

SBG STUDY

classmate

Date _____

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Alcohol and Phenol

and Ethers

Alcohols (ROH)

Hydroxy derivatives of alkanes are called Alcohols. For ex \rightarrow CH_3OH , $\text{C}_2\text{H}_5\text{OH}$ etc.

Phenols (PhOH)

Hydroxy derivatives of benzene are called Phenols


Classifications of Alcohols and Phenols on the basis of OH group.

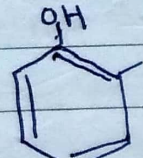
Alcohols and Phenols may be classified as monohydric, Dihydric, Trihydric and polyhydric according as they contain one, two, three or more OH group in a molecule.

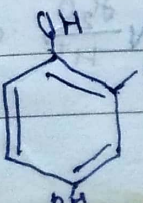
(i) $\text{CH}_3\text{OH} \rightarrow$ Methanol (Monohydric)

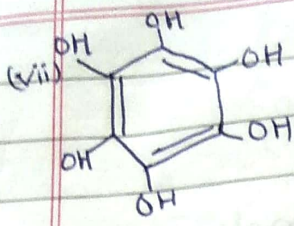
(ii) $\begin{array}{c} \text{CH}_2-\text{OH} \\ | \\ \text{CH}_2-\text{OH} \end{array} \rightarrow$ Glycol (Dihydric)

(iii) $\begin{array}{c} \text{CH}_2\text{OH} \\ | \\ \text{CH}_2\text{OH} \\ | \\ \text{CH}_2\text{OH} \end{array} \rightarrow$ Glycerol (Trihydric)

(iv)  \rightarrow Phenol (Monohydric)

(v)  \rightarrow Catechol (Dihydric)

(vi)  \rightarrow Hydroxy quinol (Trihydric)

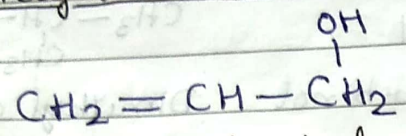


→ Hexaphenol (Polyhydric)

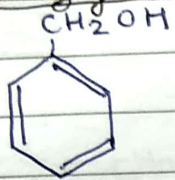
Classification of monohydric alcohols and phenols

(A) Compound containing $C_{sp^3} - OH$ bonds :-

1. Allylic Alcohol

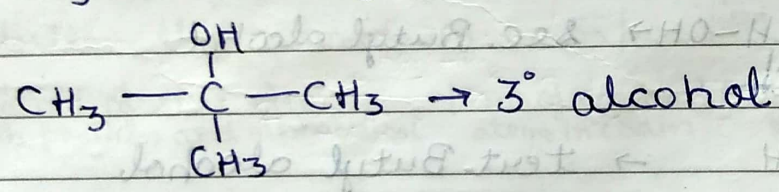
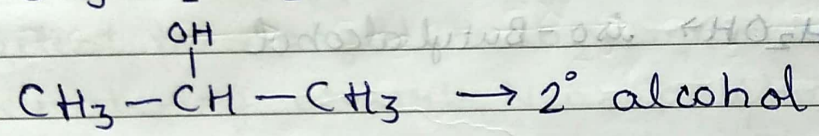
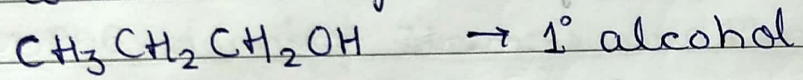


2. Benzylic alcohol



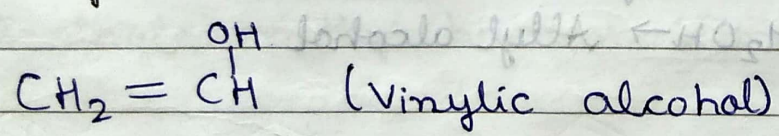
3. Alkyl alcohol

They are further classified as primary, secondary and tertiary alcohol.



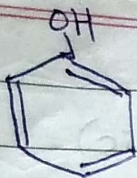
(B) Compounds containing $C_{sp^2} - OH$ bonds

1. Vinylic Alcohol



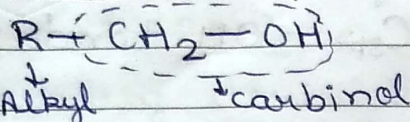
2. Phenols

Phenols are also called aromatic compounds (alcohol) and other forms of alcohol are called aliphatic alcohols.



Nomenclature of alcohols and phenols

Ex → (A) Carbinol system



Ex → CH_3OH
Carbinol

$\text{CH}_3\text{CH}_2\text{OH}$
Methyl Carbinol

$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{OH} \\ | \\ \text{CH}_3 \end{array}$
Dimethyl carbinol.

Common name

'Alkyl alcohol'

Ex → $\text{CH}_3\text{OH} \rightarrow$ Methyl alcohol

$\text{C}_2\text{H}_5\text{OH} \rightarrow$ Ethyl alcohol

$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \rightarrow$ n-propyl alcohol

$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{OH} \\ | \\ \text{CH}_3 \end{array} \rightarrow$ isopropyl alcohol

$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_2\text{OH} \\ | \\ \text{CH}_3 \end{array} \rightarrow$ iso-Butyl alcohol

$\text{CH}_3 - \text{CH}_2 - \text{CH} - \text{OH} \rightarrow$ sec. Butyl alcohol

$\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3 - \text{C} - \text{OH} \\ | \\ \text{CH}_3 \end{array} \rightarrow$ tert. Butyl alcohol

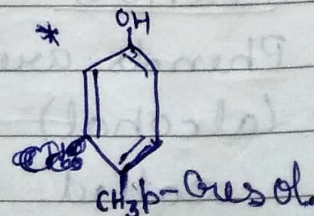
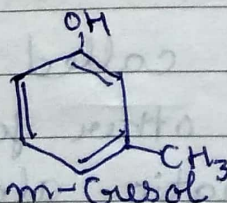
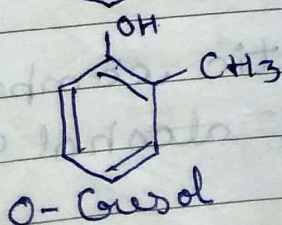
$\text{CH} \equiv \text{C} - \text{CH}_2\text{OH} \rightarrow$ Propargyl alcohol

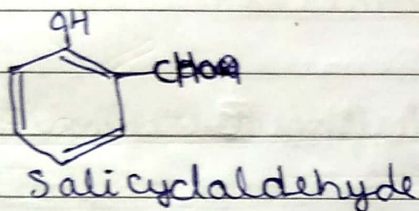
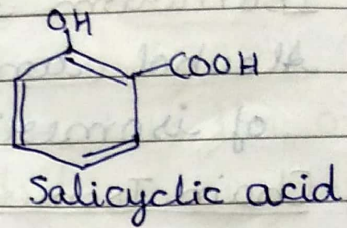
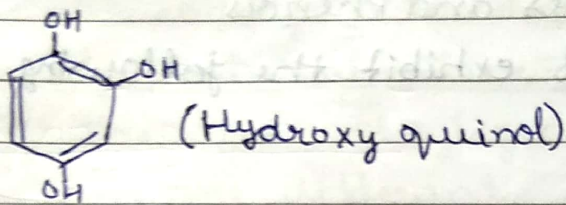
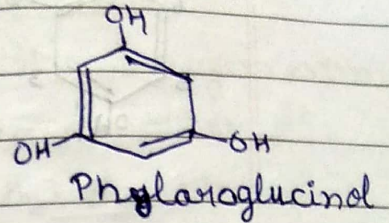
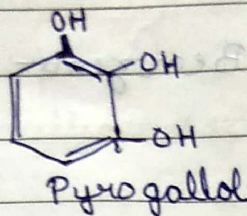
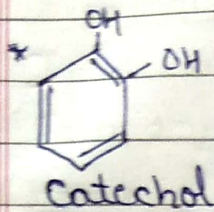
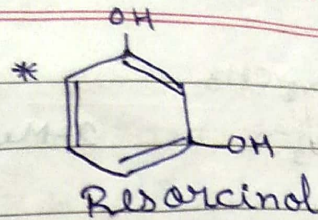
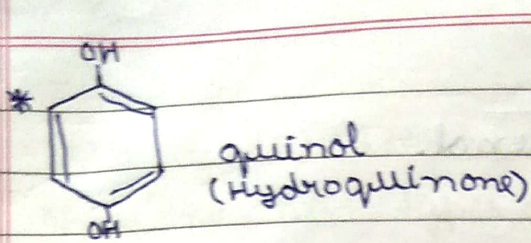
$\text{CH}_2 = \overset{\text{OH}}{\text{C}}\text{H} \rightarrow$ Vinyl alcohol.

$\text{CH}_2 = \text{CH} - \text{CH}_2\text{OH} \rightarrow$ Allyl alcohol



\rightarrow Phenol

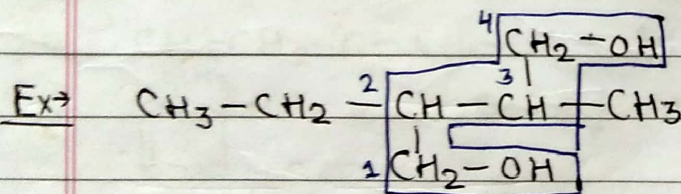




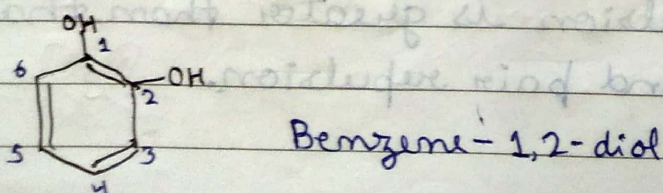
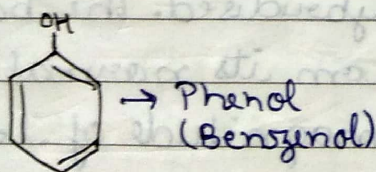
IUPAC naming of Alcohols and Phenols

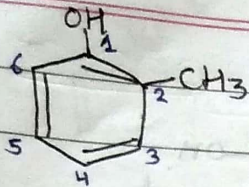
1. Select the longest carbon chain with OH group.
2. Numbering order: Near position of OH group.
3. Write the name of compound in following sequence.

Name of side chain + no. of carbon + types of bond + F. or
with position and alphabetical atoms in chain between them

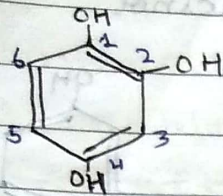


2-ethyl-3-methyl butane-1,4-diol





2-Methyl phenol.



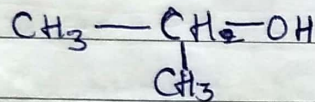
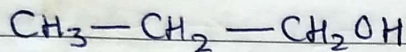
Benzene-1,2,4-Triol

Isomerism in alcohols and Phenols

Alcohol and Phenol exhibit the following type of isomerism:-

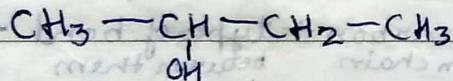
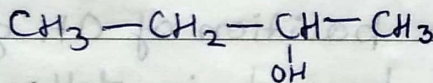
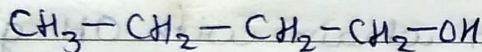
Chain Isomer

Chain isomer of C_3H_7OH



Position Isomer

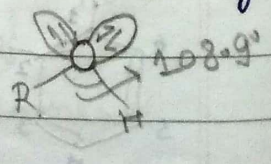
C_4H_9OH



Functional Isomer

Structure of Alcohol

In alcohol carbon atom is sp^3 hybridised and oxygen atom is also sp^3 hybridised. The bond angle $\angle COH$ decrease from its normal value (109.5°) because the magnitude of lone pair-lone pair repulsion is greater than that of bond pair-bond pair repulsion.



Ether

Alkoxy (OR) derivatives of alkane are called ether.

There are two types of ether:-

* 1. Symmetrical ether or simple ether (ROR)

If two alkyl group attached to the oxygen atom are same, it is called symmetrical ether.

For example :- CH_3OCH_3 , $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$, etc.

2. Unsymmetrical ether or Mixed ether (ROR')

If the two alkyl group attached to the oxygen atom are different, it is called unsymmetrical ether.

For example :- $\text{CH}_3\text{OCH}_2\text{CH}_3$; $\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_3$ etc.

Nomenclature of EtherCommon name

For symmetrical ether (ROR) \Rightarrow Dialkyl ether

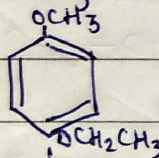
For unsymmetrical ether (ROR') \Rightarrow Alkylalkyl ether
(alphabetical order)


1. $\text{CH}_3\text{OCH}_3 \rightarrow$ Dimethyl ether

2. $\text{CH}_3\text{OCH}_2\text{CH}_3 \rightarrow$ Ethyl Methyl ether

3. $\text{CH}_3-\text{O}-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_3 \rightarrow$ Iso-propyl Methyl ether

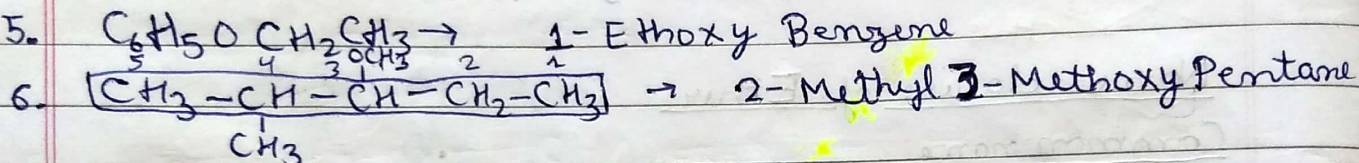
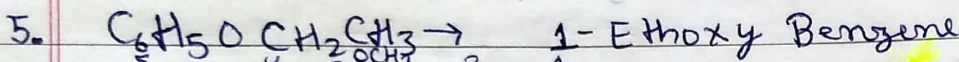
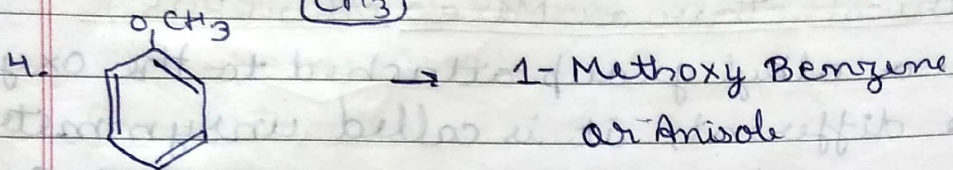
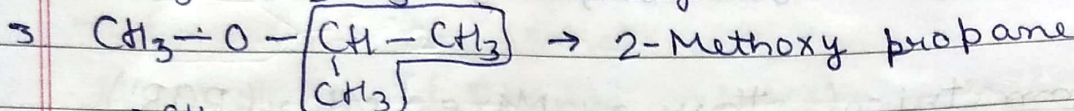
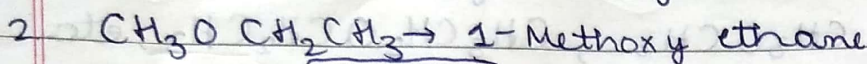
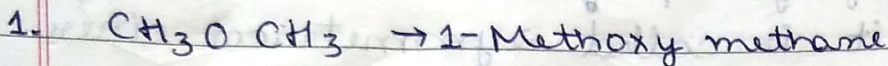
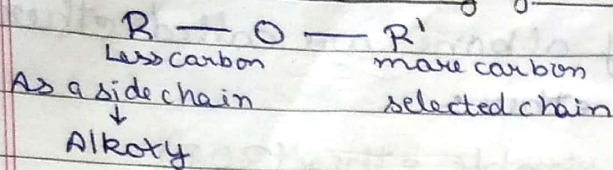
4. $\text{CH}_3-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_3 \rightarrow$ Diethyl ether

5.  \rightarrow Benzyl Methyl ether Phenyl ether or Anisole

6.  \rightarrow Benzyl ethyl ether Phenyl ether

7. $\text{CH}_3-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{O}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{CH}_3 \rightarrow$ Di(^{tertiary butyl} ~~2,2-dimethyl~~)ethyl

IUPAC naming of ether

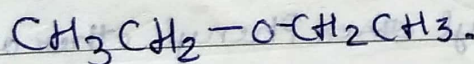
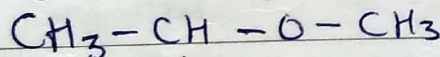
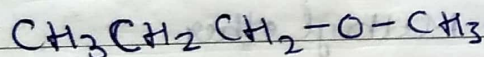


Isomerism in Ether

1. Chain Isomer

2. Functional group Isomer (Alcohol and ether are functional isomer)

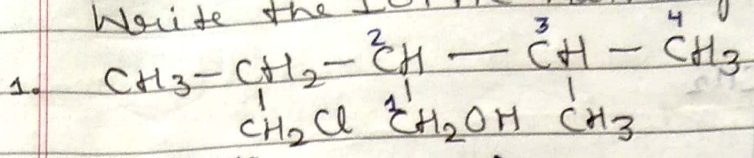
3. Metamers



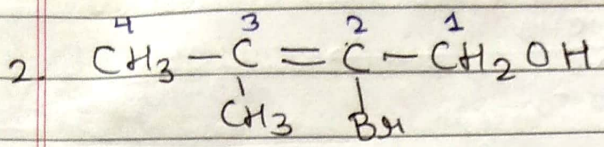
Structure of Ether

In ether, Oxygen atom is sp^3 hybridised which is surrounded by two bond pair of electrons and two lone pair of electron. The bond angle of C-O-C bond is greater from normal value (109.5°) due to large size of alkyl group.

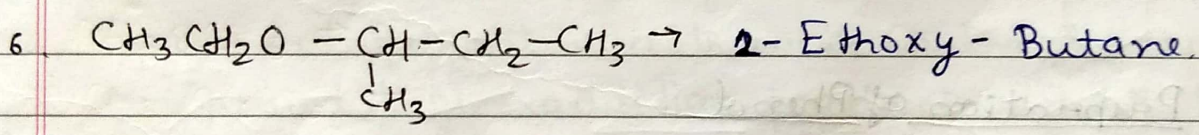
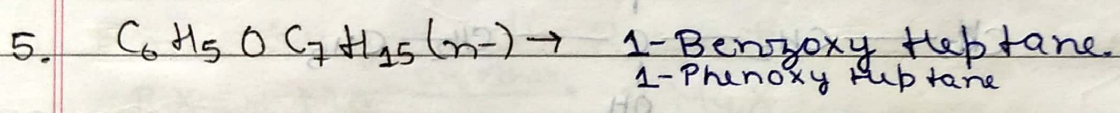
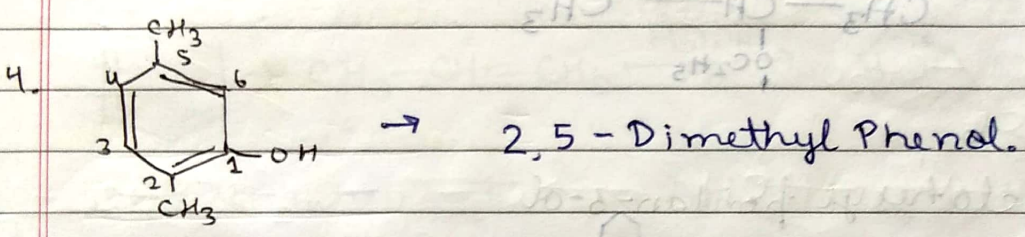
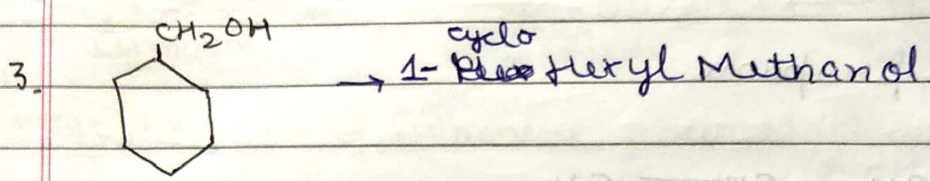
Write the IUPAC name of the following compounds:-



3-Methyl-2-(chloromethyl)butanol

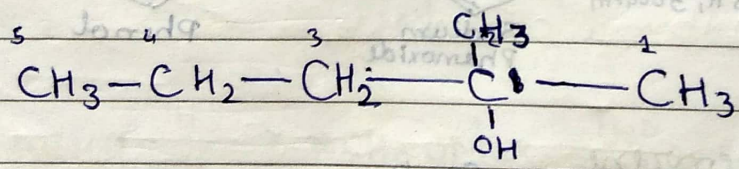


2-Bromo-3-methylbut-2-en-1-ol

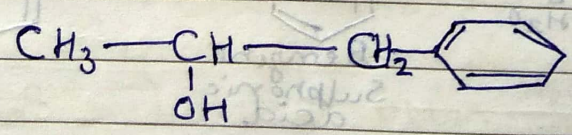


Draw the structure of the following molecules:-

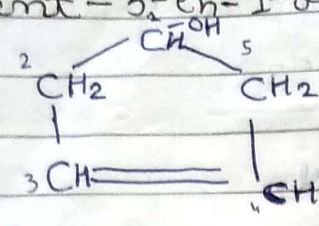
1. 2-Methylpentan-2-ol



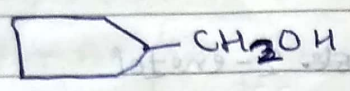
2. 1-Phenylpropan-2-ol



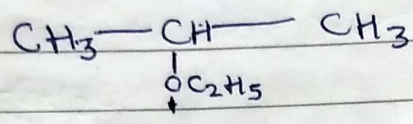
3. Cyclopent-3-en-1-ol



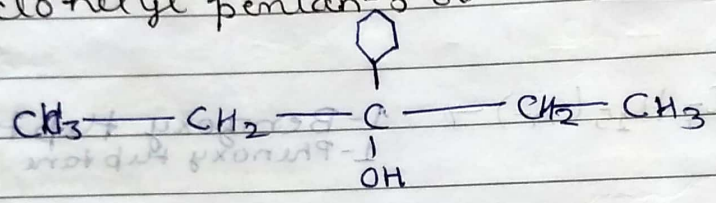
4. Cyclopentyl methanol



5. 2-ethoxy propane

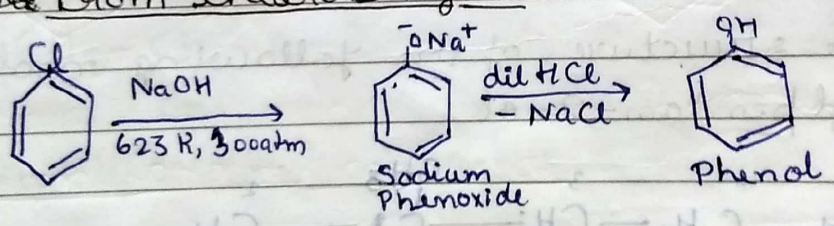


6. 3-cyclohexyl pentan-3-ol

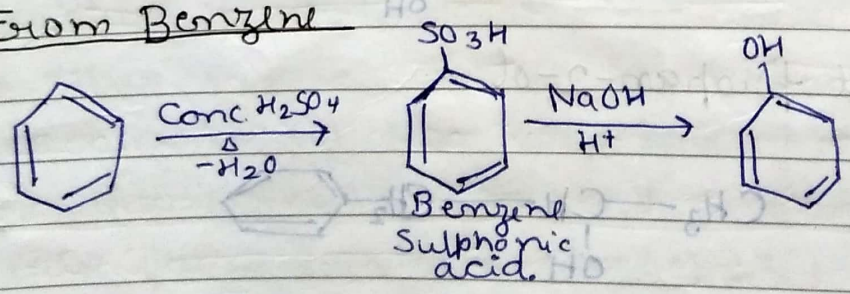


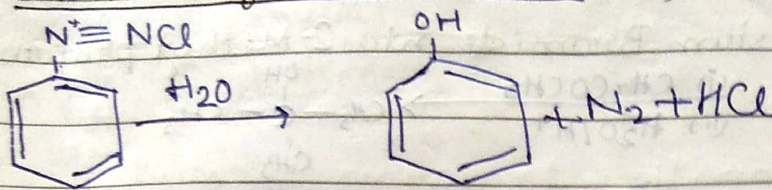
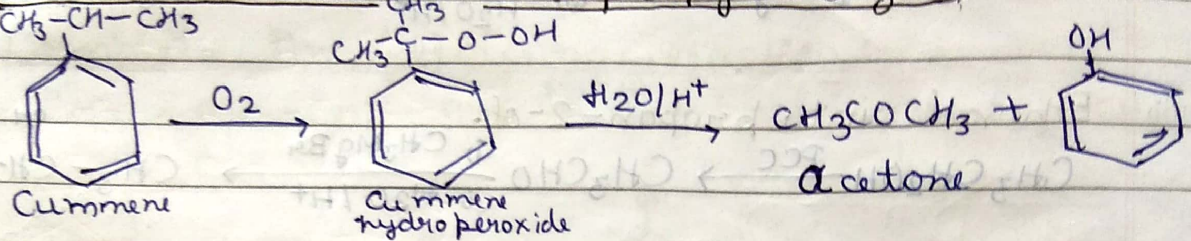
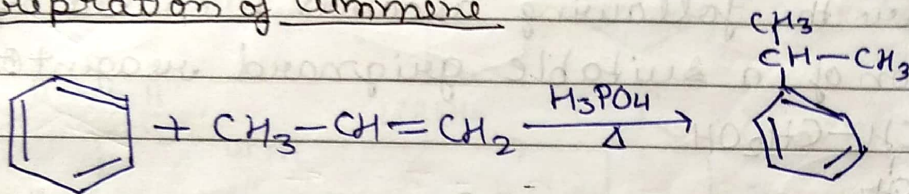
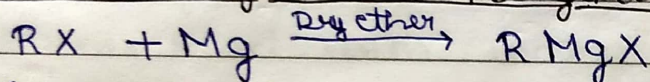
Preparation of Phenol

1. From chlorobenzene

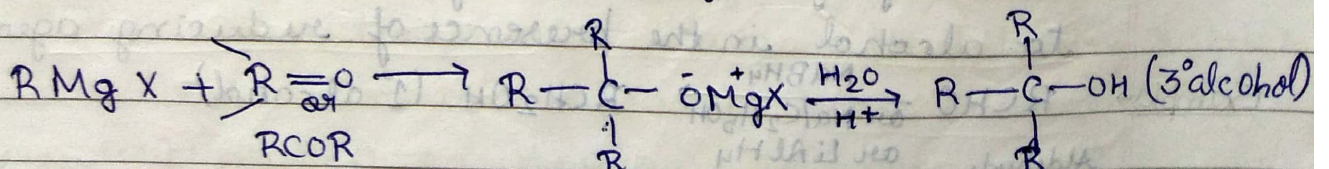
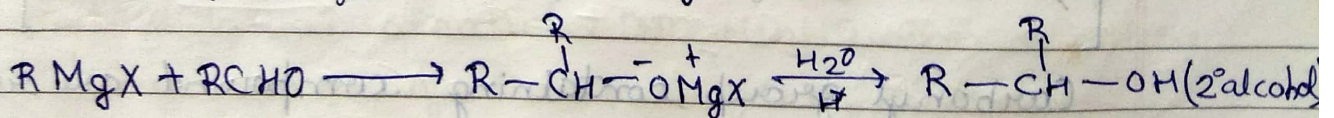
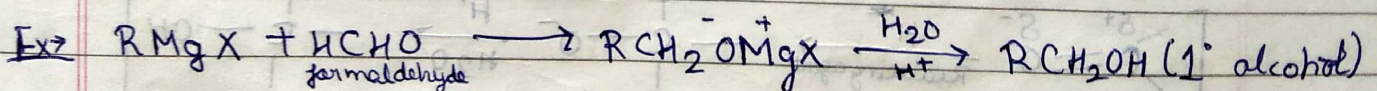
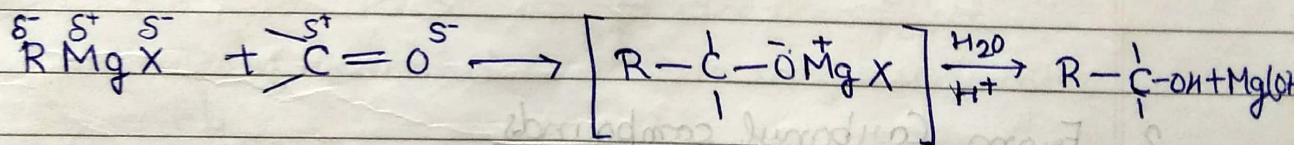


2. From Benzene

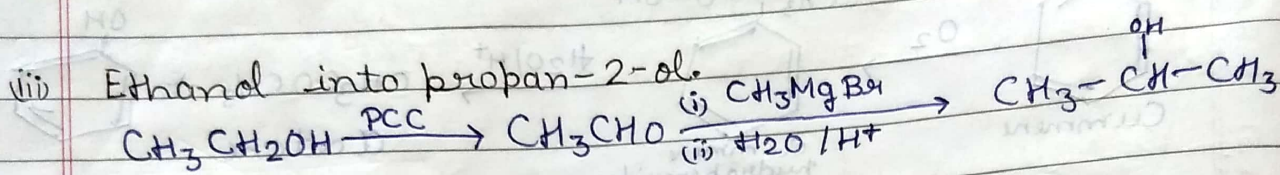
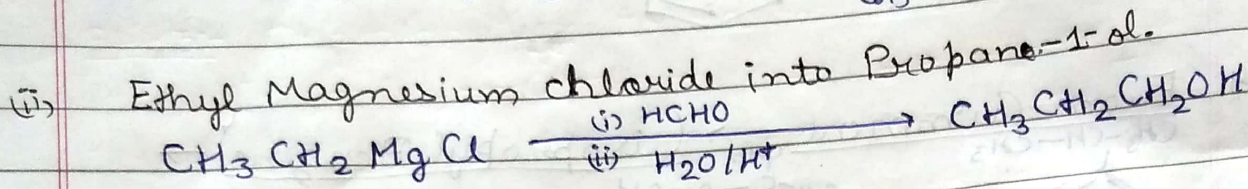
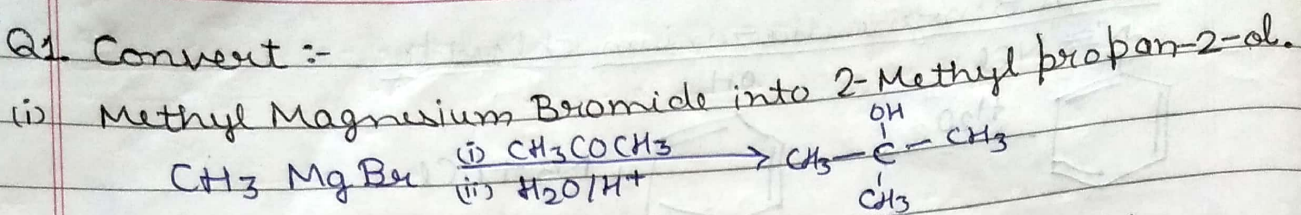


* 3. From Benzene diazonium chloride** 4. From Cumene $\xrightarrow{\text{O}_2}$ (isopropyl Benzene) \rightarrow Preparation of CumenePreparation of Alcohols:-1. From Grignard's Reagent

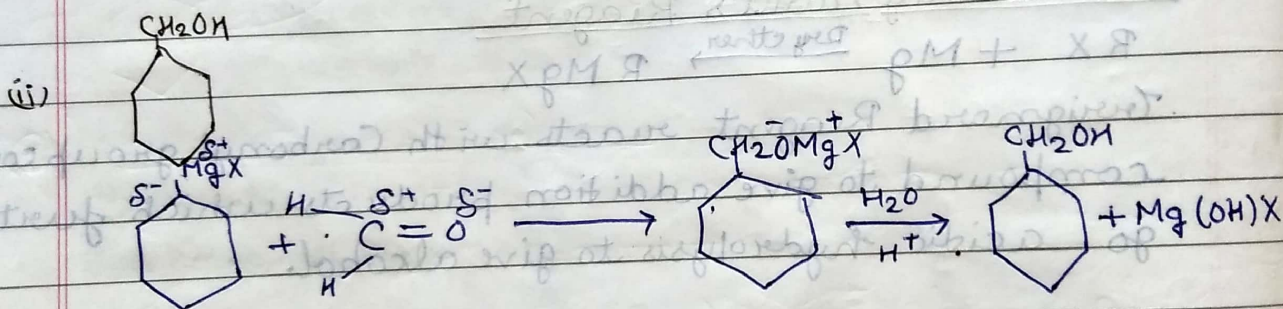
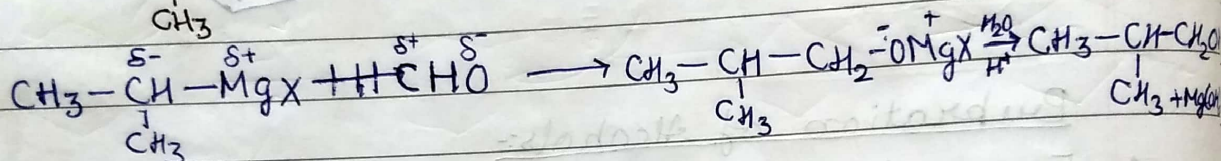
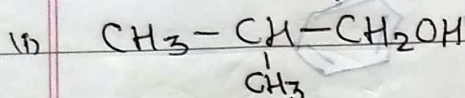
Grignard Reagent reacts with Carbonyl group containing compound to give addition products which further go acidic hydrolysis to give alcohol.



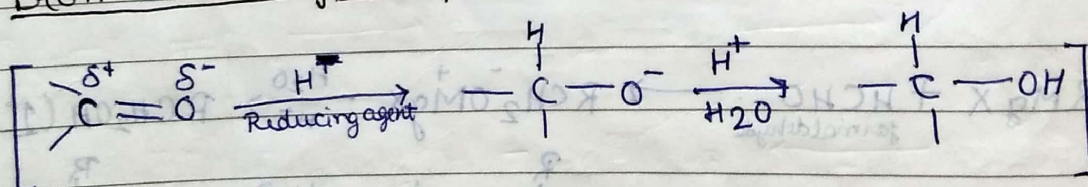
Q1. Convert :-



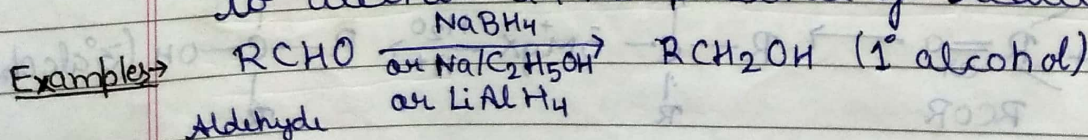
Q2 How are the following alcohols prepared by the reaction of a suitable grignard reagent on methanal?



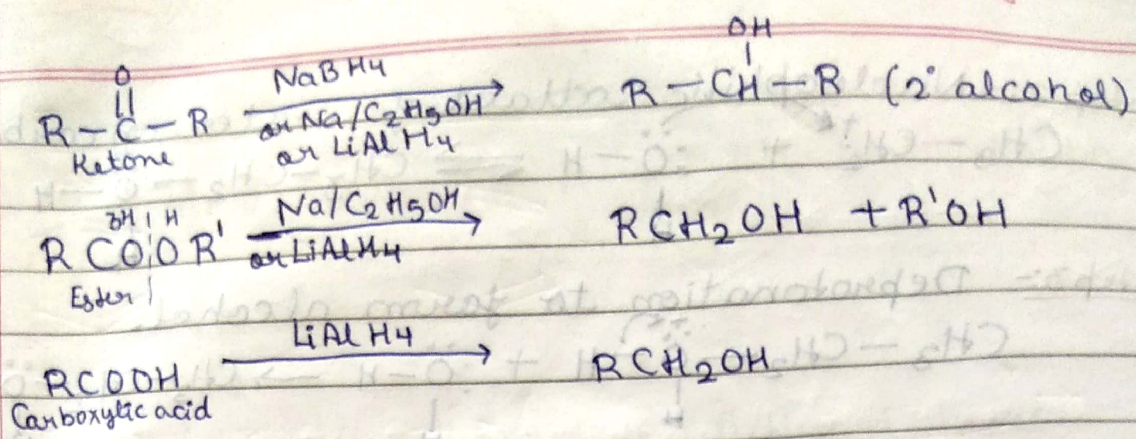
2. From Carbonyl compounds



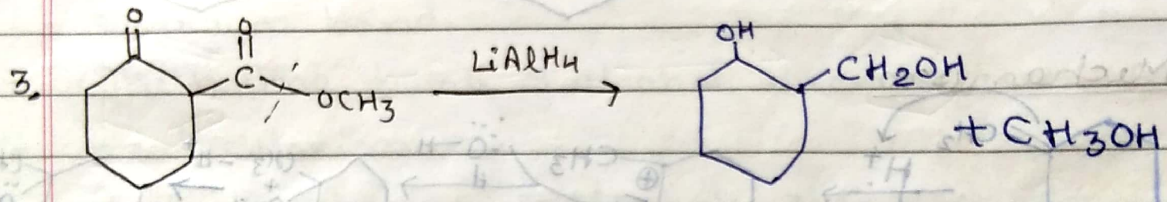
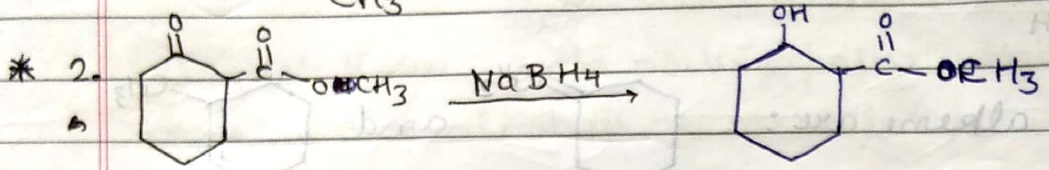
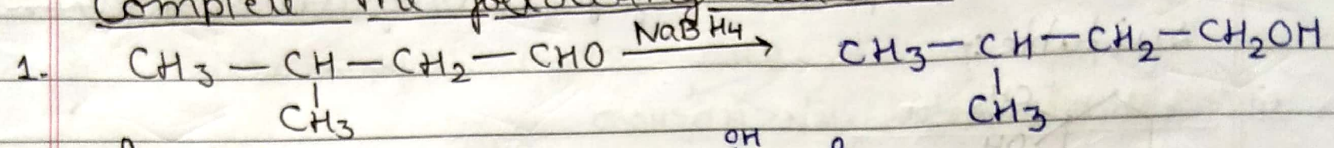
Carbonyl group containing compound are reduced to alcohol in the presence of reducing agent.



Aldehyde



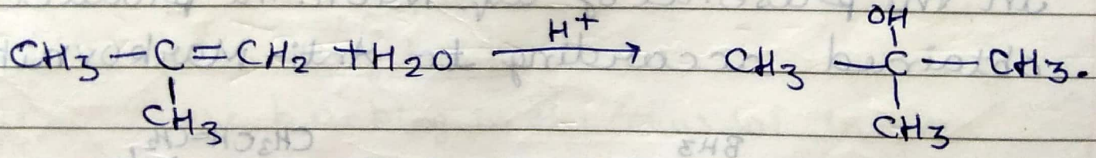
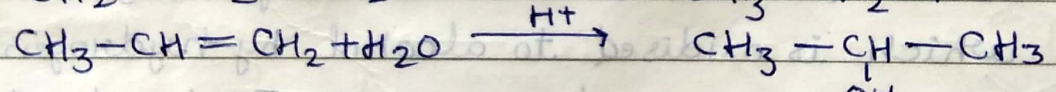
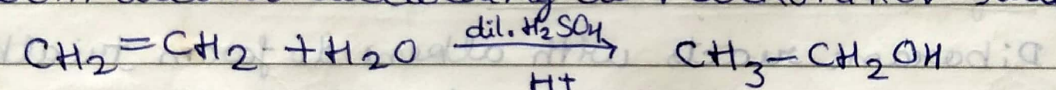
Complete the following reaction :-



3. Brom Alkene

(i) Acidic hydration of Alkenes

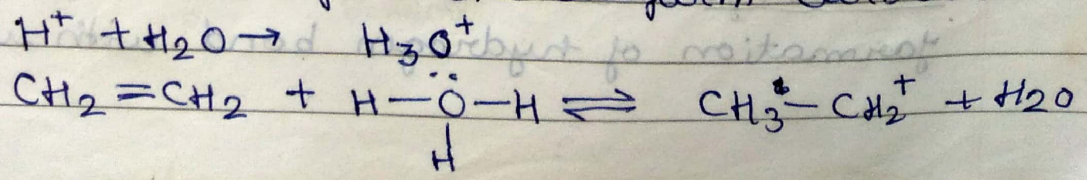
Alkenes react with water in the presence of acid to form alcohol according to Markonikov rule.



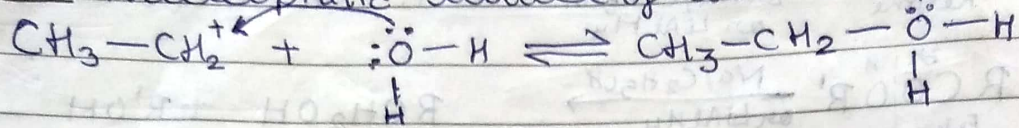
** Mechanism of acid catalysed hydration of alkenes to form alcohol + OR Mechanism of ethene hydration of ethene to form ethanol.

The reaction takes place in the following 3 steps:-

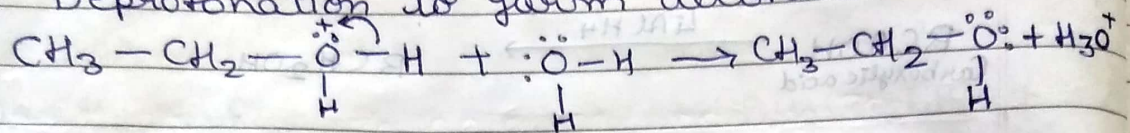
Step 1: Protonation of alkene to form carbocation:-



Step 2:- Nucleophilic attack of water on carbocation.

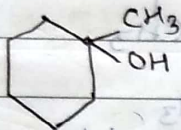


Step 3:- Deprotonation to form alcohol.

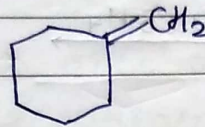


Q. Show the preparation of following alcohol from suitable:-

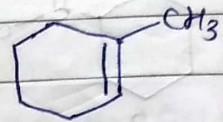
(i)



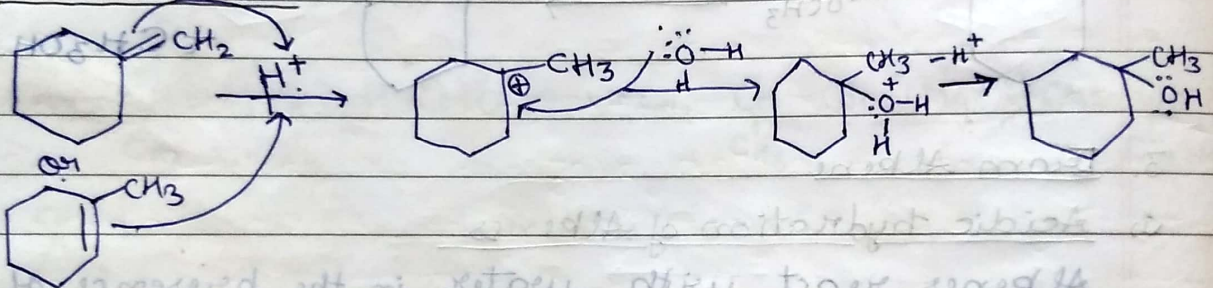
Suitable alkene are:



and

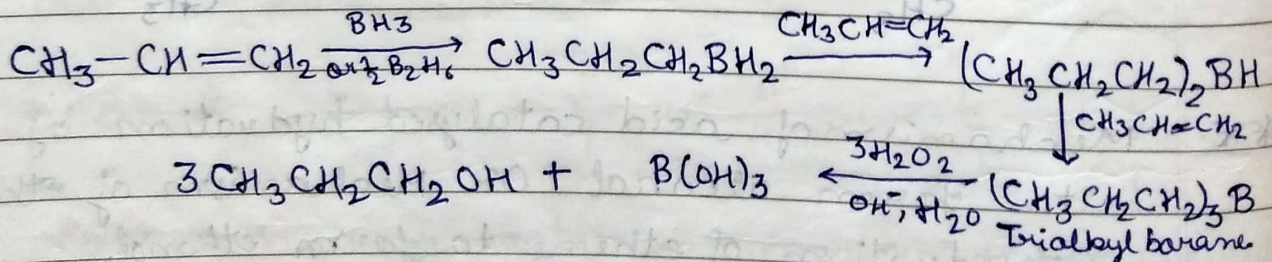


Mechanism



*** (B) Hydroboration Oxidation

Diborane reacts with alkene to form trialkyl borane which is oxidised to alcohol by hydrogen peroxide in the presence of aq. NaOH. The product is obtained according to Anti-Markovnikov rule.



Physical properties of Alcohols and Phenols

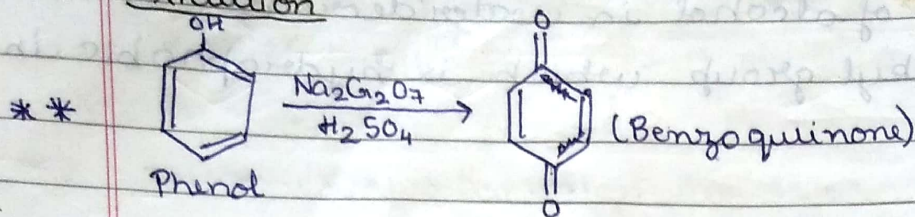
Solubility: Alcohols are soluble in water due to formation of hydrogen bond with water molecules.

* In case of phenol, ortho derivative is major product due to presence of intramolecular hydrogen bond.

classmate

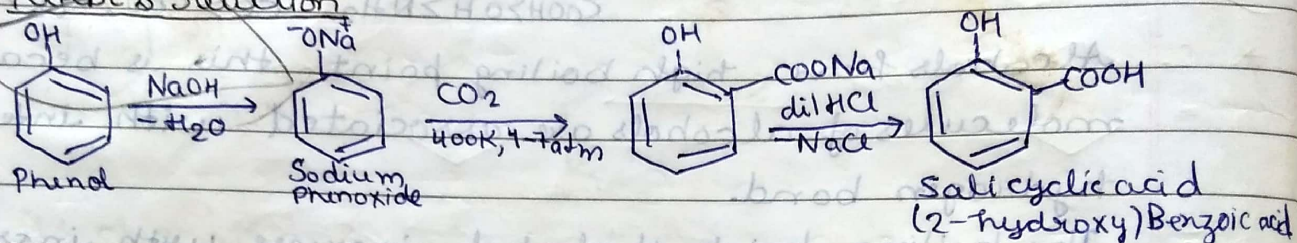
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2. Oxidation



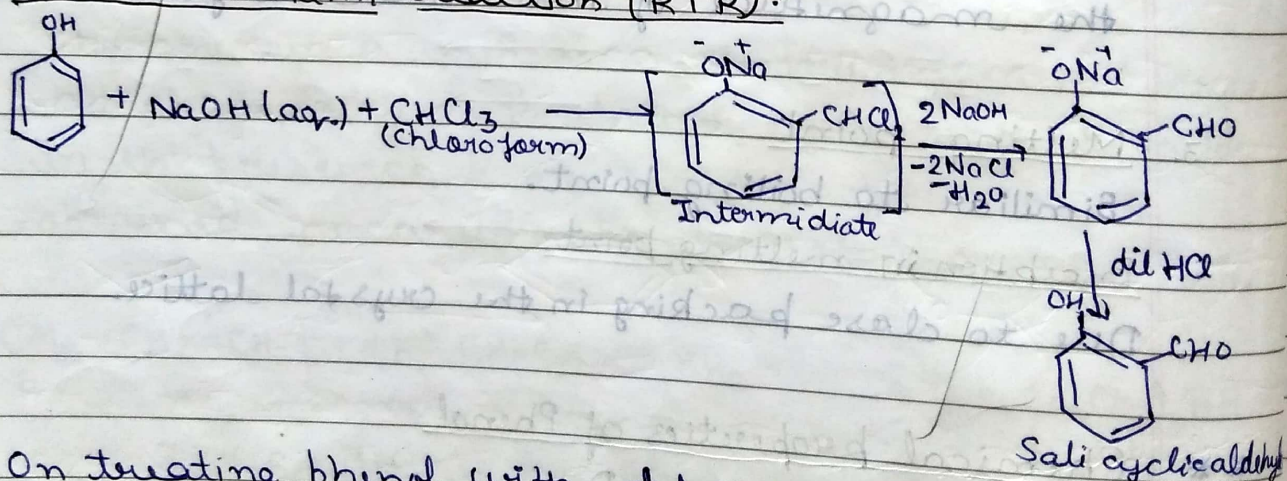
Oxidation of phenol with acidified sodium Dichromate produce a conjugated diketone known as Benzoquinone.

** 3. Kolbe's reaction



When sodium phenoxide treated with CO_2 at 400K , under the pressure of $4-7\text{atm}$, followed by acidification gives 2-Hydroxy Benzoic acid as the main product with a small amount of 4-hydroxy benzoic acid.

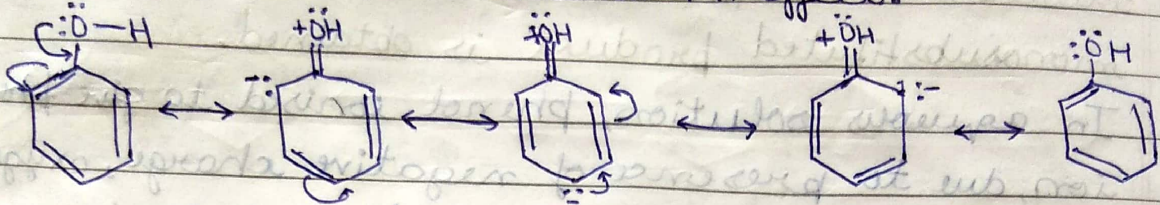
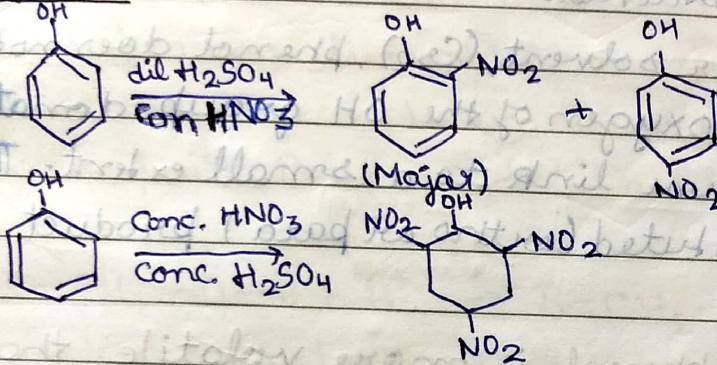
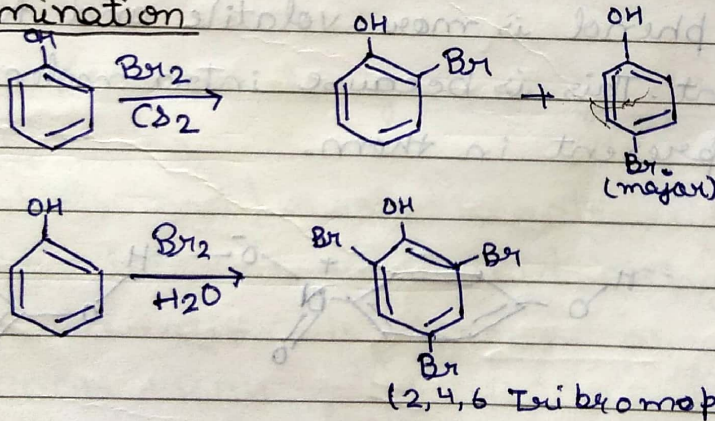
** 4. Reimer-Tiemann reaction (RTR) :-



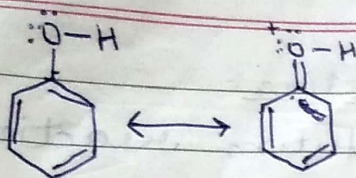
On treating phenol with chloroform in the presence of NaOH , a CHO group is introduced at ortho position of Benzene ring.

Substitution Electrophilic Reaction:-

In phenol, Electrophilic substitution reaction occur at ortho and para position. This is because OH group increase electron density more at ortho and para position. Due to its +R effect.

Ex → NitrationBrominationQ. Give reason:-

- ** (i) Protonation of phenol does not take place easily. Lone pair of electron present on oxygen atom in phenol involves in resonance and acquire positive charge therefore, phenol does not protonated easily.



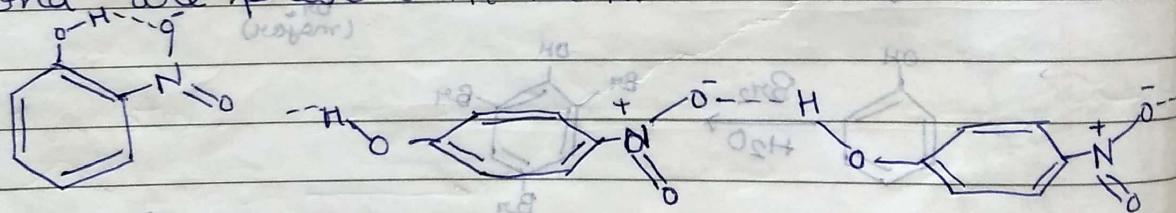
** (iii) In aqueous solution, Bromination of phenol gives trisubstituted product but in non-polar solvent, monosubstituted product is obtained.

In aqueous solution, phenol ionised to give phenoxide ion, due to presence of negative charge, oxygen of the phenoxide ion donate electron to the benzene ring to a large extent. As a result, trisubstituted product is obtained.

In non polar solvent, (C_6H_6), phenol does not ionised. As a result, oxygen of the OH group donates electron to the benzene link to a small extent. Therefore, monosubstituted (ortho or para) product is obtained.

** a. Ortho nitro phenol is more volatile than that of para nitro phenol.

Ortho nitro phenol is more volatile and has low boiling point. This is because intra molecular hydrogen bond are present in them.



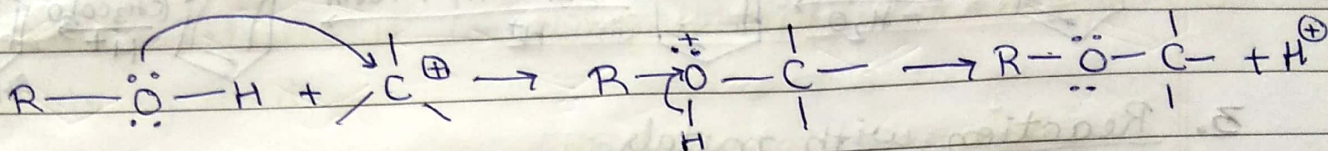
Para nitro phenol is less volatile and has high boiling point. This is because these molecules are associated with inter molecular hydrogen bond.

Chemical properties of alcohol.

Alcohol are versatile compound. Alcohols reacts both as electrophile and nucleophile.

* Alcohol as a nucleophile

When the bond between OH is broken, alcohol reacts as nucleophile.

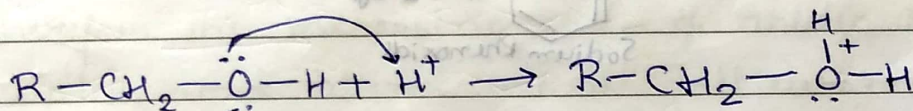


Examples i) Esterification,

ii) Reaction with metal.

* Alcohol as an electrophile

When the bond between CO is broken, alcohol reacts as electrophile. Protonated alcohol reacts in these reaction



Examples Reaction with HX

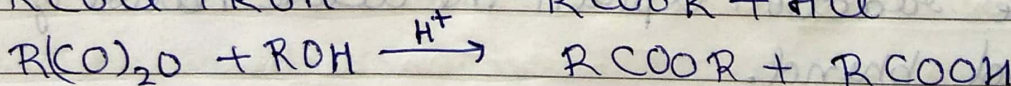
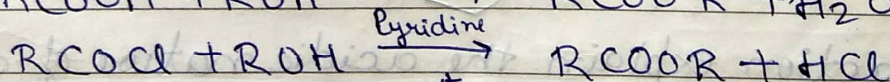
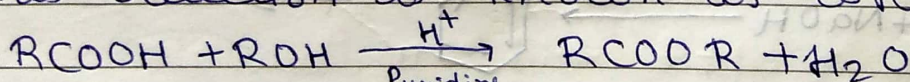
Reaction with PCl_3

Reaction involving cleavage of O-H bond

1. Esterification

Alcohols and phenols reacts with carboxylic acid, acid chloride and acid anhydride to form ester.

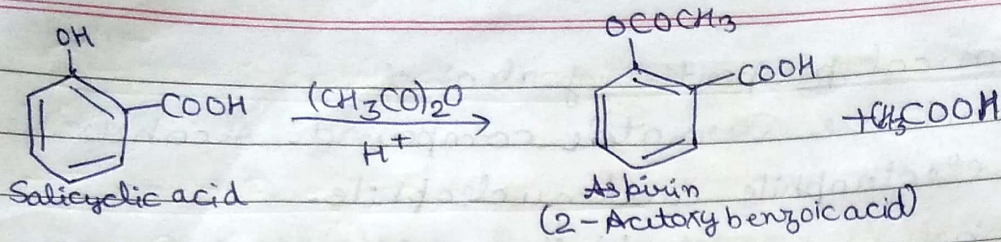
This reaction is known as esterification.



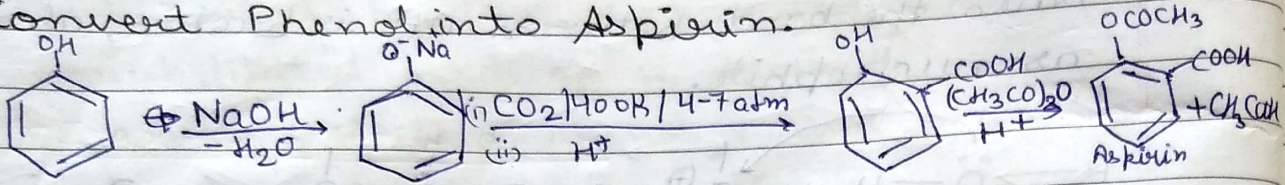
* 2. Acetylation [Acetyl (CH_3CO)]

The introduction of Acetyl (CH_3CO) group in alcohol and phenol is known as acetylation.

Ex \rightarrow Acetylation of Salicylic acid produce aspirin.

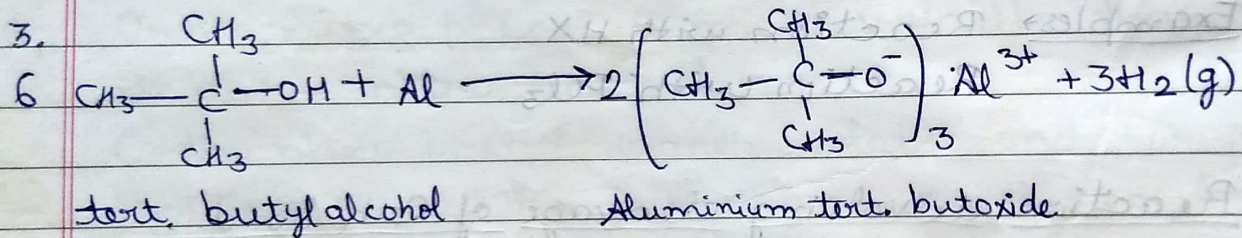
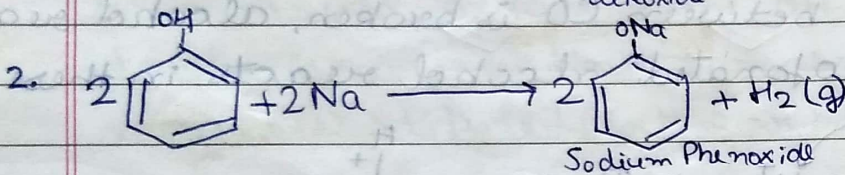
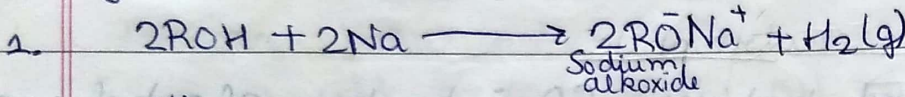


Q. Convert Phenol into Aspirin.

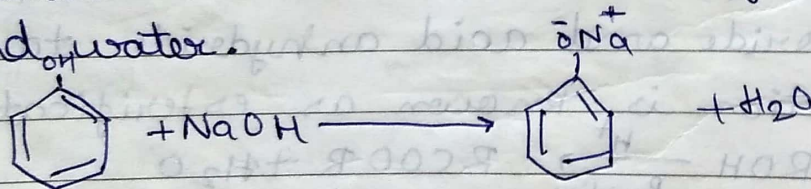


3. Reaction with metals.

Alcohol and phenol reacts with metal to give hydrogen gas.



Phenol also react with NaOH to give sodium phenoxide and water.



These reaction explain the acidic nature of alcohol and phenol.

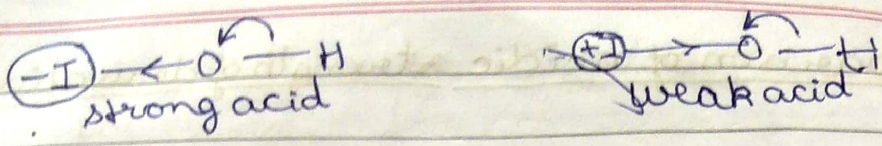
Comparison of acidic strength.

The acidic strength of alcohol and phenol depends upon inductive group as follows:

Increasing order of -I group → H < C₆H₅ < I < Br < Cl < F < NO₂
 electron withdrawing group
 strongest acid

Increasing order of +I group → H < CH₃ < CH₃CH₂ < CH₃CH₂CH₃
 electron donating group
 weakest acid

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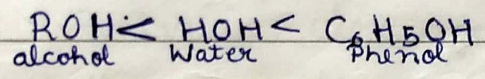


Electron withdrawing group (-I effective group) decrease electron density on oxygen atom.

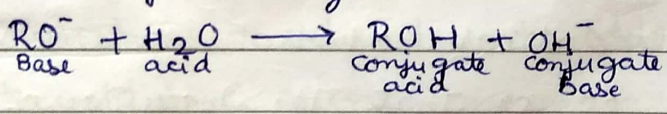
As the result, the OH bond becomes more polar and easily release H⁺ ions. Therefore, the compound becomes strong acid.

Electron donating group (+I effective group) increase electron density on oxygen atom. As a result the OH bond becomes less polar and hardly release H⁺ ions. Therefore the compound becomes weak acid.

Therefore, the increasing order of acidic strength of alcohol, water and phenol are as follows:-

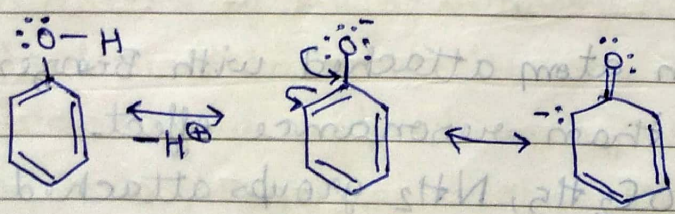


* Alcohols are weaker acid than water. This can be explained by the following reaction:-



The reaction shows that water is better proton donor than alcohol.

* Phenol is a strong acid. This is because its conjugate base (phenoxide ion) is stabilised by resonance.



Phenol Conjugate base
 Stable due to resonance

Comparison of acidic strength of derivatives of phenol

(a) +I or +R effective group

O or p < M
 ↓ ↓
 weak acid strong acid

(b) -I or -R effective group

O or p > m
 ↓ ↓
 strong acid weak acid

Arrhenius Concept ⇒ Acid ⇒ H^+ donor

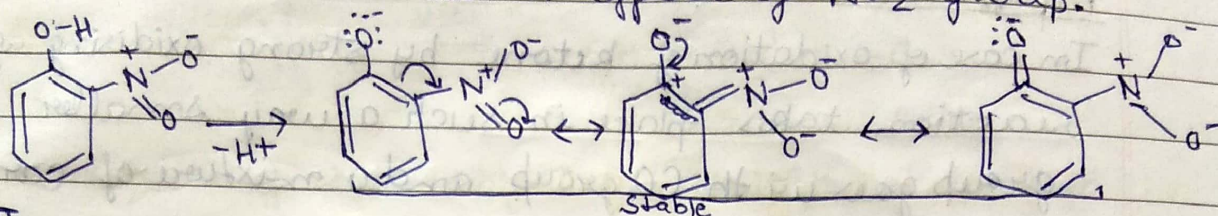
Lewis Base ⇒ Electron pair donor or lone pair of electron donor

In case of halogen atom attached with Benzene ring its -I effect prefer than resonance effect.

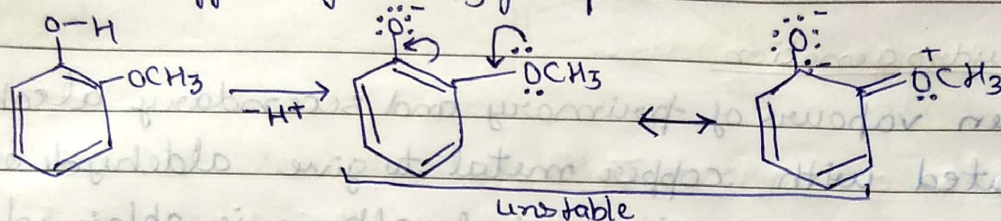
In case of OCH_3 , OC_2H_5 , NH_2 groups attached to benzene

** Q. Explain why is ortho nitro phenol more acidic than ortho methoxy phenol.

The conjugate base of ortho nitro phenol stabilised by resonance due to -R effect of NO_2 group.



The conjugate base of ortho methoxy phenol destabilised by the +R effect of OCH_3 group.



Therefore, ortho nitro phenol is more acidic than ortho methoxy phenol.

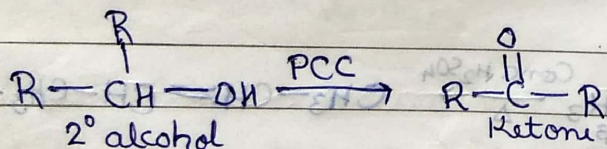
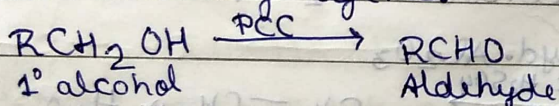
Reaction involving cleavage of C-O bond in alcohol

1. Oxidation

(a) Oxidation by weak oxidising agent (PCC or PDC or CrO_3):-

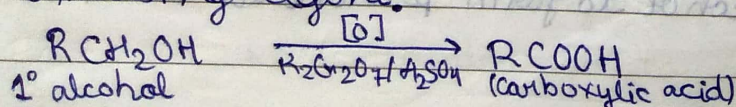
Where PCC \rightarrow Pyridinium chlorochromate and PDC \rightarrow Pyridinium dichromate

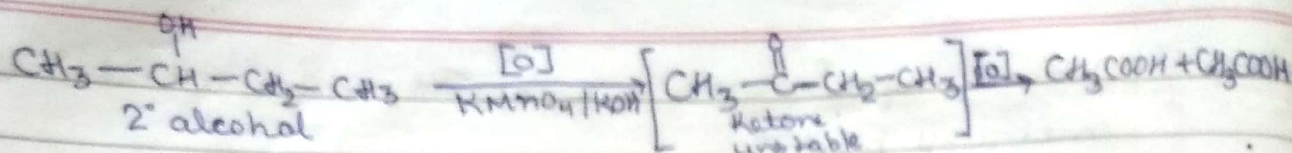
Alcohols are oxidised into aldehyde or ketone by weak oxidising agent.



(b) Oxidation by strong oxidising agent [Acidified $\text{K}_2\text{Cr}_2\text{O}_7$ or Alkaline KMnO_4 or HNO_3 conc. or chromic acid (H_2CrO_4)]

Alcohols are oxidised into carboxylic acid by strong oxidising agent.





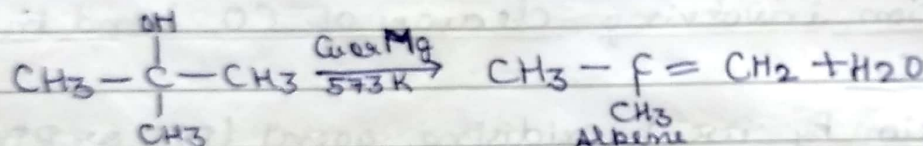
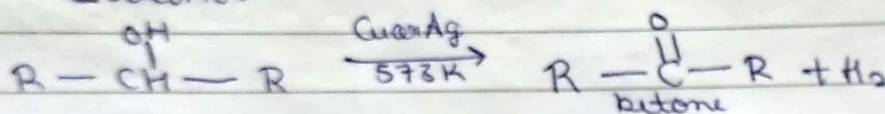
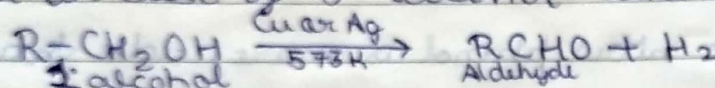
Popoff's rule

In case of oxidation of ketone by strong oxidising agent, reaction takes place in such a way smaller alkyl group goes with CO group and a mixture of carboxylic acid is obtained.

2. Dehydrogenation

When vapours of primary and secondary alcohols are treated with copper metal to give aldehyde or ketone.

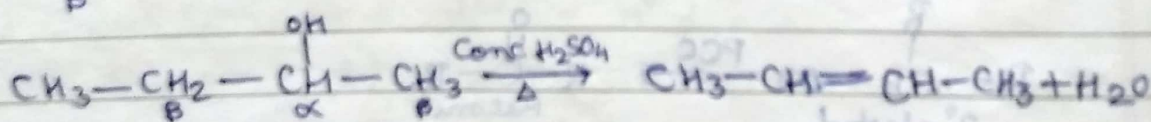
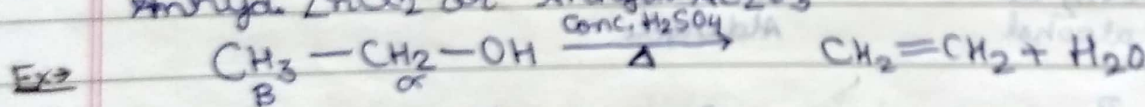
But in case of 3° alcohol alkene is obtained



3. Dehydration

Alcohols undergo dehydration to form alkenes on heating with concentrate H_2SO_4 or conc. H_3PO_4 or

Anhyd. ZnCl_2 or Anhyd. Al_2O_3



* *

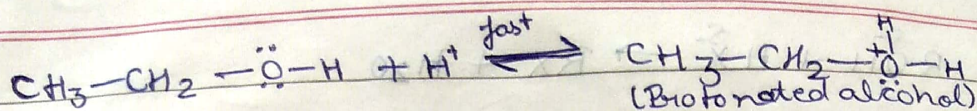
Mechanism of Dehydration of Ethanol to form ethene:

Step 1:

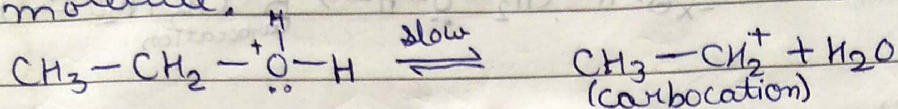
The reaction takes place in the following 3 steps:

Step 1:

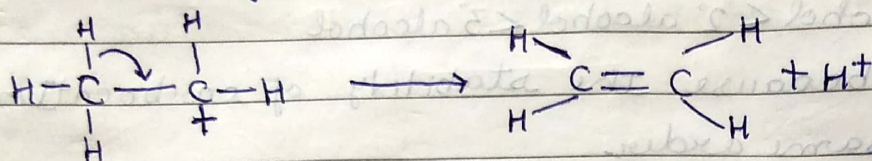
Protonation of alcohol to form protonated alcohol.



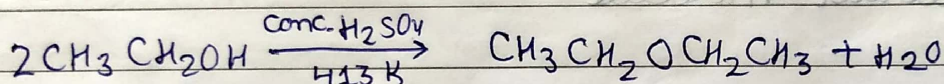
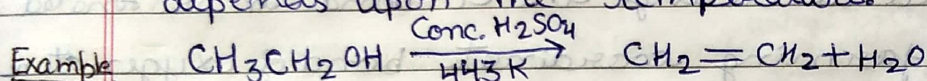
Step 2: Formation of carbocation by eliminating of water molecule.



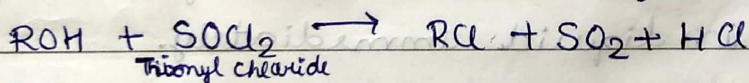
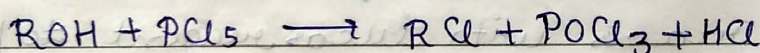
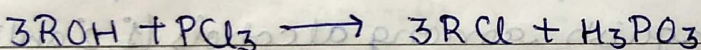
Step 3: Formation of ethene by elimination of proton.



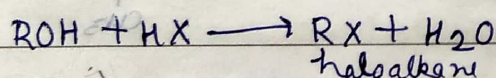
* In case of dehydration of primary alcohol, reaction depends upon the temperature.



4. Reaction with PCl_3 , PCl_5 and SOCl_2

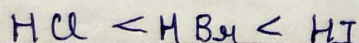


5. Reaction with HX (HCl , HBr , HI)



Reactivity order of HX

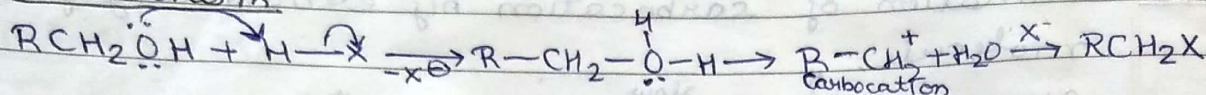
The reactivity of hydrogen halide increase in the following order:-



This is because, the strength of the nucleophile increase in the same order.

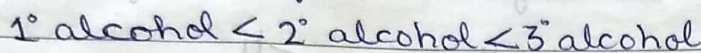


Mechanism



Reactivity order of alcohol

The reactivity of alcohol increase in the following order:



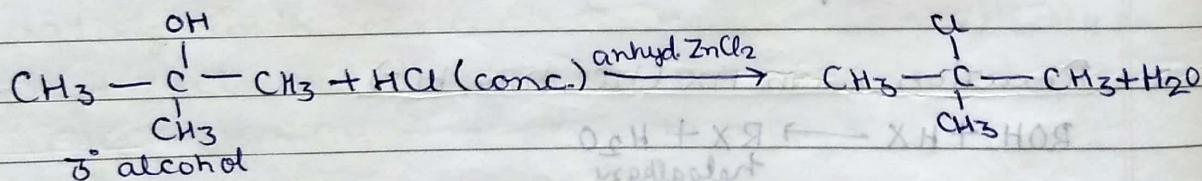
This is because the stability of carbocation increase in the same order.

Role of anhyd. $ZnCl_2$

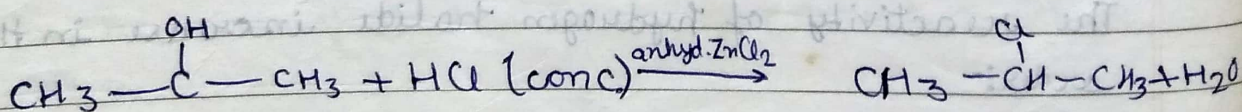
$ZnCl_2$ is used to cleave the C-O bond in protonated alcohol by forming coordinate bond of oxygen atom of water molecule.

** Lucas Reagent

1. It is a mixture of conc. HCl and Anhyd. $ZnCl_2$. It is used to distinguish among alcohols (1, 2 and 3 alcohols).
2. 3° alcohol reacts with Lucas reagent to produce turbidity in liquid immediately.



3. 2° alcohol reacts with Lucas reagent to produce turbidity after 5 minutes.

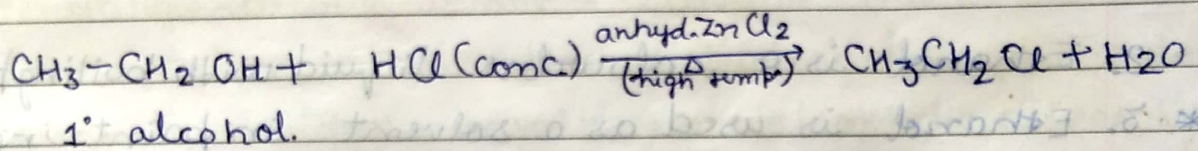
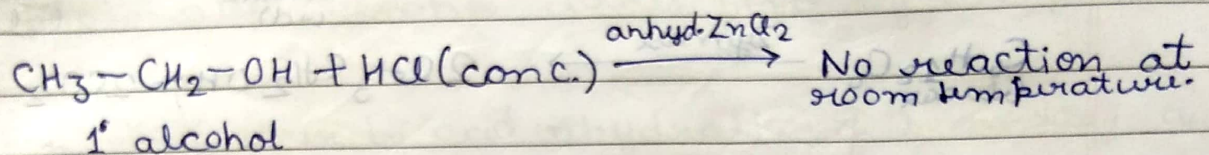


4. Primary alcohol does not react with Lucas reagent at room temperature.

* Lucas's Method

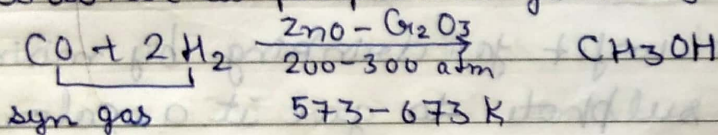
The reaction of 1° and 2° alcohols with HCl gas in the presence of anhyd. $ZnCl_2$ is called Lucas's method.

Primary alcohols does not react with Lucas reagent at room temperature. This is because 1° carbocation is unstable at room temperature.



Methanol [CH₃OH] (Wood spirit):-

Methanol is prepared from syn gas as follows:-

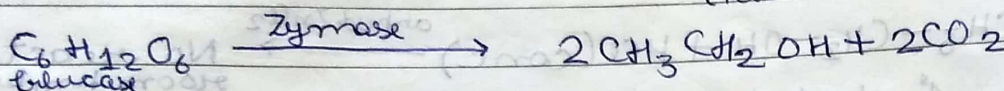
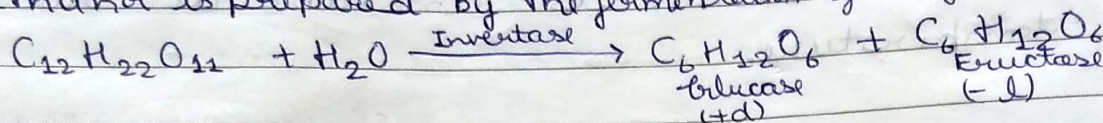


Methanol is a colourless liquid and it is highly poisonous in nature. Small quantity can cause blindness and large quantity can cause death.

It is used as a solvent for paint varnish and for making of the formaldehyde.

Ethanol (C₂H₅OH) or Spirit

1. Ethanol is prepared by the fermentation of sugar.



2. Ethanol is a colourless liquid with boiling point 351 K.
- * 3. Ethanol is used as a solvent in paint industry and in the preparation of a no. of carbon compounds.

** Denatured alcohol

Alcohol is made unfit for drinking by mixing in it some copper sulphate to give it a colour and pyridine (a foul smelling liquid). It is known as denaturation of alcohol.

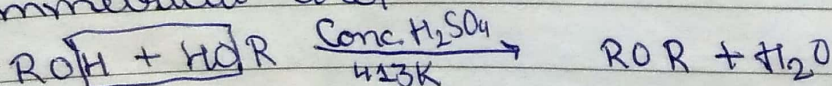
Ether

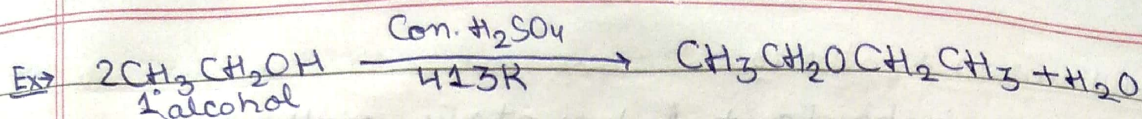
- * The preparation and properties of ether takes place by SN² path.

Preparation of Ether

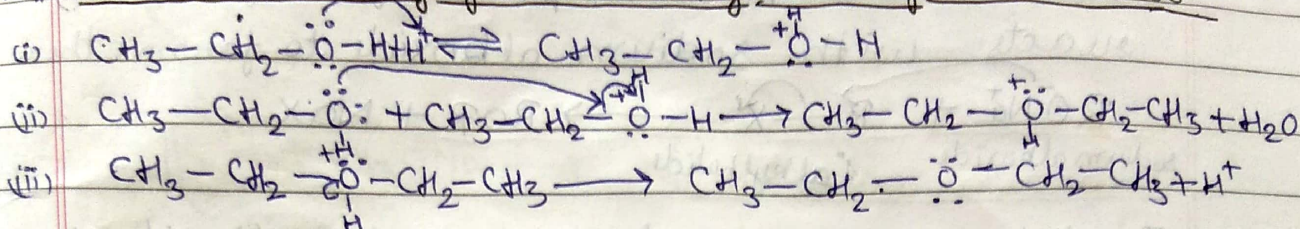
1. From Alcohol

1° alcohols on heating with conc. H₂SO₄ at 413 K. to form symmetrical ether





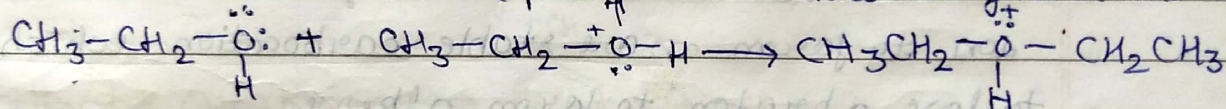
** Mechanism of formation of ether from alcohol



In this reaction, nucleophilic attack of alcohol molecule on protonated alcohol takes place by S_N^2 path.

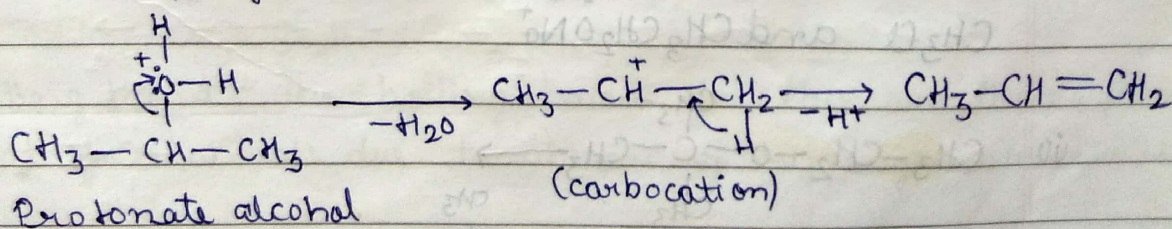
** Preparation of ether by acid dehydration of secondary and tertiary alcohol is not a suitable method. Give reasons.

Acid catalysed dehydration of 1° alcohol to form ether occurs by S_N^2 path involving nucleophilic attack by the alcohol molecule on the protonated molecule of alcohol.



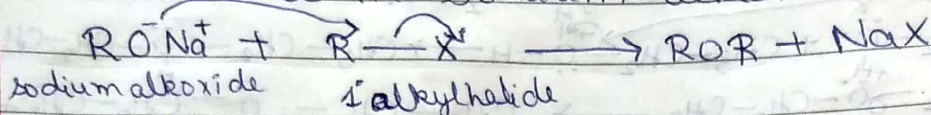
Under these conditions, 2° and 3° alcohol give alkene. This is because steric hindrance (crowding), nucleophilic attack by the alcohol molecule on the protonated alcohol molecule does not occur.

In case of 2° and 3° alcohol, protonated alcohol lose a molecule of water to form more stable carbocation which prefer to lose a proton

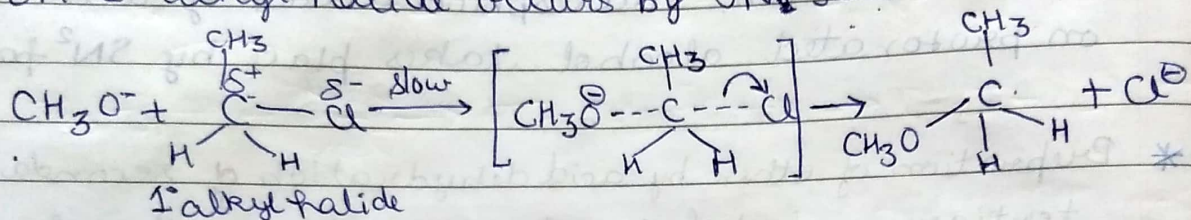


** 2. Williamson synthesis

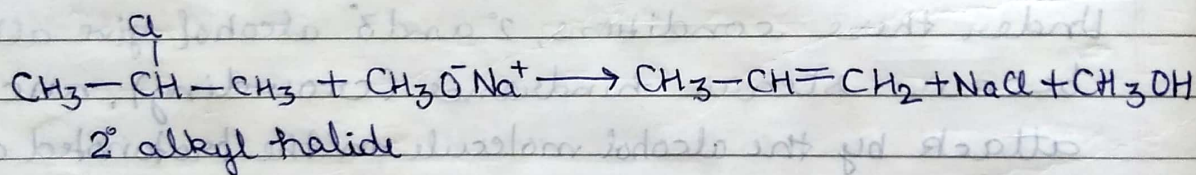
It is an important laboratory method for the preparation of symmetrical and unsymmetrical ether. In this method, primary alkyl halide reacts with sodium alkoxide to form ether.



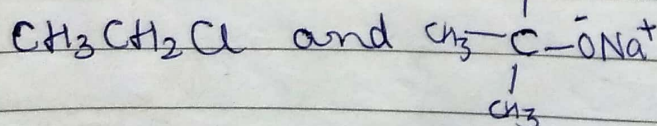
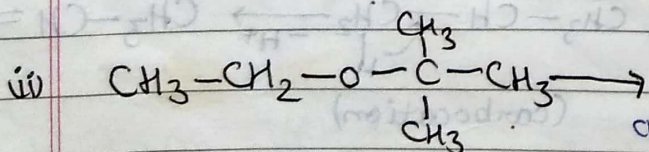
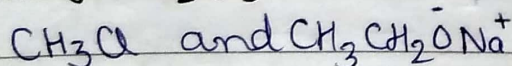
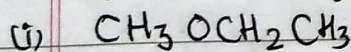
Mechanism:- In this reaction, nucleophilic attack of alkoxide ion on 1° alkyl halide occurs by $\text{S}_{\text{N}}2$ reaction.



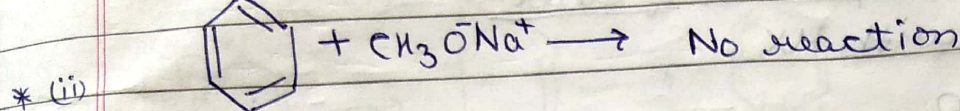
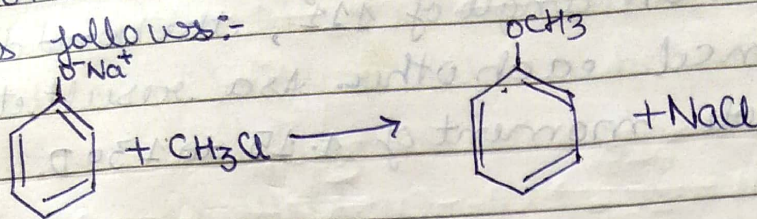
** In case of 2° and 3° alkyl halides due to steric hindrance, nucleophilic attack of alkoxide ion on alkyl halide does not occur. 2° and 3° alkyl halide lose halide ion to form more stable carbocation which prefer to lose a proton to form alkene.



Q. Write the suitable reagent for the preparation of following ether by Williamson synthesis :-

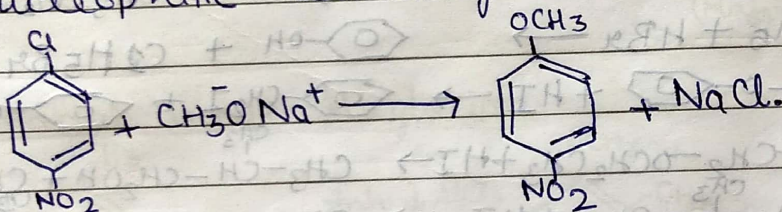


* (i) Aromatic ether like anisole, ethoxy benzene are prepared as follows:-



Aromatic ether cannot be prepared by the reaction of halobenzene with sodium alkoxide. This is because nucleophilic attack of alkoxide ion does not take place on halobenzene.

* If electron withdrawing group like NO_2 and CN are present at ortho and para-position of halobenzene, nucleophilic attack of alkoxide ion takes place.



Physical Properties of Ether

1. Solubility:- Ethers are soluble in water due to hydrogen bond formation with water molecules. The solubility decrease with increase in size of alkyl group which is hydrophobic.

2. Boiling point:- The boiling points of ether are lower than that of alcohols due to absence of hydrogen bond in it.

3. Dipole moment:-

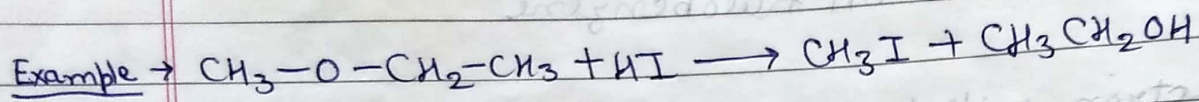
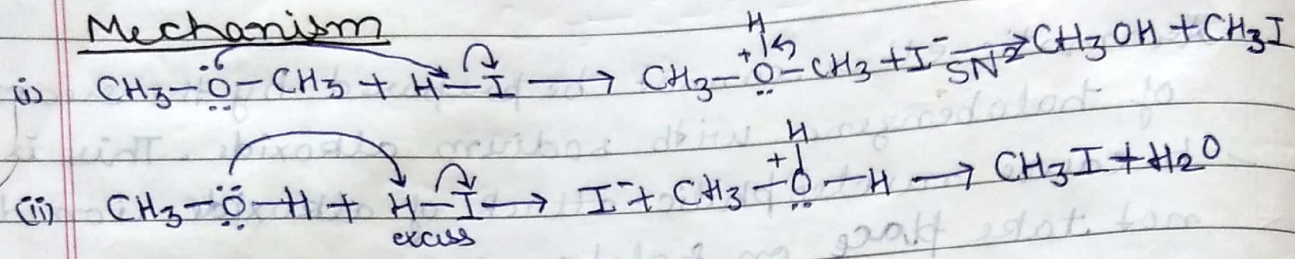
Because of greater electronegativity of oxygen than carbon C-O bonds are slightly polar and have a dipole moment.

Since the two C-O bonds in ethers are inclined to each other at an angle of 111° , the bond dipoles do not cancel each other. As a result, ether have a dipole moment of 1.15 to 1.30 D.

Chemical properties of ether

1. Reaction with HX

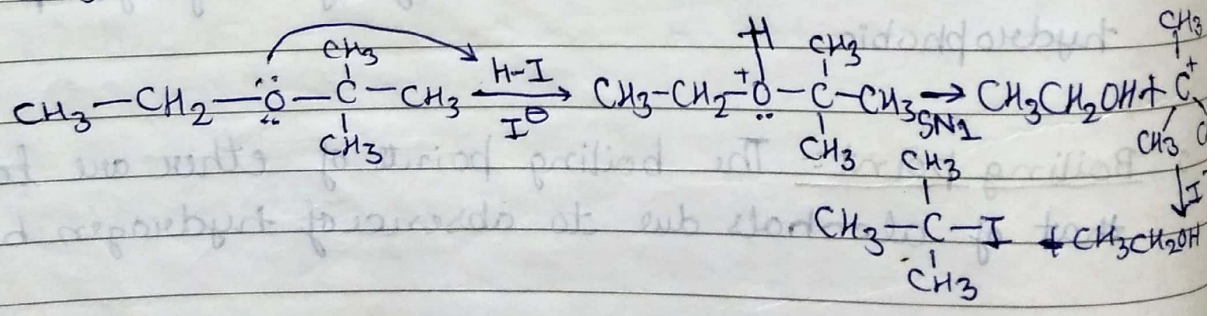
Mechanism



1. Predict the product of the following reaction:

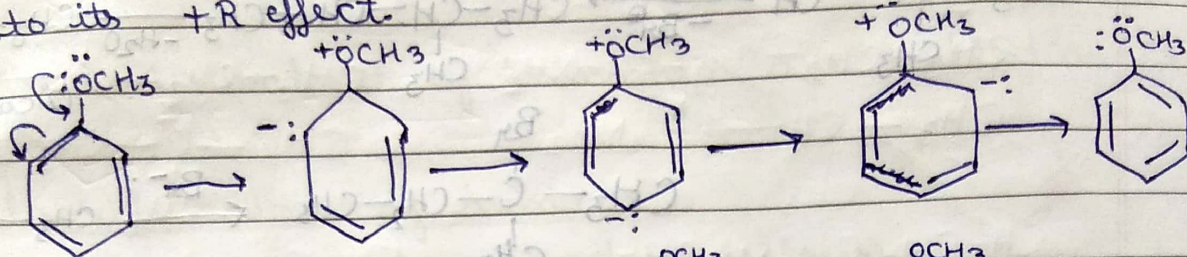
- (i) $CH_3OCH_2CH_3 + HBr \rightarrow CH_3OH + CH_3CH_2Br$
- (ii) $C_6H_5OC_2H_5 + HBr \rightarrow C_6H_5OH + C_2H_5Br$
- (iii) $C_6H_5CH_2-O-C_6H_5 + HI \rightarrow C_6H_5CH_2I + C_6H_5OH$
- (iv) $CH_3-\underset{CH_3}{CH}-CH_2-OCH_2CH_3 + HI \rightarrow CH_3-\underset{CH_3}{CH}-CH_2OH + CH_3CH_2I$
- * (v) $CH_3-CH_2-O-\underset{CH_3}{C}-CH_3 + HI \rightarrow CH_3CH_2OH + CH_3-\underset{CH_3}{C}-I$

* If 3° alkyl group attached with oxygen atom of ether reaction takes place by $SN1$ path. This is because 3° carbocation is more stable.

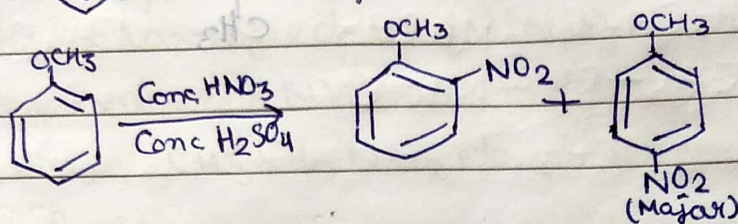


Substitution electrophilic reaction

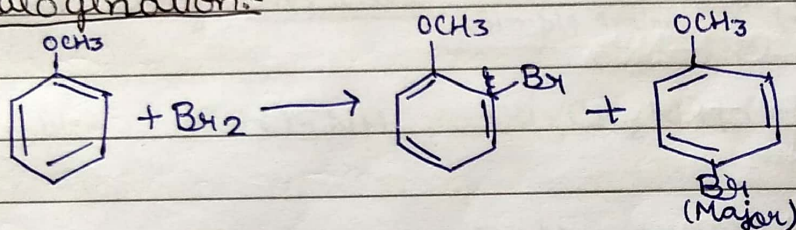
In anisole, electrophilic substitution occurs at ortho and para position. This is because OCH_3 group increases electron density more at ortho and para position due to its +R effect.



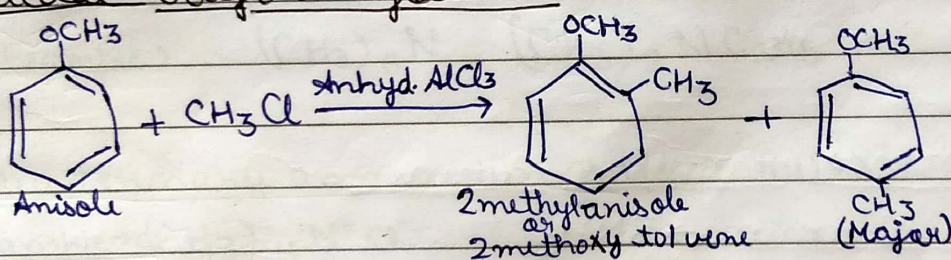
Examples \rightarrow (a) Nitration:-



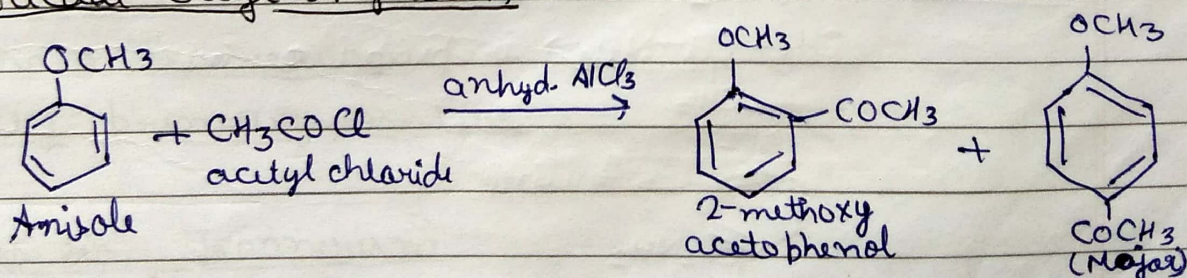
(b) Halogenation:-



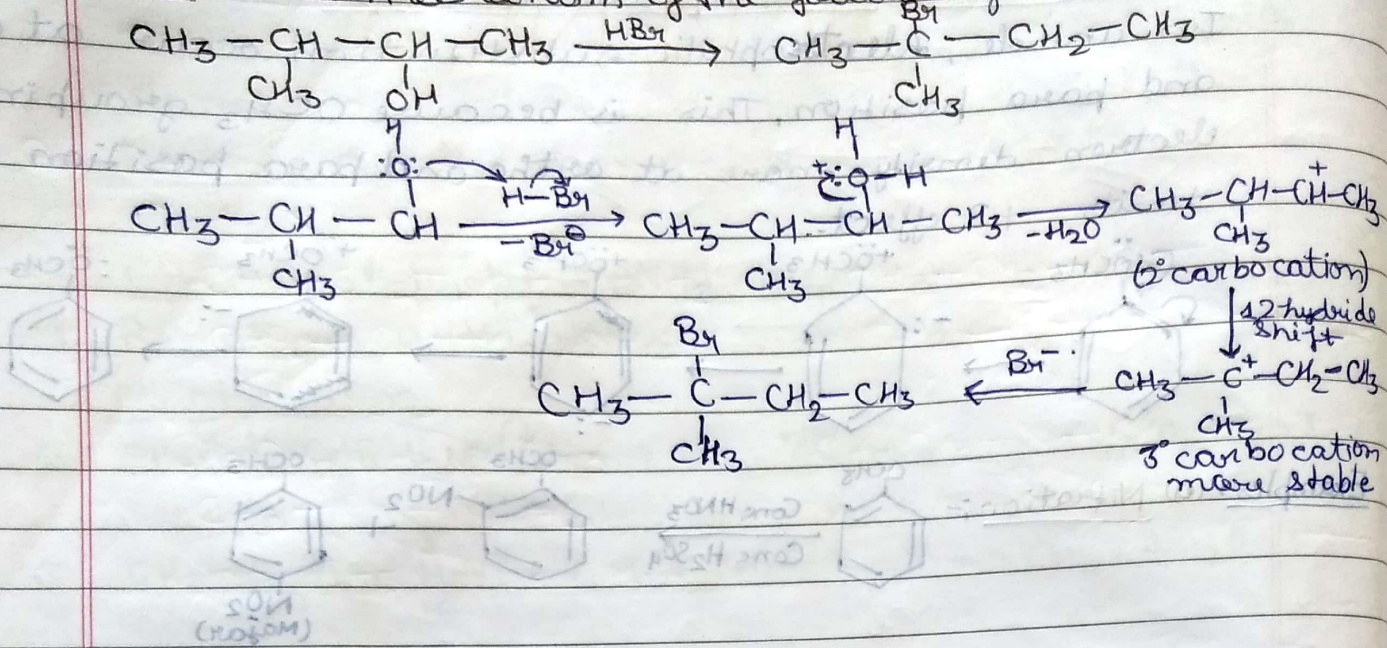
** (c) Friedel Craft Alkylation



** (d) Friedel craft Acylation



A. Write the mechanism of the following reaction:-



SBG STUDY

