Alcohol Phenol & Ether

Class XII
Board Exam

↳ These notes have been verified by top faculties & CBSE Science Toppers

↳ As per updated syllabus

↳ Target 100
↳ Previous Year Q's

Jao Ab Phodo !

Aman Dhattarwal

Flow Chart

Alcohol Phenol And Ether

- Preparation
  - Alcohol
  - Phenol
- Physical Properties
  - B.P.
  - Solubility
- Reaction of alcohal
- Reaction of Phenol
  - Electrophilic Substitution Reaction
  - Kolbe's Reaction
  - Reimer Tiemann Reaction
  - Phenal with Zn dust
  - Oxidation
- Types of monohydric Alcohal
- IUPAC Nomenclature
  - Alcohol
  - Phenol
  - Ether
- Reaction of ether
  - Preparation of ether
- ESR of Anisole
  - Halogenation
  - Nitration
  - Friedel Craft Reaction
- Conversions
- Lucas Test

Alcohols, Phenols and Ethers

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

Apni Kaksha

Monohydric Alcohols

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

- Primary Alcohol: $R-CH_2-OH$
- Secondary Alcohol: $R-CH(R)-OH$
- Tertiary Alcohol: $R-C(R)(R)-OH$
- Allylic Alcohols :- CH_2-OH (Allylic carbon) [Carbon next to double bond]
- Benzylic Alcohols :- $C_6H_5-CH_2-OH$ (Benzylic Carbon) [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

$CH_3-C(CH_3)(CH_3)-OH$: 2-Methylpropan-2-ol (tert-Butyl alcohol) : [Delhi 2012] 1M

Propan-2-ol (Isopropyl alcohol)

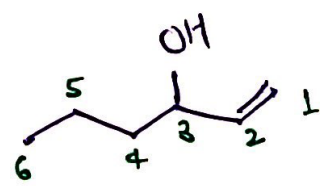
→ $C_6H_5-CH_2-CH_2-OH$: 2-Phenylethan-1-ol [CBSE 2016] 1M

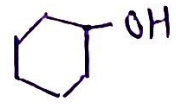
→ $CH_3-CH=C(CH_3)-CH_2-OH$: 3-Methylbut-2-en-1-ol [2015] 1M

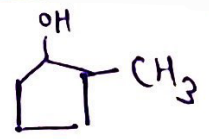
→ $CH_3-C(CH_3)(CH_2CH_3)-CH(OH)-CH_3$: 3,3-Dimethylpentan-2-ol [2018] 1M

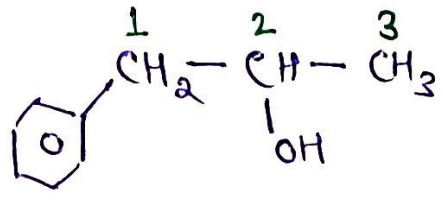
→ $CH_2(OH)-CH(OH)-CH_2(OH)$: Propan-1,2,3-triol (Glycerol) 1M

→ Hex-1-en-3-ol [Delhi 2012] 1M Structure →

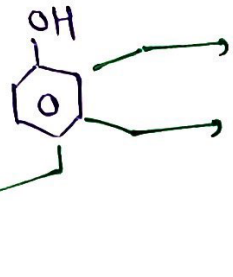


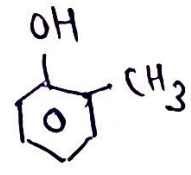
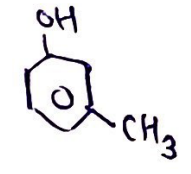
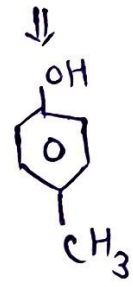
→ Cyclohexanol : 

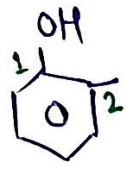
→ 2-Methyl cyclopentanol : 

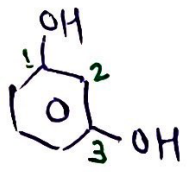
→ 1-Phenylpropan-2-ol :  (CBSE 2010) 1M

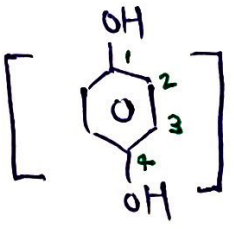
IUPAC Nomenclature of Phenols

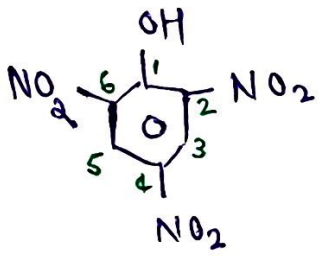
→ Phenal : 
Ortho Position
Meta Position
Para position

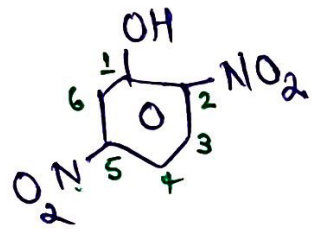
→ Cresol
- 2-Methylphenal
- o-Cresol : 
- m-Cresol : 
  → 3-Methyl phenal.
- p-Cresol : 
  → 4-Methyl phenal.

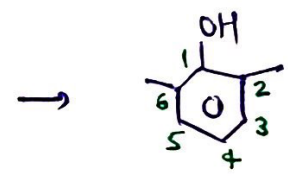
→ Catechol :  : Benzene-1,2-diol

→ Resorcinal :  : Benzene-1,3-diol

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

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

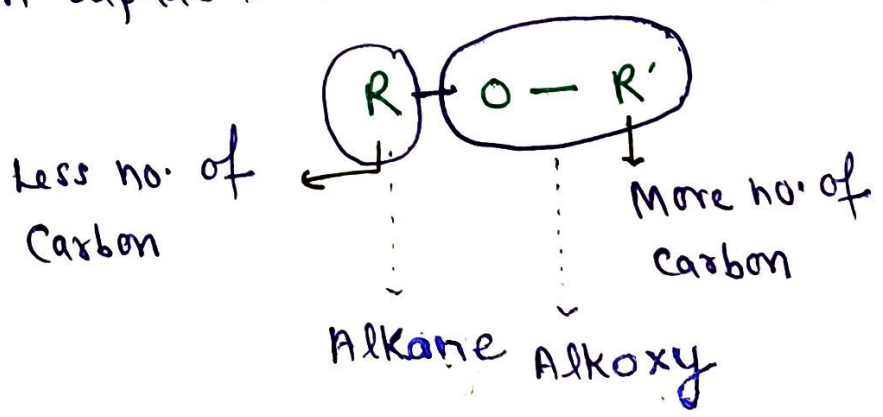
→  : 2,5-Dinitrophenol [Delhi 2015] 1M

→ 
2,6-Dimethylphenol
[2011] 1M

IUPAC Nomenclature of Ethers → Alkoxy Alkane

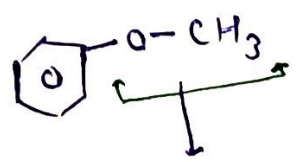
R—O—R'

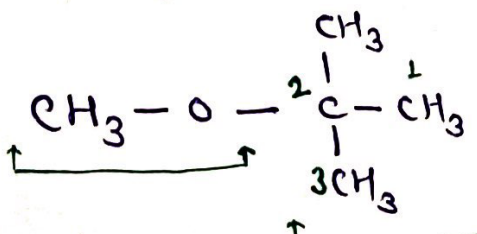
→ Common name of ethers are derived from the names of alkyl/aryl groups written as seperate words in alphabatical order and adding the word "ether" at the end.

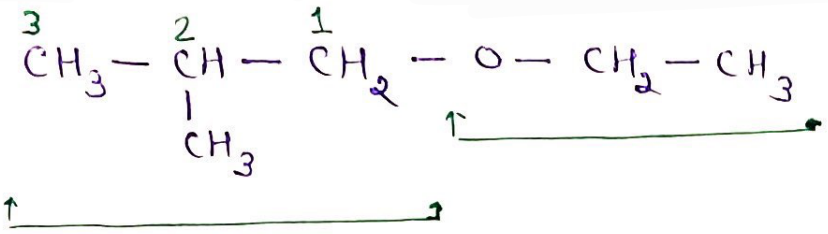


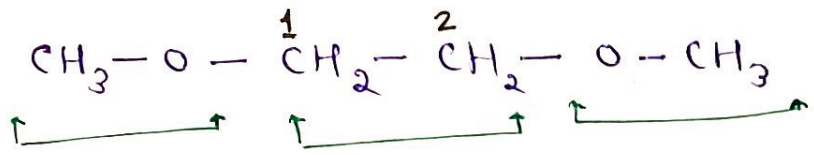
→ CH_3-O-CH_3 [Dimethyl ether]
Methoxy methane

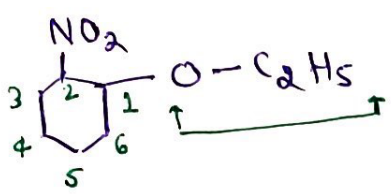
→ $CH_3-O-CH_2-CH_2-CH_3$ [Methyl n-propyl ether]
Methoxy propane

→  Methylphenyl ether
(Anisole) Methoxy benzene

→  2-Methoxy-2-methylpropane
[CBSE 2017] 1M

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

→  : 1, 2 - Dimethoxy ethane

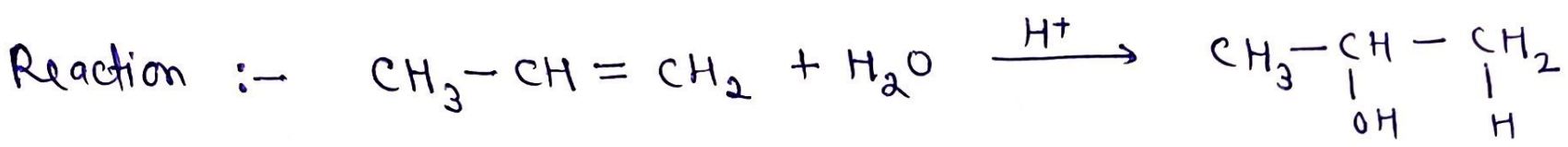
→  : 1 - Ethoxy - 2 - nitro cyclohexane [CBSE 2012 C] 1M

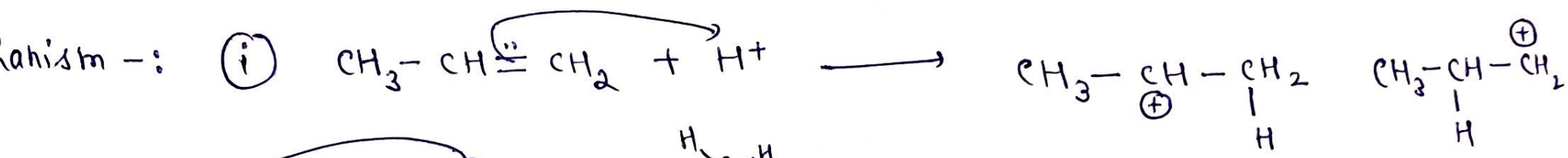
Preparation of alcohols

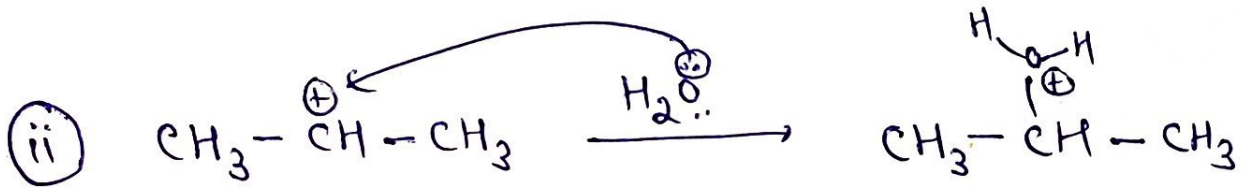
1M

1.] From alkenes :-

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

Reaction :- 

Mechanism -: (i) 

(ii)  (More stable)

(iii)  [Markovnikov's Product]

[b.] Hydroboration - Oxidation Method -:

Reaction : 

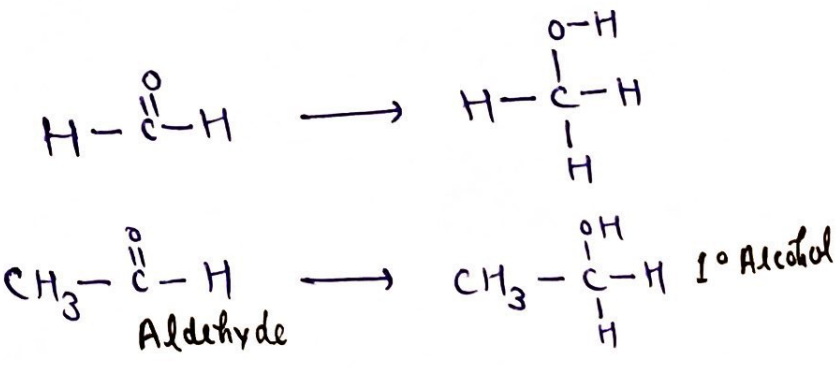
[Delhi 2013] 1M [CBSE 2016]

2.] From Carbonyl compounds -:

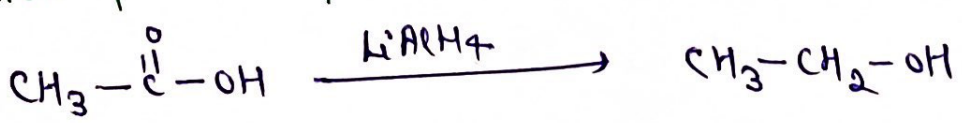
(a.) → Reduction of aldehyde and ketone :-

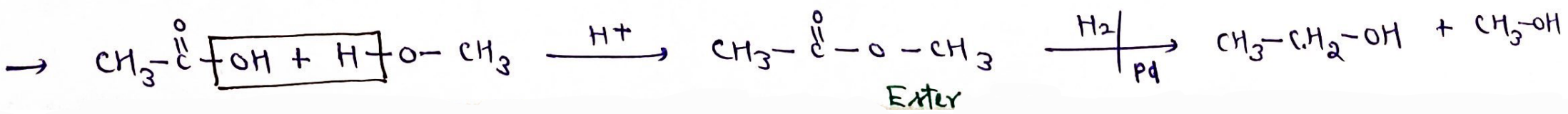
Reducing agent : $NaBH_4$ | $LiAlH_4$ | H_2 with Pd

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

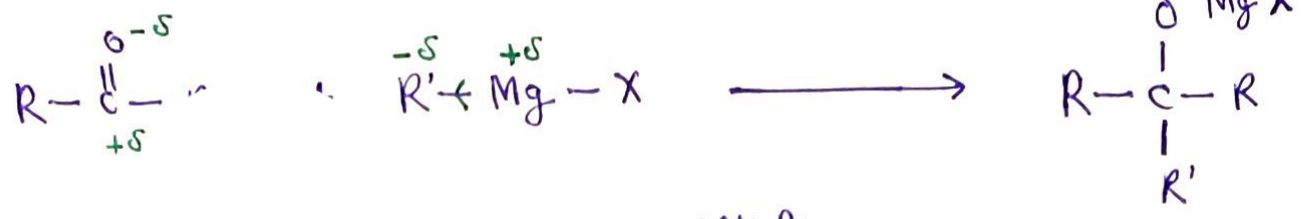


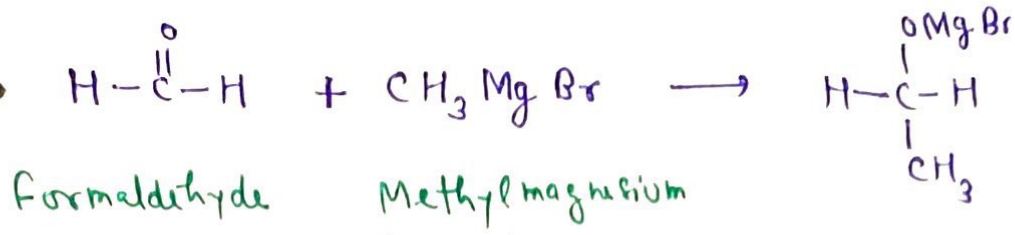
(b.) → Reduction of Carboxylic Acid -:

→ 

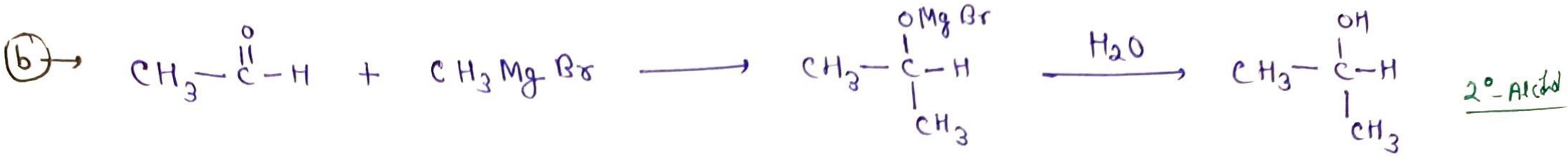
→ 

3.] From Grignard Reagents –:

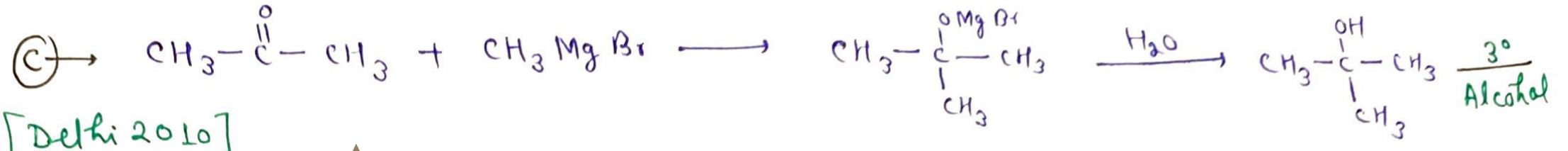
Reaction : 

(a) → 

Formaldehyde — Methylmagnesium bromide.

(b) → 

2° Alcohol

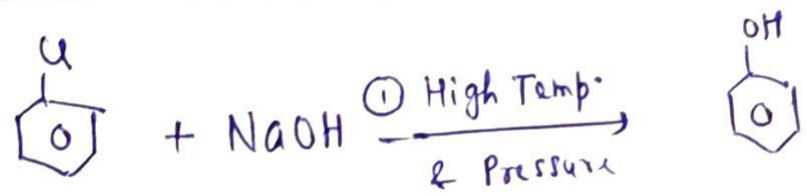
(c) → 

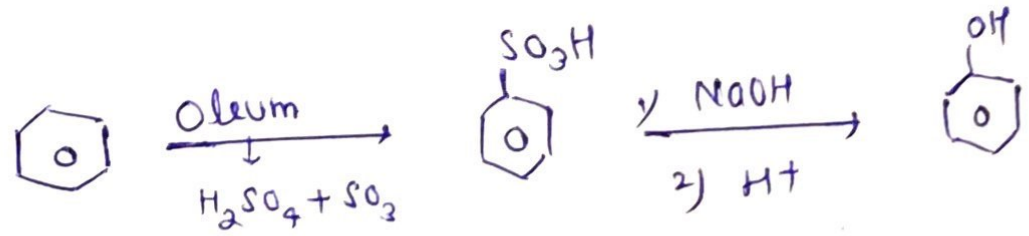
3° Alcohol

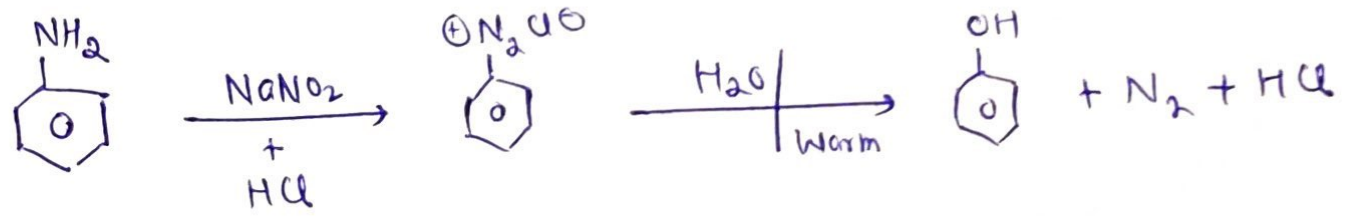
[Delhi 2010]

1M

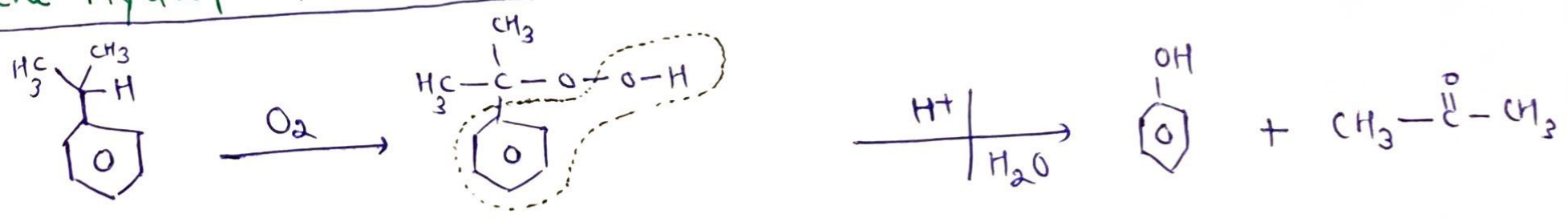
Preparation of Phenol

1. From Haloarenes –: 

2. From Benzenesulphonic Acid –: 

3. From diazonium salt –: 

Aniline

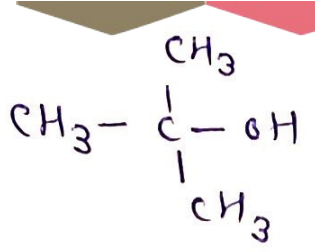
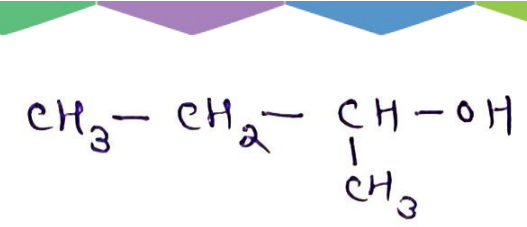
4. Cumene Hydroperoxide Method –: 

Cumene — Cumene Hydroperoxide

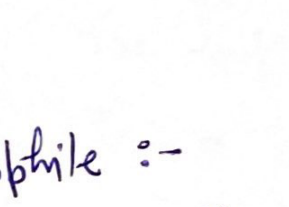
Physical Properties

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

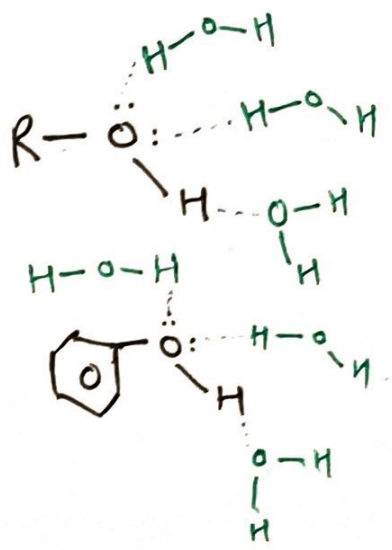
→ In alcohols –: As branching ↑es ⇒ B.P. ↓es : This is because of decrease in Vander Waals forces with decrease in surface area.

→ B.P. :  <  < $CH_3-CH_2-CH_2-CH_2-OH$

→ B.P. of alcohols and phenols (higher in comparison to hydrocarbons, ethers, haloalkanes and haloarenes of comparable molecular masses. This is because of hydrogen banding 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

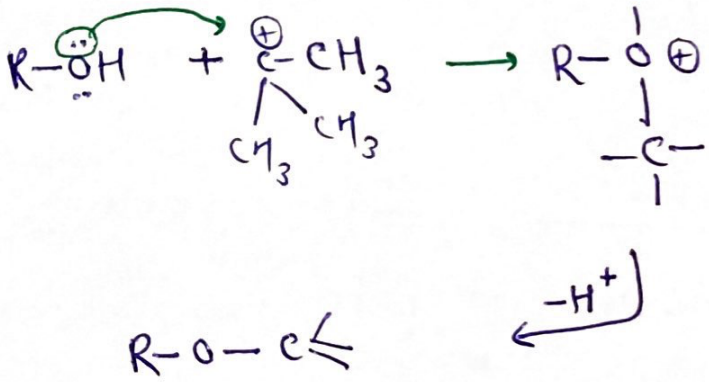
(Hydrophobic part.)

→ Solubility order :  > 

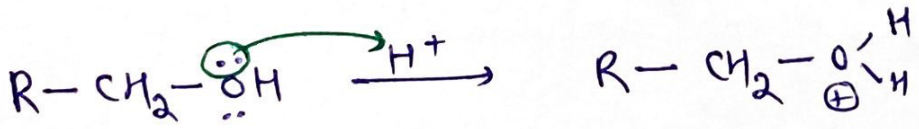
Chemical Reactions

→ R — O — H

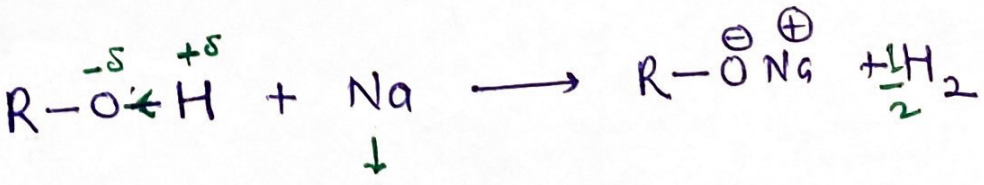
- Breaking of oxygen and hydrogen bond. → Alcohols as nucleophile :-

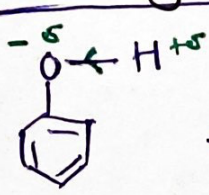
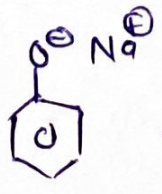


- Breaking of carbon and oxygen bond → Protonated alcohols as electrophiles



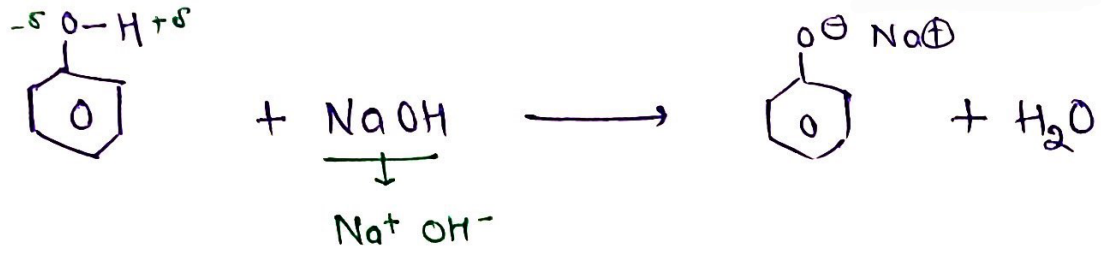
Acidity of alcohols & phenols —:



→  + Na →  + $\frac{1}{2}H_2$

Phenol — $Na^+ + e^-$ — Sodium Phenoxide

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

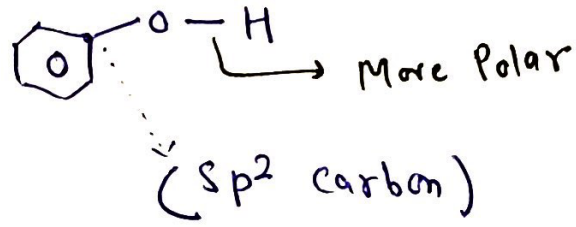
→ 

#] 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 ele n density on oxygen trending to derease the polarity of -O-H bond. This derease the acidic strength.

$$R\rightarrow CH_2\rightarrow O-H \;>\; \begin{matrix} R \\ R \end{matrix}\!\!>\!CH\rightarrow O-H \;\gg\; \begin{matrix} R \\ R \\ R \end{matrix}\!\!>\!C\rightarrow O-H$$

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

→ R-O-H and 

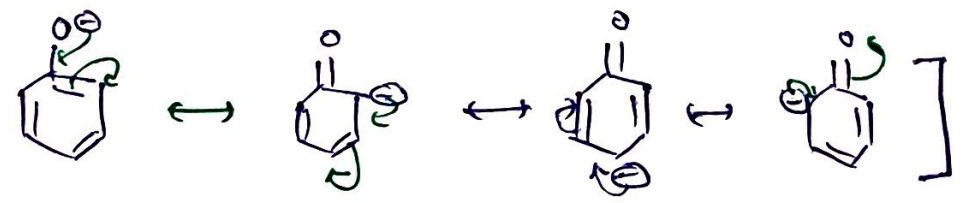
Less Polar

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

Ionisation of phenol : 

(This ⊖ve charge is delocalised due to conjugation)

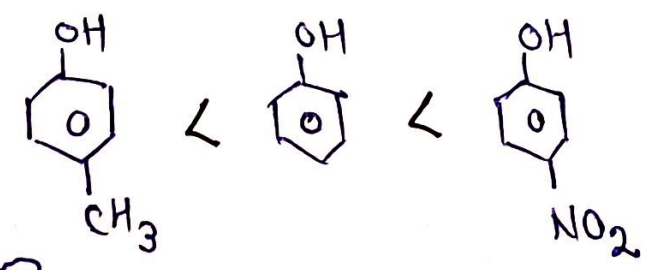
Due to resonance phenoxide is stable than alkoxide.



Resonating structure of Phenoxide Ion.

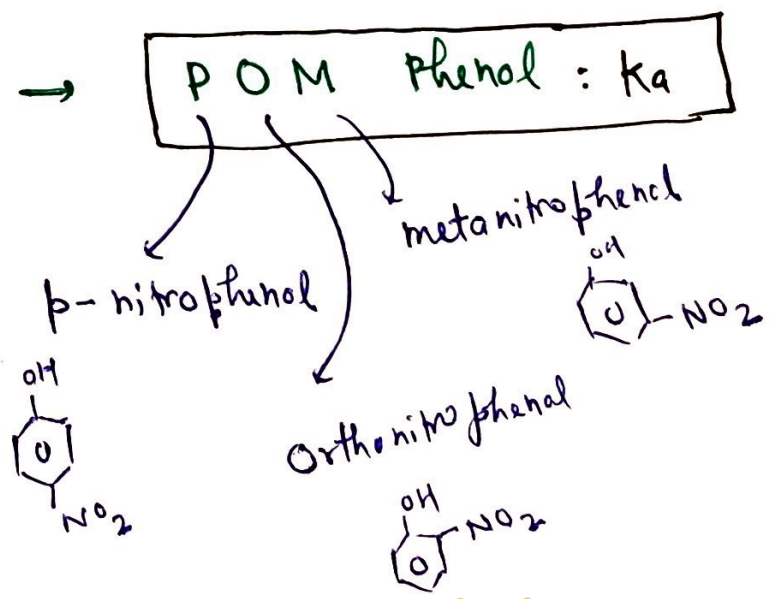
NOTE -: In resonating structure of phenoxide ion ⊖ve charge is present at ortho and para position. So, ⊖ve charge stabilising groups (-I / -M) can increase stability of substituted phenoxide ion. Thus it can increase the acidity.

→ 

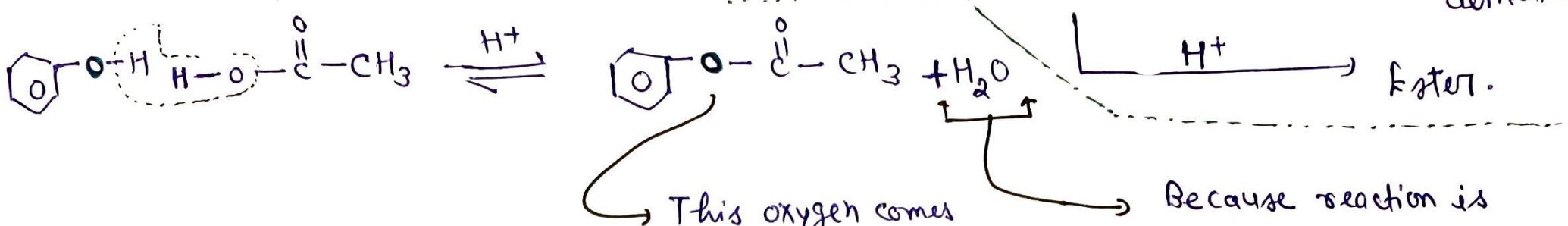
→ 

[CBSE 2017] 1M

→ POM Phenol : Ka

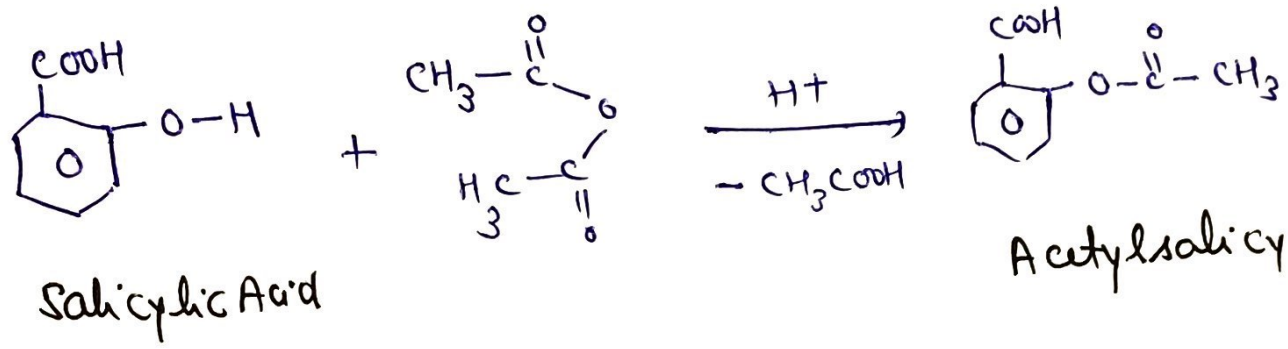


→ **Esterification :–** (Formation of ester) # Alcohols | Phenols + carboxylic acid or its derivatives

→ 

→ $CH_3-CH_2-O\overset{+}{H}\ H-O-\overset{O}{\overset{\|}{C}}-CH_3 \xrightleftharpoons{H^+} CH_3-CH_2-O-\overset{O}{\overset{\|}{C}}-CH_3$

→ $R-O\overset{+}{H} + Cl-\overset{O}{\overset{\|}{C}}-R' \xrightarrow[\text{Base}]{\text{Pyridine}} R-O-\overset{O}{\overset{\|}{C}}-R' + HCl$ → Pyridine is used to neutralise HCl and to make reaction progressive in forward direction.

→ 

Salicylic Acid

Acetylsalicylic acid [Aspirin]

→ **Reactions involving cleavage of carbon – carbon bond in alcohols –:**

1. **Reaction with HX [HCl | HBr | HI] –:** $R-\ddot{O}-H + H-I \longrightarrow R-\overset{\oplus}{O}(H)(H)$ ($H-I$: $+\delta$ $-\delta$; $I^\ominus$ attacks by S_N2)

$R-I + H_2O$

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]

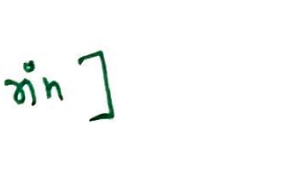
Reaction : $CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-OH \xrightleftharpoons{H^+} CH_3-\overset{CH_3}{\overset{|}{C}}=CH_2$ (Alkene)

(Alcohol)

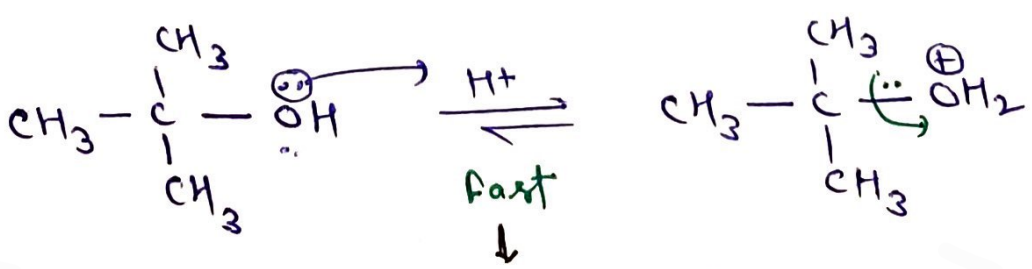
$H_3PO_4 \mid H_2SO_4$

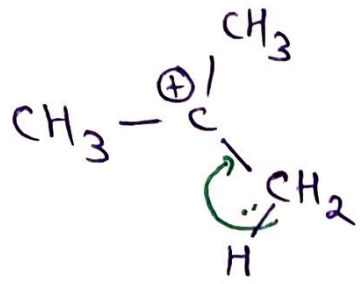
$ZnCl_2$: Lewis acid

$\uparrow -H^+$



Mechanism –:





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

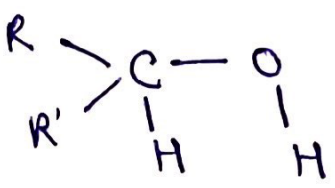
↓ H^+ ; ↑ $-H^+$

$CH_3-CH_2-\overset{\oplus}{O}H_2 \xrightarrow[(-H_2O)]{} CH_2-\overset{\oplus}{C}H_2$ (H migrates)

[CBSE 2019 | 2013 ; Delhi 2015C]

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

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 → $\left(\text{pyridinium}^+ \cdot CrO_3 \cdot HCl\right)$

$CH_3-CH_2-OH \xrightarrow[H^+]{KMnO_4} CH_3-\overset{O}{\overset{\|}{C}}-OH$

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

ter. Alcohol : $CH_3-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}-OH \xrightarrow{CrO_3} \not\rightarrow$ Because there is no C-H bond.

→ Cu / 300°C (Delhi 2015)

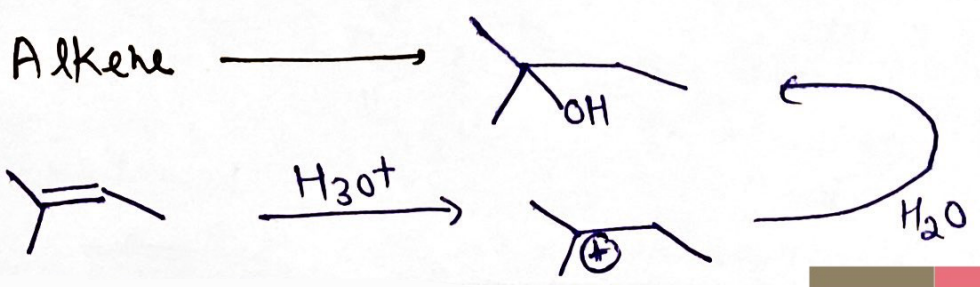
oxidation ←

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

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

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 → 

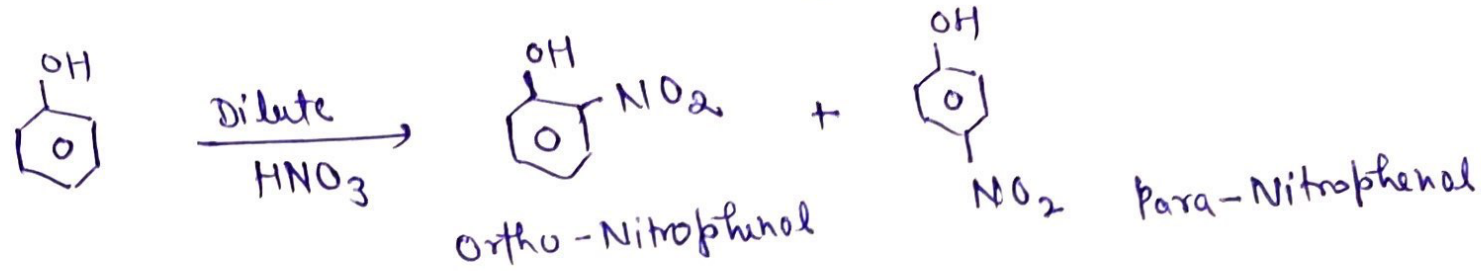
[CBSE 2019] 1M

Reactions of Phenol

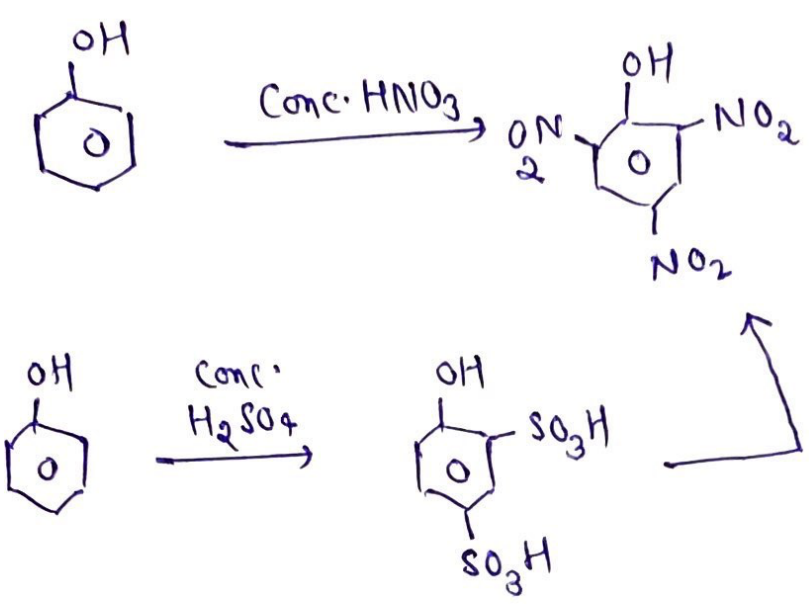
① Electrophilic aromatic substitution —: Phenol and phenoxide ion, direct the incoming electrophile to ortho and para positions in the ring as these position becomes electron rich due to resonance effect caused by $-OH$ & $-O^{\ominus}$ group.

→ Nitration :—

(a)



→

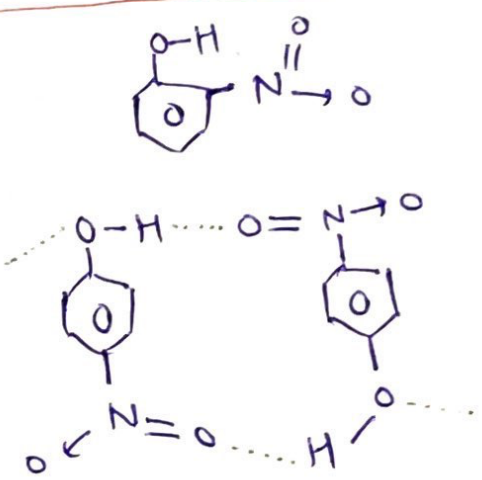


Picric acid [2, 4, 6 – Trinitrophenol]

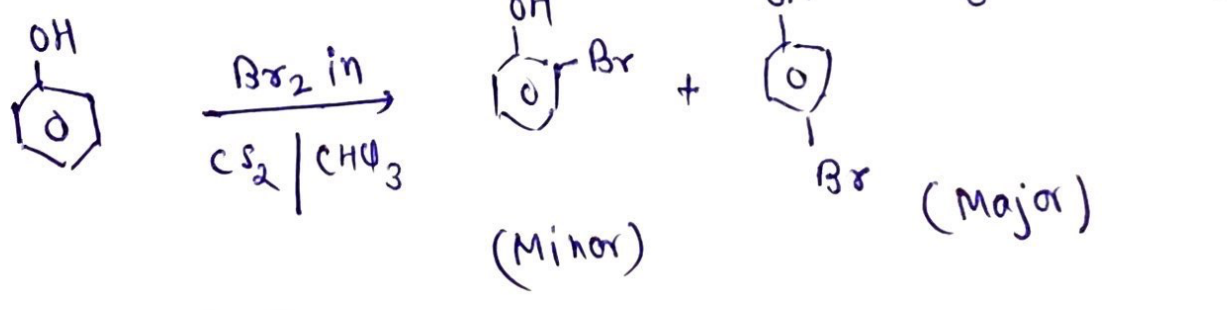
→

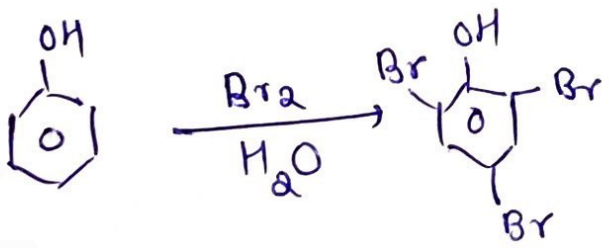
Question :— o-Nitrophenol is more steam volatile than p-Nitrophenol, Why? [Delhi 2019 / CBSE 2014]

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.



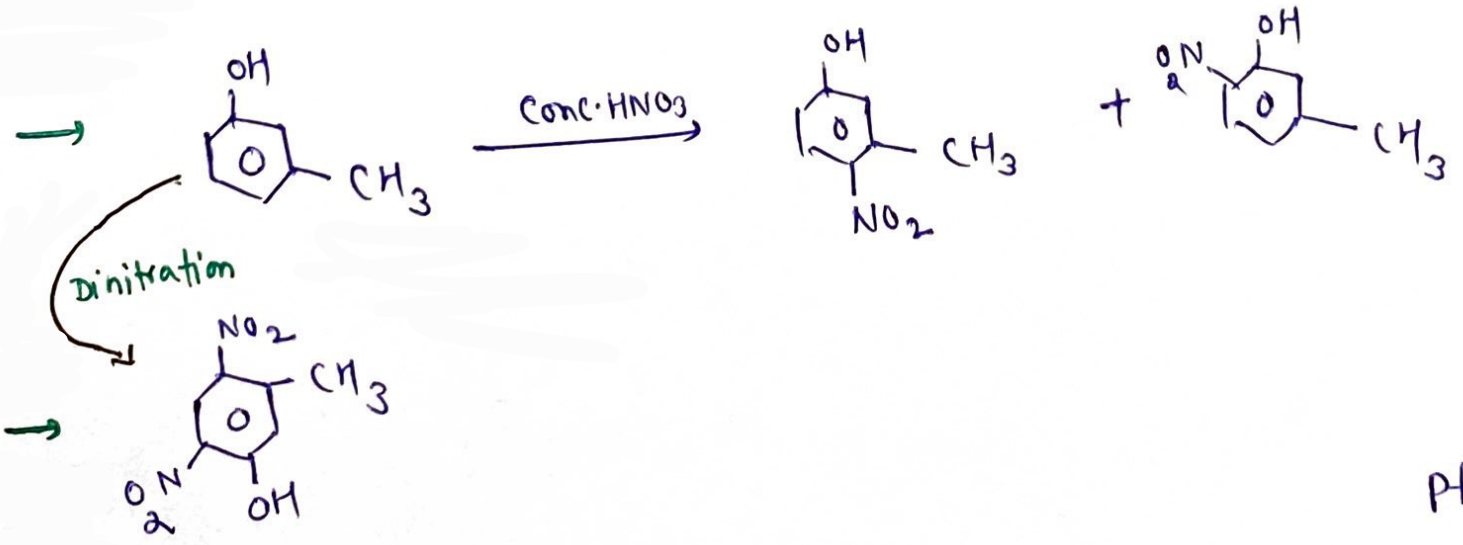
(b) Halogeration :—

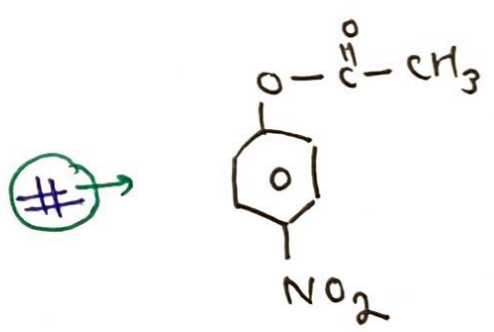


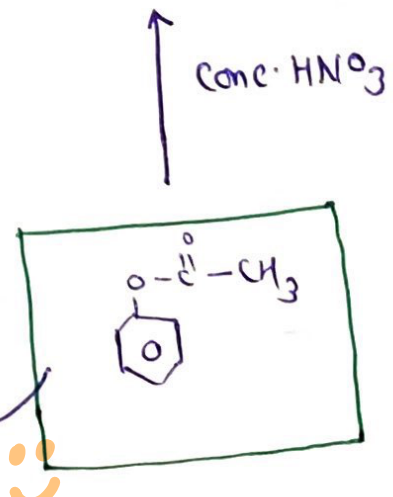


white ppt of [2, 4, 6 – Tribromophenol]

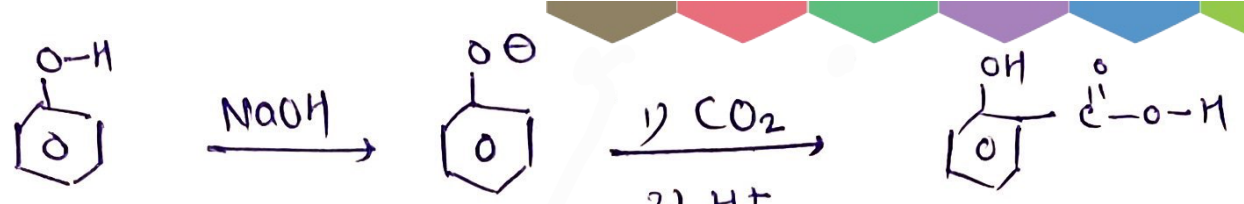
→







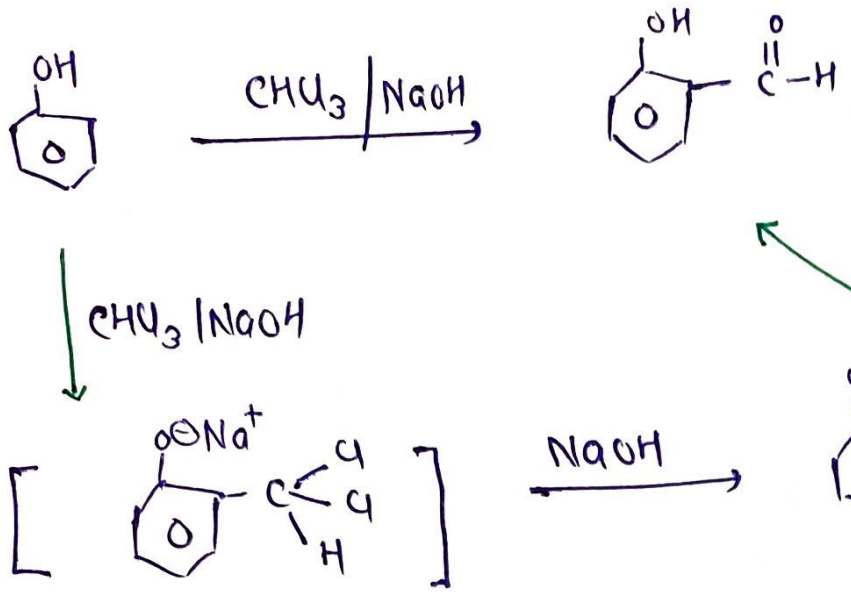
2.) **Kolbe's Reaction** —:



2–Hydroxy benzoic acid
(Salicylic acid)

[Delhi 2014C] (1M)

3. **Reimer - Tiemann Reaction** :—

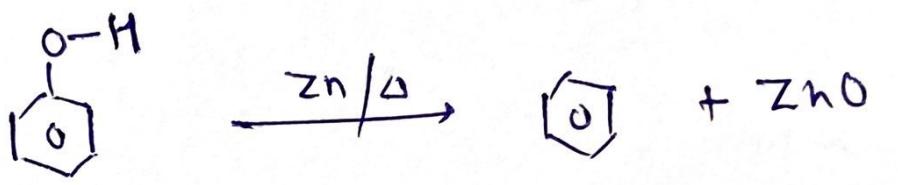


[Delhi 2015]
(1M)

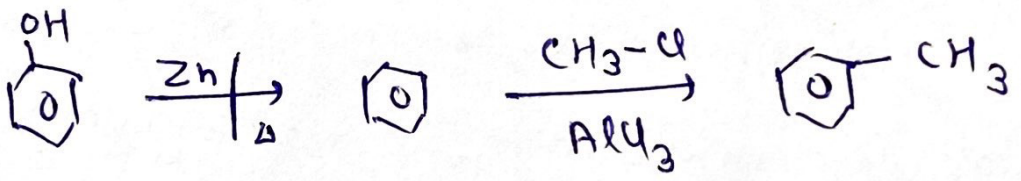
On treating phenol with chloroform and NaOH, a $-\overset{O}{\overset{\|}{C}}-H$ group is introduced at ortho position of benzene ring. This reaction is known as RT Reaction.

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

4. **Phenol with Zn dust** —:

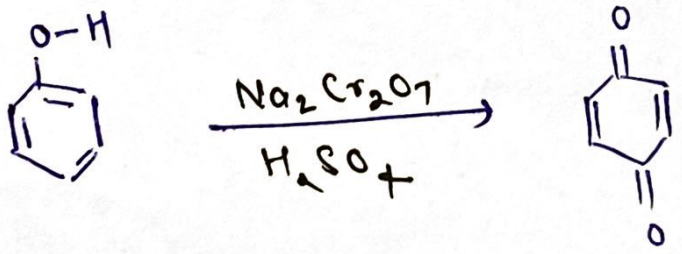


→ Phenol to toluene :



[Delhi 2013C]
(1M)

5. **Oxidation** —:

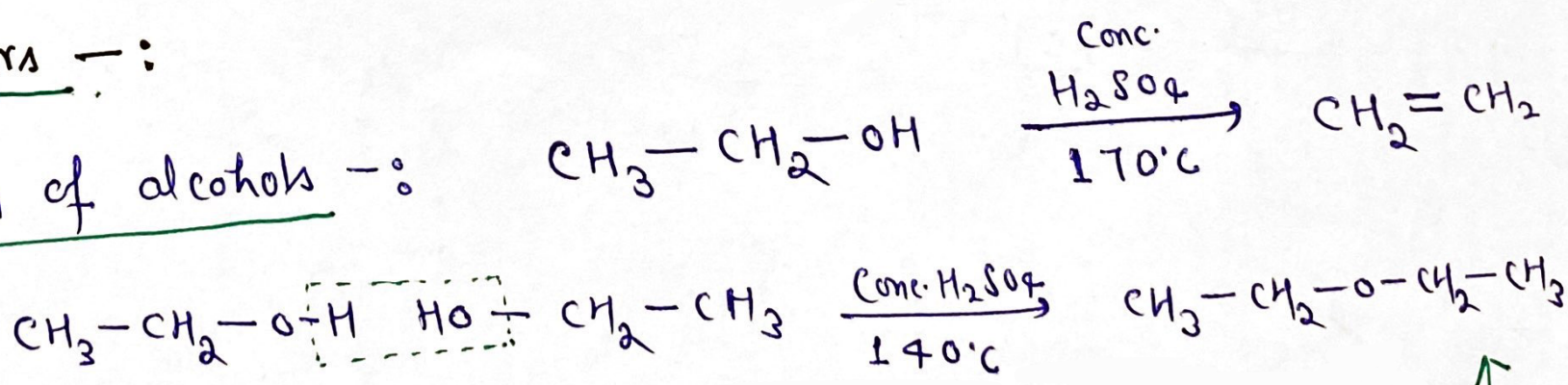


Benzoquinone

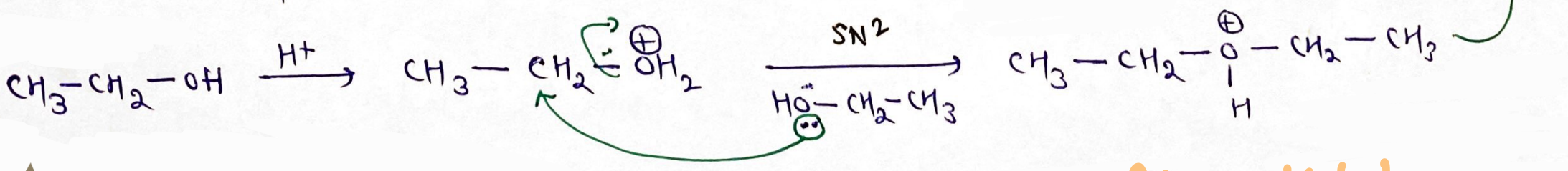
Ethers

Prepration of ethers —:

1. **By dehydration of alcohols** —:



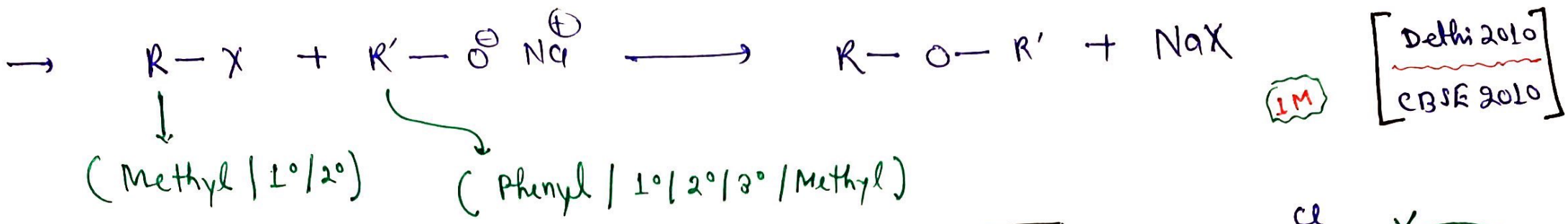
→ Formation of ether [Mechanism]

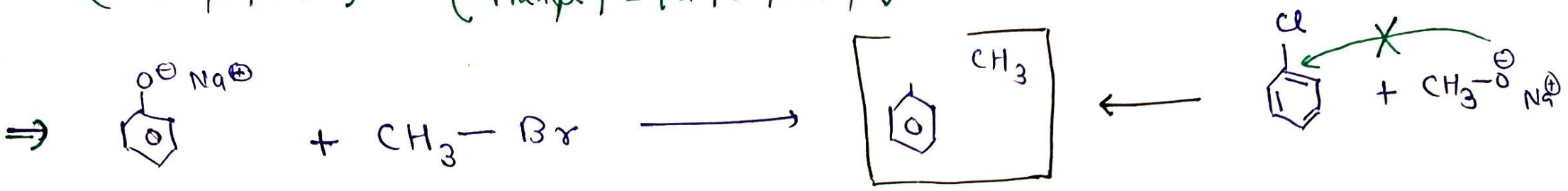


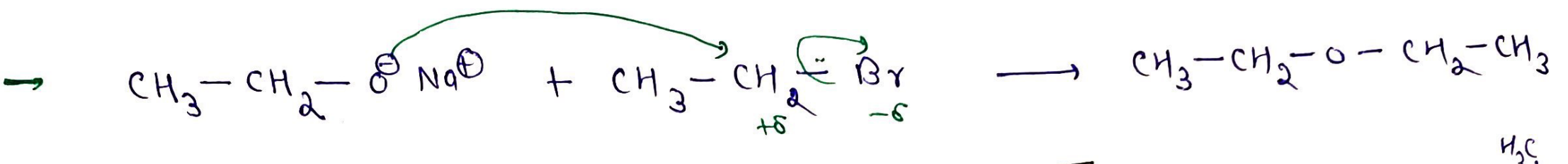
Apni Kaksha

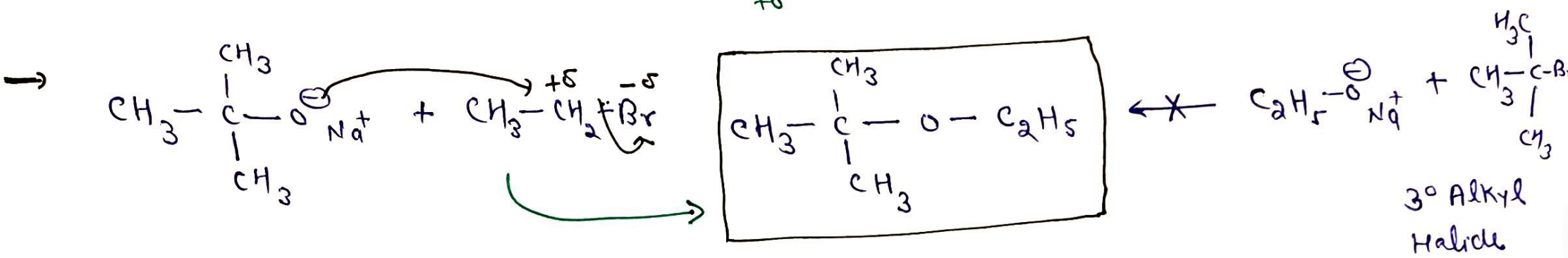
(2) Williamson synthesis —:

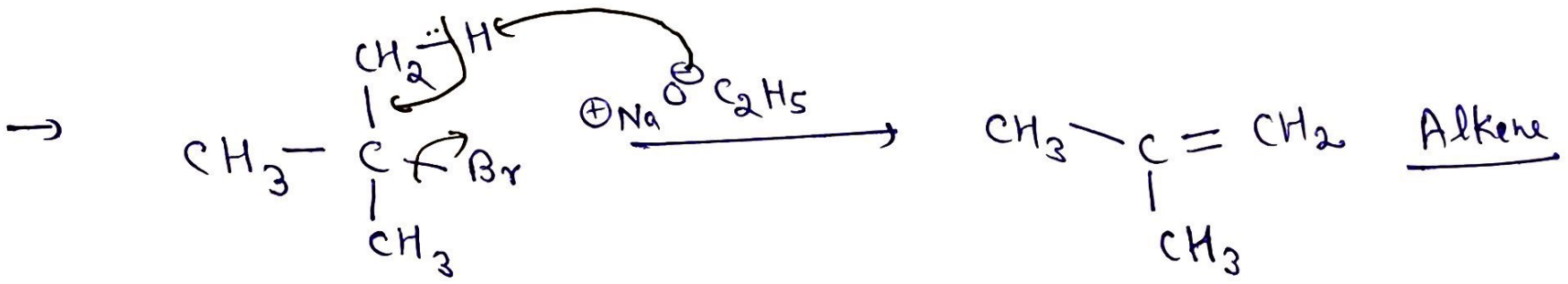
Alkyl halide + Sodium Alkoxide ⟶ Ether



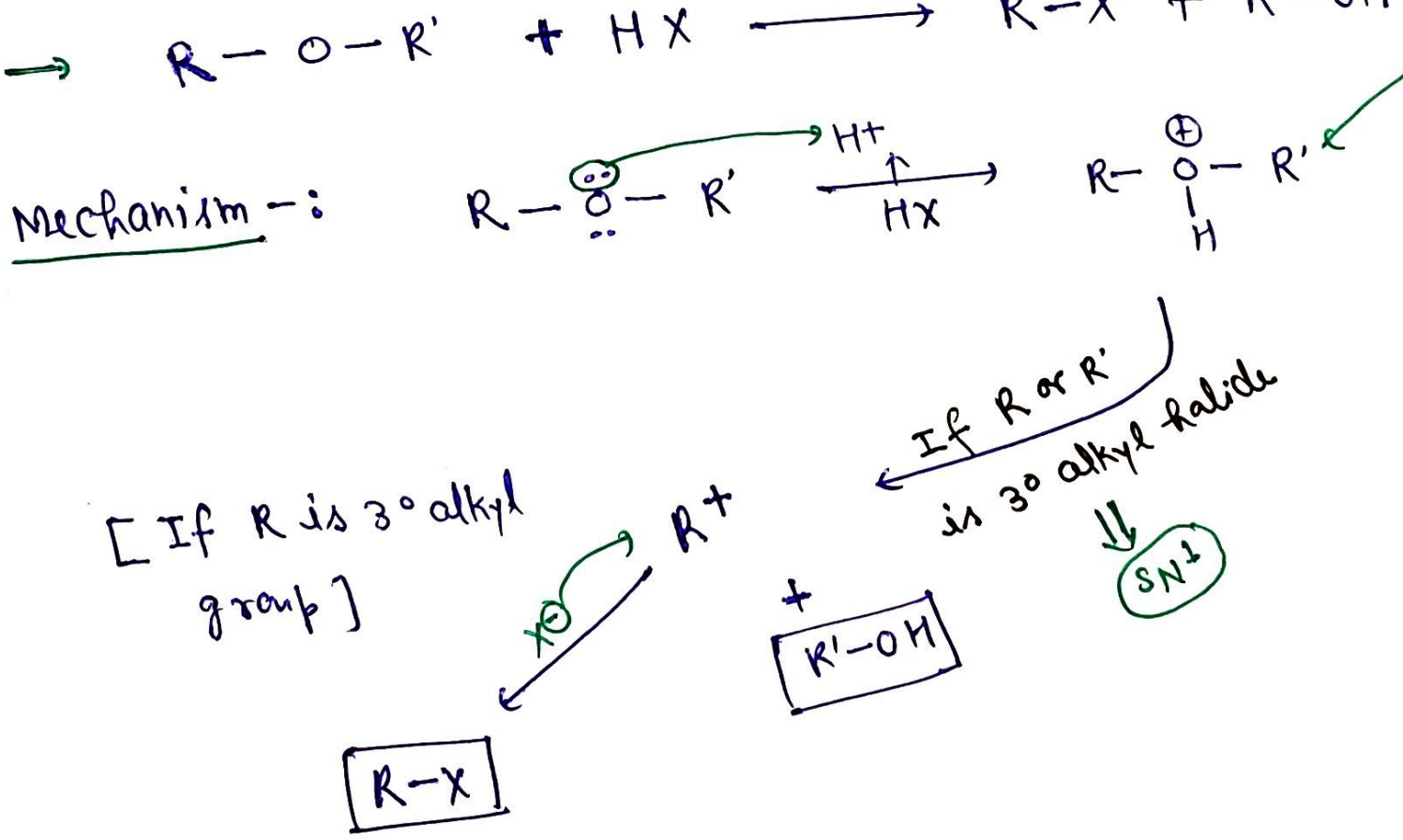


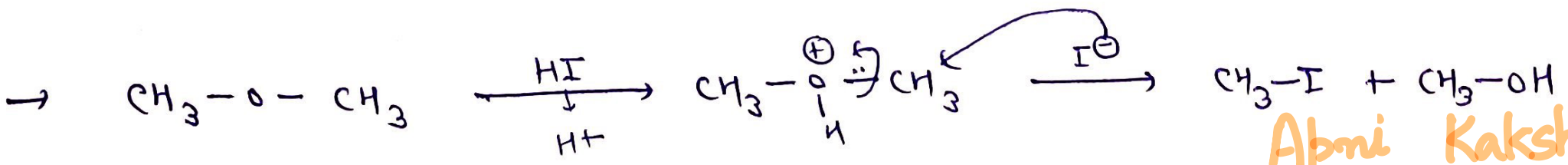






Chemical Reaction of ether





→ $CH_3-O-CH_2-CH_3$ $\xrightarrow{HI}$ $CH_3-\overset{\oplus}{O}(H)-CH_2-CH_3$ $\xrightarrow{S_N2}$ CH_3-I + CH_3-CH_2-OH

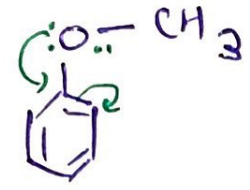
($I^\ominus$ attacks)

→ $H_3C-C(CH_3)_2-O-CH_3$ $\xrightarrow{HI}$ $\xrightarrow{H^+}$ $CH_3-C(CH_3)_2-\overset{\oplus}{O}(H)-CH_3$

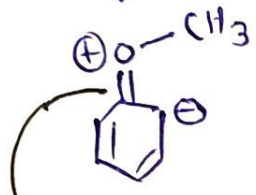
[CBSE 2015] 1M

$\rightarrow$ $H_3C-C(CH_3)_2-\overset{\oplus}{O}-CH_3$ + CH_3-OH

$I^\ominus$ attacks → **+I**

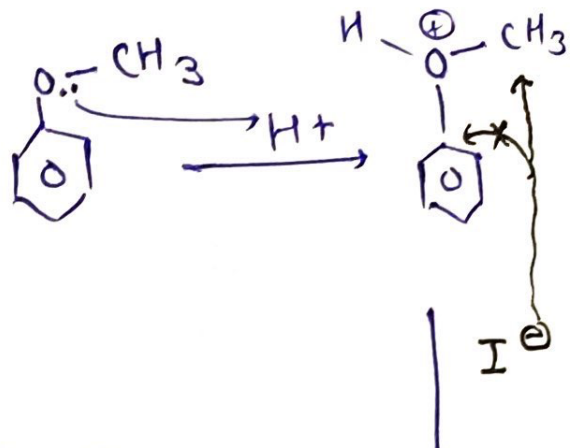
→  $\xrightarrow{HI}$  + CH_3-I

↕

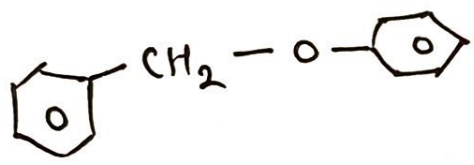
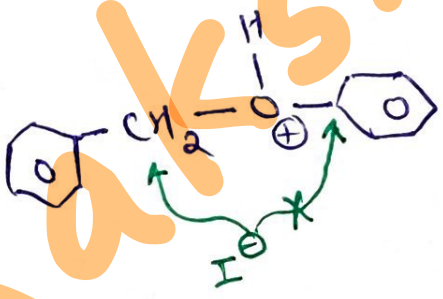
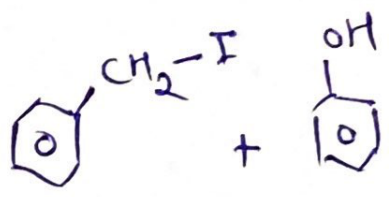


Due to Double bond character it is tough to break this bond.

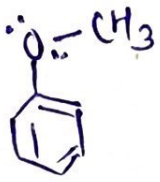
Mechanism-:



[Delhi 2010C]

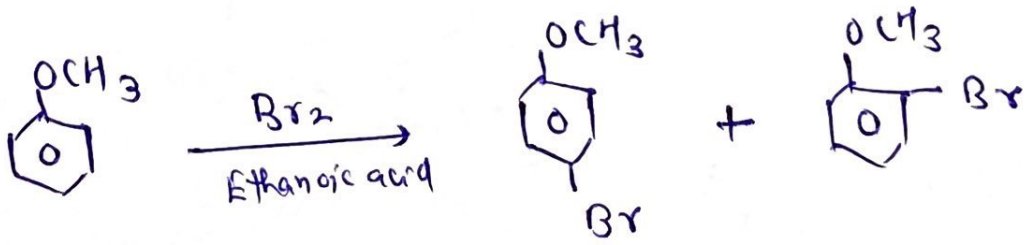
→  $\xrightarrow{HI}$  $\rightarrow$ 

Electrophilic Substitution Reaction of Anisol

→ **Anisol** :  (−O−CH_3 is a +M group which is ortho − para directing in nature)

a.) **Halogenation** :

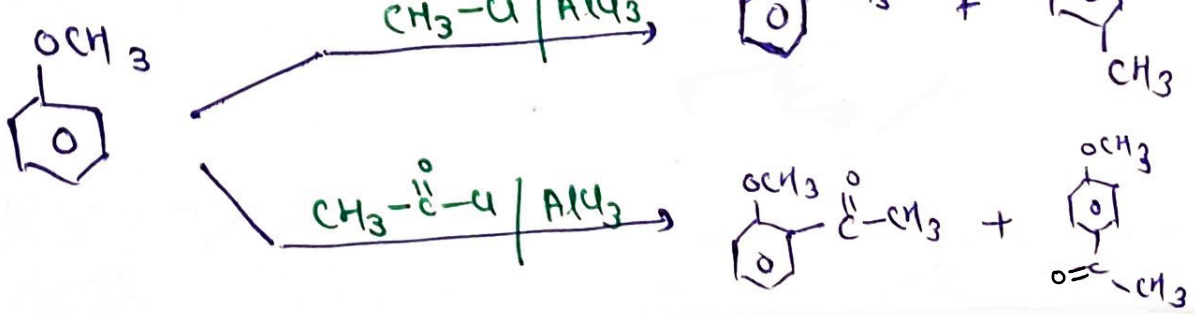
[Delhi 2015C] 1M



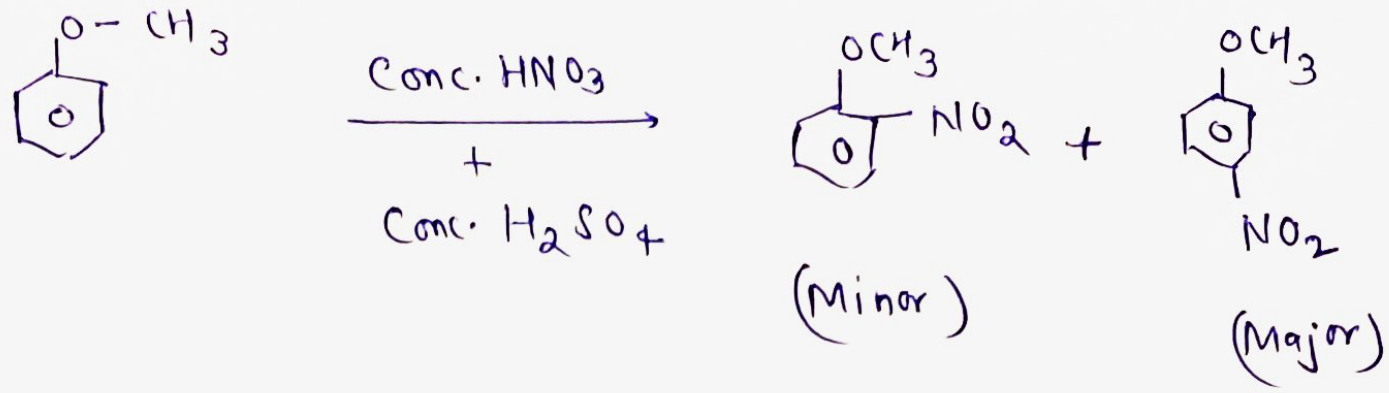
(Major) (Minor)

b.) **Friedel Crafs reaction** −:

[Delhi 2011 | 2010] 1M

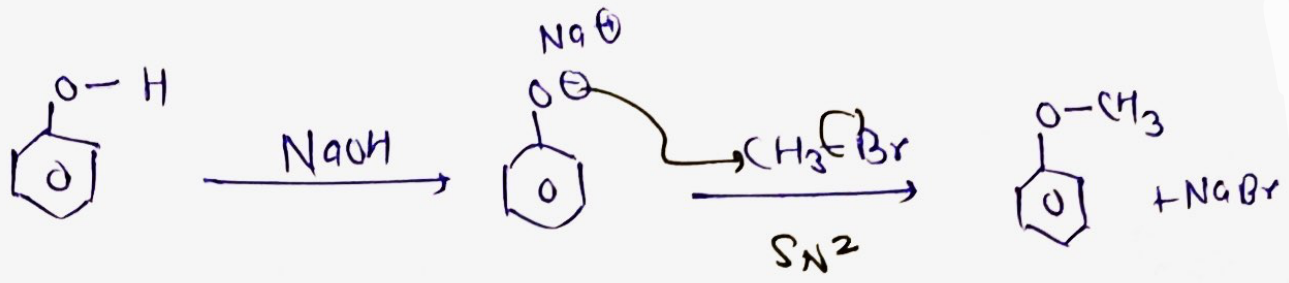


c.) Nitration :—

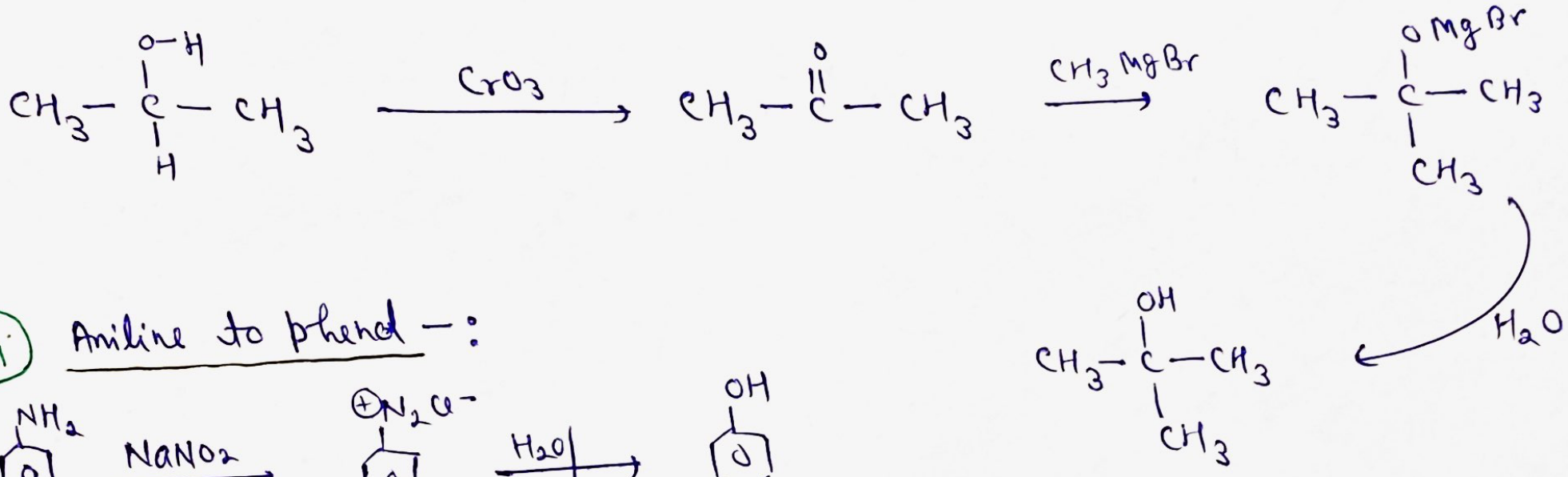


Conversions

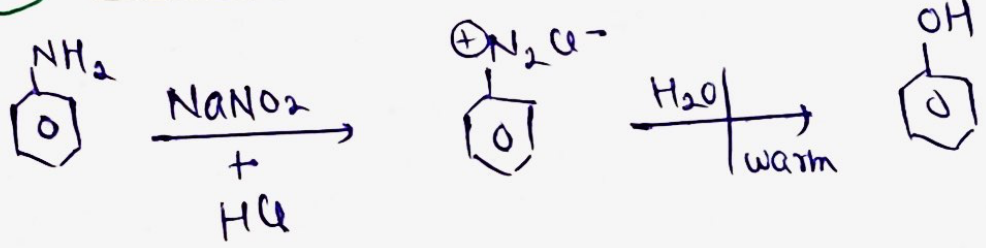
(i) Phenol to anisole :—



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



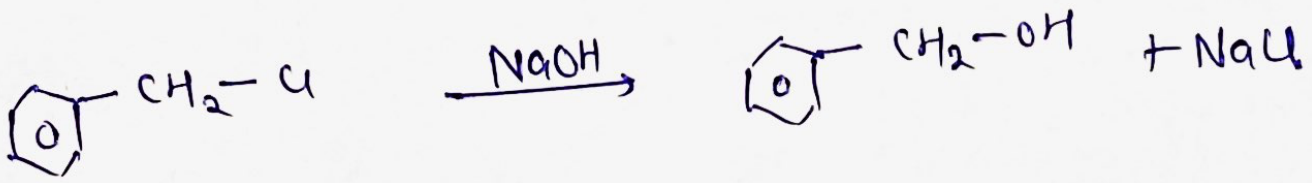
(iii) Aniline to phenol :—



Above three ← [Delhi 2015]

3M

(iv) Benzyl chloride ⟶ Benzyl Alcohol



Lucas Reagent → $ZnCl_2$ / HCl

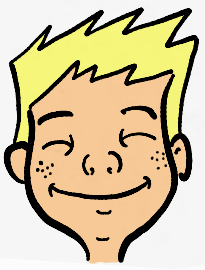
Lucas Test → To differ. 1°/2°/3° Alcohol

Phenol does not give this test.

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

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

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



समाप्त