

Chapter - 3: Alcohols, phenols, ethers

Classification of Alcohols

Monohydric

CH_3OH
Methanol

Dihydric

CH_2-OH
 CH_2-OH

Ethane 1,2 diol
(glycol)

Polyhydric.

$\text{CH}_2-\text{CH}-\text{CH}_2$
 $\text{OH} \quad \text{OH} \quad \text{OH}$

Propane 1,2,3 triol
(glycerol)

$\text{C}_{\text{sp}}^3-\text{OH}$

Alkyl

1°
 $\text{H}_3\text{CH}_2\text{CH}_2\text{OH}$
Propan-1-ol

2°
 $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}-\text{OH} \\ | \\ \text{CH}_2 \end{array}$

Butan-2-ol

3°
 $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3-\text{C}-\text{OH} \\ | \\ \text{CH}_3 \end{array}$

2 Methyl
Propan-
2-ol.

Prop-2-
en-ol

Allyl

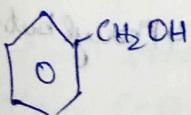
1°
 $\begin{array}{c} \text{CH}_2 \\ || \\ \text{CH} \\ || \\ \text{CH}_2-\text{OH} \end{array}$

3°
 $\begin{array}{c} \text{CH}_2 \\ || \\ \text{CH} \\ || \\ \text{CH}_3-\text{C}-\text{OH} \\ | \\ \text{CH}_3 \end{array}$

2 Methyl
But-3-en-
2-ol.

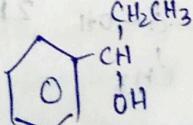
Benzyl

1°



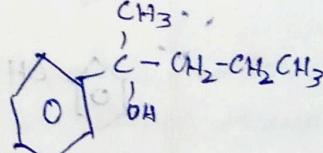
Phenyl
methanol

2°



1-Phenyl
propan-1-ol

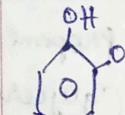
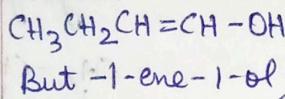
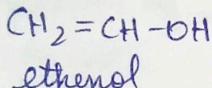
3°



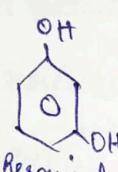
2 Phenyl
pentan-2-ol.

C_{sp^2} - OH:

Vinyl



Catechol
Benzene
1,2 diol

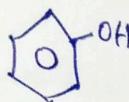


Resorcinol
Benzene
1,3 diol

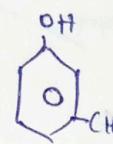


Quinol
Benzene
1,4 diol

Aryl



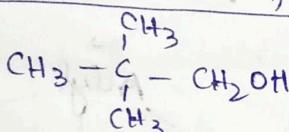
O-Cresol
2-Methyl
phenol



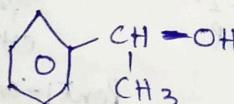
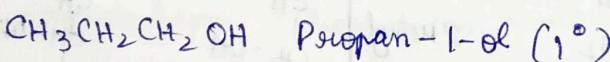
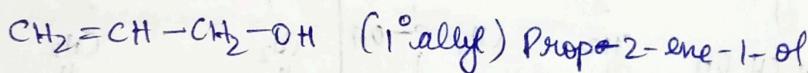
m-Cresol
3-Methyl
phenol



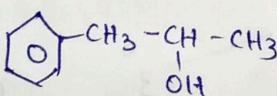
p-Cresol
4-Methyl
phenol



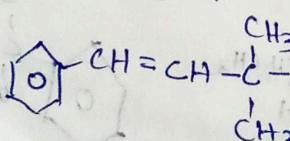
2,2-dimethylpropan-1-ol
(1°)



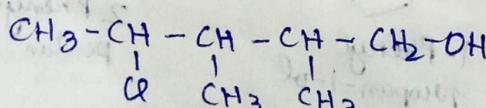
1-Phenylethanol (2° Benzyl)



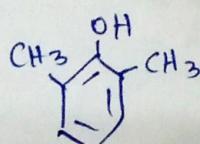
1-Phenylpropan-2-ol (2°)



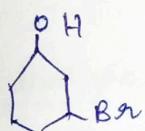
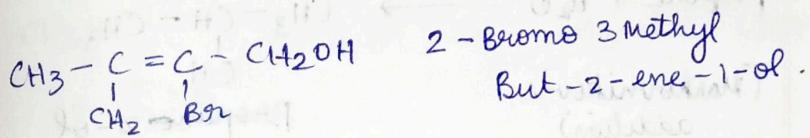
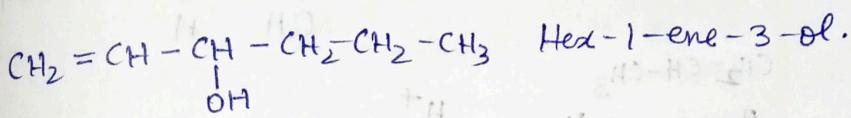
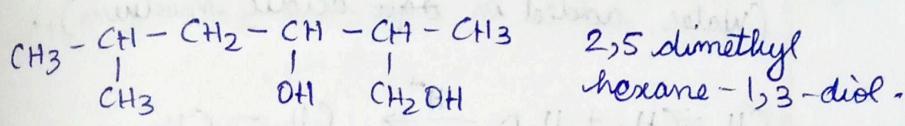
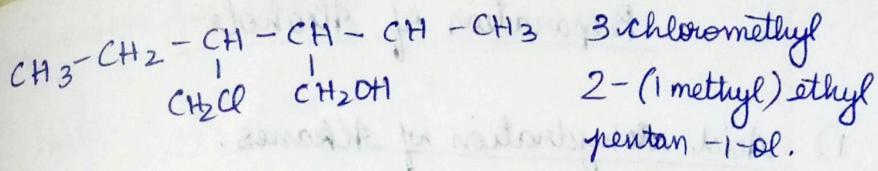
2-Methyl-4-phenylbut-3-en-2-ol.



4-chloro, 2,3-dimethyl pentan-1-ol
(1°)

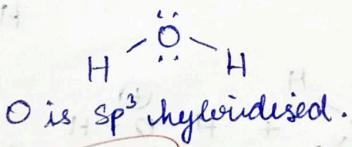


2,6-dimethyl phenol (Aryl)

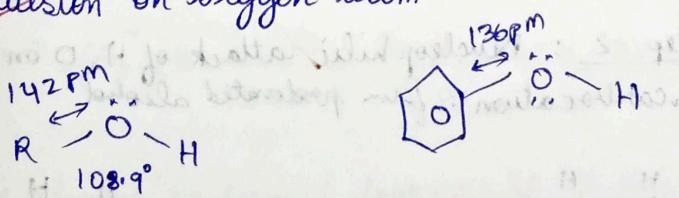


3 Bromo cyclohexanol.

structure of functional group



Bond angle < Tetrahedral angle because lp lp
 repulsion on oxygen atom .

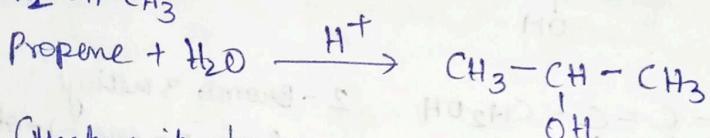
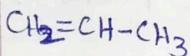
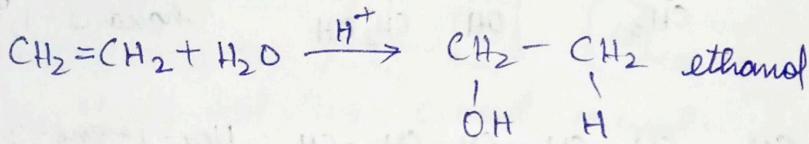


$\text{C}-\text{O}$ bond length in phenol (136 pm) is shorter
 than $\text{C}-\text{O}$ bond length in alcohol (142 pm) because
 of the partial double bond character between
 carbon and oxygen in phenol

Preparation of Alcohols

1) Acid ~~dehydration~~ of Alkanes.

(Water added in acidic medium)

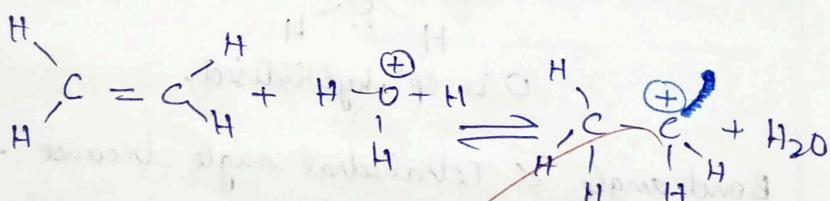
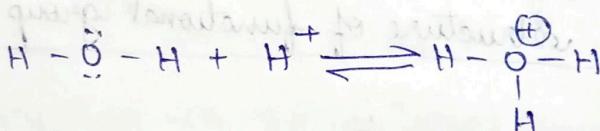


(Markovnikov's addition)

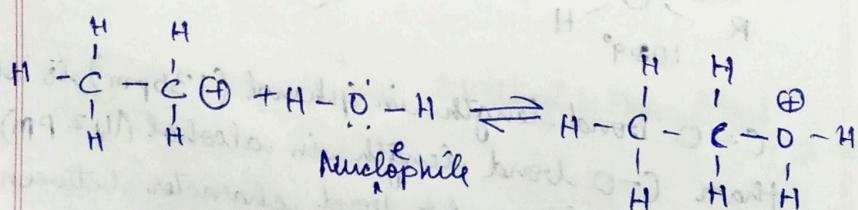
Propane-2-ol

Mechanism

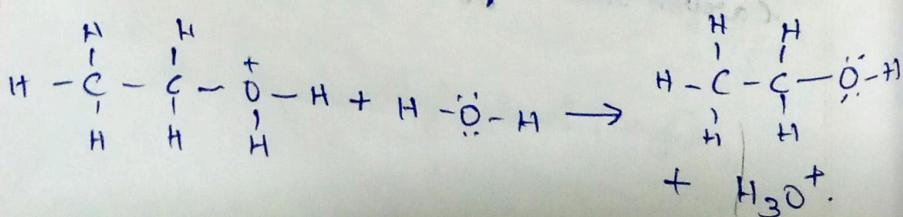
Step-1: Formation of carbocation



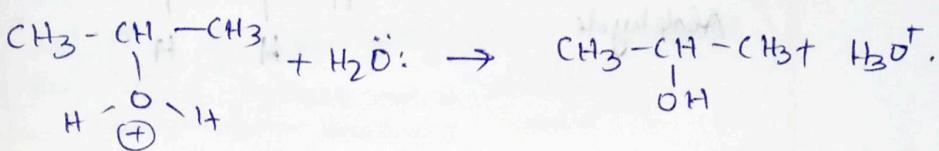
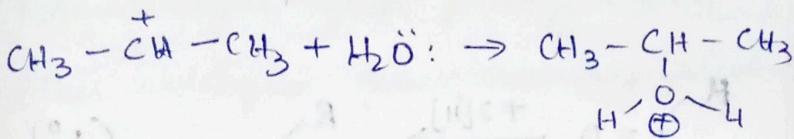
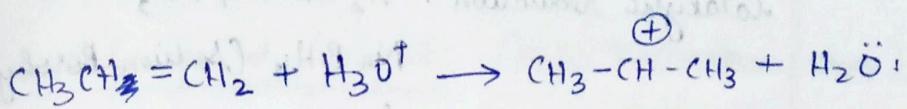
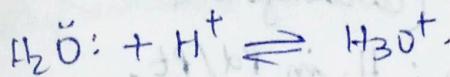
Step-2: Nucleophilic attack of H_2O on carbocation to form protonated alcohol



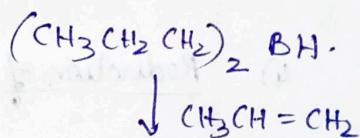
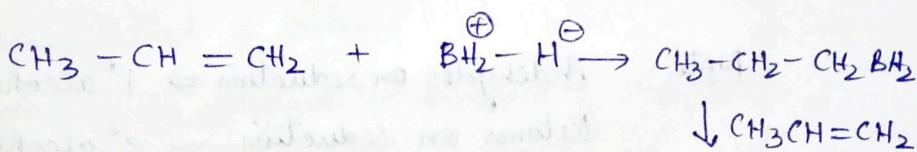
Step-3: Deprotonation to form alcohol



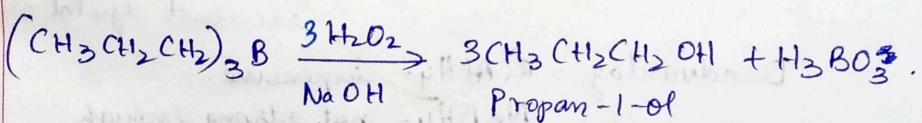
Mechanism for propene -



2) Hydroboration oxidation:



trialkyl Borane. $(\text{CH}_3\text{CH}_2\text{CH}_2)_3\text{B}$

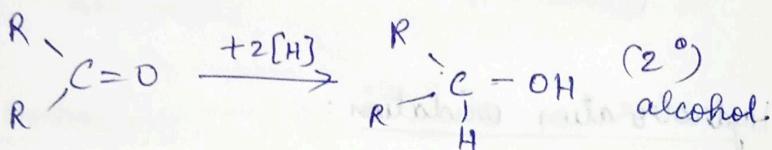
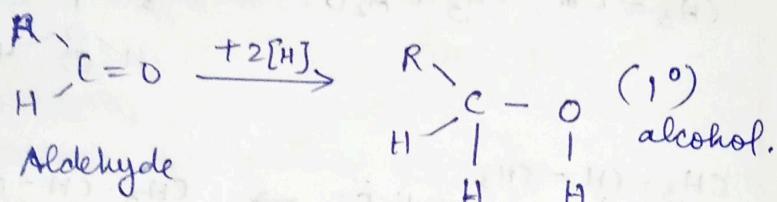


The alcohol so formed looks as if it has been formed by addition of H_2O to alkene in a way opposite to the Markovnikov's rule. In this reaction alcohol is obtained in excellent yield

3) By reduction of aldehydes and ketones:
 (Carbonyl compounds)

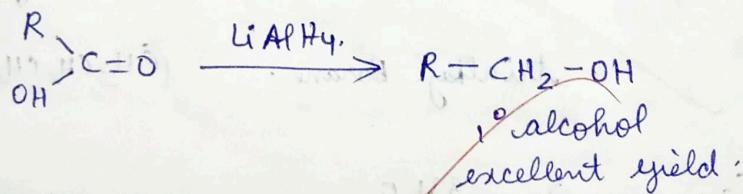
Catalytic reduction: H_2 in Pd/Pt ,

NaBH_4 (Sodium Borohydride)
 LiAlH_4 .



Note: Aldehydes on reduction $\Rightarrow 1^\circ$ alcohol
 Ketones on reduction $\Rightarrow 2^\circ$ alcohol.

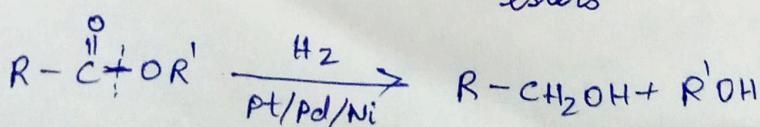
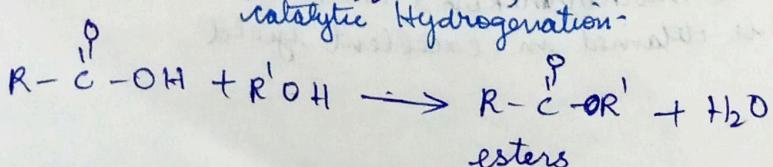
4) Reduction of carboxylic acids and esters

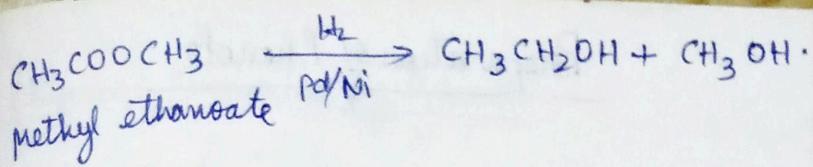


Disadvantage: LiAlH_4 - expensive.

NaBH_4 - not strong enough
 to reduce $\text{R}-\text{COOH}$.

Solution = Convert $\text{R}-\text{COOH}$ to esters
 by esterification, then use cheaper
 catalytic Hydrogenation-





5) From Leymus Reagent: (Refer Haloalkane chap)

Formaldehyde gives primary alcohol

Other aldehydes give secondary alcohol

Ketones give tertiary alcohol.

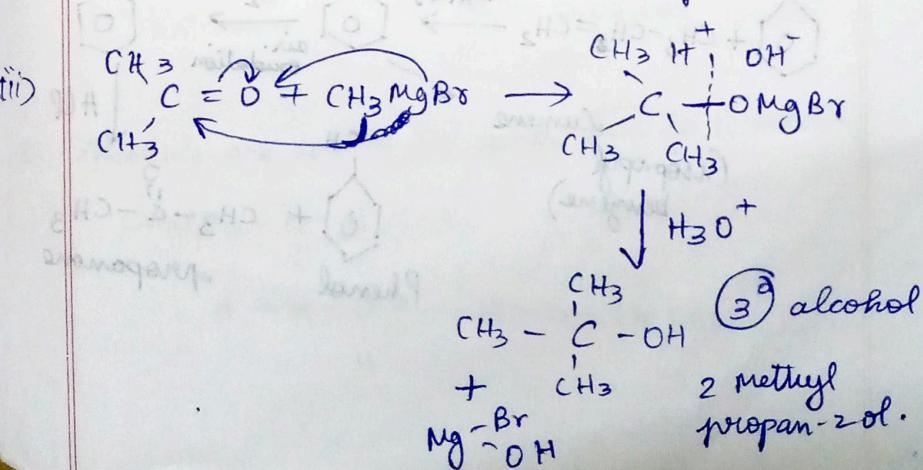
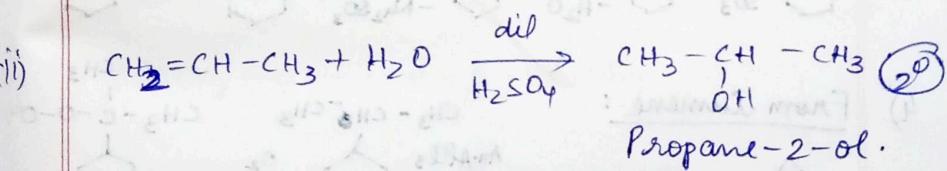
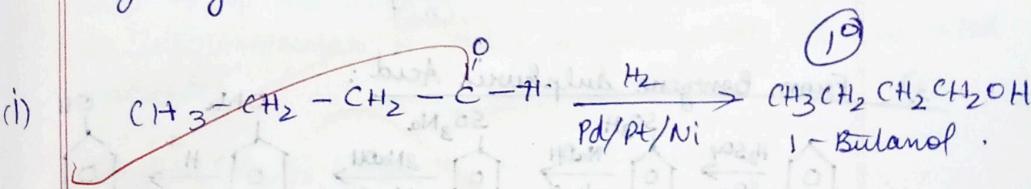
→ (Reduction of other aldehydes → ${}^1\text{O}$ alcohol)
 Reduction of Ketones → ${}^2\text{O}$ alcohol)

Give the structure and IUPAC names of the products expected from the following exns.

(i) Catalytic Red. of Butanal

(ii) Hydration of propene in presence of dil H_2SO_4

(iii) Reaction of propanone with MgBr followed by hydrolysis

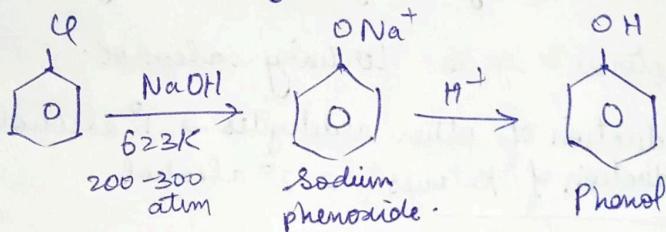


Preparation of Phenols

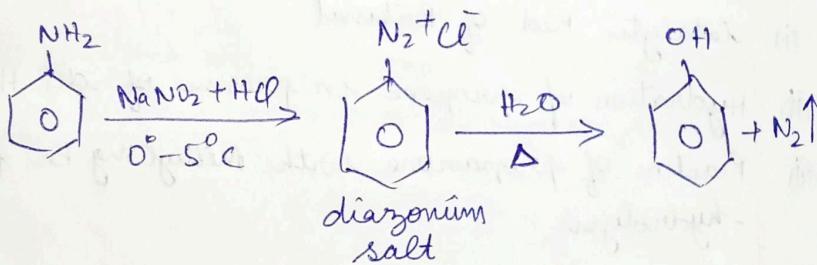
1) Dow's Process :

Nu. subs. rxn of Chlorobenzene,
drastic conditions of High P and Temp

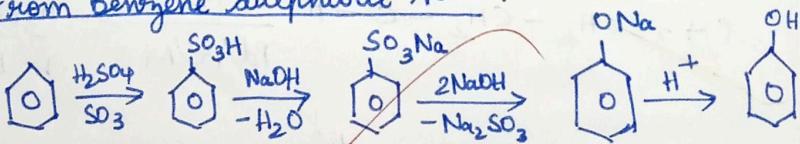
Chlorine replaced by $\text{O}^- \text{Na}$, then OH^- .



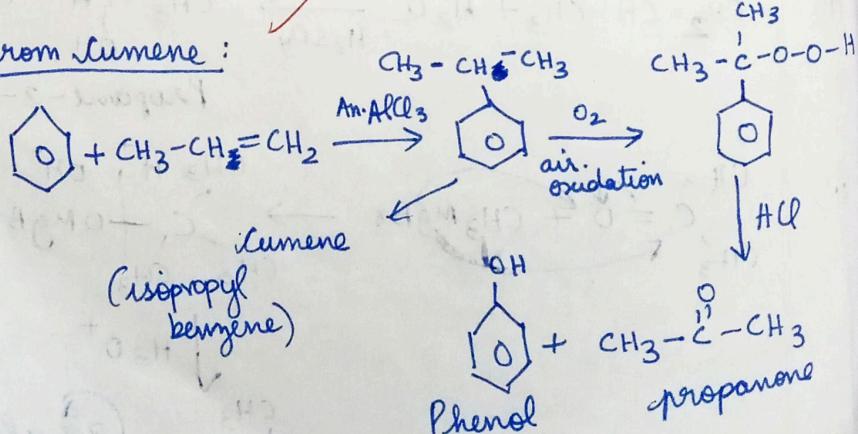
2) From Diazonium Salt :



3) From Benzene Sulphuric Acid :

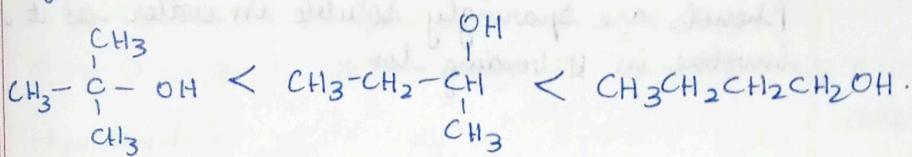


4) From Cumene :

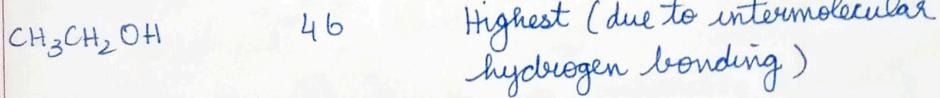
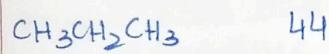


Physical Properties of Phenol

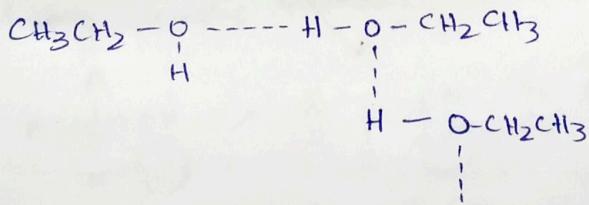
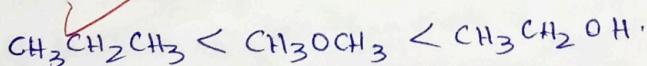
- As the no. of C atom increases, bp increases, since surface area decreases, Van der Waals forces increases.
- Among isomeric alcohols as branching increases, surface area decreases, Van der Waals forces decreases, hence boiling point decreases. n-isomer has the highest bp.



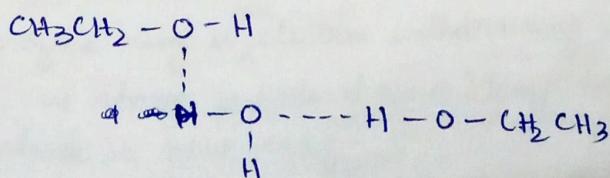
- Molar mass : Boiling point



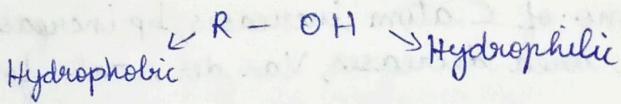
- Alcohols have higher bp than ethers and hydrocarbons of comparable molar mass as they involve in ~~intermolecular H-bonding~~ and exist as associated molecules



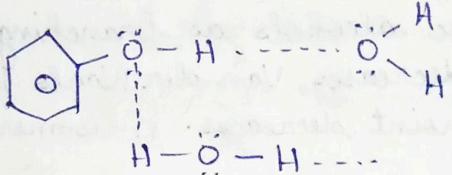
- Alcohols are soluble in water due to H bonding



Solubility of alcohol decreases as the chain length of hydrophobic alkyl group increases.

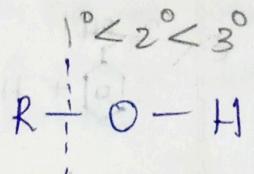
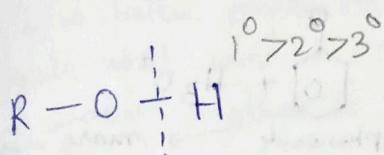


6.



Phenols are sparingly soluble in water as it can involve in H bonding too.

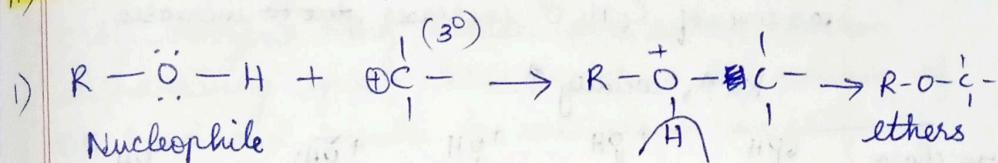
Chemical Properties



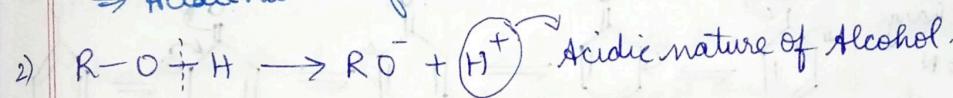
Cleavage of O-H
out as nucleophiles

Cleavage of R-O.
act as electrophiles
(protonated alcohol)

A) Reactions involving cleavage of O-H bonds.



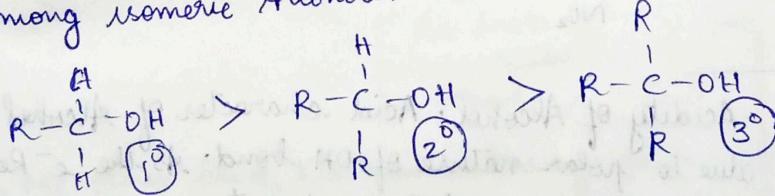
↳ Alcohols act as nucleophiles due to presence of lone pair on oxygen atom and involve in cleavage of ~~O-H~~ bond. \Rightarrow Acidic nature of alcohol



H-O-H and $\text{R}-\overset{\cdot}{\underset{\cdot}{\text{O}}}-\text{H} \Rightarrow$ Comparison of Acidity.
 $\downarrow +I$ effect

-ve charge is intensified (due to +I effect of R group) on the oxygen. $\therefore \text{H}^+$ ion is more strongly bonded to O^- . Hence release of H^+ has become difficult. \therefore Acidity of Alcohols is less than that of water.

Among Isomeric Alcohols:



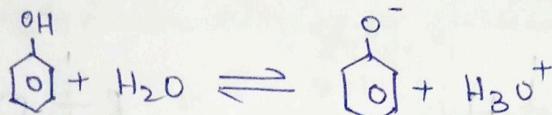
Between Phenol and H_2O : H-O-H and $\text{O}^{\cdot\cdot}\text{H}$.

Benzene ring is ^{an} electron withdrawing group.

\therefore -ve charge is reduced on O atom. Hence H^+ ion release is now easy.

\therefore Phenol is more acidic than water, which is in turn more acidic than water.

Another reason of why Phenols are more acidic :



phenoxide ion

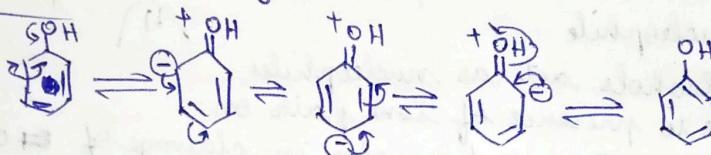
more resonance stability than phenol.
∴ phenoxide ion is released more.

$$K_a = \frac{[\text{C}_6\text{H}_5\text{O}^-][\text{H}_3\text{O}^+]}{[\text{C}_6\text{H}_5\text{OH}]}$$

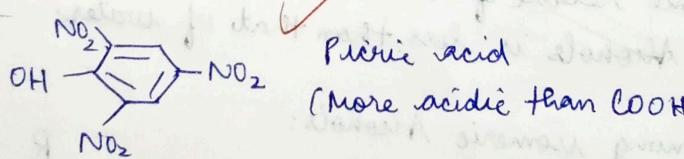
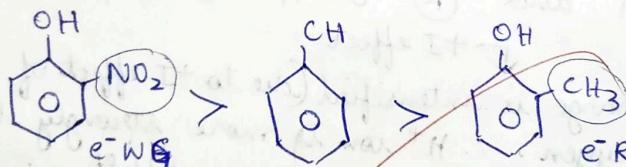
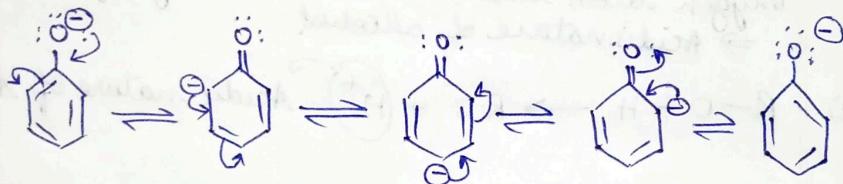
as conc. of $\text{C}_6\text{H}_5\text{O}^-$ increases, K_a increases.

$K_a \uparrow$, acidity \uparrow .

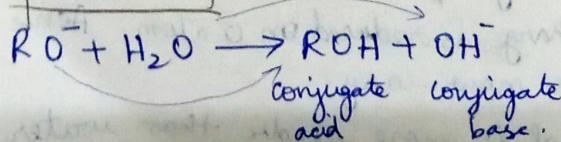
+ve charge
on EN
Oxygen atom



-ve charge
on EN
Oxygen atom



Acidity of Alcohol : Acid character of Alcohol is due to polar nature of OH bond. As the e^- Releasing group increases, electron density on oxygen atom increases, thereby decreasing the polarity of OH bonds. Acidic character of alcohols decreases in the order : $1^\circ > 2^\circ > 3^\circ$



H_2O - strong acid than alcohol. The alkoxide ion is a better proton acceptor than OH ion, which suggests that sodium alkoxide is a stronger base than sodium hydroxide ($\text{RONa} > \text{NaOH}$)

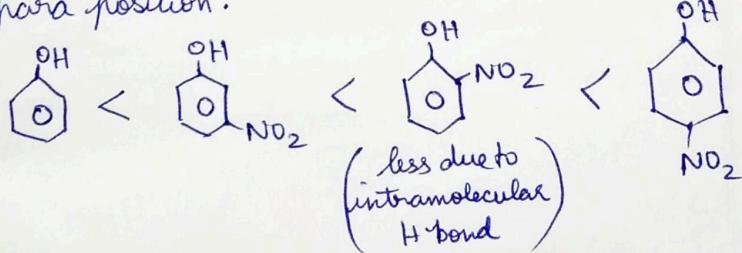
Acidity of Phenols:

Phenols are more acidic than alcohols, this is because OH group is directly attached to sp^2 hybrid carbon of benzene ring, which acts as an electron withdrawing group. This increases the polarity of OH bond and results in increase in ionisation of phenols than in alcohols.

The phenoxide ion formed is more stabilised by resonance.

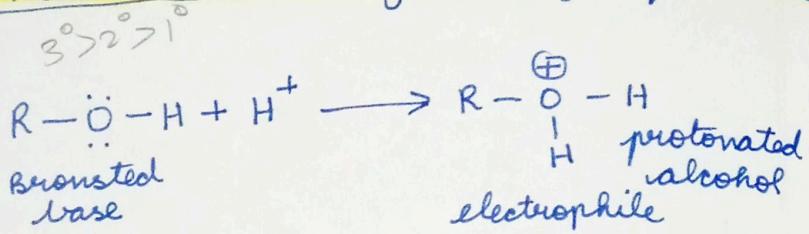
Phenol molecule is less stable than phenoxide ~~molecule~~ ^{ion} as the resonance structure of phenol have charge separation.

In substituted phenols, in presence of e^- withdrawing groups such as NO_2 , enhances the acidic strength of phenols. This effect is more pronounced when the substituent is in para position.



On the other hand, electron releasing group such as alkyl groups ~~do~~ not favour the formation of phenoxide ion resulting in decrease in acid strength

[B] Reactions involving cleavage of C-O bond

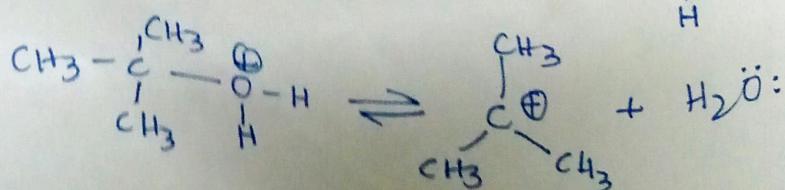
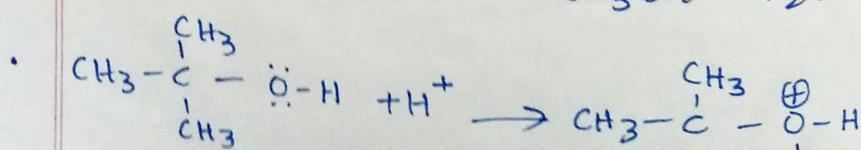
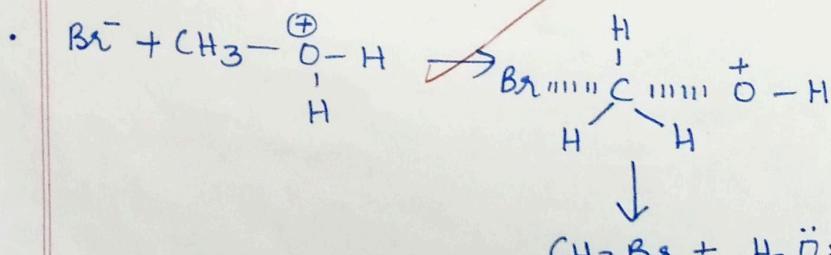
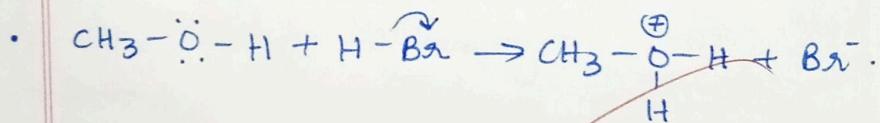


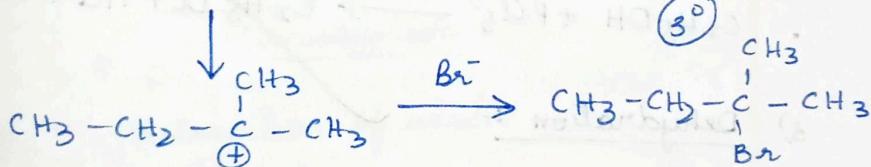
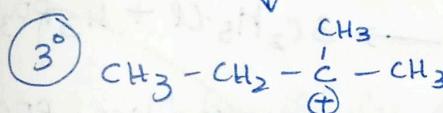
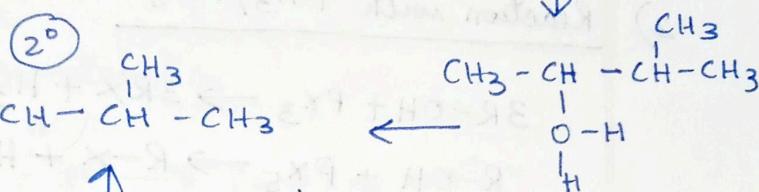
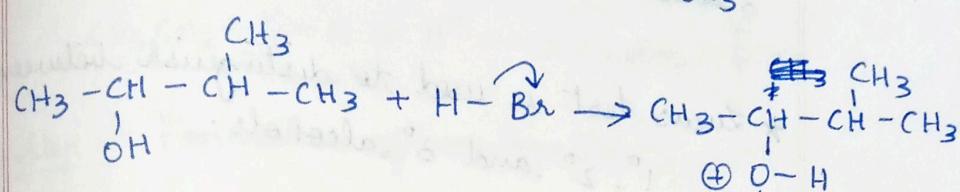
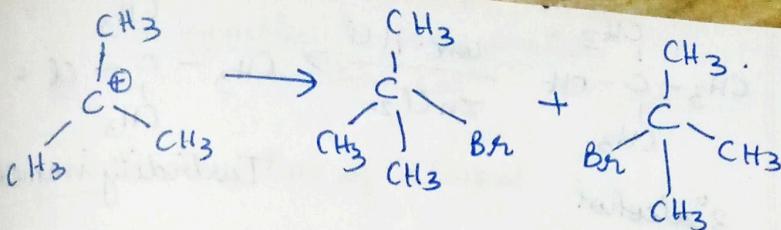
- Alcohol act as bronsted bases and accepts a proton to form protonated alcohol which acts as an electrophile.
- This leads to cleavage of C-O bond.



1) Reaction with HX :-

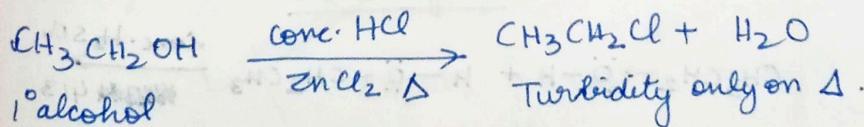
- order of reactivity towards cleavage of C-O bond, $3^\circ > 2^\circ > 1^\circ$



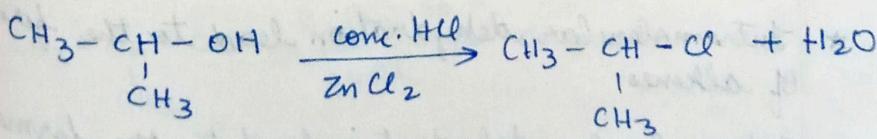


Lucas Reagent: Alcohol to Haloalkane

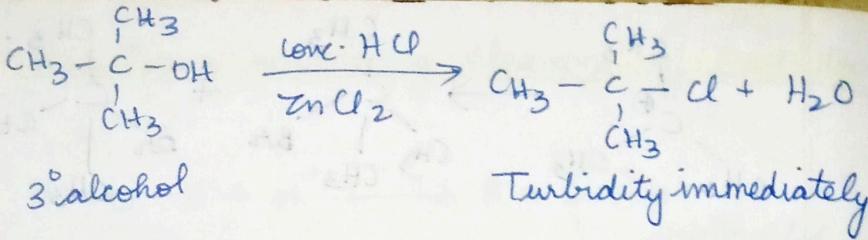
(Conc. HCl + ZnCl₂)



* 1° alcohols give turbidity only on heating.

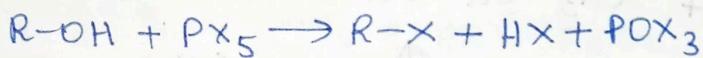


Turbidity after 5-10 mins.

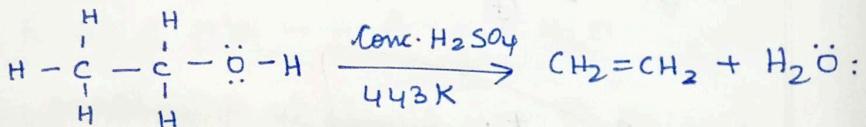


- * Lucas test is used to distinguish between 1° , 2° and 3° alcohols.

2) Reaction with PX_3/PX_5 :-

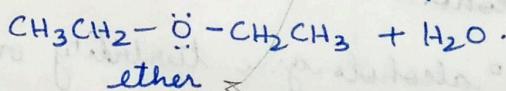
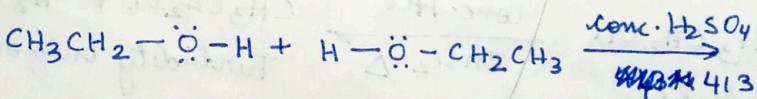


3) Dehydration :-



inter - ether
intra - alkene

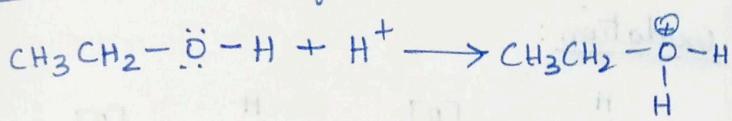
Intramolecular dehydration (Inter)



- * Intramolecular dehydration lead to the formation of alkenes
- * Intermolecular dehydration lead to the formation of ethers.

Intramolecular dehydration mechanism

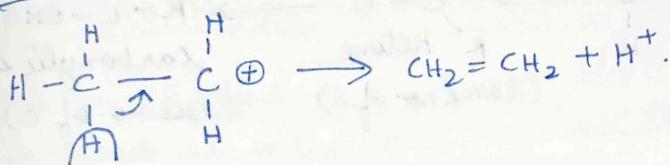
Step 1: Protonation of alcohol



Step 2: Formation of carbocation

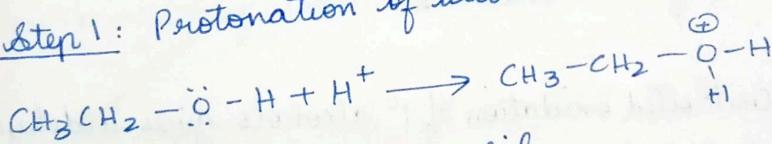


Step 3: Deprotonation

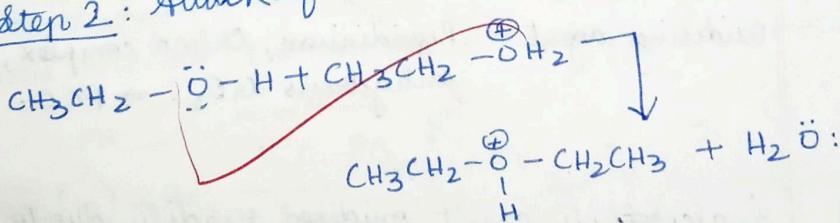


Intermolecular dehydration mechanism

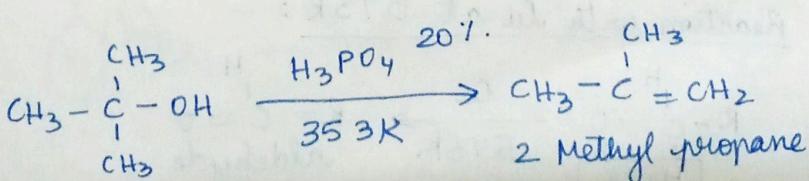
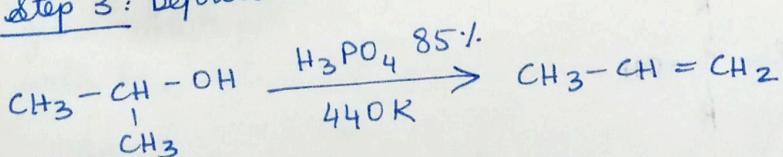
Step 1: Protonation of alcohol



Step 2: Attack of nucleophile



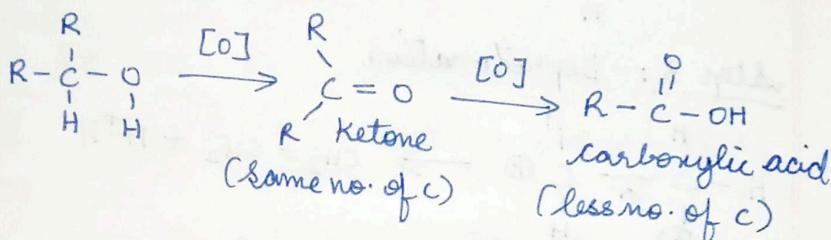
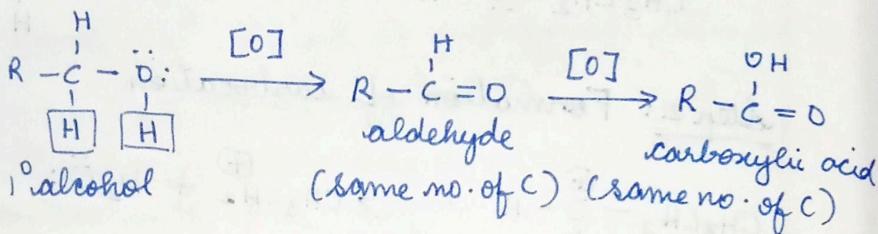
Step 3: Deprotonation



* Order of reactivity towards dehydration

$3^\circ > 2^\circ > 1^\circ$ - stability of carbocation

4) Oxidation:

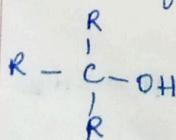


* Strong oxidising agents acidified KMnO_4 oxidise
 1° alcohol to carboxylic acid
 2° alcohol to carboxylic acid with lesser
no. of carbon atoms.

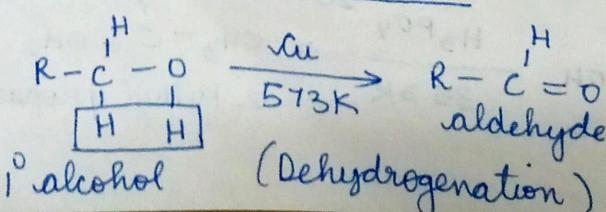
* Controlled oxidation of 1° alcohols gives aldehydes &
 2° alcohols give ketones.

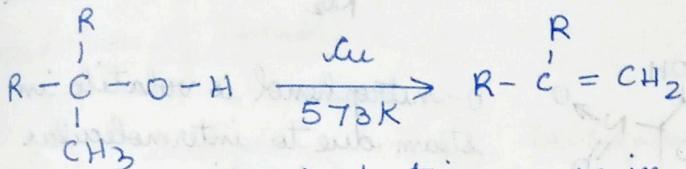
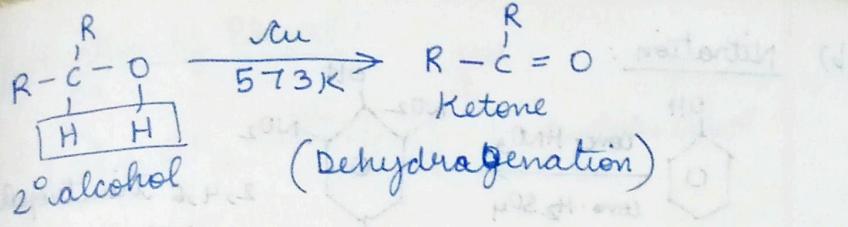
Oxidising agent = Pyridinium, Chloro complex,
anhydrous Cr_2O_7 . \Rightarrow P.C.C.

* 3° alcohols aren't oxidised readily due to
absence of α Hydrogen atom.



5) Reaction with Cu at 573 K:

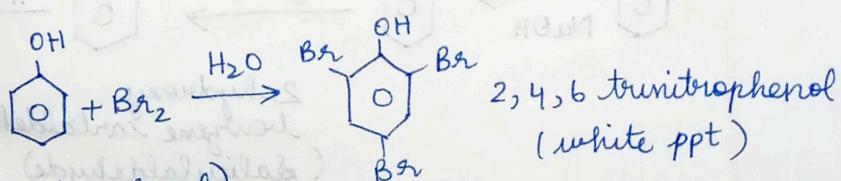




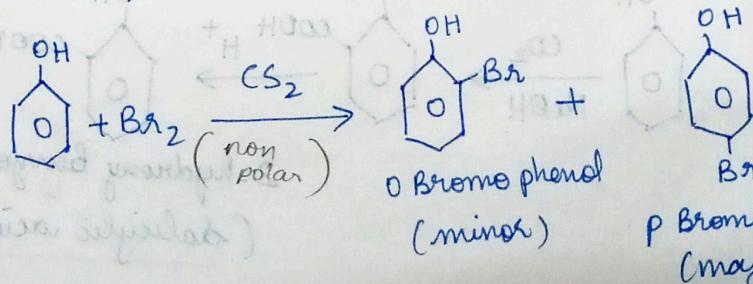
Dehydration occurs in 3° alcohols to give alkenes.

ELECTROPHILIC SUBSTITUTION RXN OF PHENOLS

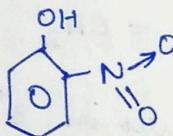
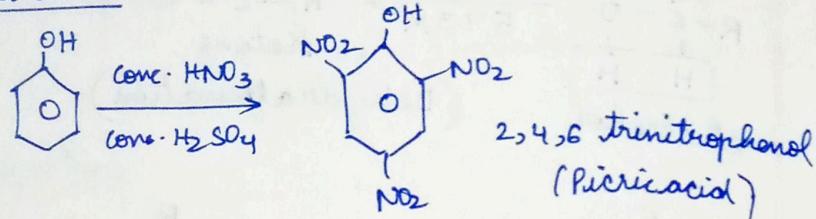
- * Due to $+R$ effect of OH group, the e^- density increases at ortho and para positions of the Benzene ring, hence O-H group is highly activating and ortho - para directing in nature.
- * Phenols undergo electrophilic substitution reaction more readily than benzene
- a) Bromination: OH - poor leaving group $\Rightarrow S\text{N}2$
- * OH is highly activating, so halogenation reaction can proceed even in the absence of Lewis acid.



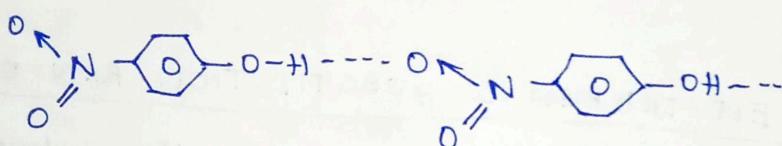
(Test for phenol)
gives white ppt
with $\text{Br}_2/\text{H}_2\text{O}$.



b) Nitration:

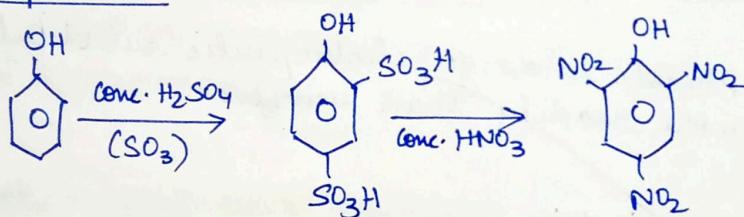


o-nitrophenol is volatile in steam due to intermolecular hydrogen bonding.

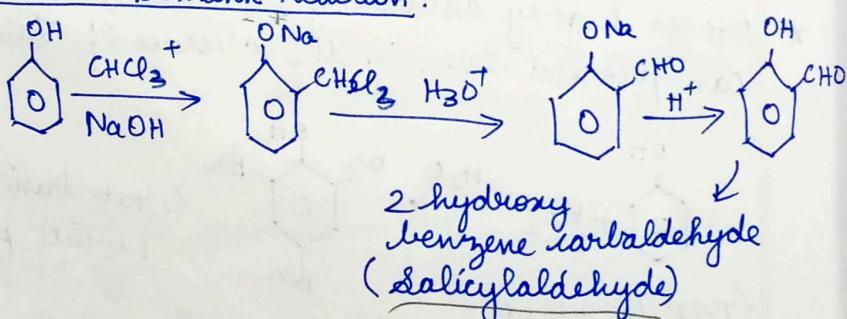


p-nitrophenol has higher bp and not volatile due to intermolecular Hydrogen bonding.

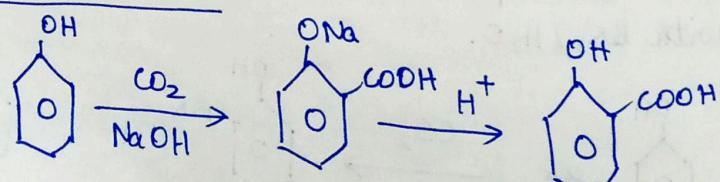
c) Sulphonation:



d) Riemer - Tiemann Reaction:

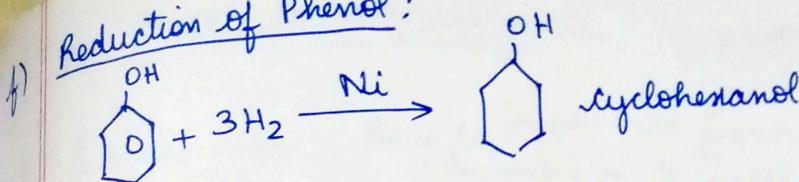


e) Kolbe's Reaction:

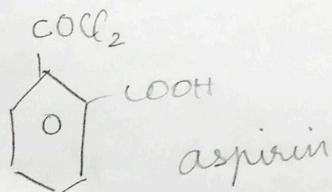
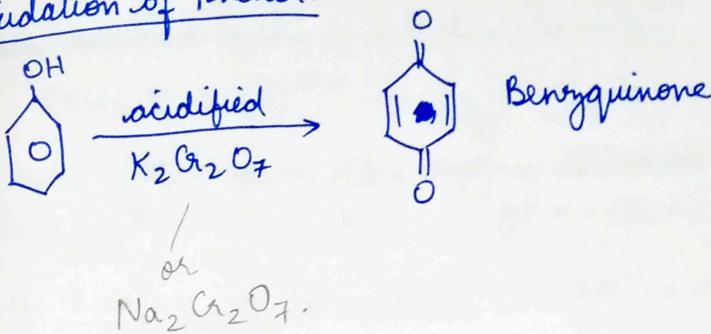


2 hydroxy Benzoic acid
 (Salicylic acid)

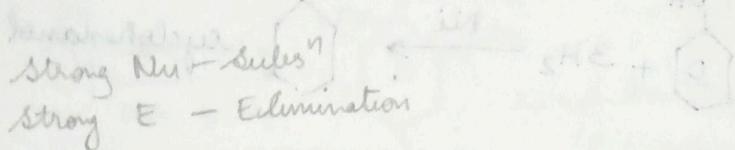
f) Reduction of Phenol:



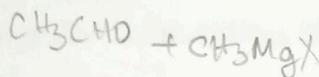
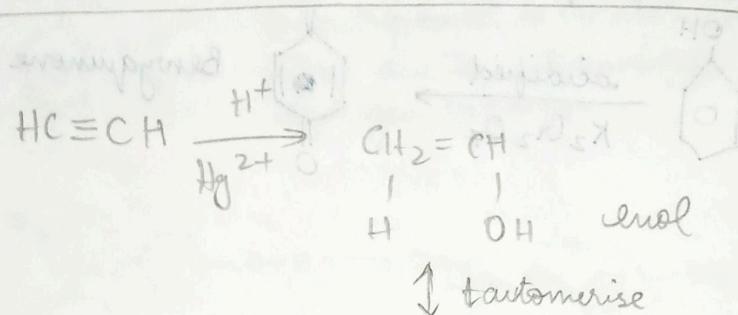
g) Oxidation of Phenol:



Alkoxide - strong base than hydroxide



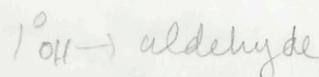
Reactions involving cleavage of O-H bond



Only reaction in breaking C=O bond in phenols

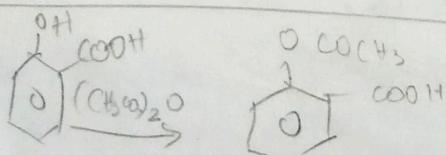
Zinc dust - to give O^-

Controlled oxidation - PCC



Methoxy benzene - anisole

allyl = benzyl $> 3^\circ > 2^\circ > 1^\circ >$ Aryl $>$ Vinyl



Carboxic acid - Phenol

Alcohols
are
Bronsted acids
Lewis base
Reducing

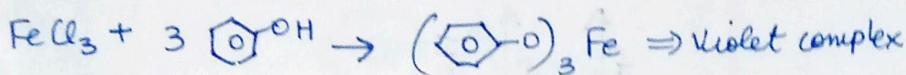
Test for Phenols

Fehling
Aldohyde & Ketone

1) Litmus test : Blue to Red

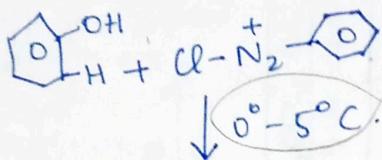
2) With Br_2 water : White ppt.

3) With neutral FeCl_3 : Violet colouration .



not only with phenols, any enol gives characteristic colour with neutral FeCl_3 . ($-\text{CH}=\text{CH}-\text{OH}$)

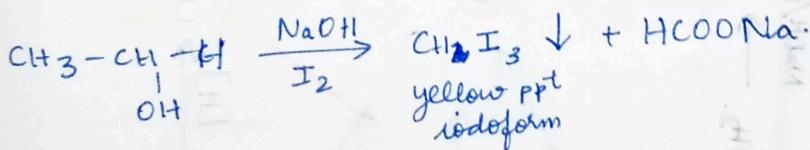
4) With Benzene o-diazonium chloride \rightarrow orange dye



P-bihydroxy arylbenzene (orange dye)

5) Iodoform Test:

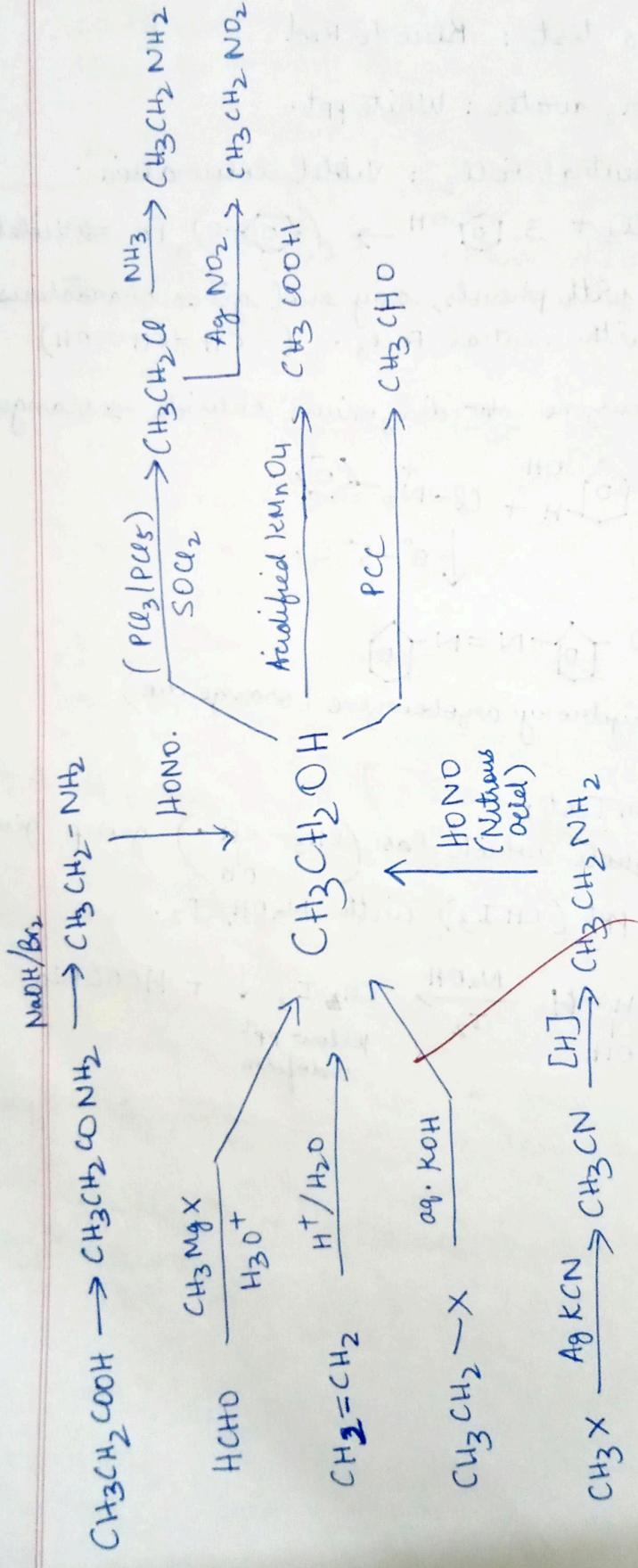
All alcohols which has $(\text{CH}_3-\text{CH}-\text{H})$ group gives yellow ppt (CHI_3) with NaOEt/I_2 .

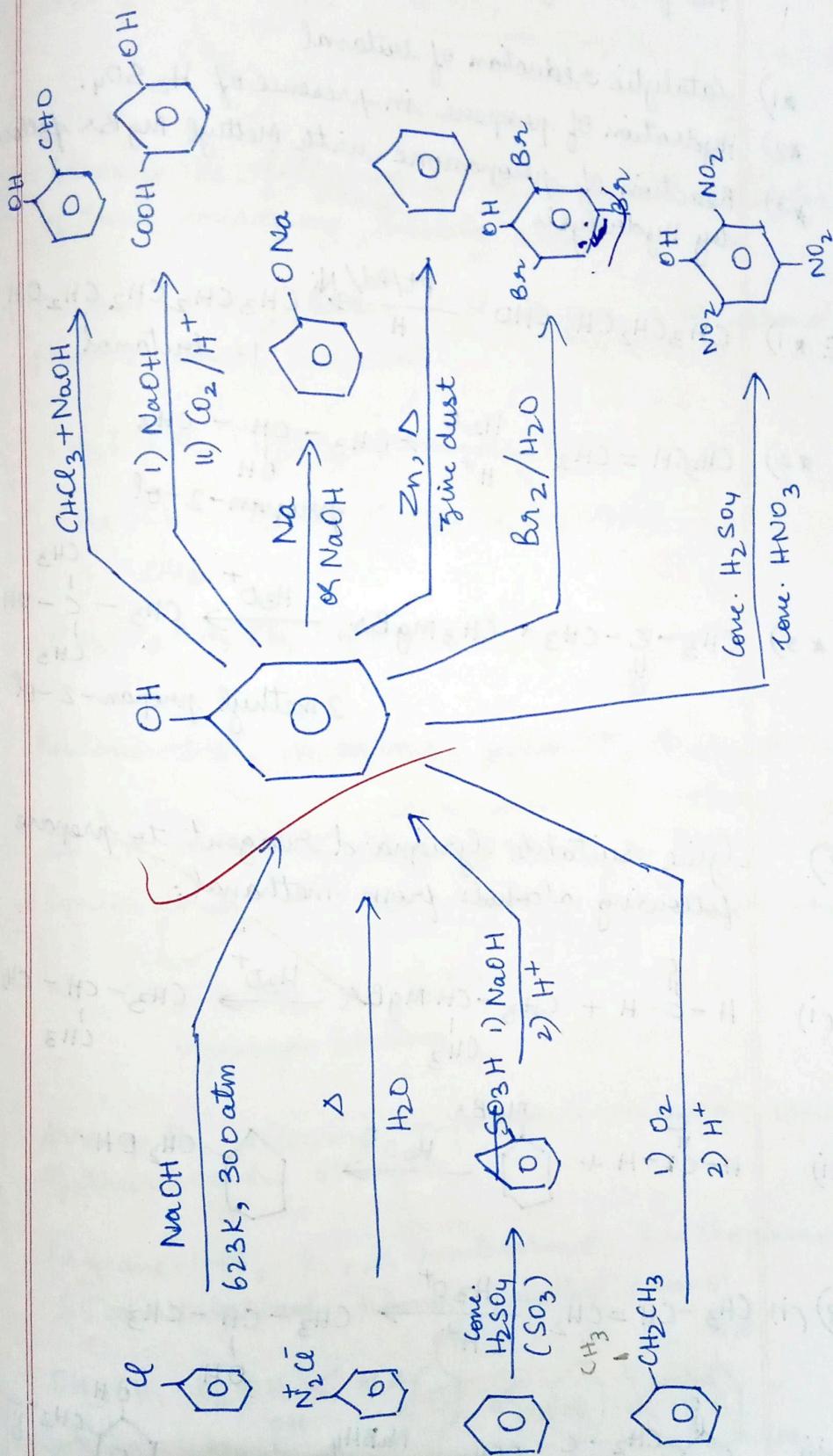


6) 1° alcohol heating with Cu $\xrightarrow[573]{\text{Cu}} \text{Aldehyde}$

1° & 2° & 3° distinguishing — linear test
 $\text{ZnCl}_2 + \text{H}_2\text{O}$

Pyridine, conc. HCl + CrO_2





Ethers

a) Simple ether: $R-O-R$ (symmetric)

e.g. CH_3OCH_3 methoxy methane

$C_2H_5OC_2H_5$ ethoxy ethane

$C_6H_5O C_6H_5$ phenoxybenzene

b) Mixed ether: $R-O-R'$ (Unsymmetric)

e.g. $CH_3O C_2H_5$ methoxy ethane

$C_6H_5OCH_3$ methoxybenzene (Anisole)

$C_6H_5O C_7H_{15}$ phenoxyheptane

$C_6H_5OC_2H_5$ ethoxybenzene (Phenetole)

Isomerism

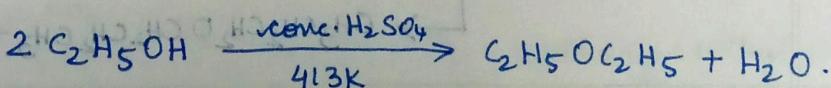
• Functional isomerism: Alcohols and ethers

• Position isomerism: $CH_3CH_2CH_2OCH_3$ + $CH_3CH_2CH_2O$

• Metamerism: $CH_3CH_2OCH_2CH_3$ + $CH_3OCH_2CH_2CH_3$

Preparation of Ethers

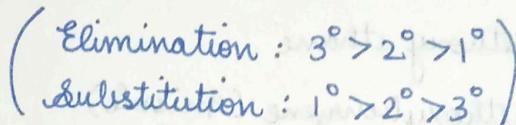
1) Intermolecular dehydration of alcohols.



This method is suitable for preparation of ethers having 1° alkyl groups only.

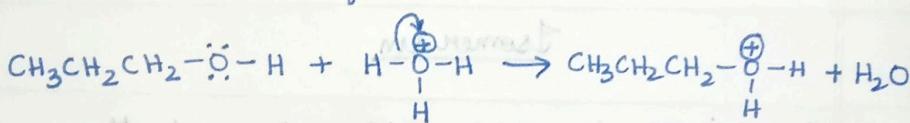
The alkyl groups should be unhindered sterically and the temperature must be kept low, or else it favours the formation of alkenes (by elimination). Low temperature favours substitution and H₂O. High temperature favours elimination.

Dehydration of 2° and 3° alcohols to give corresponding ethers is unsuccessful as elimination competes over substitution and alkenes are formed.

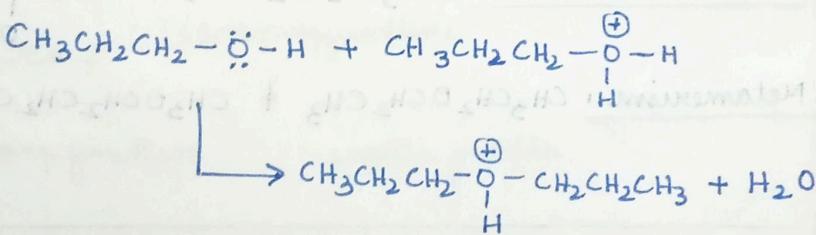


Mechanism of dehydration of propan-1-ol

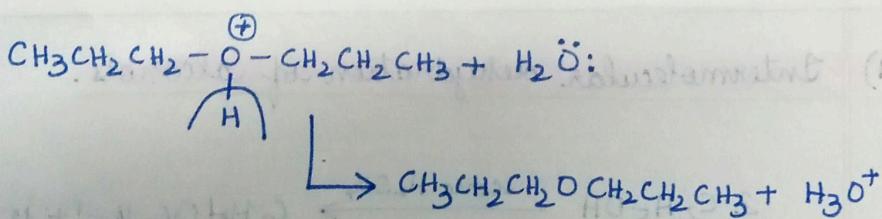
Step 1: Protonation of alcohol



Step 2: Attack of nucleophile

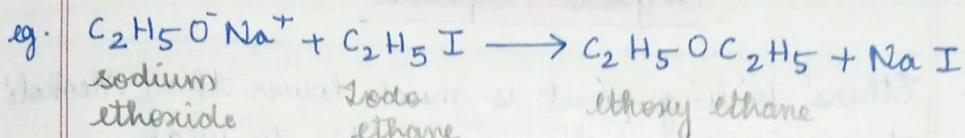
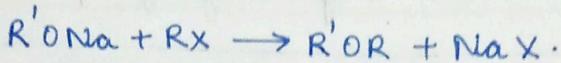


Step 3: Deprotonation

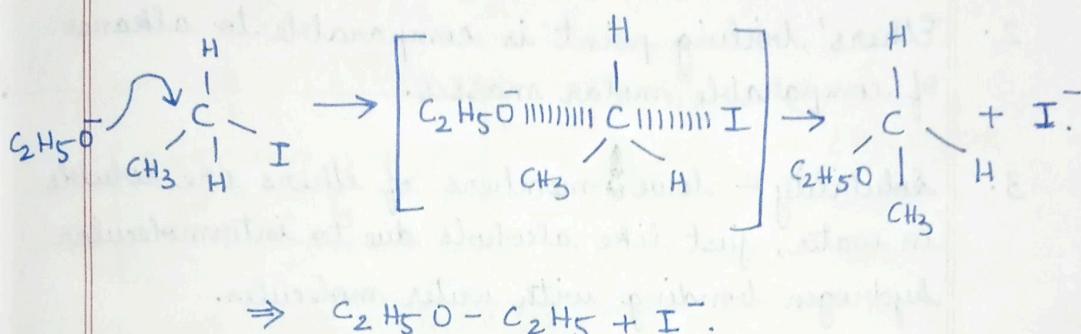


2) Williamson's Synthesis

Sodium alkoxide + Alkyl halide \rightarrow Ether + Sodium halide

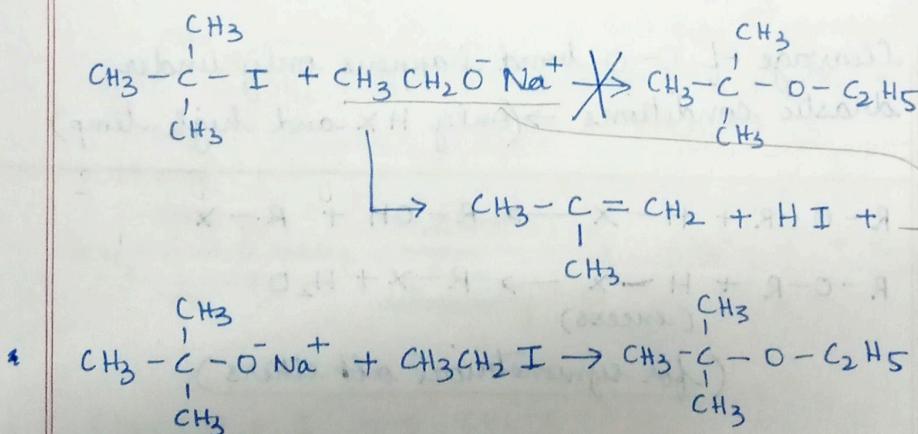


Mechanism: $SN2$ (No $SN1$)

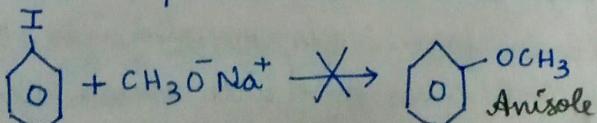


Limitations of Williamson's synthesis

- 3° alkyl halides preferably undergo elimination reaction to form alkenes



- Aryl halides do not undergo Nucleophilic substitution reaction due to partial double bond character of $C-X$



Structure of ether: Bond angle is slightly greater than tetrahedral angle (119°) due to repulsion between bulky alkyl groups.

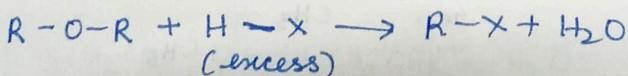
Physical Properties

1. Ethers' boiling point is much lower than Alcohols' of comparable molar masses due to weak polarity of these molecules.
2. Ethers' boiling point is comparable to alkanes of comparable molar masses.
3. Solubility - lower members of ethers are soluble in water, just like alcohols due to intermolecular hydrogen bonding with water molecules.

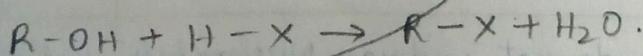
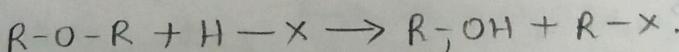
Chemical Properties

Among all functional bonds, ethers are the least reactive.

Cleavage of C-O bond happens only under drastic conditions \rightarrow (only HX and high temp)

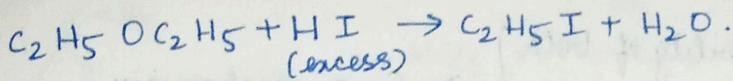
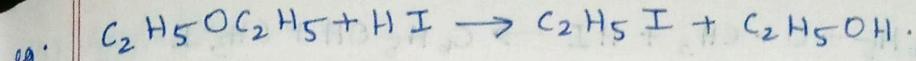


(for symmetrical ethers)



\therefore if $R-O-R$ reacts with excess HX,
all $R-OH$ formed gets converted into $R-X$.

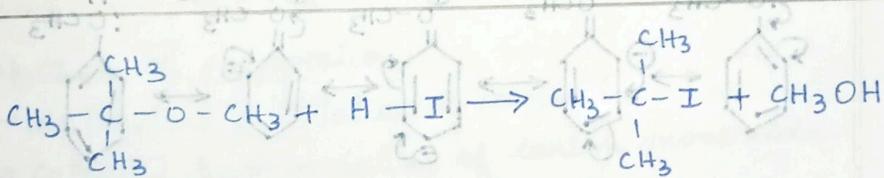
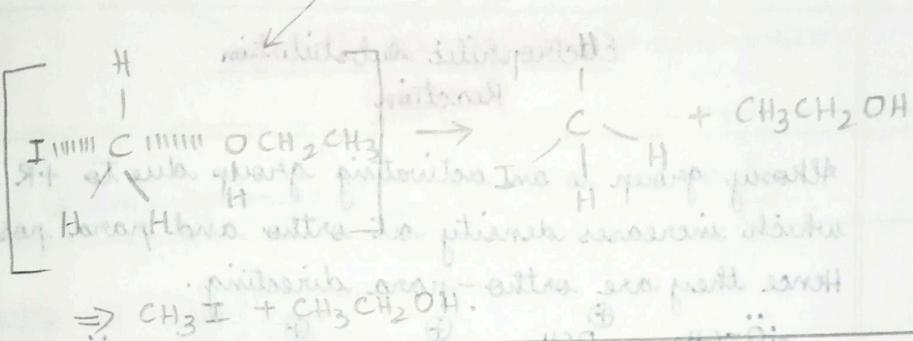
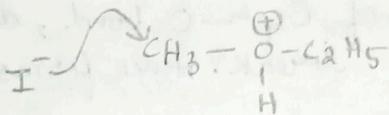
$\therefore R-O-R$ gives $R-X$ with excess HX



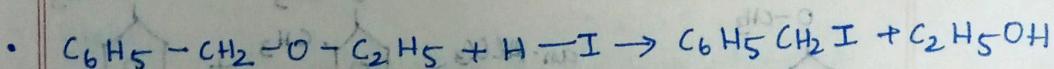
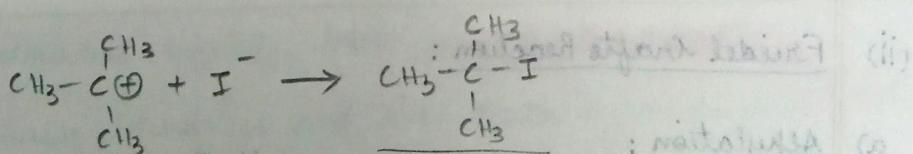
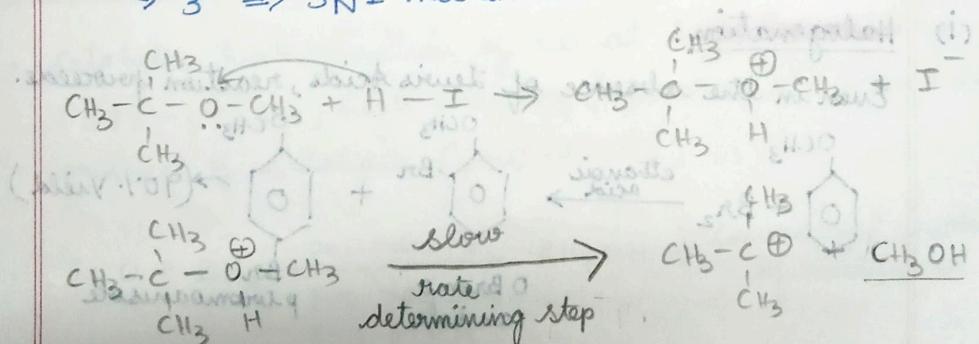
b) for unsymmetrical ethers:



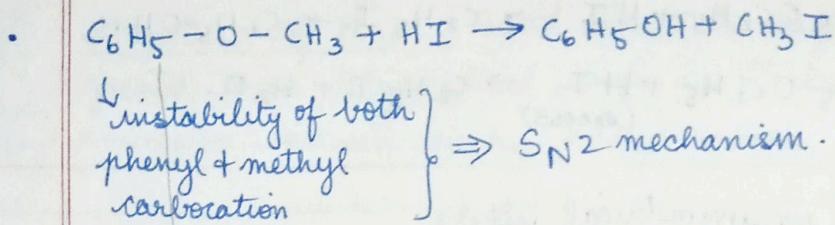
$\hookrightarrow 1^\circ \Rightarrow \text{S}_{\text{N}}2$ mechanism.



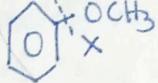
$\hookrightarrow 3^\circ \Rightarrow \text{S}_{\text{N}}1$ mechanism



$\left. \begin{array}{l} \text{stability of benzyl} \\ \text{carbocation} \end{array} \right\} \Rightarrow \text{S}_{\text{N}}1$ mechanism.

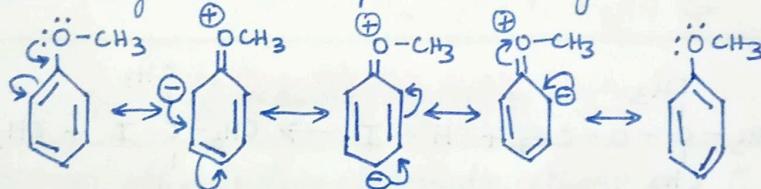


Note: $C_6H_5OH + HI \rightarrow$ no reaction
(cannot react in excess of HI to give C_6H_5I)

Why? -  partial double bond character of Csp^2-O bond, difficult to break. Hence forms alcohol

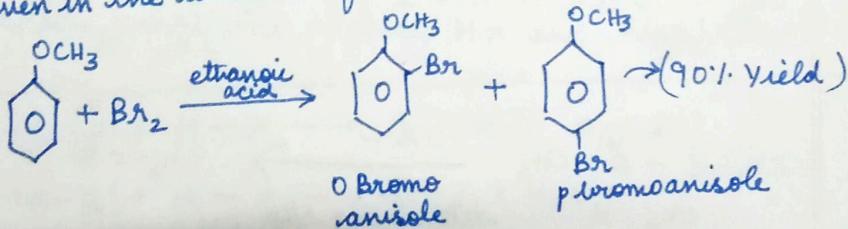
Electrophilic Substitution Reaction

Alkoxy group is an activating group due to $+R$ effect which increases density at ortho and para positions. Hence they are ortho-para directing.



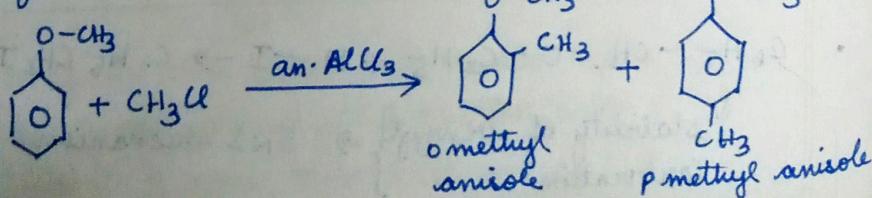
(i) Halogenation:

Even in the absence of Lewis acids, reaction proceeds.

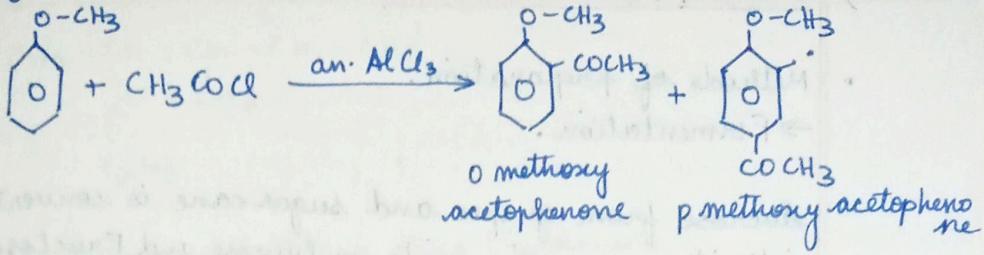


(ii) Friedel-Crafts Reaction:

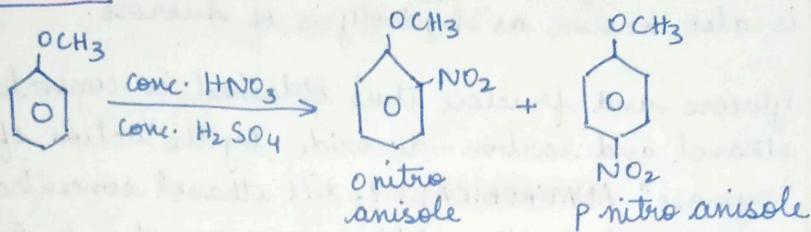
a) Alkylation:



(b) Acylation:



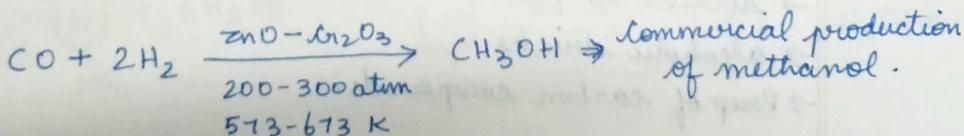
(iii) Nitration:



Some commercially important alcohols:

1) Methanol (Wood spirit):

- Methods of preparation:
 - destructive distillation of wood
 - catalytic hydrogenation of carbon monoxide.
- catalytic hydrogenation of CO at high temperature (573-673 K), high pressure (200-300 atm) and in presence of catalysts ($\text{ZnO}-\text{Cr}_2\text{O}_3$)



- colourless liquid, boils at 337 K, poisonous.
- causes blindness and even death.
- Uses:
 - solvent in paints and varnishing purposes.
 - Produces methanal - formaldehyde (HCHO)

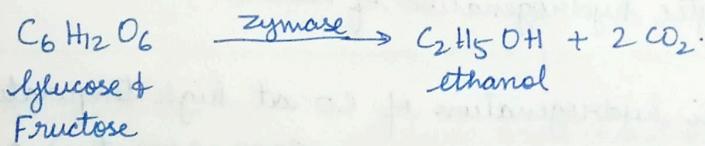
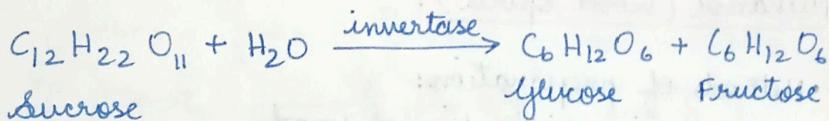
2) Ethanol (edible alcohol):

- Methods of preparation:
→ Fermentation.

sucrose from grapes and sugar cane is converted into its monomeric units - glucose and Fructose by the action of an enzyme called "invertase". This is also known as hydrolysis of sucrose.

Glucose and fructose thus obtained is converted to ethanol and carbon-di-oxide by the action of "zymase" ANAEROBICALLY, till ethanol concentration reaches 14% (after which zymase's action is inhibited by high concentrations of ethanol).

- Anaerobic conditions are ensured to avoid oxidation of ethanol to ethanoic acid.



- Uses:

- Solvent in paints
- alcoholic drinks
- Prep of carbon compounds.

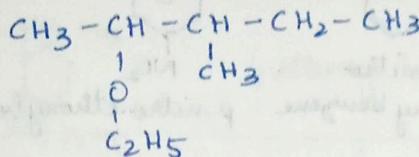
- Denatured alcohol $\Rightarrow \text{CuSO}_4 + \text{Pyridine} + \text{Ethanol}$.

becomes unfit for drinking due to foul smell of pyridine.

found in laboratories.

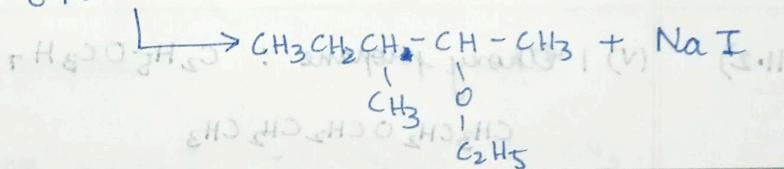
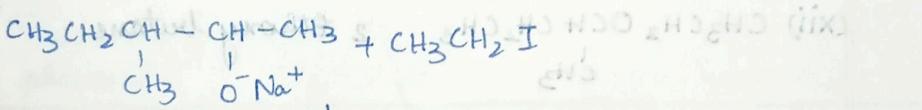
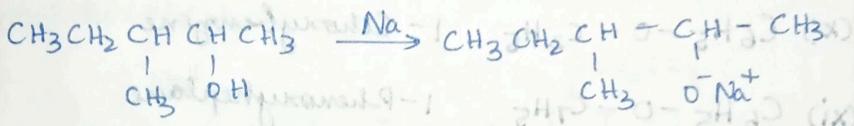
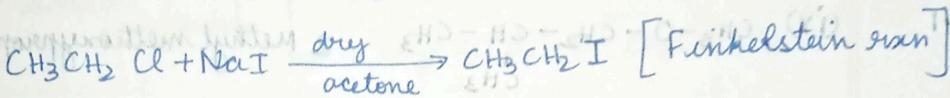
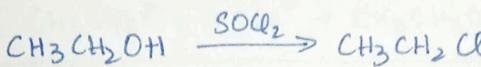
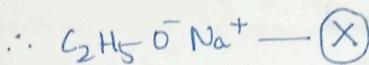
In-text Questions

II.10)

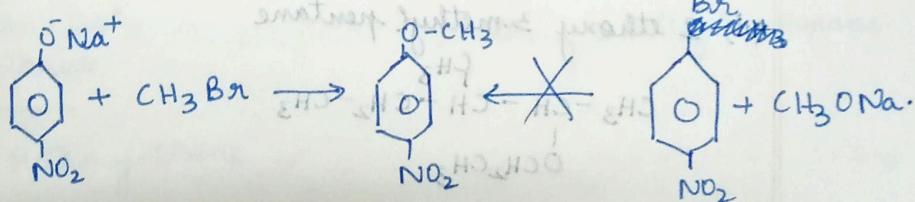


2° alkoxide - less basic than 1° alkoxide.

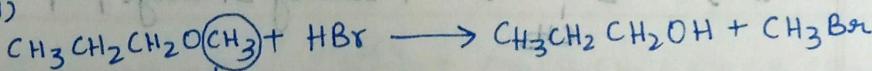
hence undergoes elimination to produce alkene.



II.11) (iii)



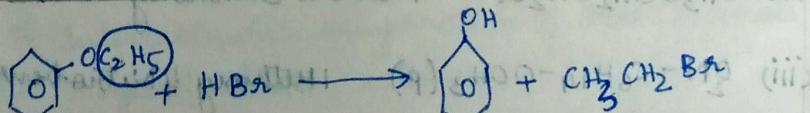
II.12) (i)



SN2

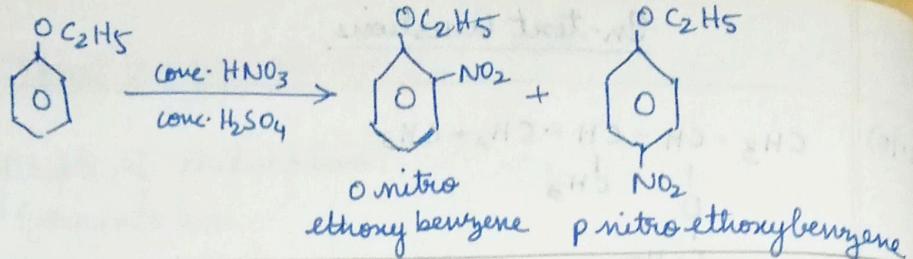
(less steric hindrance, forms CH_3X)

ii)

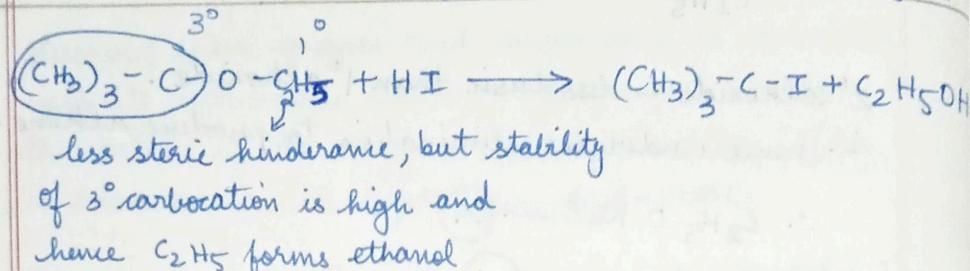


\downarrow
 C-O bond can't be broken
 due to $[\text{C}_{\text{sp}^2}\text{O}]$'s partial double bond character

(iii)

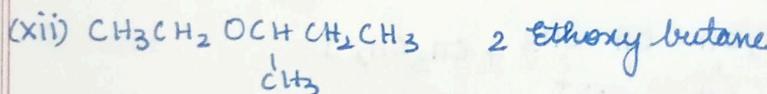
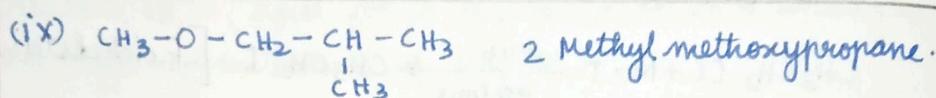


(iv)

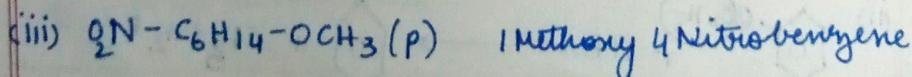
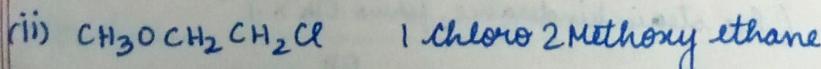
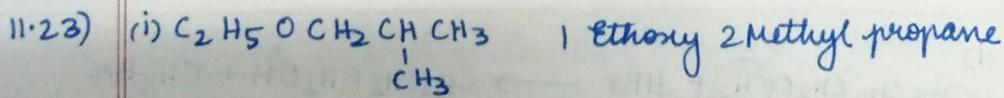
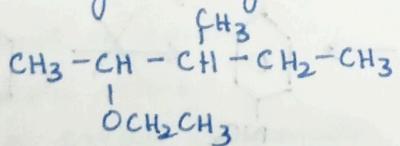
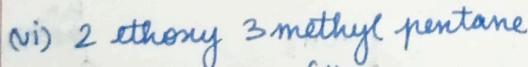
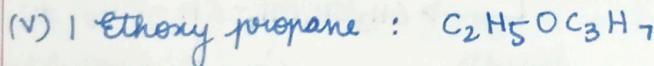


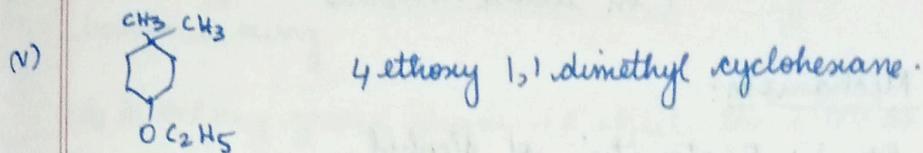
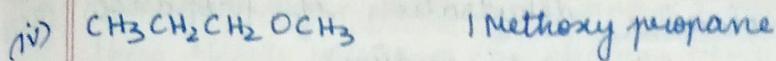
Exercises

U.1

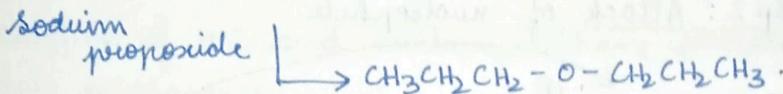
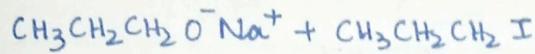


U.2)

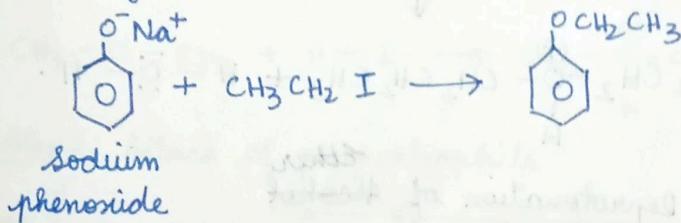




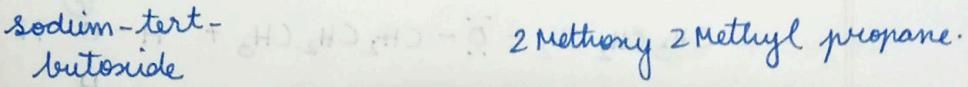
11.24) i) Propoxypyropane



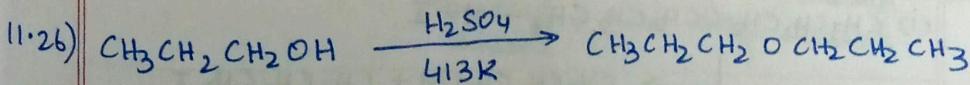
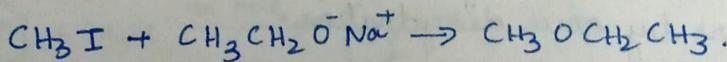
ii) Ethoxybenzene



iii) 2 Methoxy
2 Methylpropane.



iv) 1 Methoxyethane



\Rightarrow Intermolecular dehydration of Alkohols

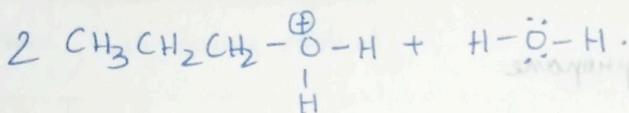
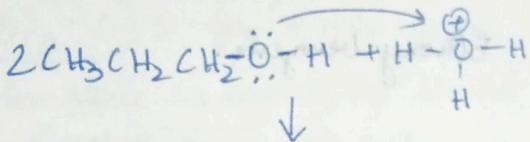
yield ethers, whereas

Intramolecular dehydration of Alcohols
yield alkenes.

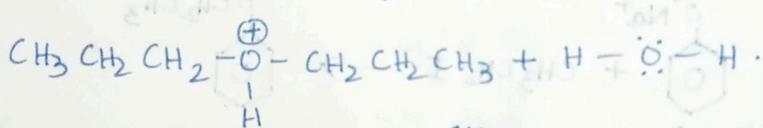
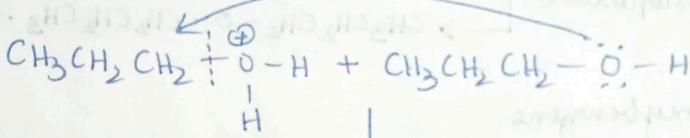
Intermolecular dehydration of propanol (in acidic medium)

Mechanism:

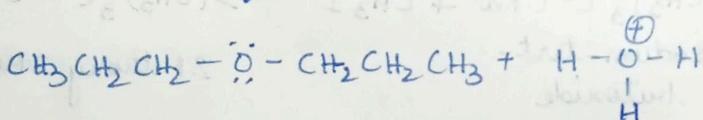
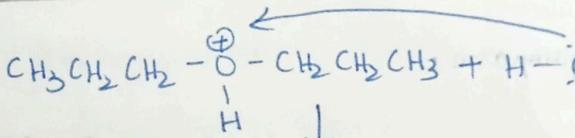
Step 1: Protonation of Alcohol



Step 2: Attack of nucleophile

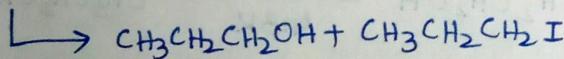


Step 3: Deprotonation of Alcohol



II.27) 2° and 3° alcohols undergo elimination to form alkenes. Hence they are not suitable in preparing ethers by acid dehydration.

II.28) (i) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_3 + \text{H}-\text{I} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{CH}_3\text{CH}_2\text{CH}_2\text{I}$

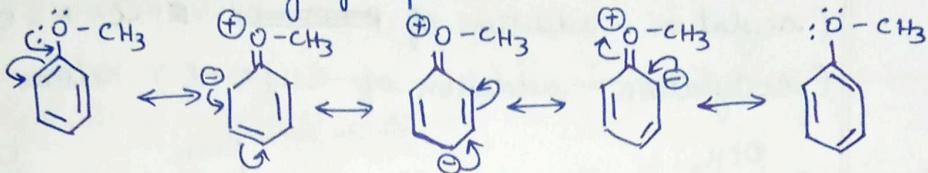


(ii) $\text{CH}_3\text{OC}_6\text{H}_5 + \text{H}-\text{I} \rightarrow \text{C}_6\text{H}_5\text{OH} + \text{CH}_3\text{I}$
phenol

(iii) $\text{C}_6\text{H}_5\text{CH}_3\text{OCH}_2\text{CH}_3 + \text{H}-\text{I} \rightarrow \text{C}_6\text{H}_5\text{CH}_3\text{I} + \text{CH}_3\text{CH}_2\text{OH}$.

- 11.29) i) Alkoxyl group shows +R and -I effect, and both these effects increase the electron density at in benzene ring.
- (ii) As Alkoxyl group shows +R effect, the electron density is increased at ortho and para positions.

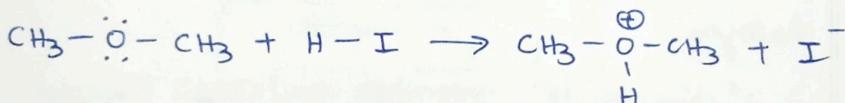
(σ and p directing group)



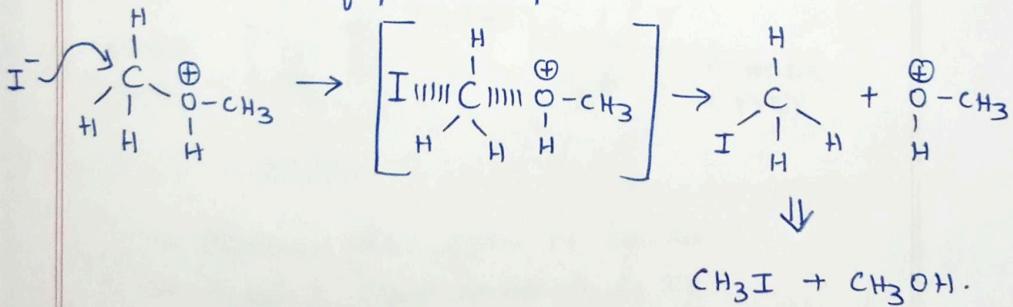
Resonance effect (+R) shown by alkoxyl group.

- 11.30) Reaction of HI and methoxymethane proceeds by S_N2 mechanism:

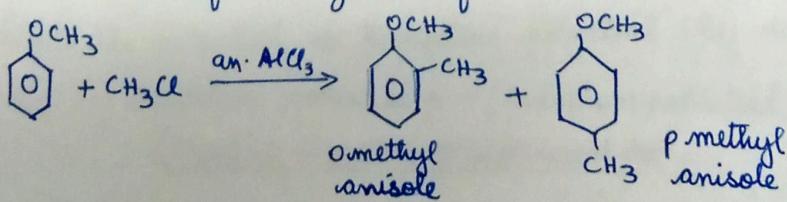
Step 1: Protonation



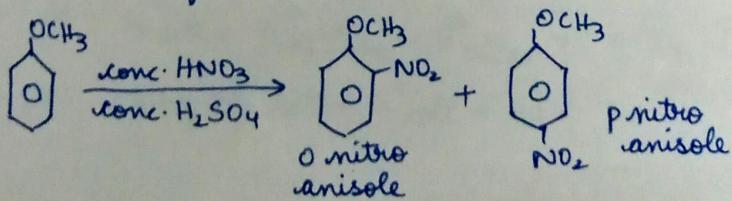
Step 2: Attack of $\rho\pi$ nucleophile



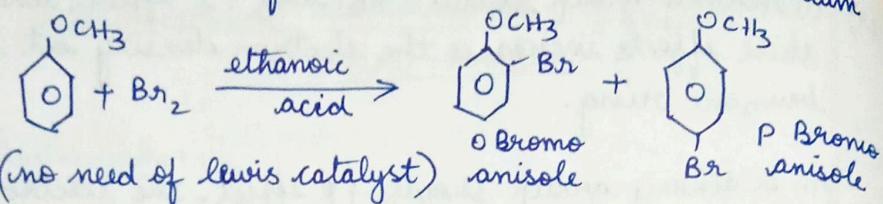
- 11.31) i) Friedel-Crafts alkylation of anisole



ii) Nitration of anisole



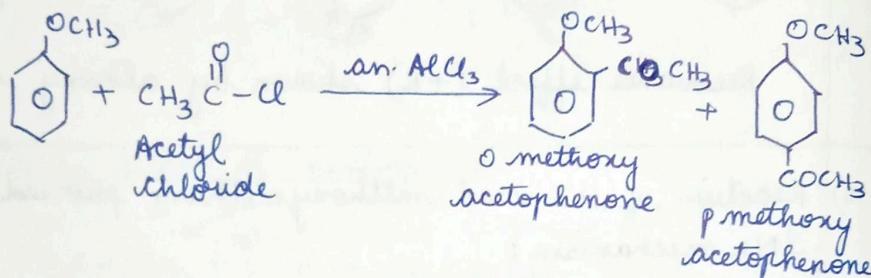
(iii) Bromination of anisole in ethanoic acid medium



(iv) Friedel-Crafts acylation of anisole.

(acylation - addition of $\text{C}_2\text{H}_5\text{COCl}$) Ketone

(acetylation - addition of CH_3COCl) Ketone



2 1° compounds - $\text{S}_{\text{N}}2$, one with less C gets the halogen.

2 2° compounds - one with less C gets halogen