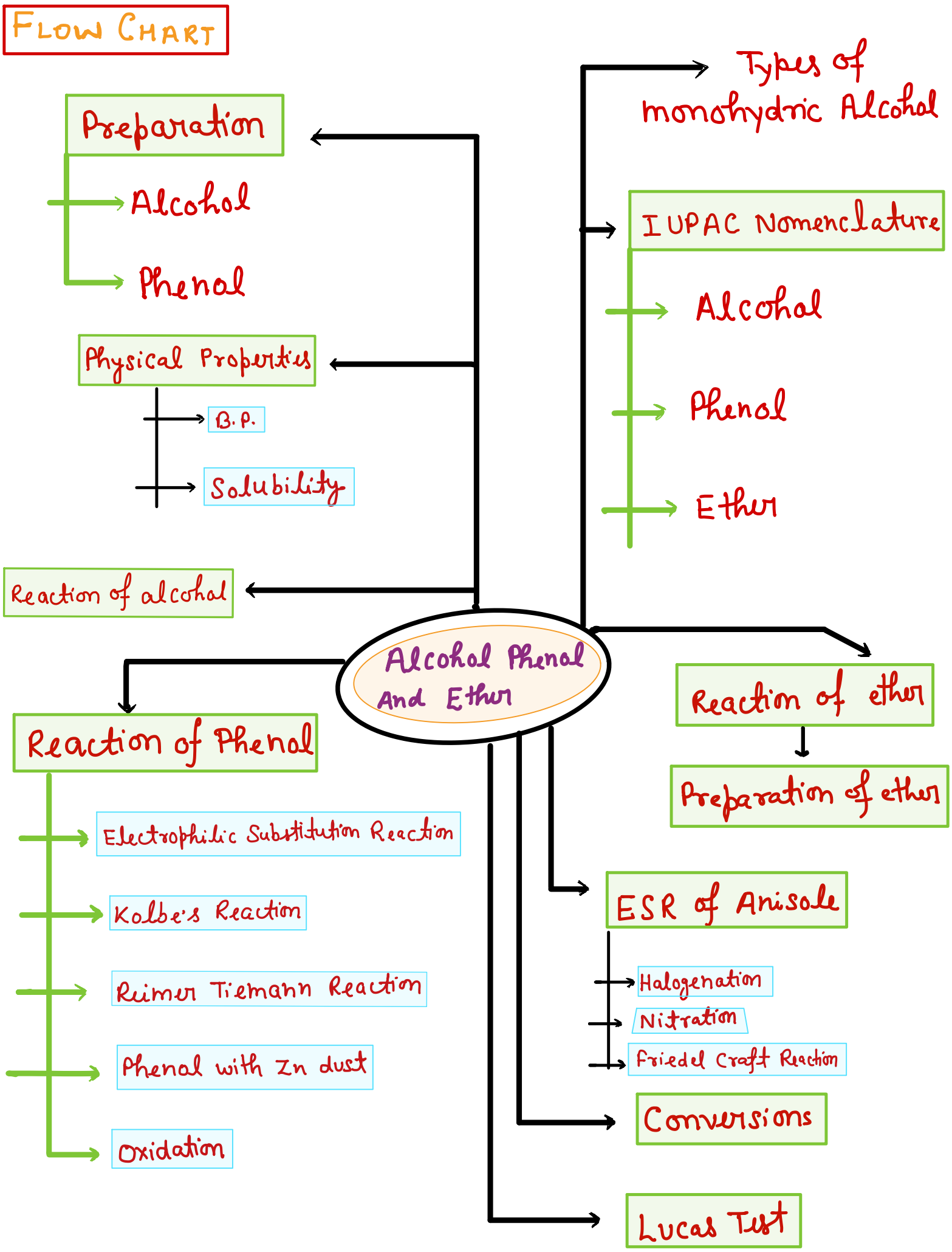
Flow Chart
Alcohol Phenol And Ether
Preparation
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Phenol
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Reaction of Phenol
Electrophilic Substitution Reaction
Kolbe's Reaction
Reimer Tiemann Reaction
Phenal with Zn dust
Oxidation
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Phenol
Ether
Reaction of ether
Preparation of ether
ESR of Anisole
Halogenation
Nitration
Friedel Craft Reaction
Conversions
Lucas Test

# Alcohols, Phenols and Ethers

$R-OH$ | $Ph-OH$ | $R-O-R'$

## Monohydric Alcohols

Compounds containing $C_{sp^3}-OH$ bond

- Primary Alcohol: $R-CH_2-OH$
- Secondary Alcohol: $R_2CH-OH$
- Tertiary Alcohol: $R_3C-OH$

### Allylic Alcohols :-

$CH_2=CH-CH_2-OH$

↳ Allylic carbon

[ Carbon next to double bond ]

### Benzylic Alcohols :-

Benzylic Carbon → $C_6H_5-CH_2-OH$

[ Carbon next to benzene ]

## IUPAC Nomenclature of Alcohols

→ The longest carbon chain is numbered starting at the end nearest to the hydroxyl group (-OH).

Alkane - e + ol = Alkanol

Examples :- $CH_3-OH$ : Methanol ( Methyl alcohol ) ; $CH_3-CH(OH)-CH_3$

↳ IUPAC ↳ Common Name

Propan-2-ol

( Isopropyl alcohol)

$(CH_3)_3C-OH$ : 2-Methylpropan-2-ol

( tert-Butyl alcohol) : [Delhi 2012] 1M

→ $C_6H_5-CH_2-CH_2-OH$ : 2-Phenylethan-1-ol → $CH_2(OH)-CH=C(CH_3)_2$ [2015] 1M

[CBSE 2016] 1M

: 3-Methylbut-2-en-1-ol

→ $CH_3-C(CH_3)_2-CH(OH)-CH_3$ : 3,3-Dimethylpentan-2-ol

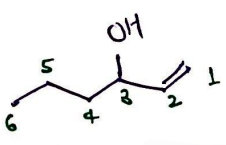
[2018] 1M

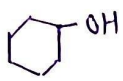
→ $CH_2(OH)-CH(OH)-CH_2(OH)$ : Propan-1,2,3-triol

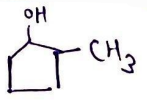
(Glycerol) 1M

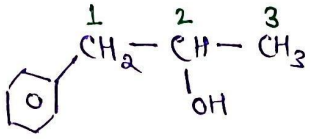
→ Hex-1-en-3-ol

Delhi 2012] 1M Structure →

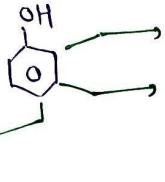


→ Cyclohexanol : 

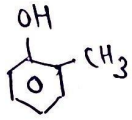
→ 2-Methyl cyclopentanol : 

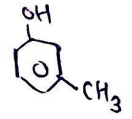
→ 1-Phenylpropan-2-ol :  (CBSE 2010) 1M

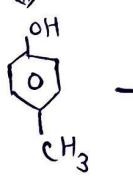
## IUPAC Nomenclature of Phenols

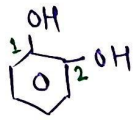
→ Phenol : 
Ortho Position
Meta Position
Para position

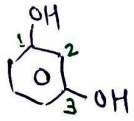
→ Cresol → 2-Methylphenol.

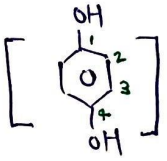
o-Cresol : 

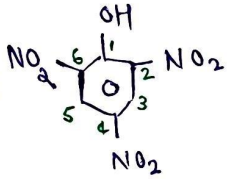
m-Cresol : 
↳ 3-Methyl phenol.

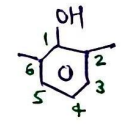
p-Cresol : 
→ 4-Methyl phenol.

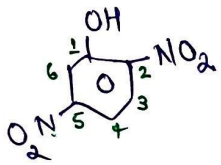
→ Catechol :  : Benzene-1,2-diol

→ Resorcinal :  : Benzene-1,3-diol

→ Quinal (Hydroquinone) : Benzene-1,4-diol 

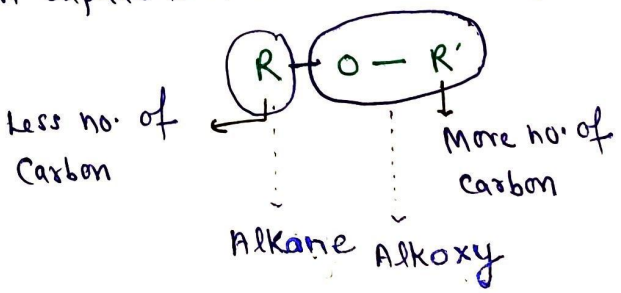
→ Picric Acid :  : 2,4,6-Trinitrophenal.

→ 
2,6-Dimethylphenol [2011] 1M

→  : 2,5-Dinitrophenol [Delhi 2015] 1M

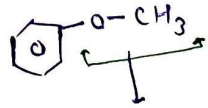
## IUPAC Nomenclature of Ethers → Alkoxy Alkane
R-O-R'

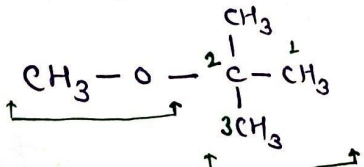
→ Common name of ethers are derived from the names of alkyl / aryl groups written as seperate words in alphabatical order and adding the word "ether" at the end.

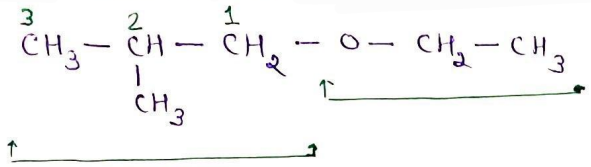


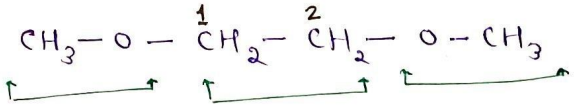

→ $CH_3-O-CH_3$ [Dimethyl ether]
Methoxymethane

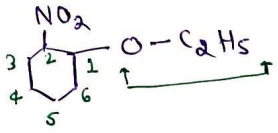
→ $CH_3-O-CH_2-CH_2-CH_3$ [Methyl n-propyl ether]
Methoxypropane

→ 
Methylphenyl ether
(Anisole) Methoxybenzene

→ 
2-Methoxy-2-methylpropane [CBSE 2017]

→  : 1 - Ethoxy - 2 - methyl propane [CBSE 2015] 1M

→  : 1, 2 - Dimethoxy ethane

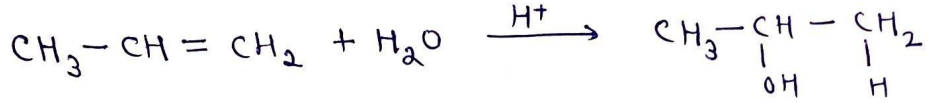
→  : 1 - Ethoxy - 2 - nitrocyclohexane [CBSE 2012C] 1M

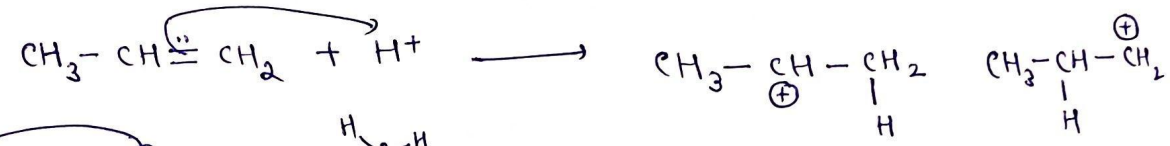
## Preparation of alcohols

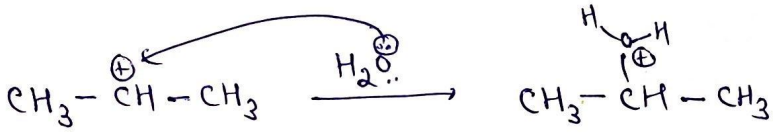
1M

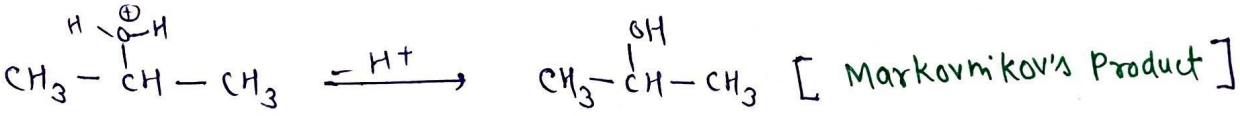
### 1.] From alkenes :-

[a.] Acid catalysed hydration :- [Delhi 2013]

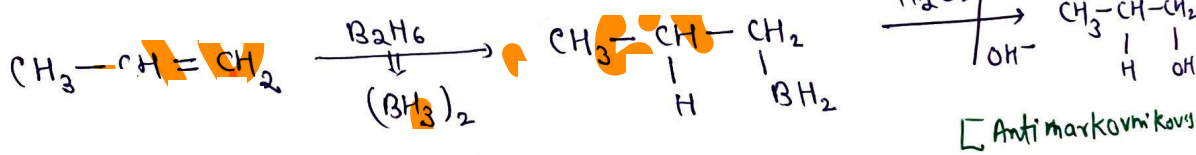
Reaction :-  Propan-2-ol

Mechanism -: (i) 

(ii)  (More stable)

(iii)  [ Markovnikov's Product ]

[b.] Hydroboration - Oxidation Method -:

Reaction : 

[Delhi 2013] 1M [CBSE 2016]

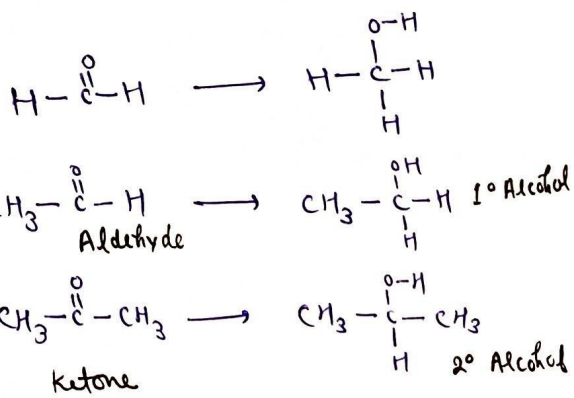
[ Anti markovnikovs Product ]

### 2.] From Carbonyl compounds -:

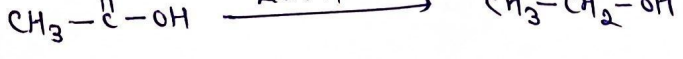
(a.) → Reduction of aldehyde and ketone :-

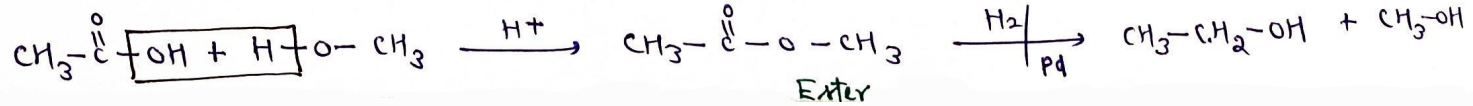
Reducing agent : $NaBH_4$ | $LiAlH_4$ | $H_2$ with Pd

Only for ketone/Aldehyde ↵ ↳ Ketone / Aldehyde / Acid Ester



(b.) → Reduction of carboxylic Acid -:

→ 

→ 

3.] From Grignard Reagents –:

Reaction : $R-\overset{\overset{O}{\|}}{C}-R + R'-Mg-X \longrightarrow R-\underset{R'}{\overset{O-MgX}{\underset{|}{C}}}-R \xrightarrow[H-OH]{H_2O} \underset{R'}{\overset{OH}{\underset{|}{R-C-R}}}$ + $Mg(OH)X$

(a) $H-\overset{\overset{O}{\|}}{C}-H$ + $CH_3MgBr \longrightarrow H-\overset{OMgBr}{\underset{CH_3}{\underset{|}{C}}}-H \xrightarrow{H_2O} H-\overset{OH}{\underset{CH_3}{\underset{|}{C}}}-H$ (1°- Alcohol)

Formaldehyde — Methylmagnesium bromide.

(b) $CH_3-\overset{\overset{O}{\|}}{C}-H + CH_3MgBr \longrightarrow CH_3-\overset{OMgBr}{\underset{CH_3}{\underset{|}{C}}}-H \xrightarrow{H_2O} CH_3-\overset{OH}{\underset{CH_3}{\underset{|}{C}}}-H$ 2°- Alcohol

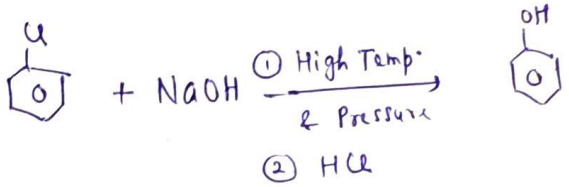
(c) $CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + CH_3MgBr \longrightarrow CH_3-\overset{OMgBr}{\underset{CH_3}{\underset{|}{C}}}-CH_3 \xrightarrow{H_2O} CH_3-\overset{OH}{\underset{CH_3}{\underset{|}{C}}}-CH_3$ 3° Alcohol

[Delhi 2010]

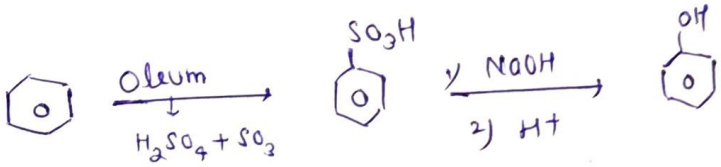
1M

## Preparation of Phenol

1. From Haloarenes –:

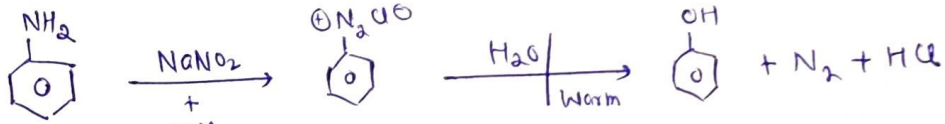



2. From Benzenesulphonic Acid –:

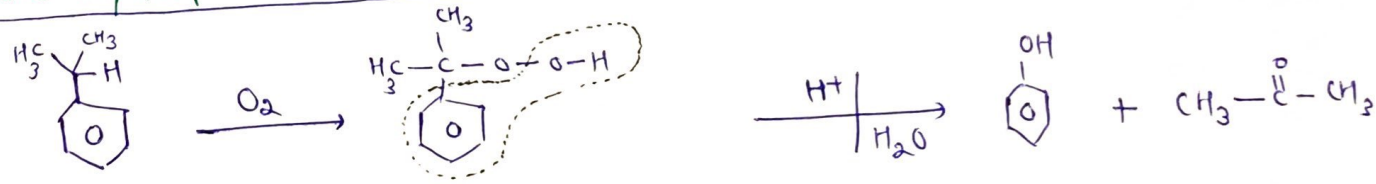



3. From diazonium salt –:

Aniline




4. Cumene Hydroperoxide Method –:




Cumene — Cumene Hydroperoxide

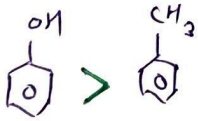
## Physical Properties

Boiling Point –: B.P. of alcohols and phenols ↑ as no. of carbon atoms increases

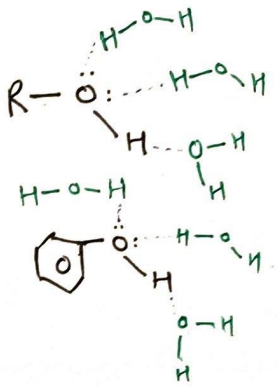
→ In alcohols –: As branching ↑es ⇒ B.P. ↓es : This is because of decrease in Vander Waals forces with decrease in surface area.

→ B.p. : $CH_3-\underset{\underset{CH_3}{|}}{\overset{CH_3}{\overset{|}{C}}}-OH$ < $CH_3-CH_2-\underset{CH_3}{\underset{|}{CH}}-OH$ < $CH_3-CH_2-CH_2-CH_2-OH$

→ B.p. of alcohols and phenols are higher in comparison to hydrocarbons, ethers haloalkanes and haloarenes of comparable molecular masses. This is because of hydrogen bonding in alcohols and phenols. [CBSE 2012] 1M

→  : B.p. similarly B.p. order : 

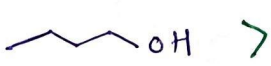
→ $CH_3-CH_2-OH$ > $CH_3-O-CH_3$ : B.p.



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

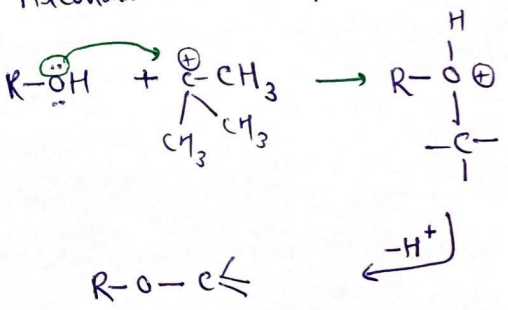
→ Solubility ↓es ⇒ size of alkyl / aryl group ↑es

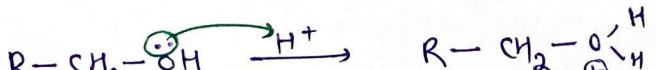
(Hydrophobic part.)

→ Solubility order :  > 

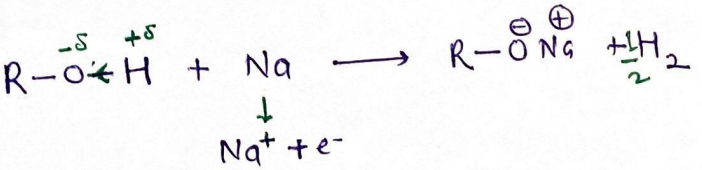
## Chemical Reactions

→ R—O—H

- Breaking of oxygen and hydrogen bond.
  - Alcohols as nucleophile :-
  
- Breaking of carbon and oxygen bond
  - Protonated alcohols as electrophiles



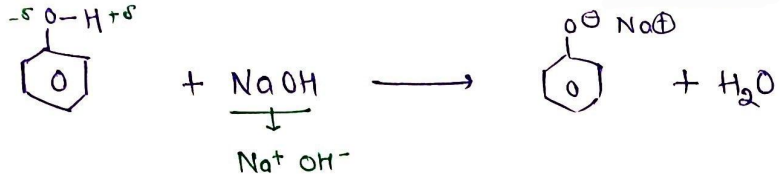
**Acidity of alcohols & phenols** –:



→ 

Phenol — Sodium Phenoxide

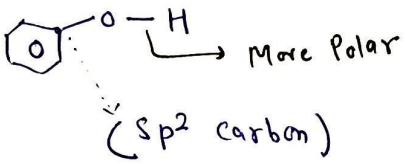
# This reaction shows that alcohols and phenols can donate $H^+$, means that they are acidic.

→ 


#] The acidic character of alcohols is due to the polar nature of −O−H bond. An electron releasing group (−$CH_3$ / −$C_2H_5$ etc.) increases electron density on oxygen trending to decrease the polarity of −O−H bond. This decrease the acidic strength.

$$R\rightarrow CH_2\rightarrow O-H \;>\; \underset{R}{\overset{R}{\searrow}}CH\rightarrow O-H \gg \underset{R}{\overset{R}{\searrow}}\underset{\uparrow R}{C}\rightarrow O-H$$

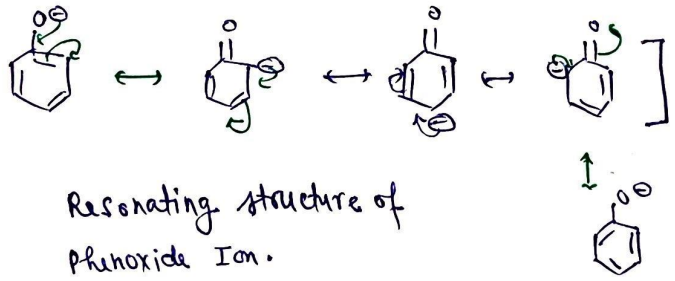
#] Phenols are more acidic than alcohols ? [CBSE 2015] (1M)

→ R−O−H and 


→ Ionisation of alcohol : $R-O-H \rightleftharpoons R-O^{\ominus} + H^+$ (This ⊖ charge is localised on oxygen atom.)

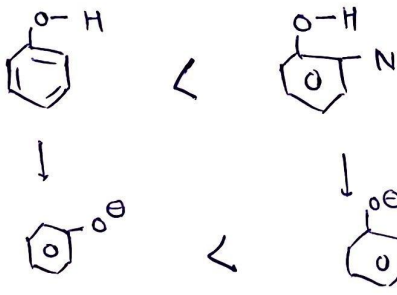
Ionisation of phenol : 


Due to resonance phenoxide is stable than alkoxide.

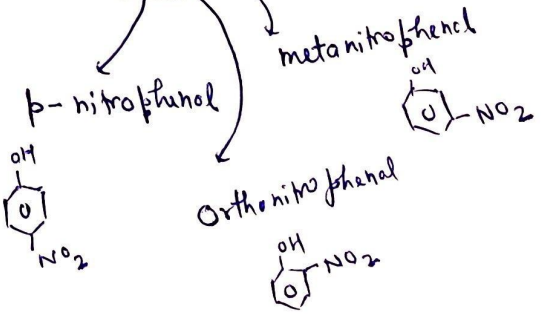


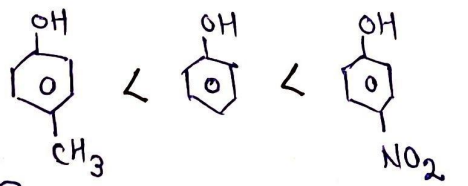
Resonating structure of phenoxide Ion.

NOTE −: In resonating structure of phenoxide ion ⊖ve charge is present at ortho and para position. So, ⊖ve charge stabilising groups (−I / −M) can increase stability of substituted phenoxide ion. Thus it can increase the acidity.

→ 

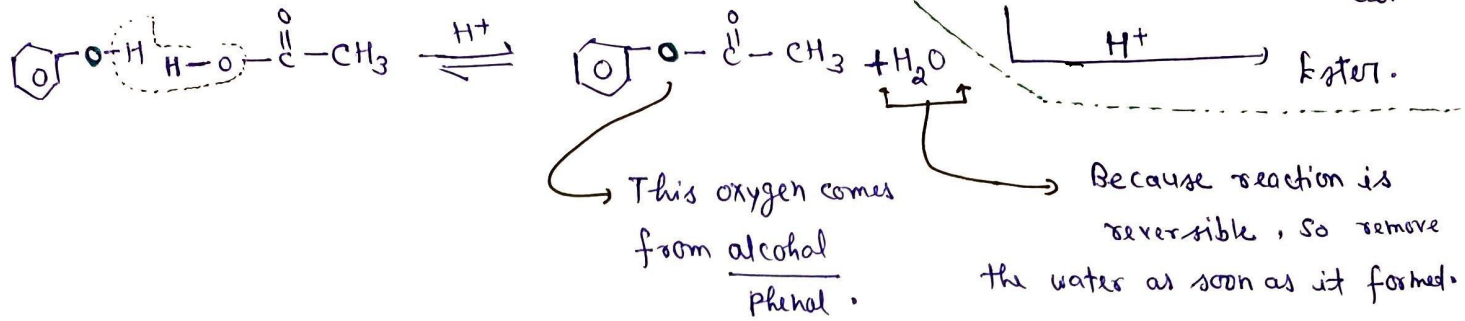

→ POM Phenol : Ka

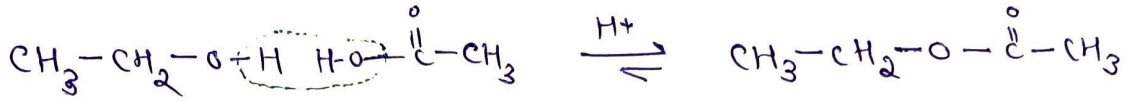


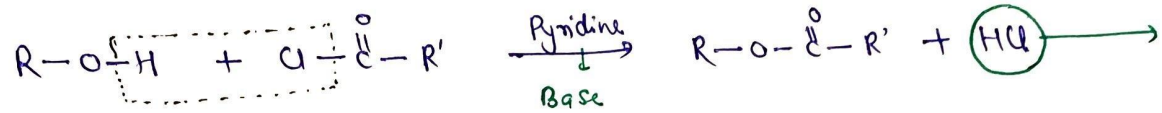

→ 

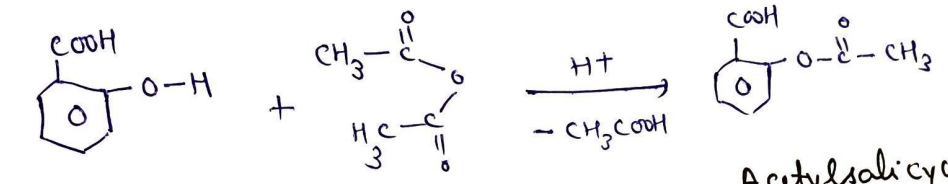

[CBSE 2017] (1M)

→ **Esterification :–** (Formation of ester) # Alcohols | Phenols + carboxylic acid or its derivatives

→ 


→ 


→ 

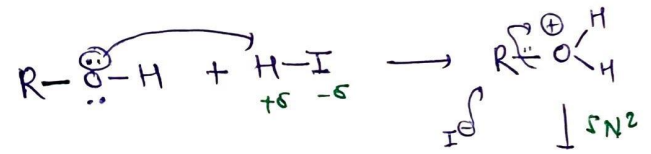

→ 


Salicylic Acid

Acetylsalicylic acid [ Aspirin ]

## Reactions involving cleavage of Carbon – oxygen bond in alcohols :–

**1. Reaction with HX [ HCl | HBr | HI ] :–**

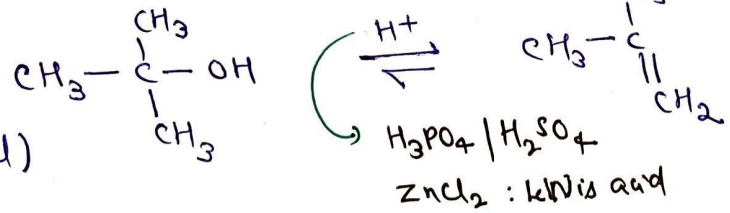


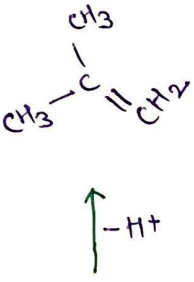

**2. Reaction with $SOCl_2$ | $PCl_3$ | $PCl_5$ :–**

$CH_3-CH_2-OH \xrightarrow[PCl_3 \text{ or } PCl_5]{SOCl_2 \text{ or}} CH_3-CH_2-Cl$ [CBSE 2015C] (1M)

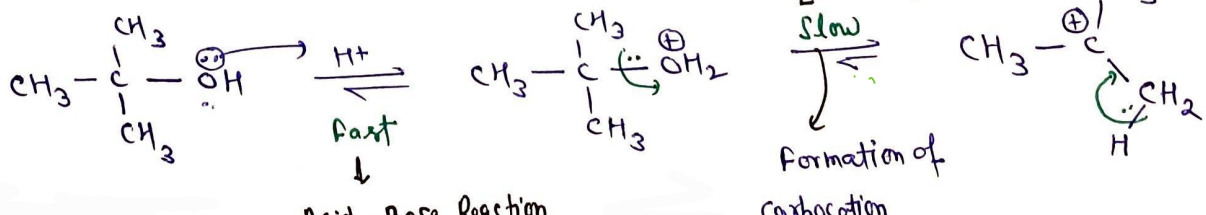
**3. Dehydration :–** [ Removal of $H_2O$ from a molecule ]

**Reaction :**




**Mechanism :–**



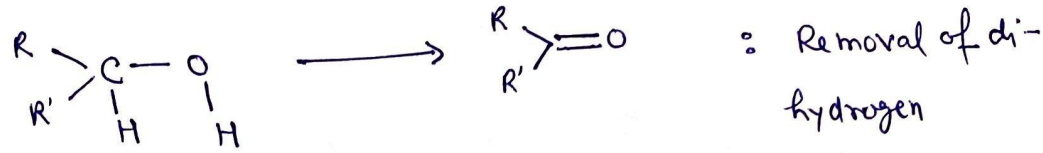
→ $CH_3-CH_2-OH \xrightarrow[\Delta]{H^+} CH_2=CH_2$

[CBSE 2019 | 2013 Delhi 2015C]

$CH_3-CH_2-OH \xrightarrow{H^+} CH_3-CH_2-\overset{\oplus}{O}H_2 \xrightarrow{(-H_2O)} CH_2-\overset{\oplus}{C}H_2 \xrightarrow{-H^+} CH_2=CH_2$

→ $CH_3-\underset{OH}{\underset{|}{CH}}-CH_3 \xrightarrow[\Delta]{85\%\ H_3PO_4} CH_3-CH=CH_2$

## 4.) Oxidation :-



: Removal of di-hydrogen ⇓ Dehydrogenation

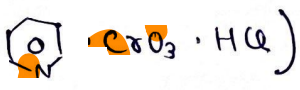
Alcohal → Ketone / Aldehyde

PCC / $CrO_3$ ← Weak oxidising agent

# 1° Alcohol → Aldehyde → Acid

Strong oxidising agent ↳ $KMnO_4/H^+$

→ $CH_3-CH_2-OH \xrightarrow{CrO_3} CH_3-\overset{O}{\overset{\|}{C}}-H$

PCC : Pyridinium Chlorochromate → (  )

$\xrightarrow[H^+]{KMnO_4}$ → $CH_3-\overset{O}{\overset{\|}{C}}-OH$

# Sec- Alcohal : $CH_3-\underset{OH}{\underset{|}{CH}}-CH_3 \xrightarrow{CrO_3} CH_3-\overset{O}{\overset{\|}{C}}-CH_3$ : Ketone.

# ter. Alcohal : $CH_3-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}-OH \xrightarrow{CrO_3} \times$ Because there is no C-H bond.

→ Cu / 300°C

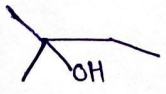
Delhi 2015

oxidation ←

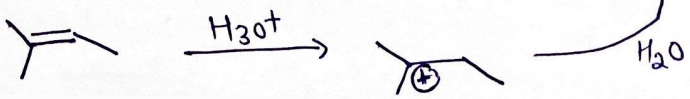
a.) $CH_3-CH_2-OH \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-H$

b.) $CH_3-\underset{OH}{\underset{|}{CH}}-CH_3 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

Dehydration : c.) $CH_3-\underset{CH_3}{\overset{CH_2-H}{\overset{|}{\underset{|}{C}}}}-OH \xrightarrow{(-H_2O)} CH_3-\underset{CH_3}{\overset{CH_2}{\overset{\|}{C}}}$

**Question :-** Alkene → 

[CBSE 2019] 1M

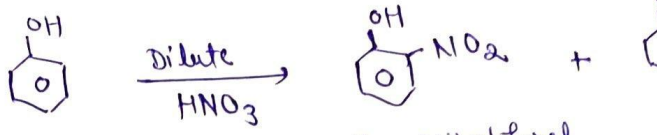


# Reactions of Phenol

① Electrophilic aromatic substitution —: Phenol and phenoxide ion, direct the incoming electrophile to ortho and para positions in the ring as these position becomes electron rich due to resonance effect caused by $-OH$ & $-O^{\ominus}$ group.

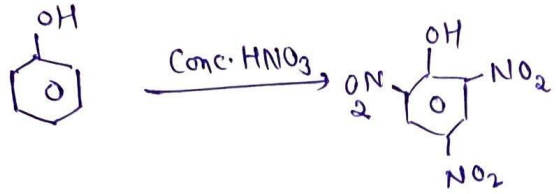
→ Nitration :—

(a)



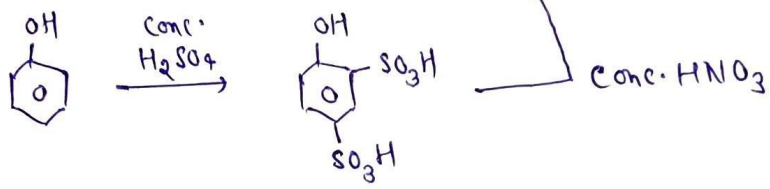

Ortho-Nitrophenol  Para-Nitrophenol

→



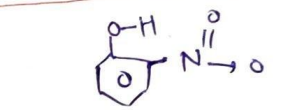

Picric acid [2, 4, 6-Trinitrophenol]

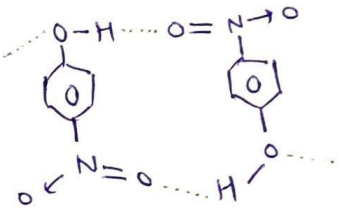
→



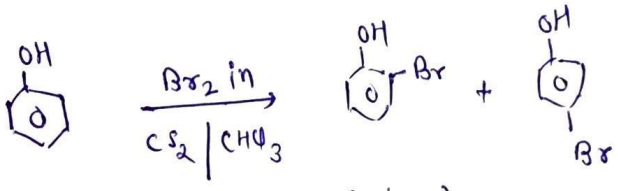

**Question :—** o-Nitrophenol is more steam volatile than p-Nitrophenol, Why? [Delhi 2019 / CBSE 2014]

**Answer —:** o-Nitrophenol is steam volatile due to intramolecular hydrogen bonding while p-nitrophenol is less volatile due to intermolecular hydrogen bonding which causes the association of molecules.

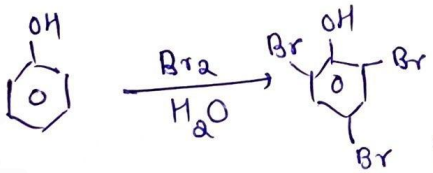


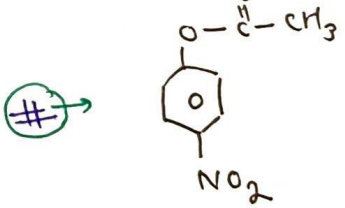

(b) Halogeration :—




(Minor)  (Major)



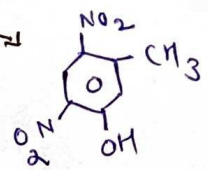

white ppt of [2, 4, 6-Tribromophenol]



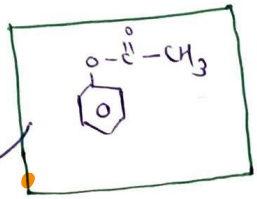

→


Dinitration

→



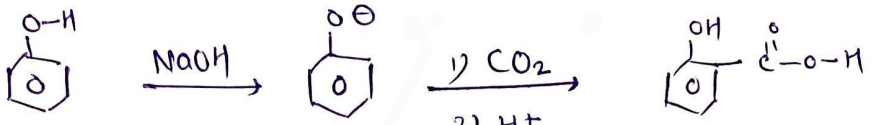

Conc. $HNO_3$




Phenyl methanoate

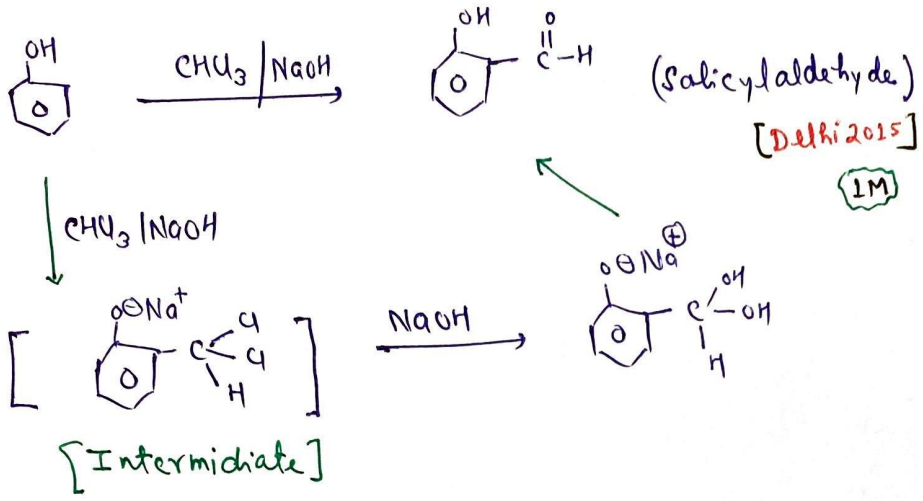
2.) **Kolbe's Reaction** :-

[Delhi 2014C] (1M)




2-Hydroxy benzoic acid
(Salicylic acid)

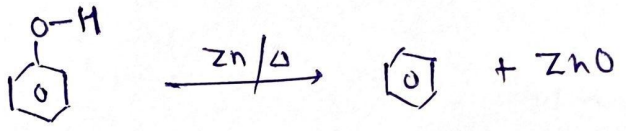
3. **Reimer-Tiemann Reaction** :-



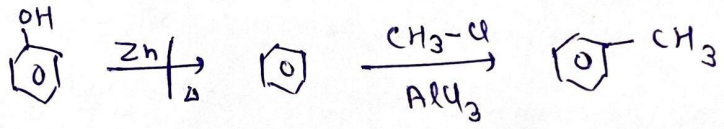

# On treating phenol with chloroform and NaOH, a $-\overset{O}{\overset{\|}{C}}-H$ group is introduced at ortho position of benzene ring. This reaction is known as RT Reaction.

(1M) [ 2011 | 2012 | 2019 ] CBSE

4. **Phenol with Zn dust** :-

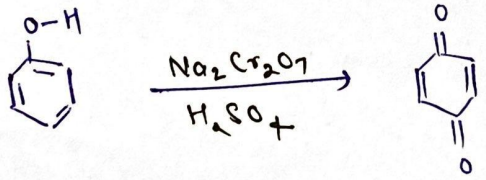



→ Phenol to toluene :




[Delhi 2013C]
(1M)

5. **Oxidation** :-




Benzoquinone

## Ethers

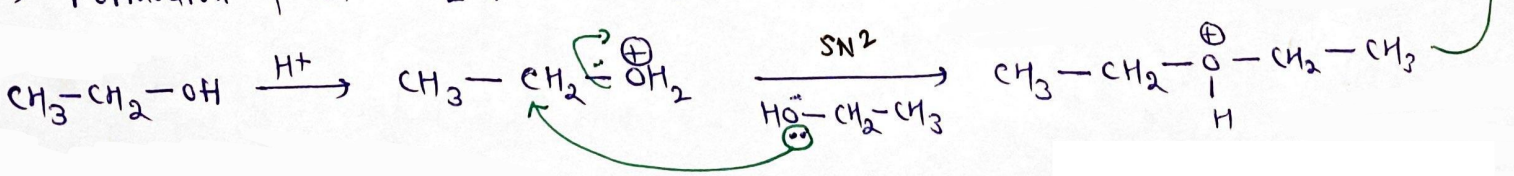
**Prepration of ethers** :-

1. **By dehydration of alcohols** :-

$$CH_3-CH_2-OH \xrightarrow[170^\circ C]{\text{Conc. } H_2SO_4} CH_2=CH_2$$

$$CH_3-CH_2-\overset{+}{O}H_2 \; HO^- + CH_2-CH_3 \xrightarrow[140^\circ C]{\text{Conc. } H_2SO_4} CH_3-CH_2-O-CH_2-CH_3$$

→ Formation of ether [Mechanism]



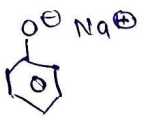
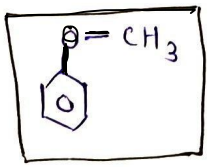
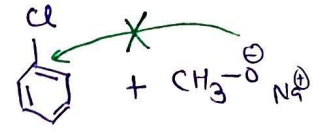
## ② Williamson Synthesis —:

**Alkyl halide + Sodium Alkoxide ⟶ Ether**

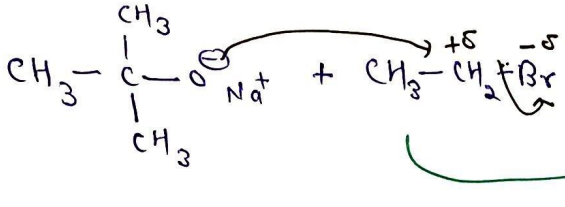
→ $R-X + R'-O^{\ominus}Na^{\oplus} \longrightarrow R-O-R' + NaX$ (1M)

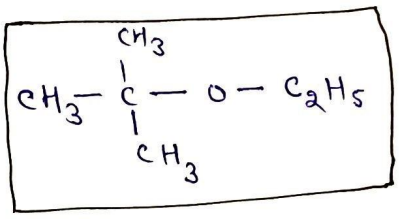
[Delhi 2010, CBSE 2010]

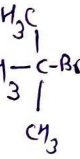
($R$ = Methyl | 1°/2°) ($R'$ = Phenyl | 1°/2°/3°/Methyl)

⇒  + $CH_3-Br$ ⟶  ⟵ 

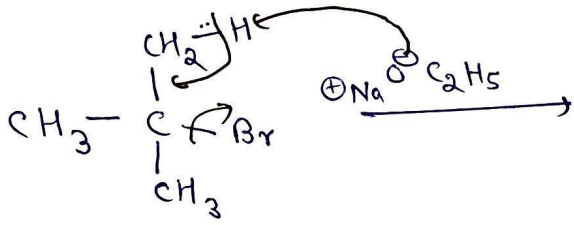
→ $CH_3-CH_2-O^{\ominus}Na^{\oplus} + CH_3-\overset{\delta+}{CH_2}\overset{\delta-}{\cdots}Br \longrightarrow CH_3-CH_2-O-CH_2-CH_3$

→ 



⟵ $C_2H_5-O^{\ominus}Na^{+}$ + 

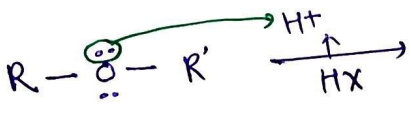
3° Alkyl Halide

→ 

Alkene

## Chemical Reaction of ether

→ $R-O-R' + HX \longrightarrow R-X + R'-OH$

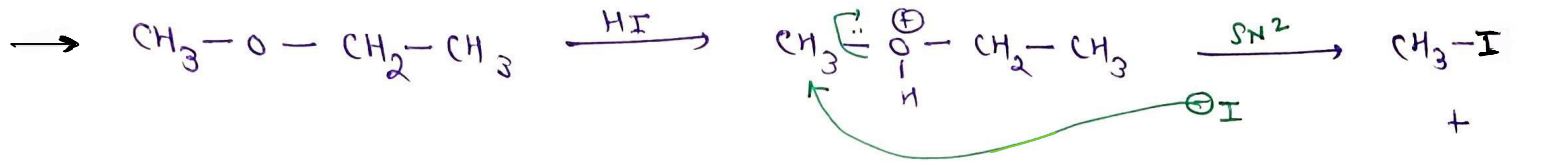
Mechanism —: 

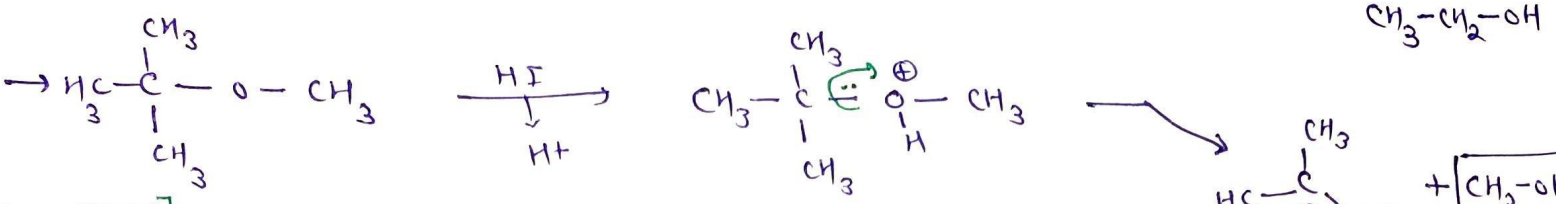
If R' is a small alkyl group then → $S_N2$ → $R'-X$ + $R-OH$

If R or R' is 3° alkyl halide → $S_N1$ → $R^+$ + $R'-OH$

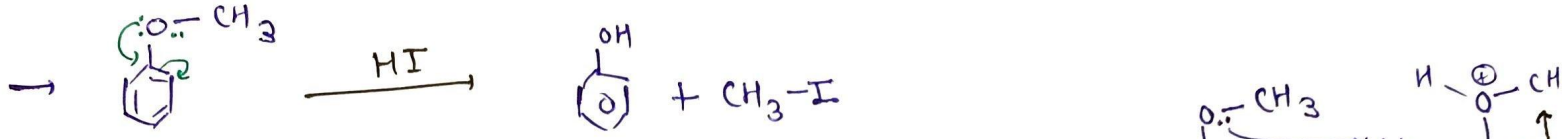
[If R is 3° alkyl group] → $R^+ + X^{\ominus}$ → $R-X$

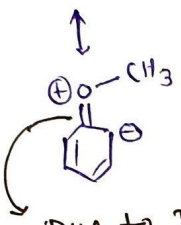
→ $CH_3-O-CH_3 \xrightarrow[H^+]{HI} CH_3-\overset{\oplus}{O}(H)-CH_3 \xrightarrow{I^{\ominus}} CH_3-I + CH_3-OH$



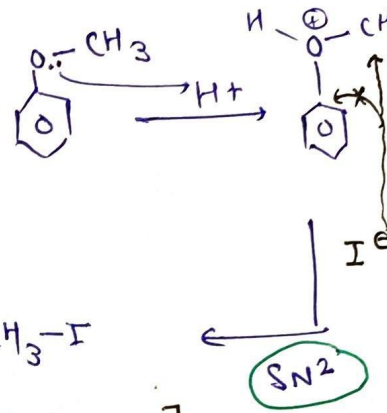

[CBSE 2015] 1M

Due to Double bond character it is tough to break this bond.

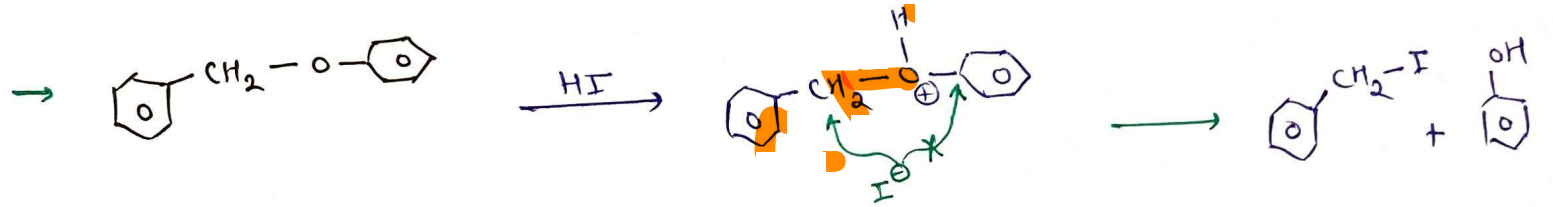
Mechanism-:





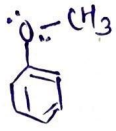


[Delhi 2010C]



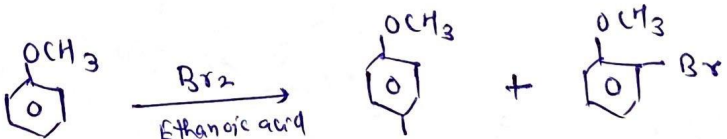

## Electrophilic Substitution Reaction of Anisol

→ **Anisol** :



(−O−CH3 is a +M group which is ortho − para directing in nature)

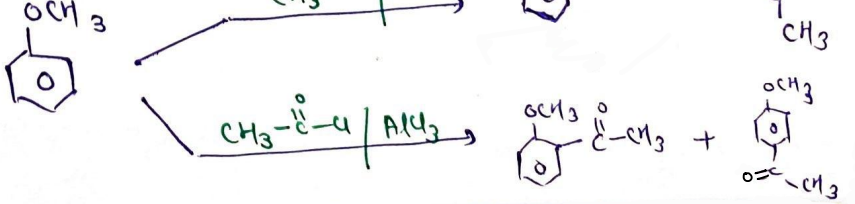
q.> **Halogenation** :




(Major) (Minor)

[Delhi 2015C] 1M

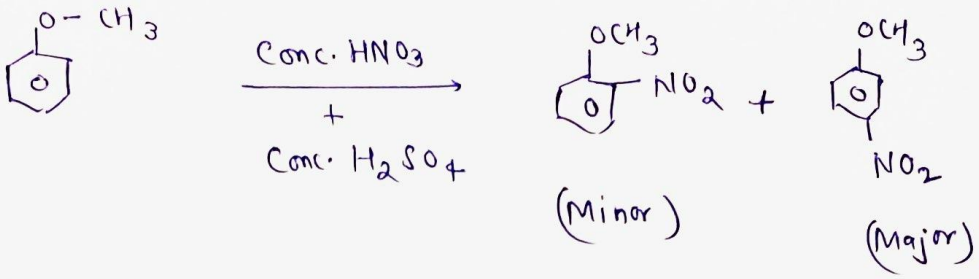
b.> **Friedel Crafs reaction** −:




Minor Major

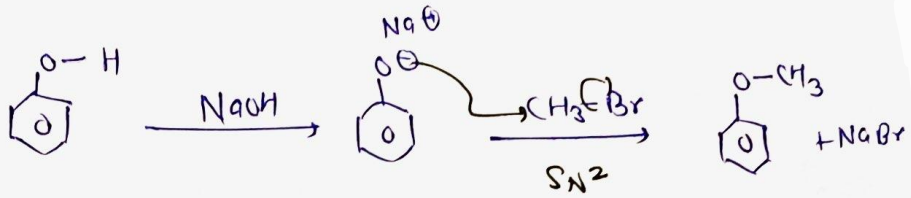
[ Delhi 2011 / 2010] 1M

c.) **Nitration :—**

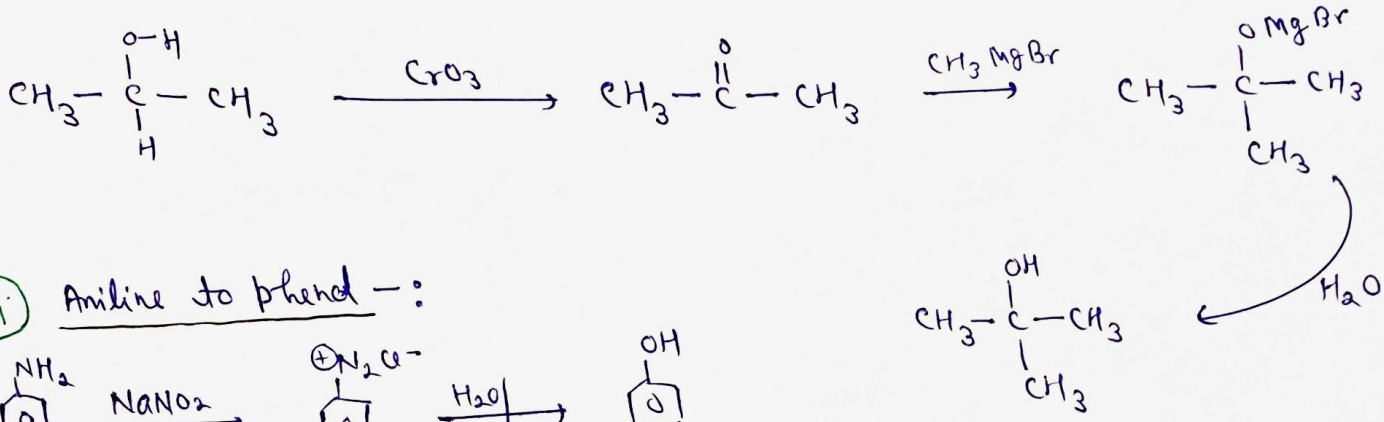



## Conversions

(i) **Phenol to anisole :—**




(ii) **Propan-2-ol to 2-methyl propan-2-ol :—**



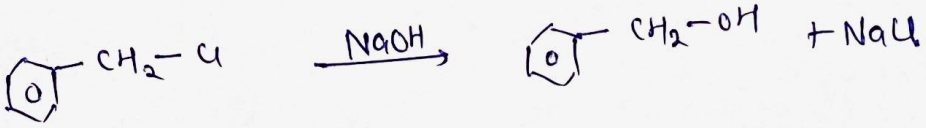

(iii) **Aniline to phenol —:**




Above three ← [ Delhi 2015 ]

3M

(iv) Benzyl chloride ⟶ Benzyl Alcohol




**Lucas Test** → To differ. 1°/2°/3° Alcohol

→ phenol does not give this test.

**Lucas Reagent** → $ZnCl_2$ + HCl

(1) $R-CH_2-OH \xrightarrow[HCl]{ZnCl_2} R-CH_2-Cl$ → Turbidity after 30 min.

(2) $R-\underset{\underset{R}{|}}{CH}-OH \xrightarrow[HCl]{ZnCl_2} R-\underset{\underset{R}{|}}{CH}-Cl$ : Turbidity within 5 min.

(3) $R-\overset{\overset{R}{|}}{\underset{\underset{R}{|}}{C}}-OH \xrightarrow[HCl]{ZnCl_2} R-\overset{\overset{R}{|}}{\underset{\underset{R}{|}}{C}}-Cl$ : Turbidity with second.

# Commercial use of Ethanol & Methanol

Methanol and ethanol are among the two commercially important alcohols.

## 1. Methanol

Methanol, $CH_3OH$, also known as 'wood spirit', was produced by destructive distillation of wood. Today, most of the methanol is produced by catalytic hydrogenation of carbon monoxide at high pressure and temperature and in the presence of $ZnO - Cr_2O_3$ catalyst.

$$CO + 2H_2 \xrightarrow[\substack{200\text{-}300\ atm\\ 573\text{-}673\ K}]{ZnO\text{-}Cr_2O_3} CH_3OH$$

Methanol is a colourless liquid and boils at 337 K. It is highly poisonous in nature. Ingestion of even small quantities of methanol can cause blindness and large quantities causes even death. Methanol is used as a solvent in paints, varnishes and chiefly for making formaldehyde.

## 2. Ethanol

Ethanol, $C_2H_5OH$, is obtained commercially by fermentation, the oldest method is from sugars. The sugar in molasses, sugarcane or fruits such as grapes is converted to glucose and fructose, (both of which have the formula $C_6H_{12}O_6$), in the presence of an enzyme, invertase. Glucose and fructose undergo fermentation in the presence of another enzyme, zymase, which is found in yeast.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{Invertase} \underset{Glucose}{C_6H_{12}O_6} + \underset{Fructose}{C_6H_{12}O_6}$$

$$C_6H_{12}O_6 \xrightarrow{Zymase} 2C_2H_5OH + 2CO_2$$

In wine making, grapes are the source of sugars and yeast. As grapes ripen, the quantity of sugar increases and yeast grows on the outer skin. When grapes are crushed, sugar and the enzyme come in contact and fermentation starts. Fermentation takes place in anaerobic conditions i.e. in absence of air. Carbon dioxide is released during fermentation.