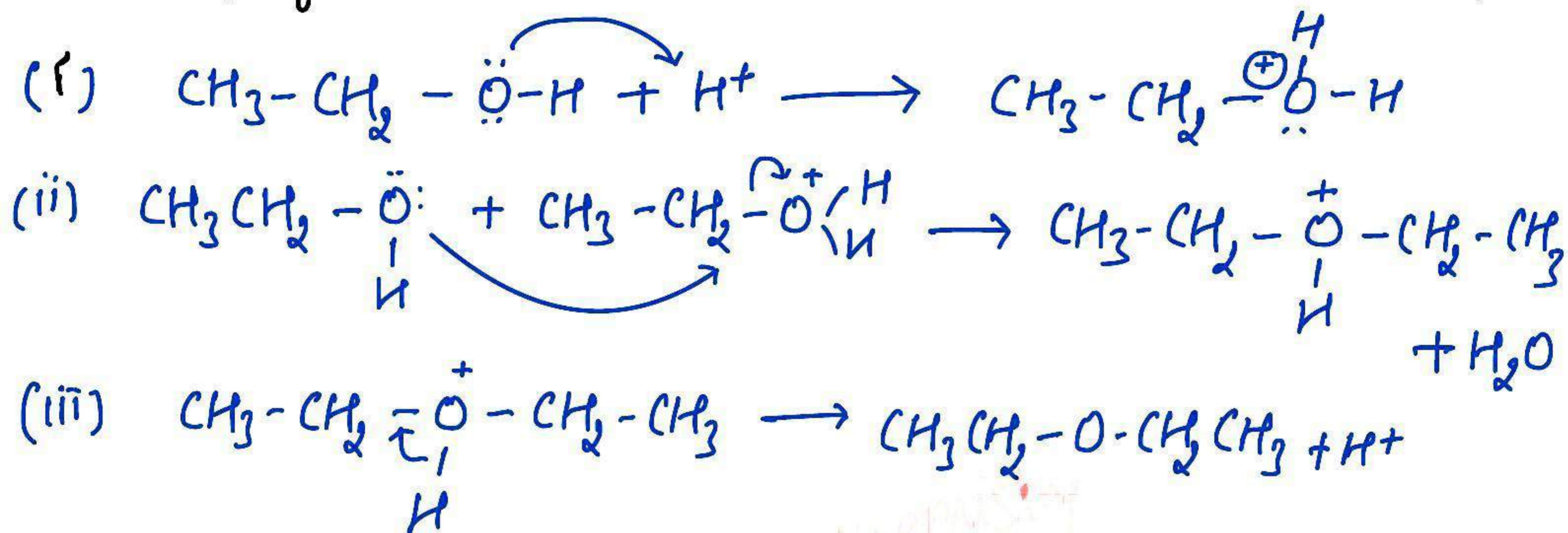
Preparation of Ethers

- By dehydration of alcohol



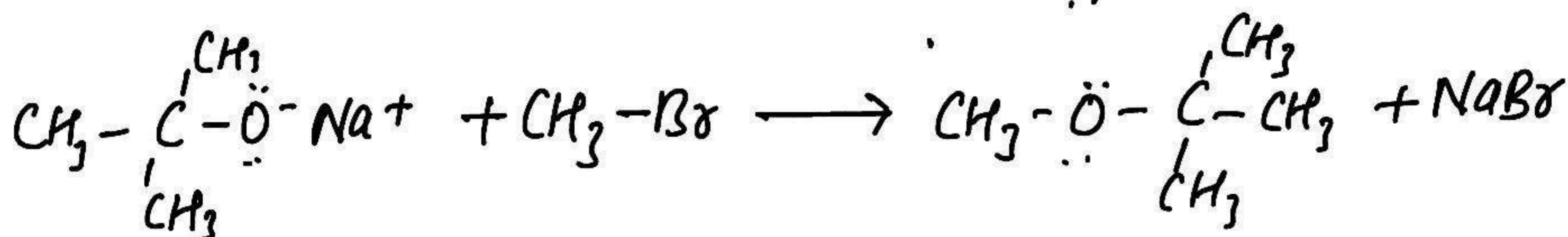
Mechanism

The formation of ether is S_N2 involving the attack of alcohol molecule on a protonated alcohol.

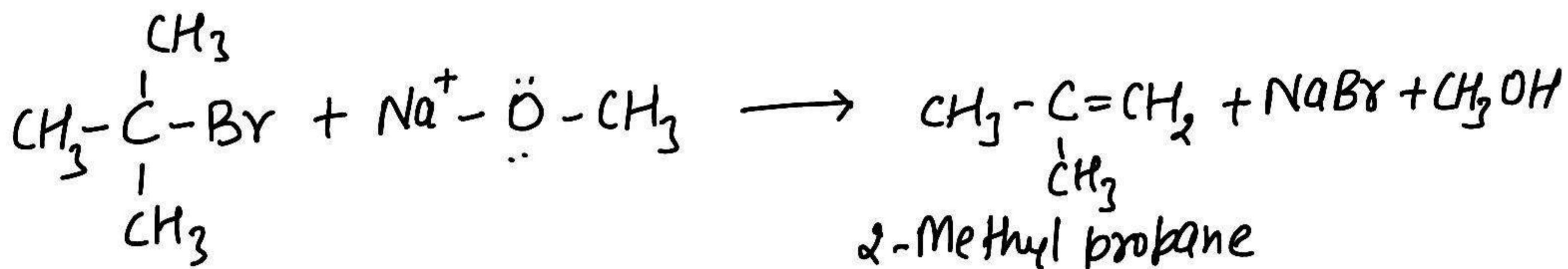


Williamson Synthesis

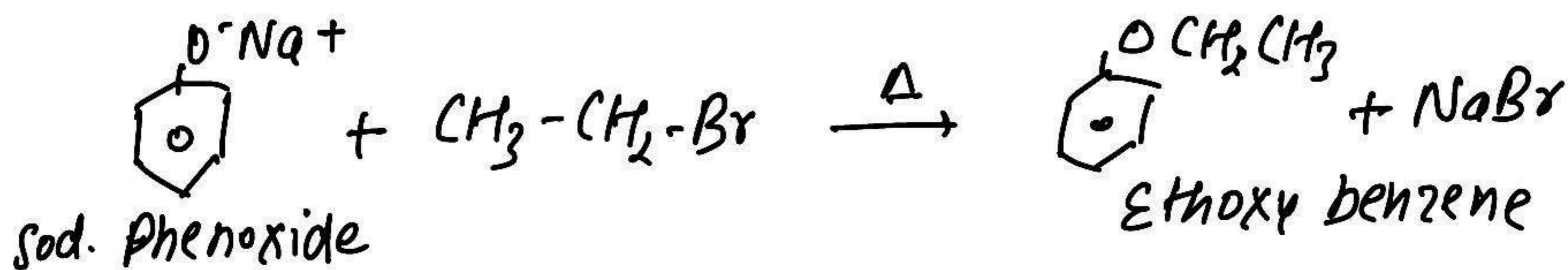
When sodium or potassium alkoxide are heated with alkyl halide, then ether is formed. This takes place by S_N2 mechanism.



In case of 2° and 3° alkyl halides, elimination completes over substitution. If a 3° alkyl halide is used an alkene is the only reaction product and no ether is formed.



Phenols are also converted to ethers by this method.

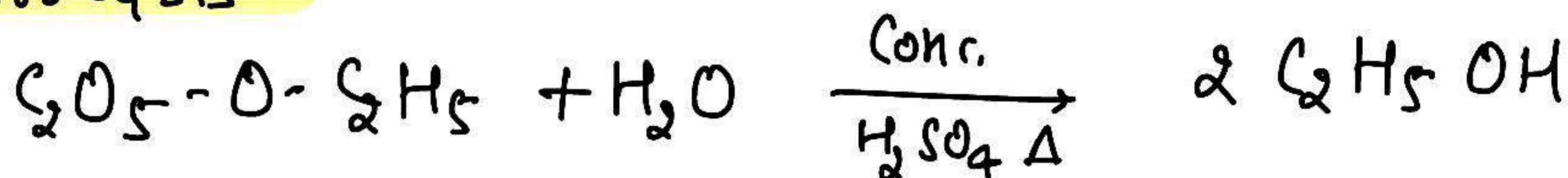


Physical Properties of Ethers

-) Dimethyl ether and diethyl ether are gaseous and other ethers are liquid in nature.
-) Ethers are lighter than water i.e. density is less than water.
-) Ethers are highly volatile in nature.
-) **Solubility** ethers are partially soluble in water and are highly soluble in chloroform and benzene.
-) **Boiling Point** The b.pt of ether is very less than compare to isomeric alcohol because in ether intermolecular H-bonding is not present.
The b.pt of ether is similar to the molecular wt. of alkane.

Chemical Properties

i) Hydrolysis

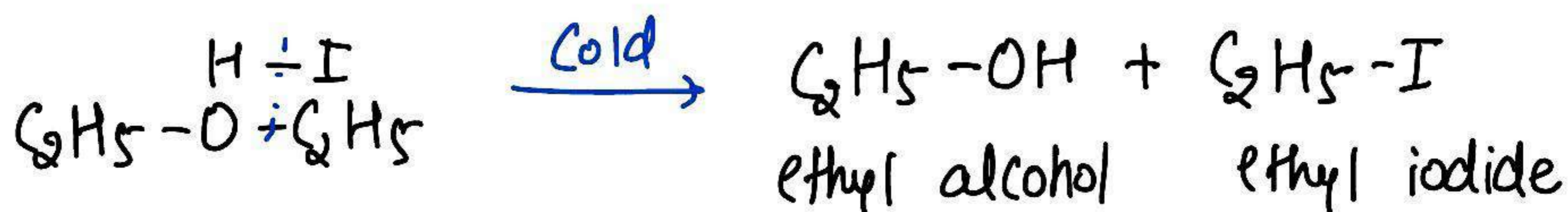
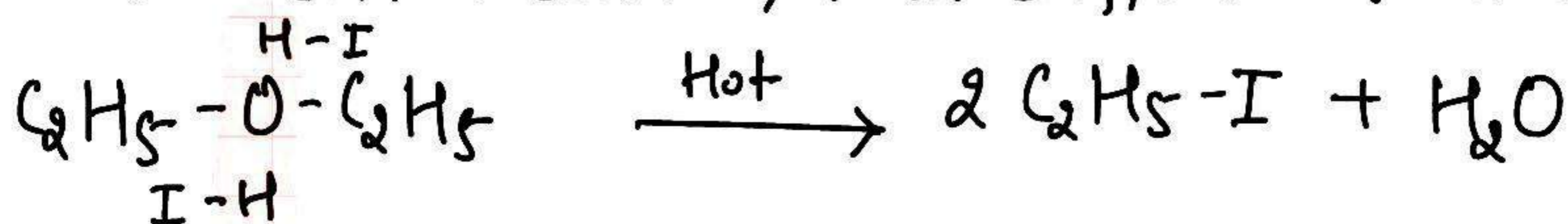


ii) Rxn with Halogen Acids:



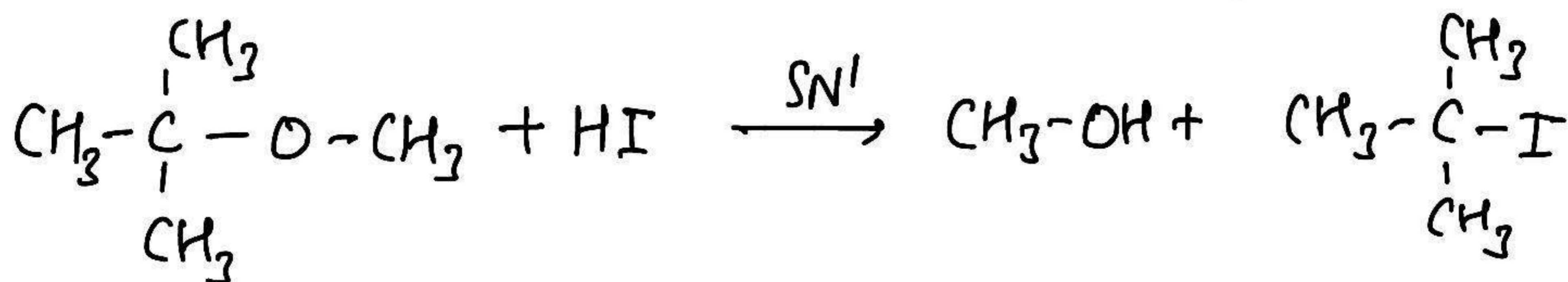
Reaction with HI:

when ether react with HI in hot and cold medium, then different product is formed

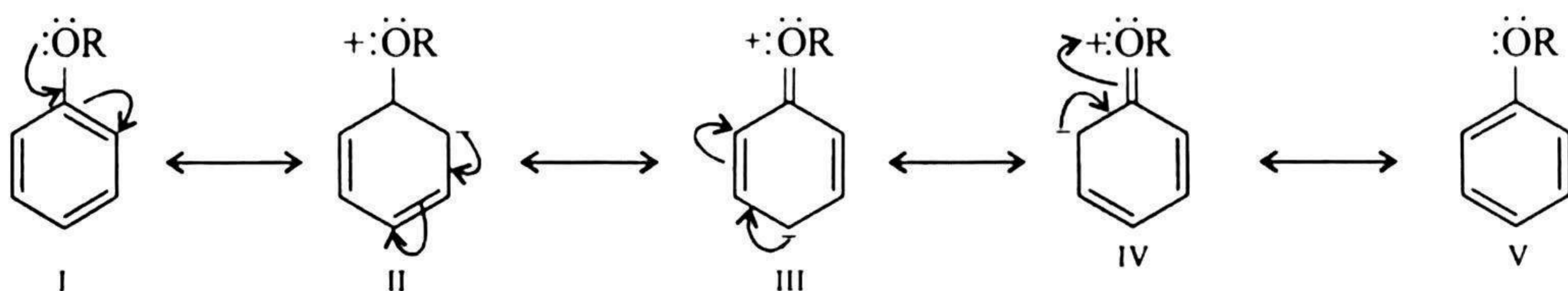


Note

When one of the alkyl group is a tertiary group, the halide ion is formed is a tertiary halide.

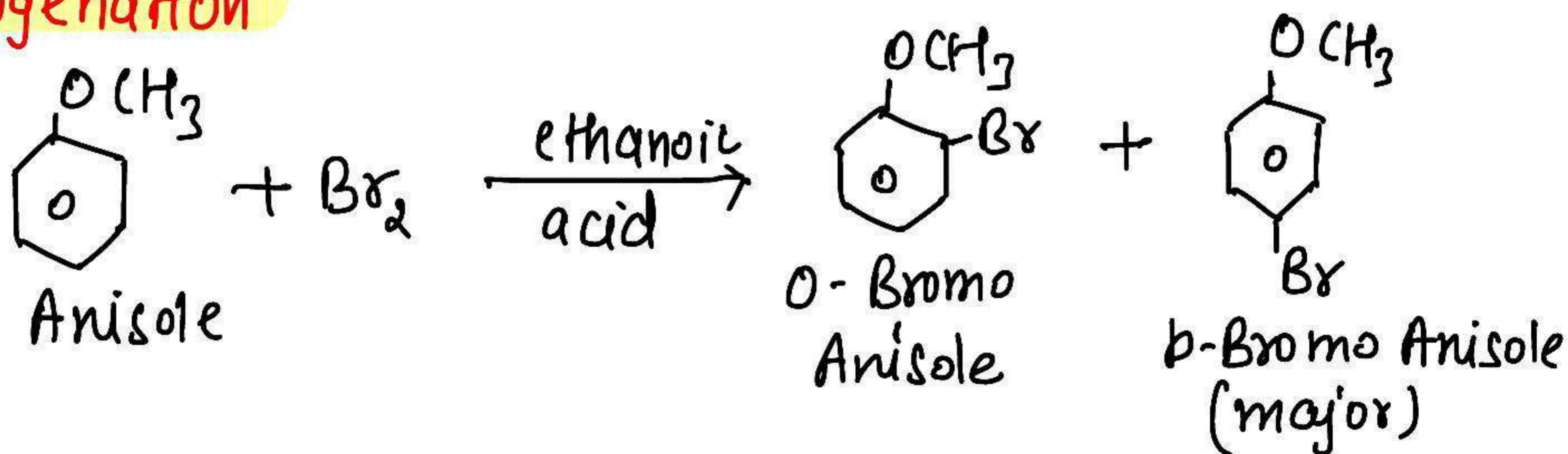


• Electrophilic Substitution Reaction

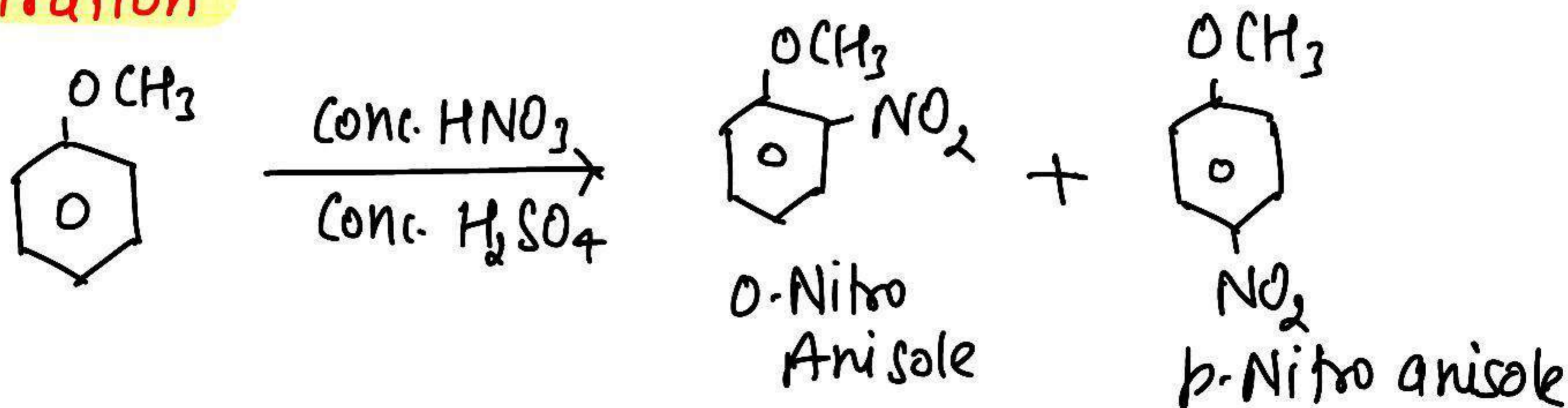


-OR group is ortho and para directing. Therefore electrophilic substitution takes place on ortho and para position of benzene ring.

• Halogenation

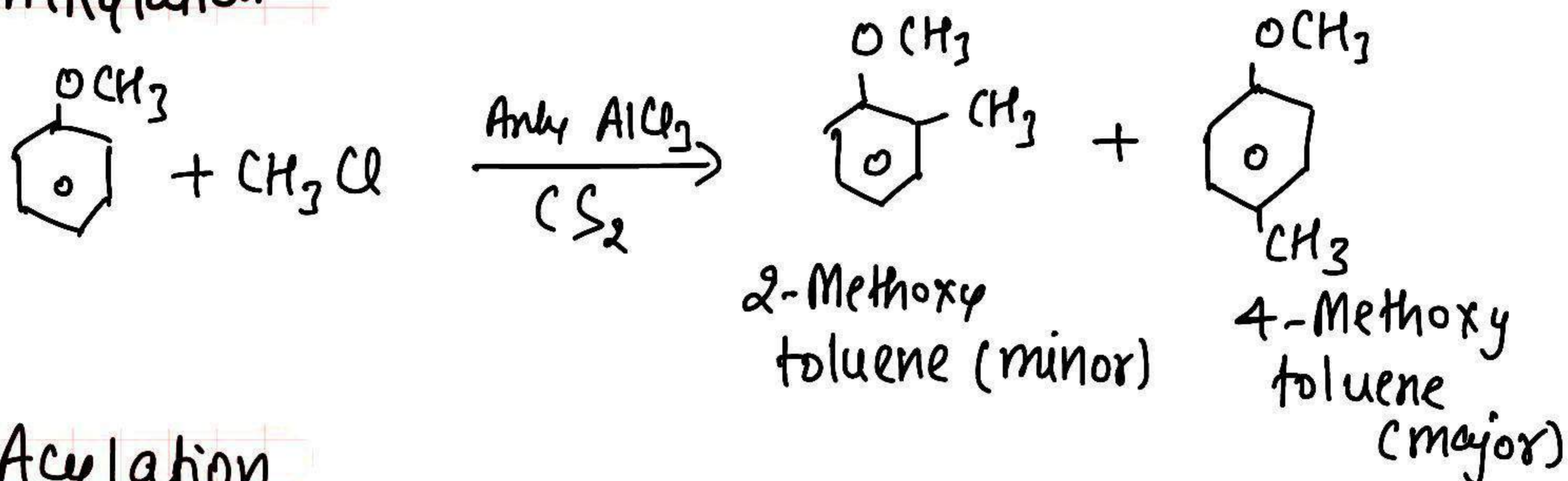


• Nitration

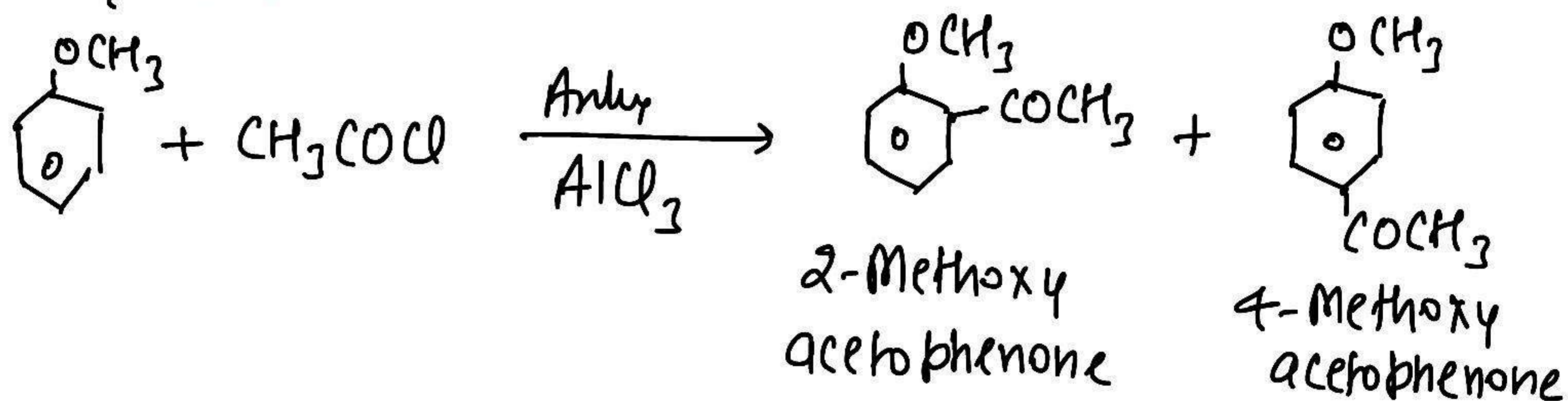


Friedel Craft Reaction

Alkylation



Acylation



Denaturation of Alcohol

The commercial alcohol is made unfit for drinking by mixing it with some copper sulphate and methyl alcohol.

Power Alcohol -

Absolute alcohol mixed with petrol (roughly in the ratio 20:80) is used in internal combustion engines. This is known as power alcohol. Mixing is done in presence of 1% benzene or 1% ether.

ALCOHOLMETRY -

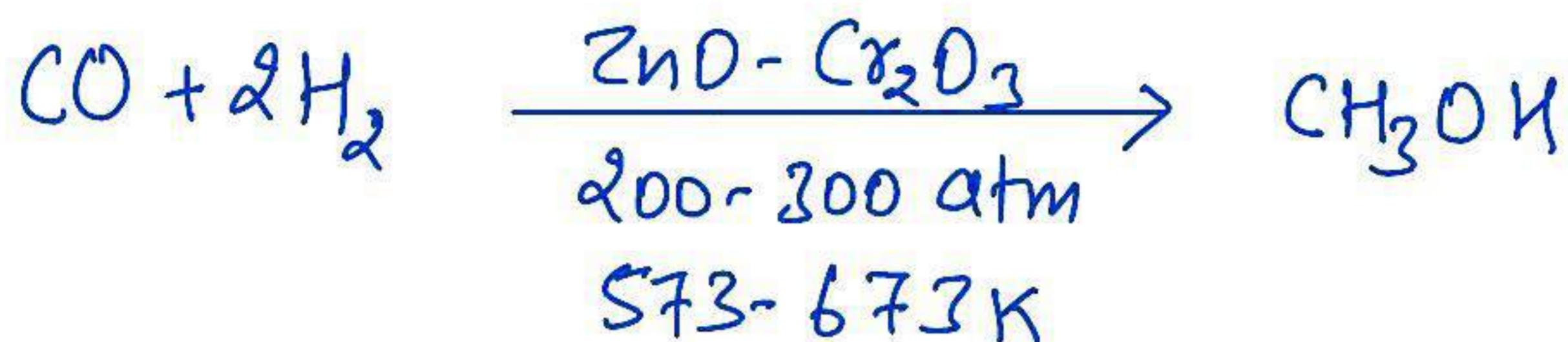
The determination of the percentage of alcohol in a liquid, especially in alcohol is known as alcoholmetry.

SOME COMMERCIALY IMPORTANT ALCOHOLS

1. Methanol, CH_3OH \rightarrow also known as wood spirit

Preparation

By catalytic hydrogenation of carbon monoxide at high pressure and temp. in the presence of $\text{ZnO} \cdot \text{Cr}_2\text{O}_3$ catalyst



Properties

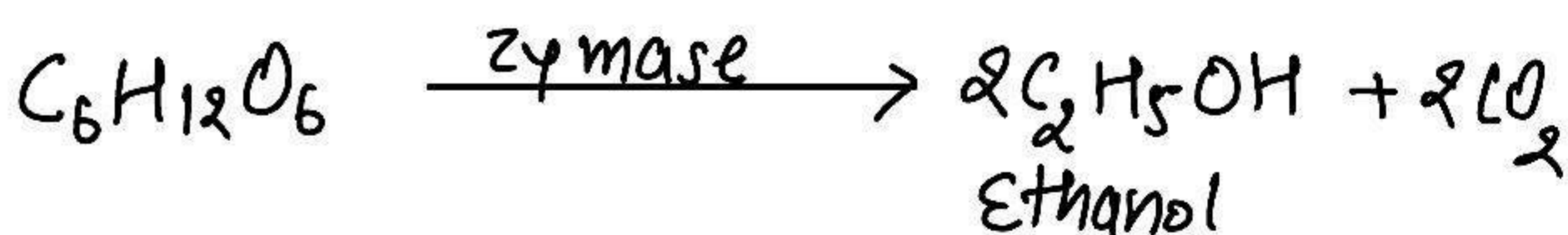
- it is a colourless liquid and highly poisonous
- It is completely soluble in water.

Uses

- It is used as a solvent for paints.
- It is used for the manufacture of formaldehyde
- It is used as an antifreeze for automobile radiators.
- It is used for denaturing ethyl alcohol.

2. Ethanol ($\text{C}_2\text{H}_5\text{OH}$)

Ethanol is mainly obtained commercially by fermentation of sugar.



Properties

Ethanol is a colourless liquid

The boiling point of ethanol is higher than methanol.

USES -

- as a solvent in paint industry
- it is used as an antiseptic in the form of ^{rectified spirit}
- in the preparation of a no. of compounds such as ether, acetic acid, chloroform, iodoform etc.