13/11/23

CHAPTER-7
ALCOHOLS, PHENOLS AND ETHERS

☆ INTRODUCTION

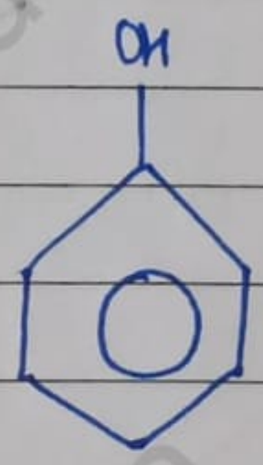
- **ALCOHOL**

When one or more than one hydroxyl group (-OH) is attached to aliphatic hydrocarbons (open chain), then they are ~~reffered~~ referred as alcohol.

R - OH

- **PHENOL**

When OH is directly attached to the carbon of aromatic compound, it is referred as phenol.

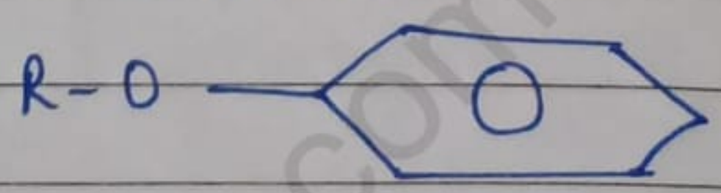


- **ETHER**

Substitution of H of hydrocarbon (R-H) is done by -OR or -O-⬡

⇒ referred as ether

R-O-R



☆ CLASSIFICATION OF ALCOHOL AND PHENOLS

- **ON THE BASIS OF ALCOHOLIC GROUP [No. of OH group]**

(A) **MONOHYDRIC** ⇒ when only one OH group is present in compound

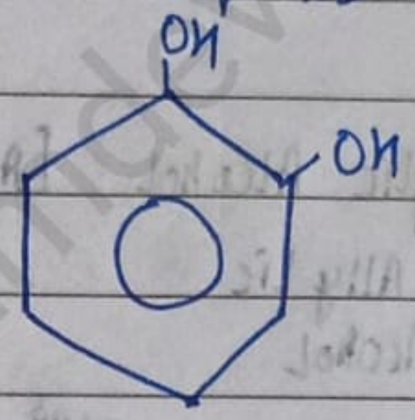
Examples: CH_3OH Methanol

Phenol

CH_3CH_2OH Ethanol

(B) DIHYDRIC ⇒ When two OH groups are present in compound

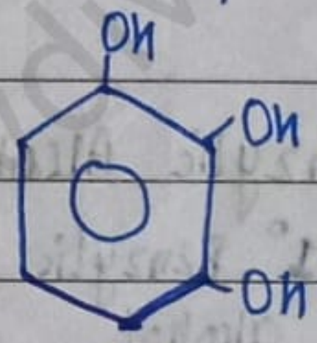
Examples: $CH_2(OH)-CH_2(OH)$ (Glycol) → common name



(Catechol) → common name

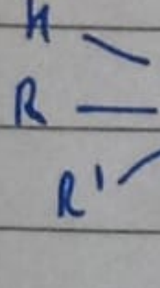
(C) TRIHYDRIC ⇒ When three OH groups are present in compound

Examples: $CH_2(OH)-CH(OH)-CH_2(OH)$ (Glycerol) → common name

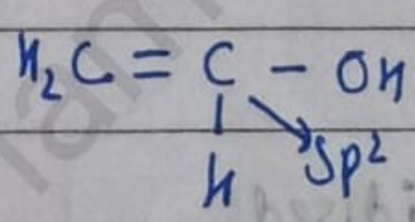


- MONOHYDRIC COMPOUND ON THE BASIS OF HYBRIDISATION

sp^3 hybridised



sp^2 hybridised



(A) sp^3 hybridised

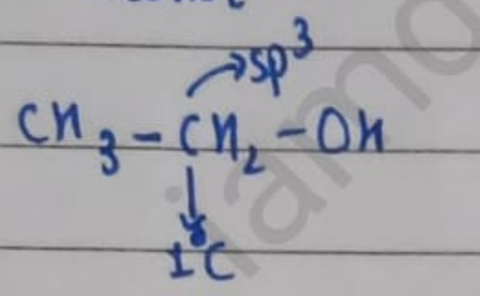
(a) General aliphatic alcohol

CH_3OH (No degree)

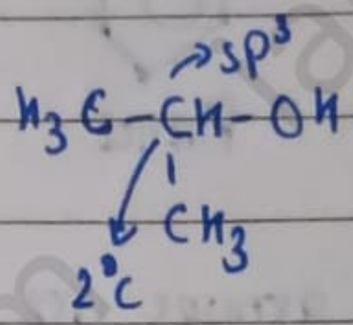
sp^3

* ~~Monohydric~~ [Hydridisation of C bonded with OH group]

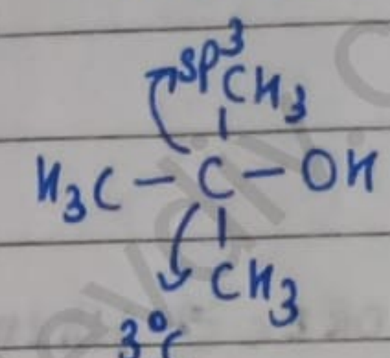
1° Monohydric alcohol



2° Monohydric alcohol

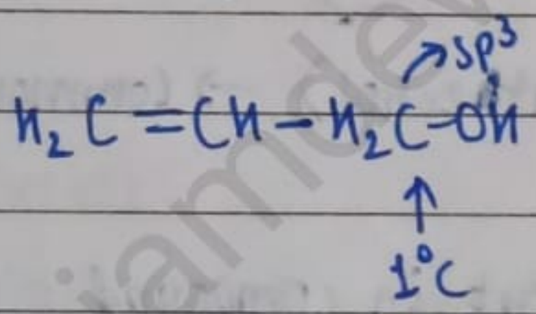


3° Monohydric alcohol

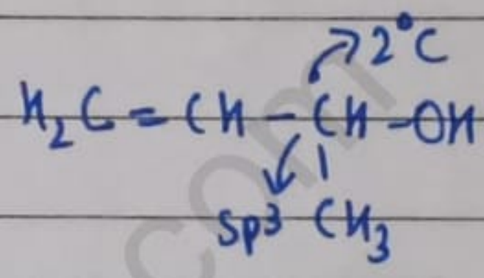


(b) Allylic Alcohol [Alcohol attached to C which is further bonded with C of double bond]

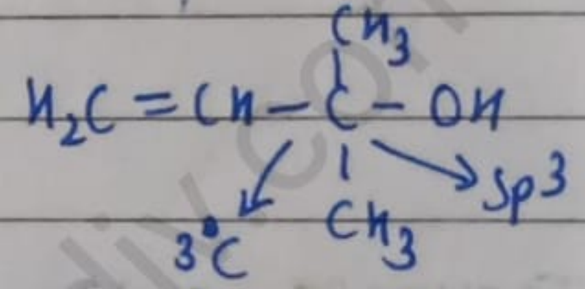
1° Allylic alcohol



2° Allylic alcohol

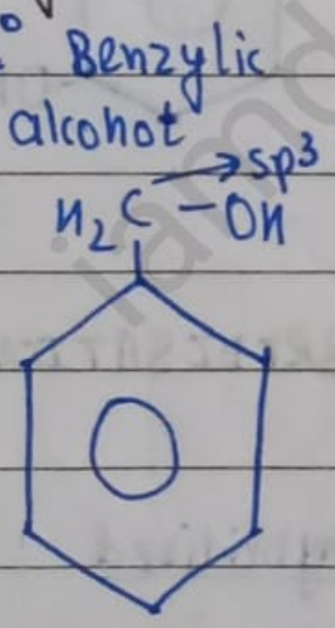


3° Allylic alcohol

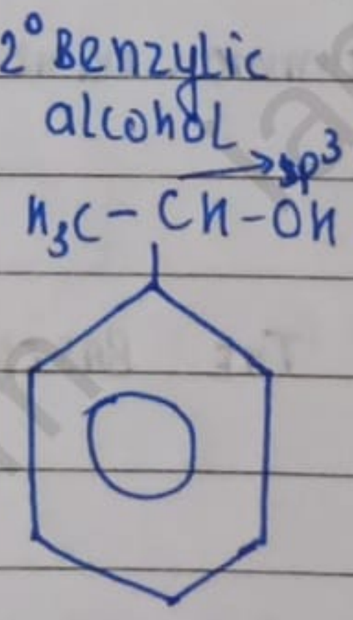


(c) Benzylic Alcohol

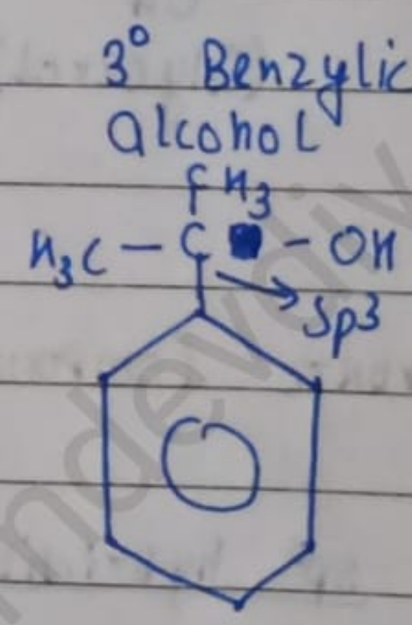
1° Benzylic alcohol



2° Benzylic alcohol

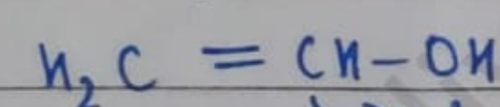


3° Benzylic alcohol

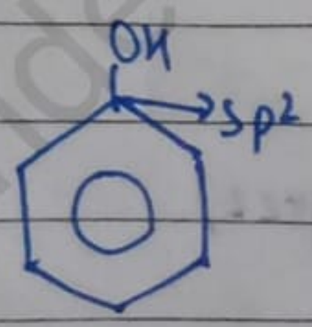


(B) sp^2 hybridised

(a) Vinylic alcohol



(b) Phenol



★ CLASSIFICATION OF ETHERS

- SYMMETRICAL

  R-O-R

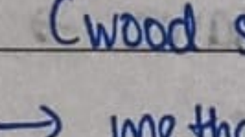
  Examples: $CH_3 - O - CH_3$

  $C_2H_5 - O - C_2H_5$

- NON-SYMMETRICAL

  R-O-R'

  Examples: $CH_3 - O - C_2H_5$

  $CH_3 - O -$ 

★ NOMENCLATURE OF ALCOHOLS, PHENOLS AND ETHERS

- ALCOHOLS (R-OH)

  IUPAC → Alkanol

  Common name → Alkyl Alcohol

  Examples: CH_3OH (wood spirit) OR (carbinol)

  IUPAC → methanol

  Common name → methyl alcohol

  $CH_3CH_2CH_2OH$

  IUPAC → Propanol

  common name → propyl alcohol

  $CH_3 - \underset{\underset{OH}{|}}{CH} - CH_3$

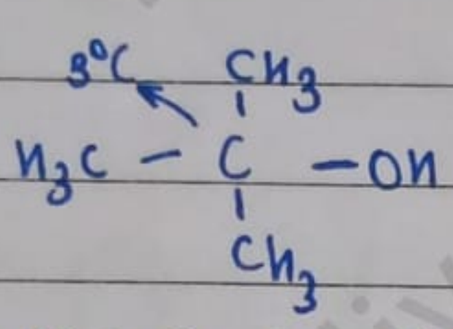
  IUPAC → Propan-2-ol

  Common name → Isopropyl alcohol

$CH_3CH_2CH_2CH_2OH$

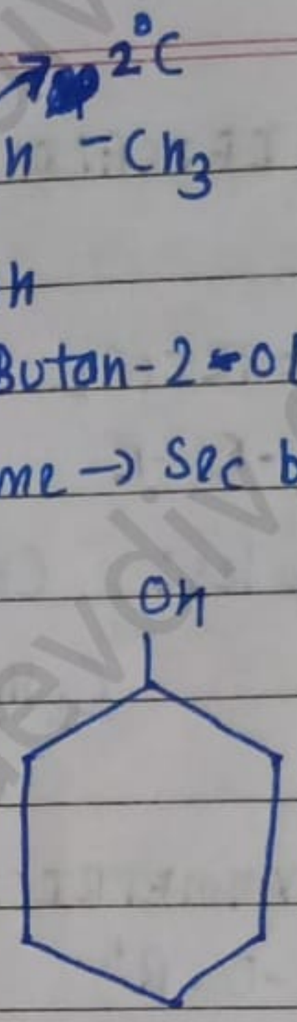
IUPAC → Butanol

Common name → Butyl alcohol



IUPAC → 2-methyl propan-2-ol

common name → Tertiary butyl alcohol



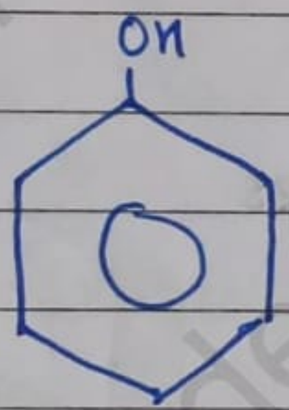
IUPAC → Butan-2-ol

Common name → Sec butyl alcohol

(This is not phenol!)

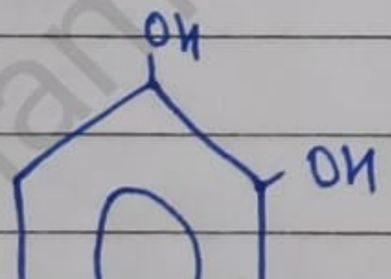
Cyclo Hexanol

- PHENOLS



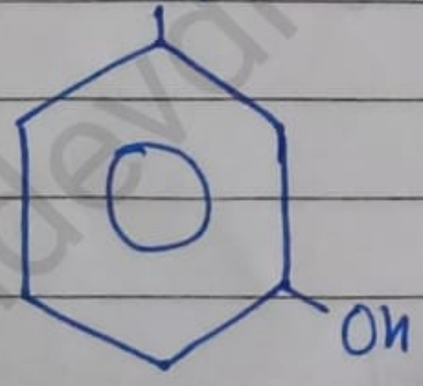
IUPAC → Phenol

Common name → Phenol



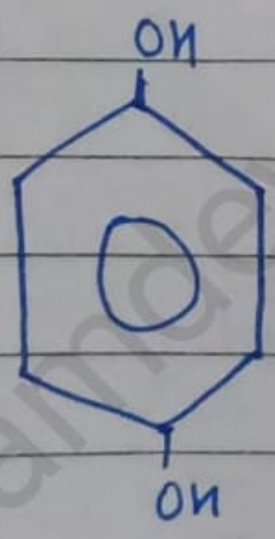
IUPAC → Benzene-1,2-diol

Common name → Catechol



IUPAC → Benzene-1,3-diol

Common name → Resorcinol



IUPAC → Benzene-1,4-diol

Common name → Quinol

- ETHERS

Symmetrical (R-O-R)

~~IUPAC → diethyl ether~~

· IUPAC → alkoxyalkane

Common name → dialkylether

Example: CH_3-O-CH_3

Common name → dimethylether

IUPAC → methoxymethane

Non symmetrical (R-O-R')

↗ CH

IUPAC → alkoxyalkane

Common name → alkylalkyl ether

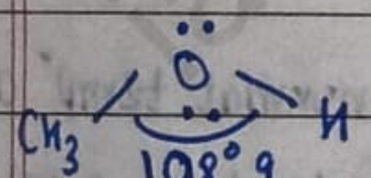
Example: $CH_3-O-C_2H_5$

Common name → ethylmethylether

IUPAC → methoxyethane

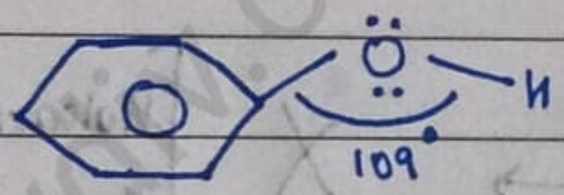
★ BOND ANGLE

Alcohol



(Repulsion of lone pairs)

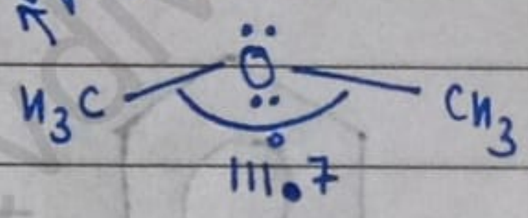
Phenol



(Lp-Lp repulsion and bp-Lp repulsion)

Ether

Bulky group



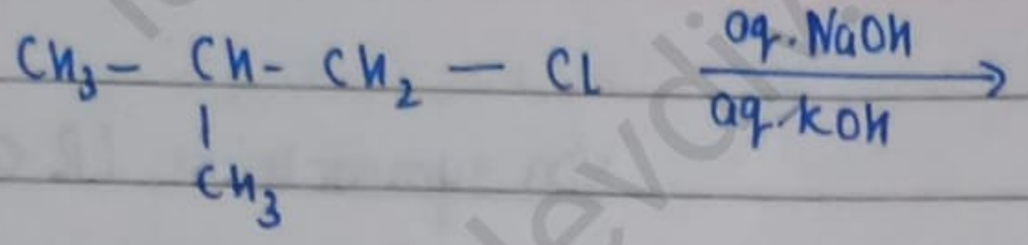
(bp repulsion > Lp repulsion)

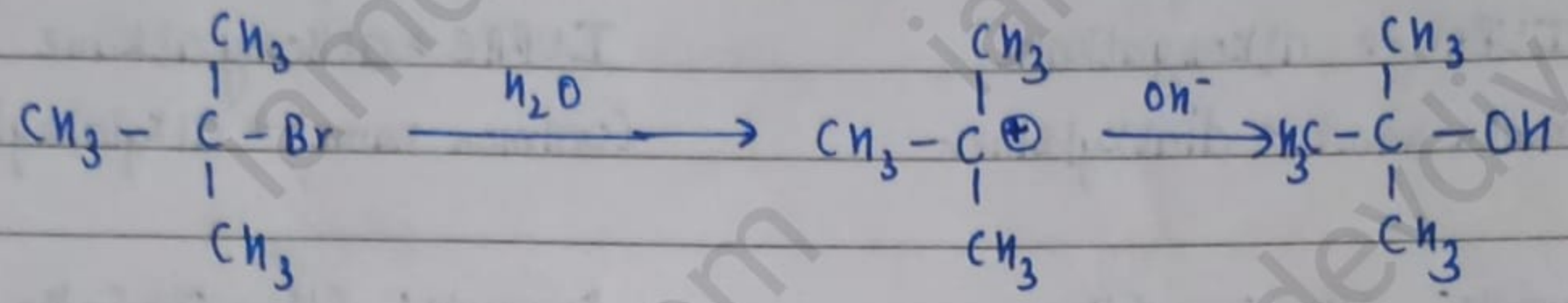
★ PREPARATION OF ALCOHOLS

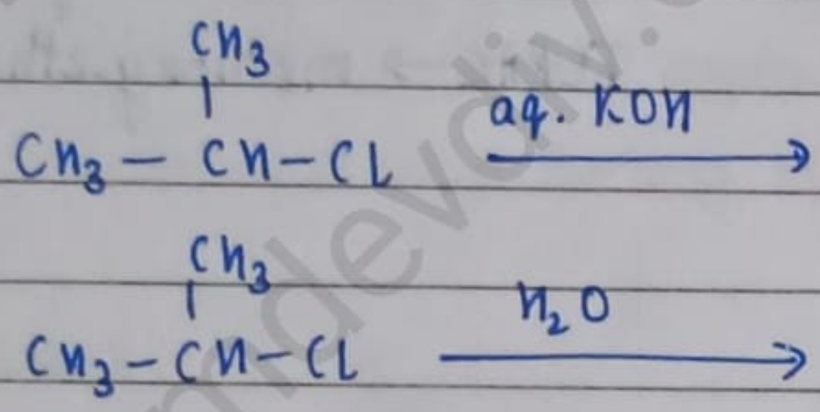
- BY ALKYL HALIDE

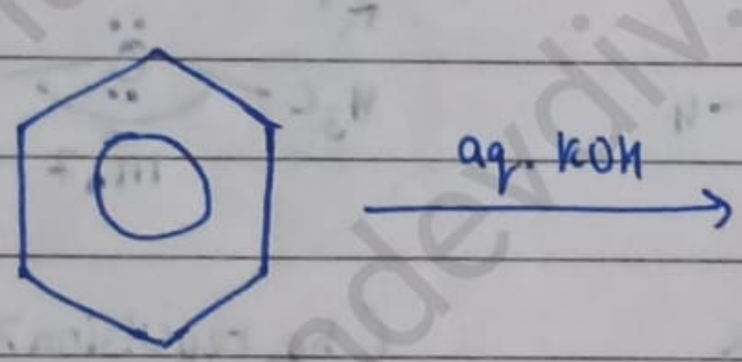
$$\underset{[1^\circ/2^\circ]}{R-X} \xrightarrow[\text{aq. KOH}]{\text{Strong } Nu^\ominus} R-OH + KX \quad (SN^2 \text{ Mechanism})$$

$$\underset{[3^\circ/2^\circ]}{R-X} \xrightarrow[\text{Polar protic solvent}]{H_2O} R^\oplus \xrightarrow{OH^-} R-OH \quad (SN^1 \text{ Mechanism})$$





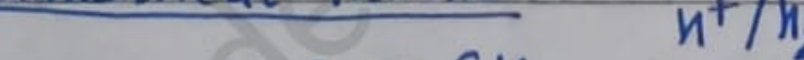




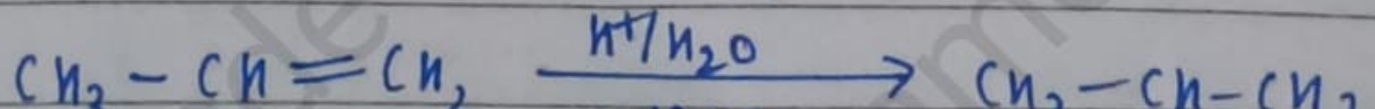
- BY ALKENES

* DIRECT METHOD
[ACID CATALYSED REACTION]

Symmetrical Alkene



Unsymmetrical Alkene

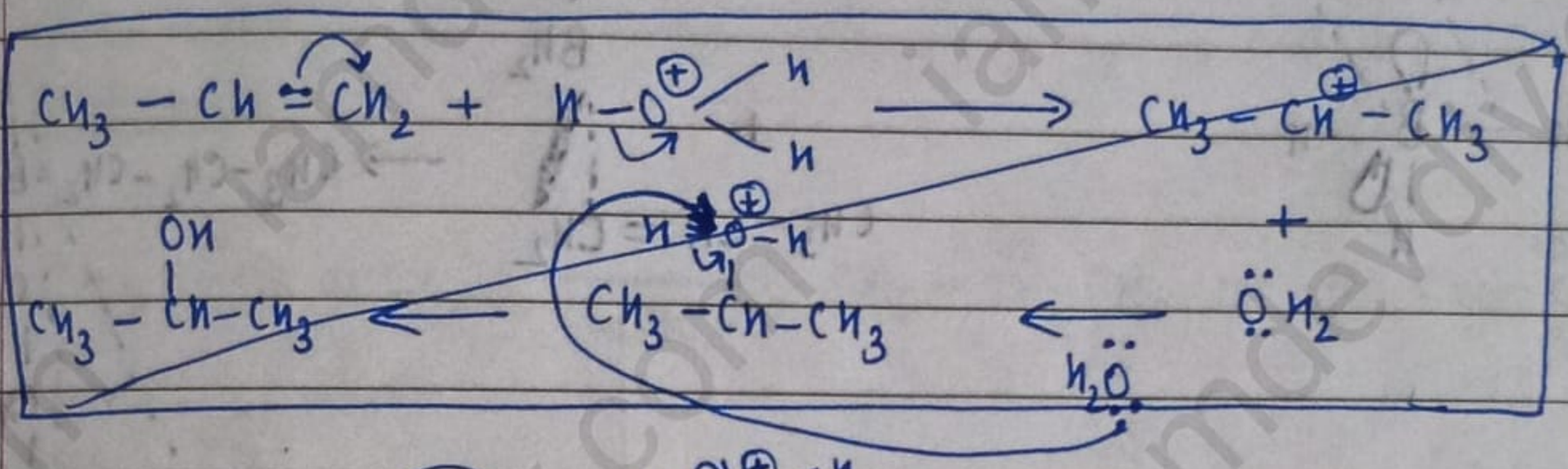


(Markonikov Rule)

Mechanism

$$H^+ + H_2\ddot{O} \longrightarrow H_3O^+$$

(Hydronium ion)



* INDIRECT METHOD

(i) [HYDROBORATION OXIDATION]

- Symmetrical Alkene

$$CH_2 = CH_2 \xrightarrow[H_2O_2]{BH_3} CH_3 - CH_2 - OH$$

BH_3 → provides H

H_2O_2 → provides OH

Unsymmetrical Alkene

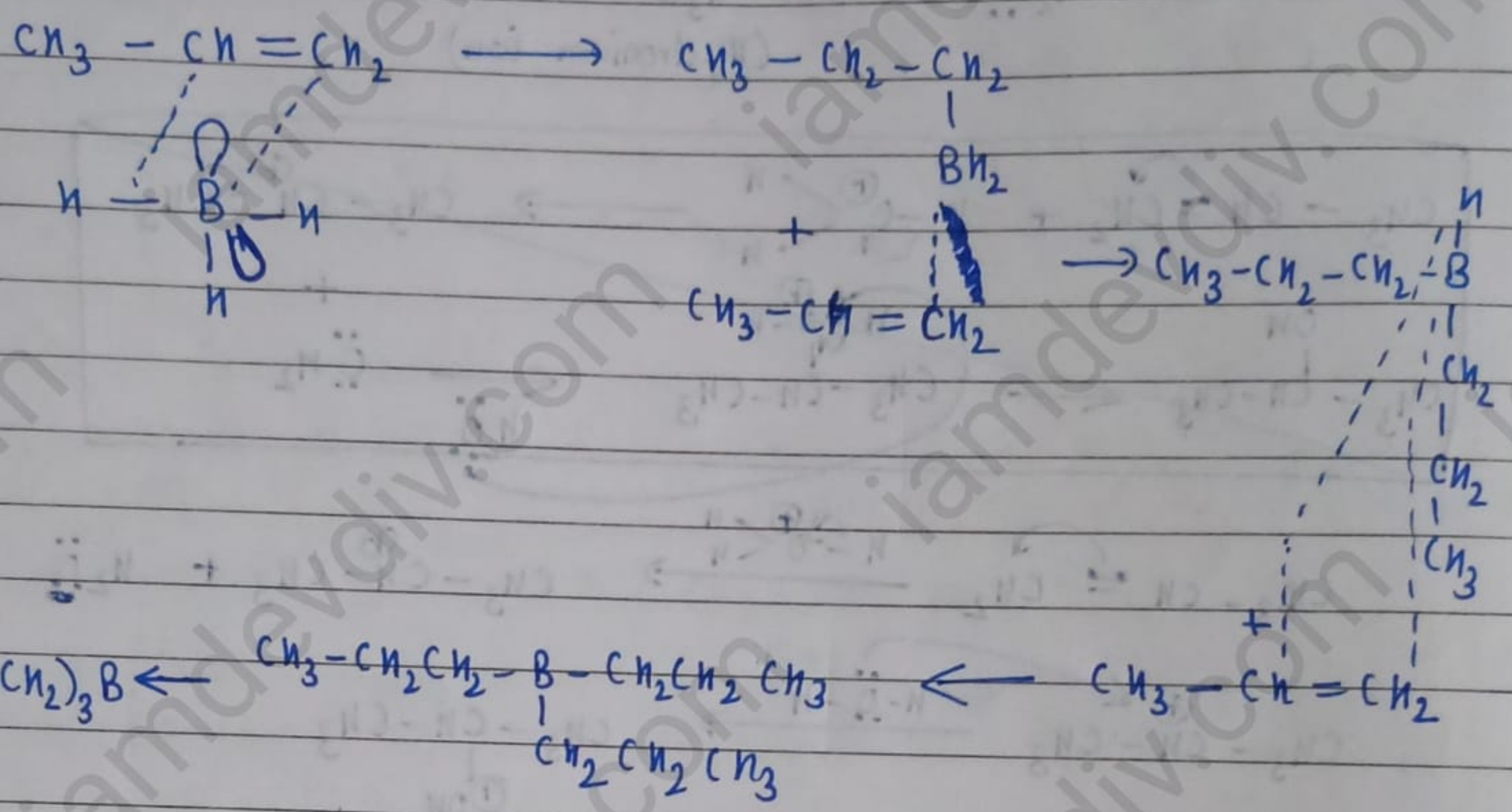
$$CH_3 - CH = CH_2 \xrightarrow[H_2O_2]{BH_3} CH_3 - CH_2 - CH_2 - OH$$

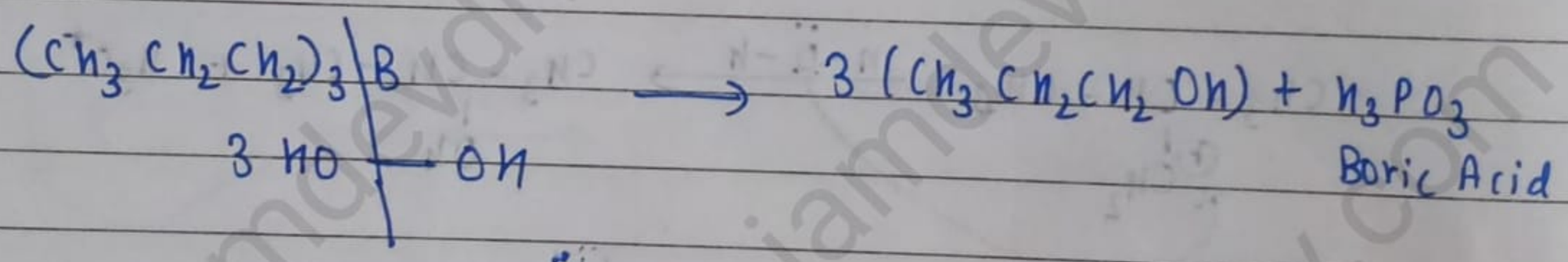
(Anti markonikov Rule)

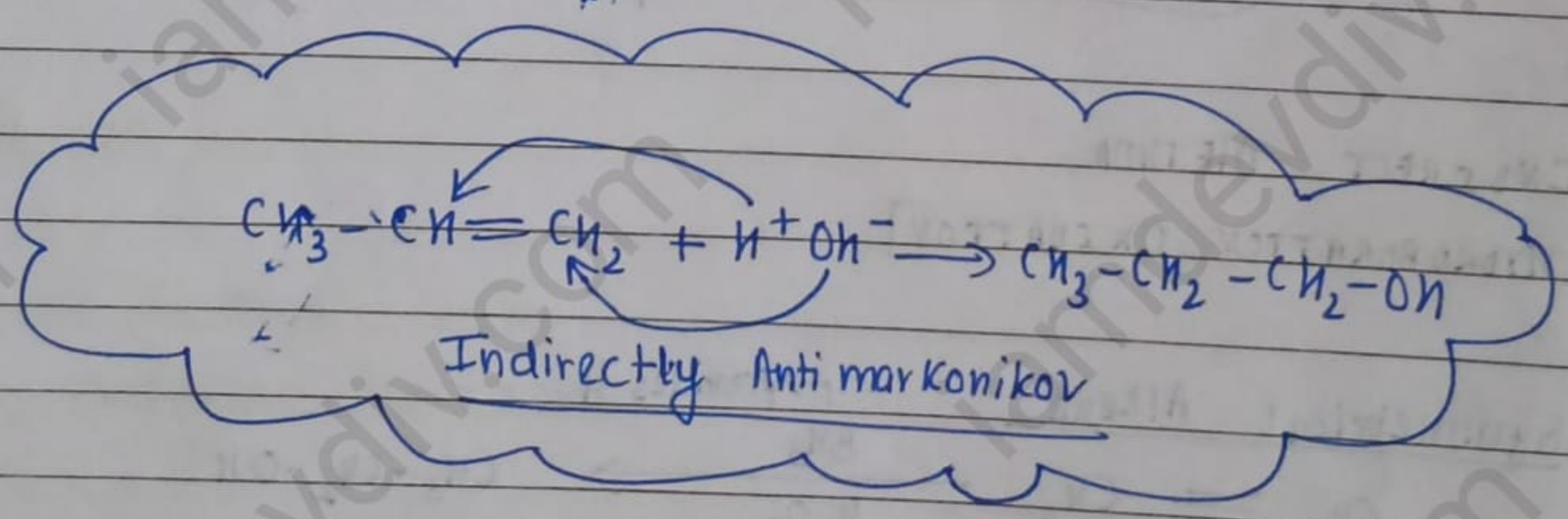
→ No rearrangement

→ No carbocation

Mechanism







(iii) [OXYMERCURATION DEMERCURATION]

→ Mercury acetate [$Hg(OAc)_2$]

→ $NaBH_4$ (Reducing agent)

→ Markonikov Rule (Unsymmetrical Alkene)

→ Rearrangement is not possible

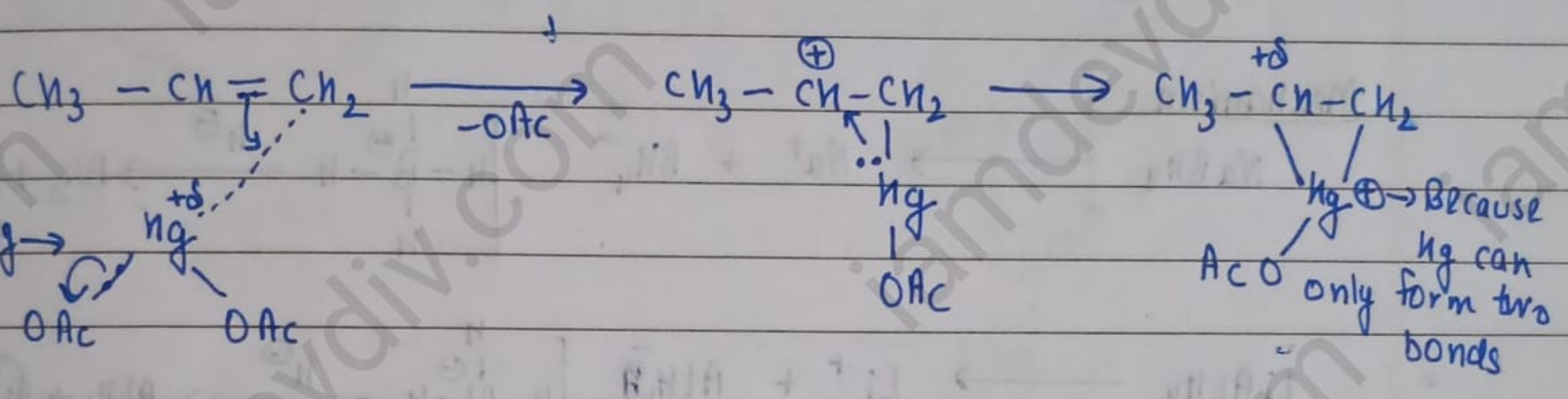
Symmetrical Alkene

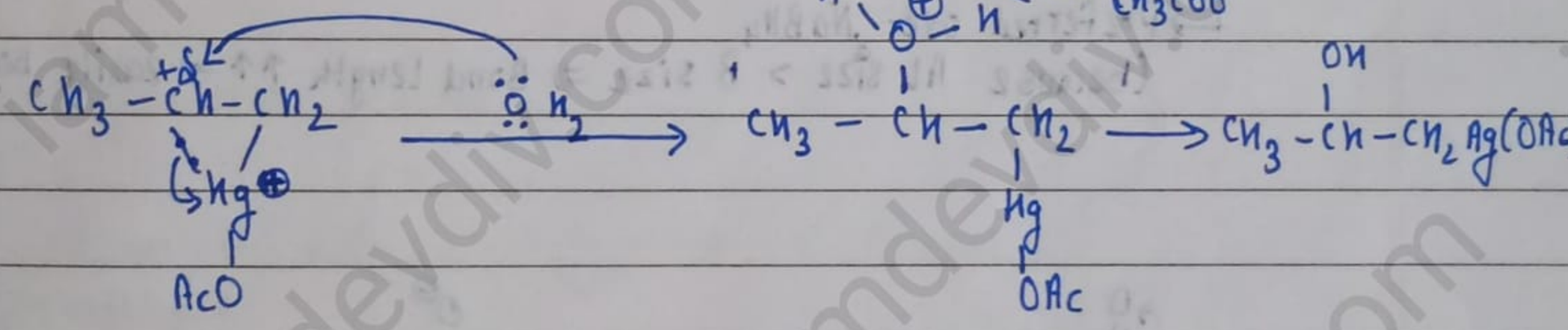
$$CH_2 = CH_2 \xrightarrow[NaBH_4]{Hg(OAc)_2 + H_2O} CH_3 - CH_2 - OH$$

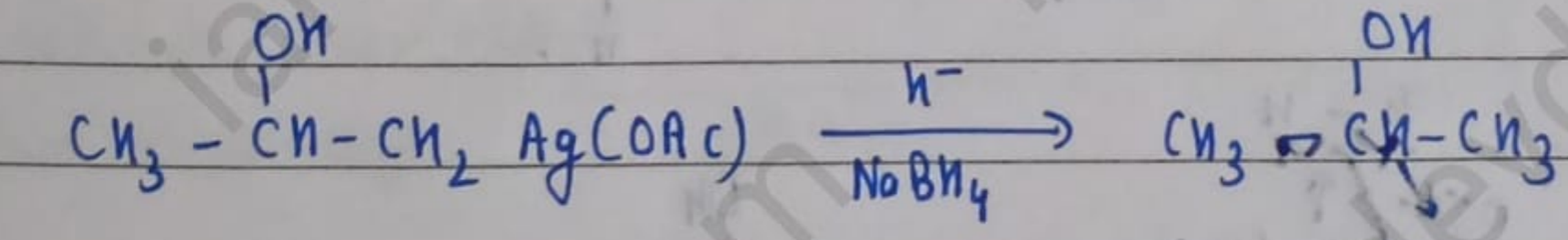
Unsymmetrical Alkene

$$CH_3-CH=CH_2 \xrightarrow[NaBH_4]{Hg(OAc)_2 + H_2O} CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$$

Mechanism







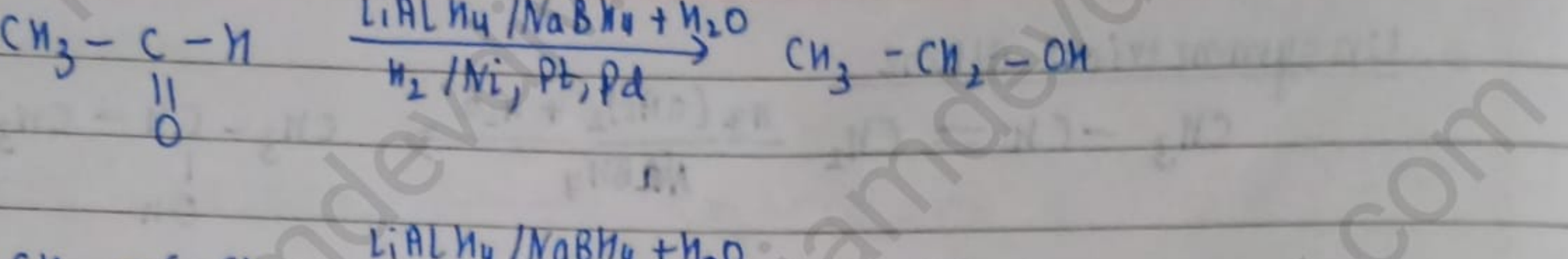
- FROM CARBONYL COMPOUND

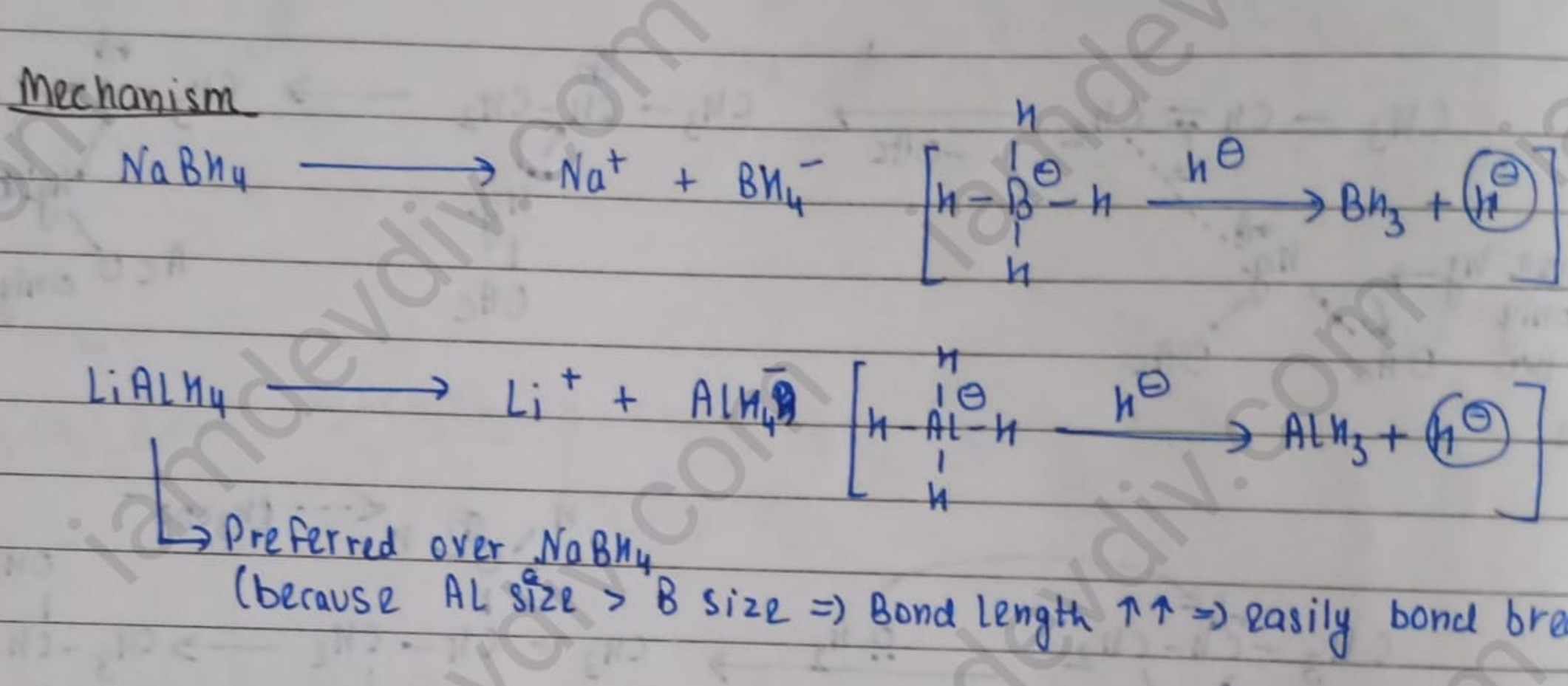
$$\text{L}\rightarrow -\underset{\underset{O}{\|}}{C}- \quad \left[\ \underset{R-\underset{\underset{O}{\|}}{C}-H}{\text{Aldehyde}} \qquad \underset{R-\underset{\underset{O}{\|}}{C}-R}{\text{Ketone}} \qquad \underset{R-\underset{\underset{O}{\|}}{C}-OH}{\text{Carboxylic acid}}\ \right]$$

* FROM ALDEHYDE AND KETONE

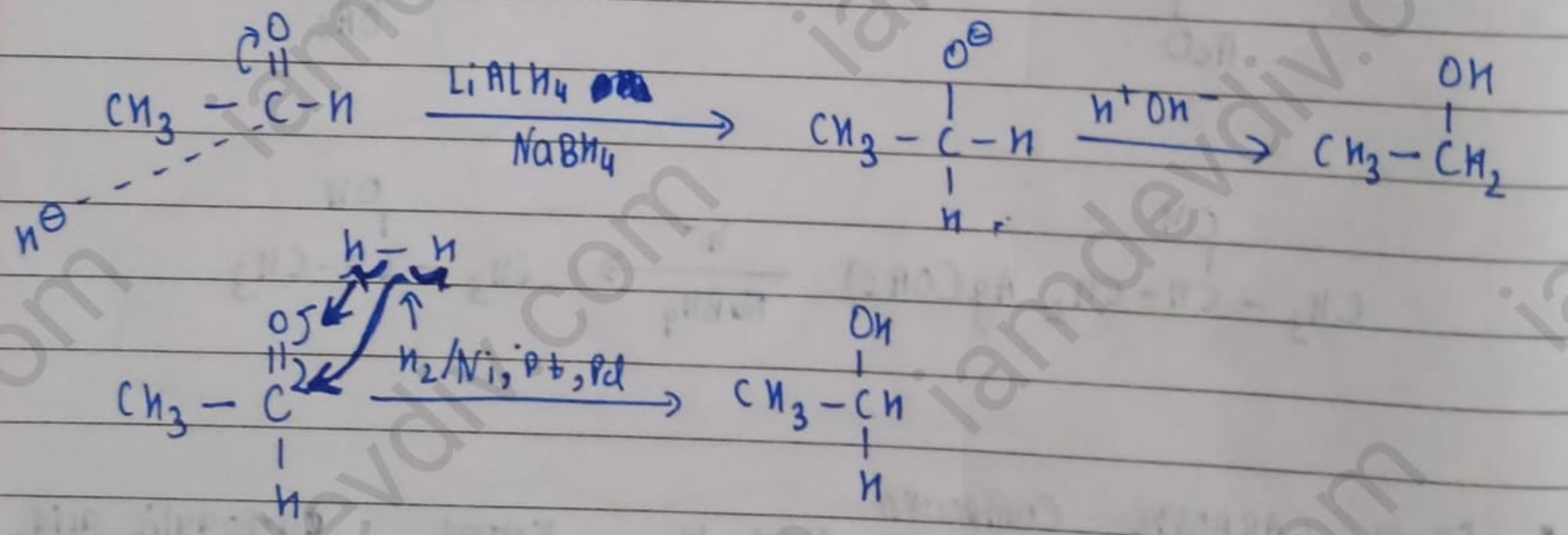
$$H-\underset{\underset{O}{\|}}{C}-H \xrightarrow[H_2/Ni,Pt,Pd]{LiAlH_4/NaBH_4+H_2O} H-CH_2-OH \Rightarrow CH_3OH$$

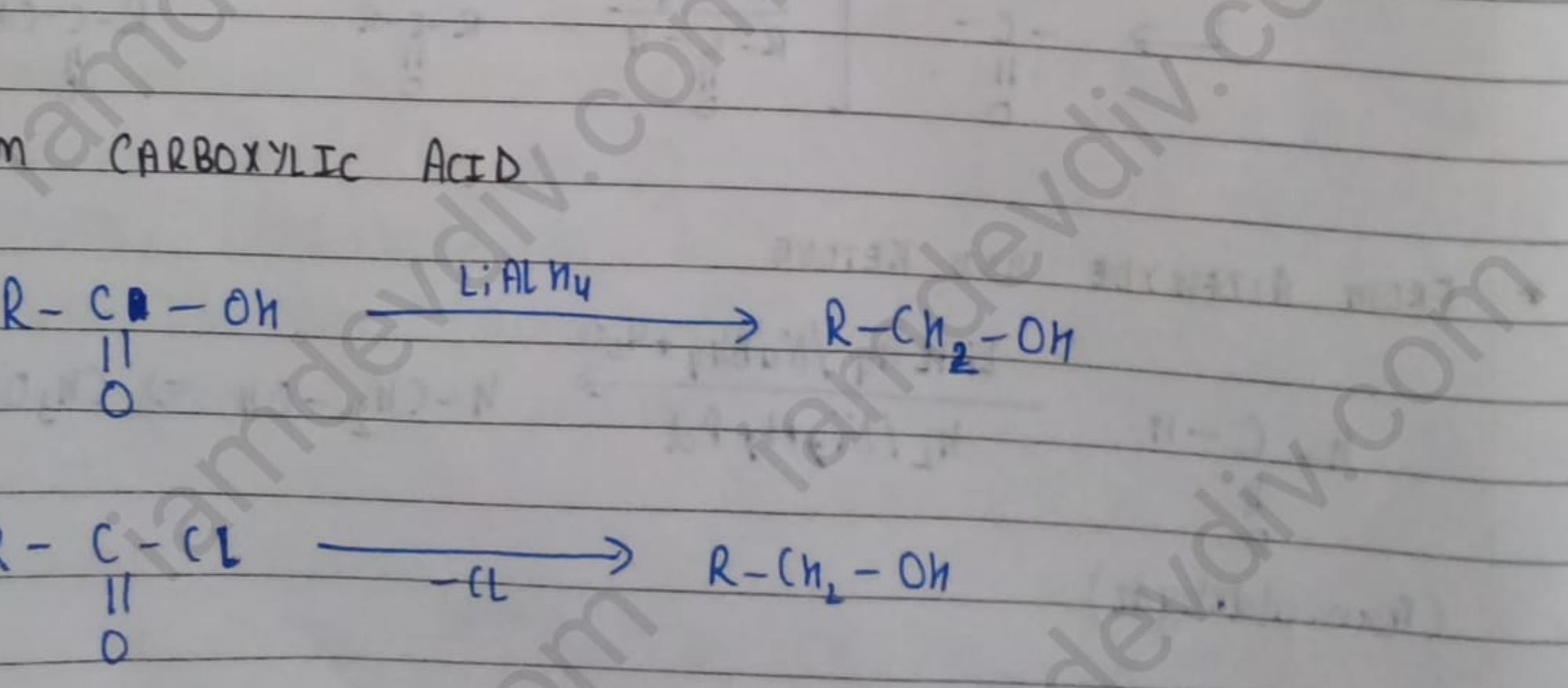
(Formaldehyde)



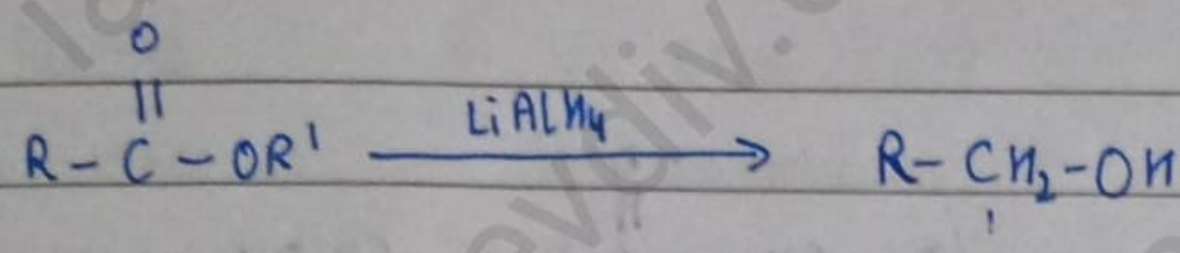


Mechanism

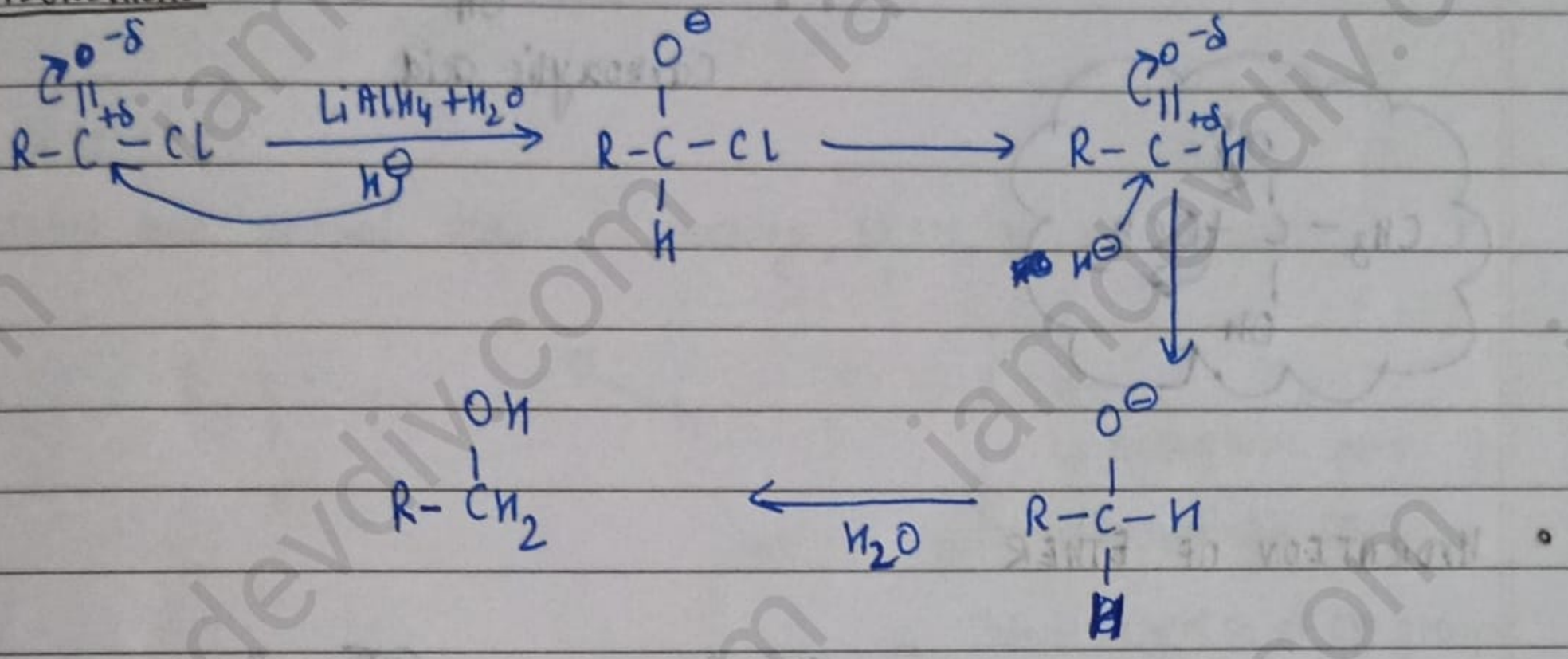




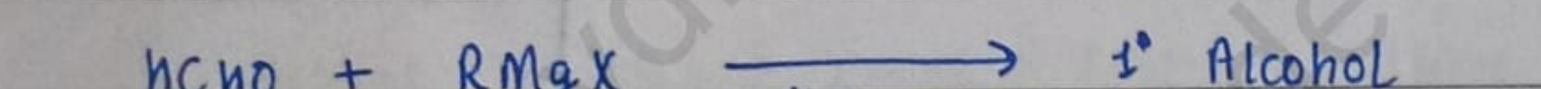
* FROM CARBOXYLIC ACID

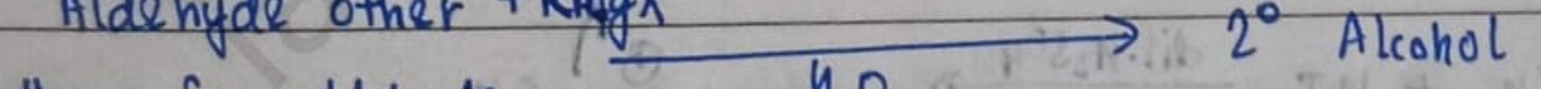


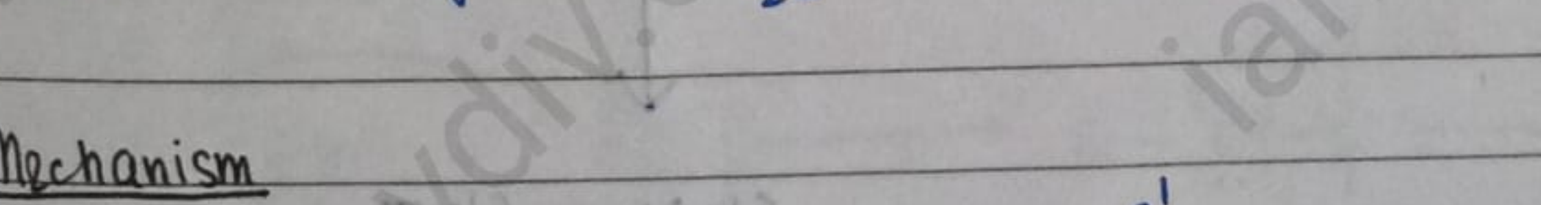
Mechanism



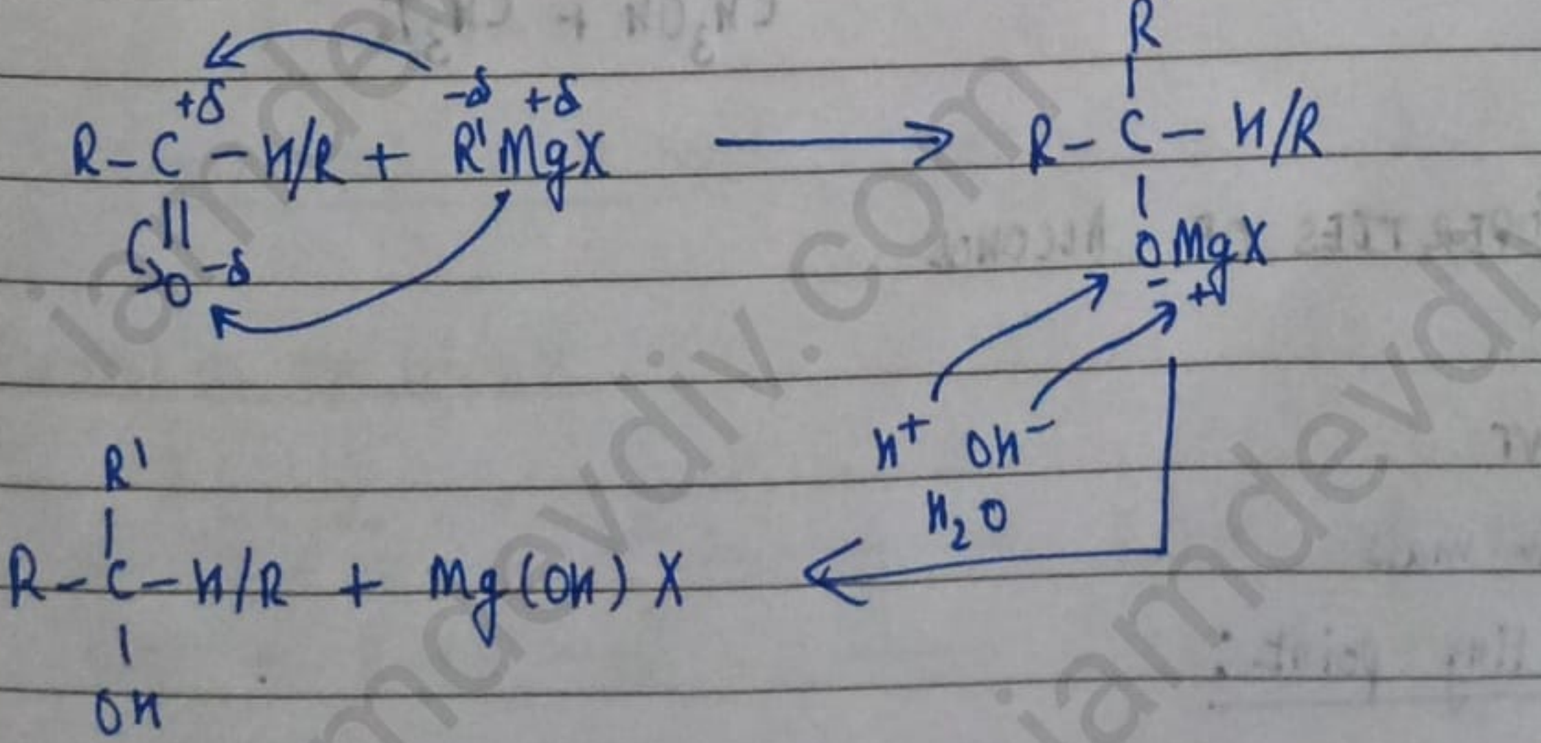
* FROM GRIGNARD REAGENT



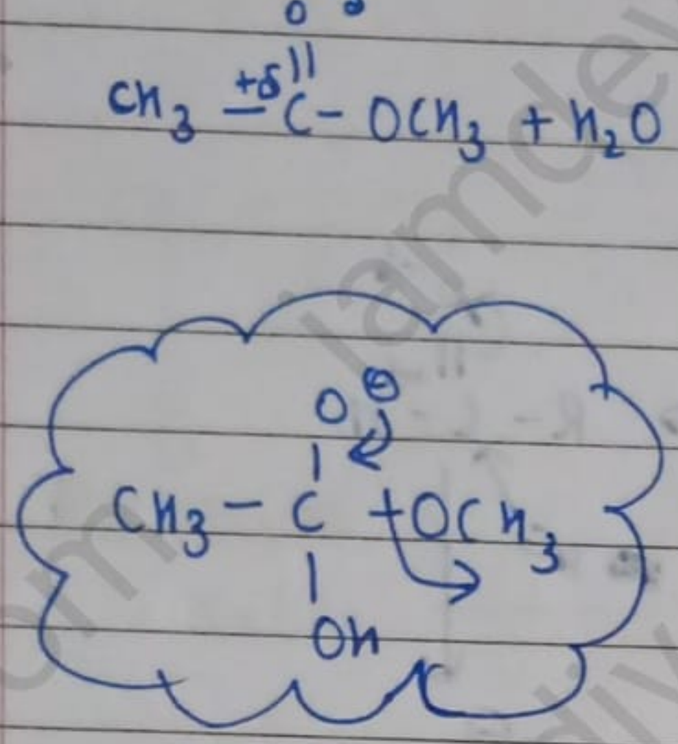




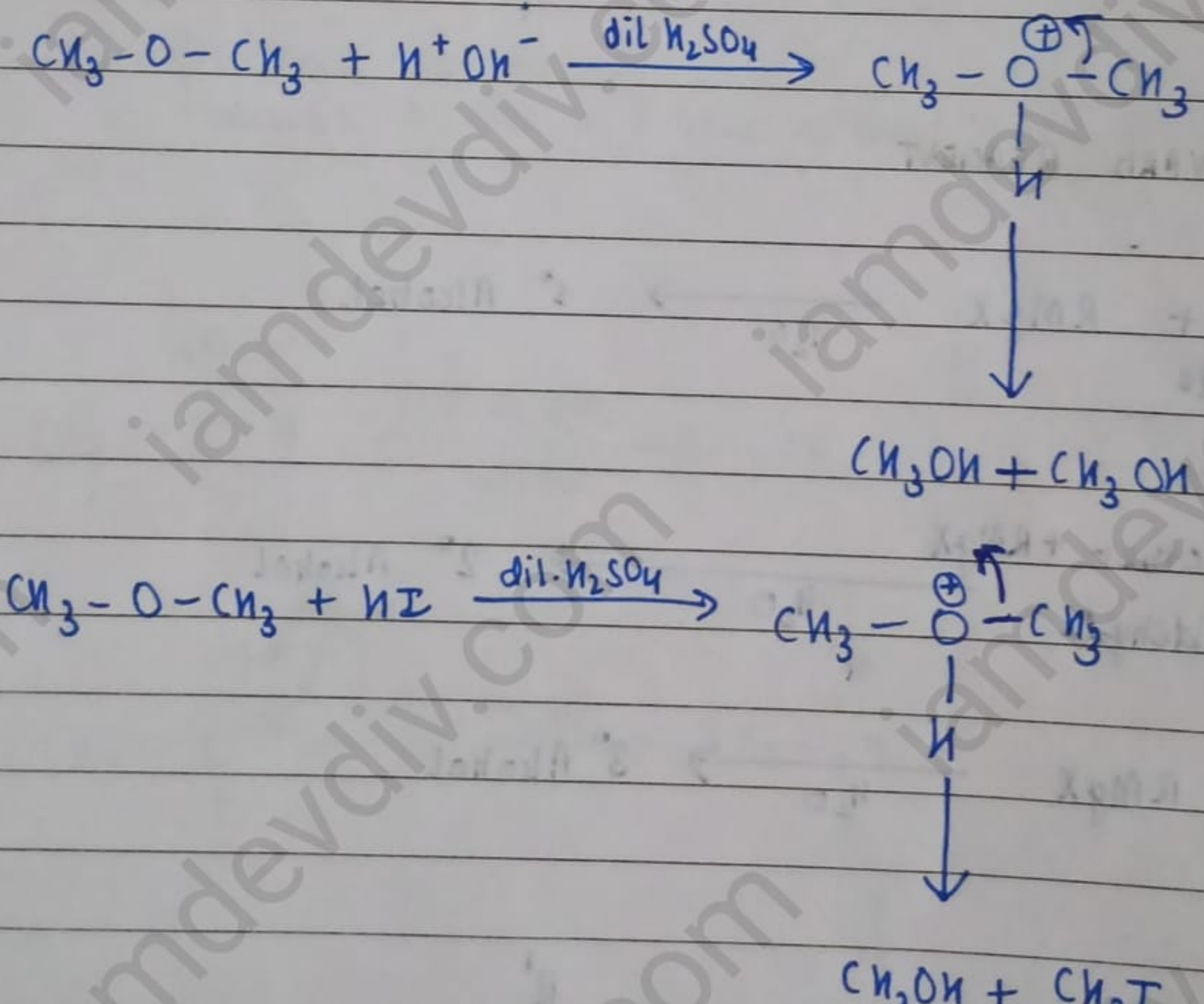
Mechanism



- HYDRATION OF ESTER



- HYDRATION OF ETHER



★ PHYSICAL PROPERTIES OF ALCOHOL

- BOILING POINT

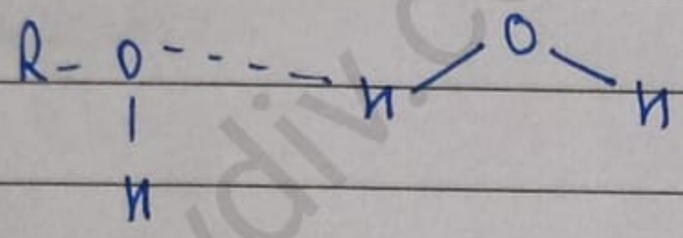
BTα Molecular mass

Order of boiling point:

Alcohol	>	Ether	>	Alkane
(Intermolecular H bonding)		(No intermolecular H bonding but it is polar)		(Non-polar)

- **SOLUBILITY**

Alcohol and phenol show H-bonding, so are soluble in water.



R-OH
↳ hydrophilic part
↳ hydrophobic part

Solubility $\propto$ No. of OH group $\propto \frac{1}{\text{No. of R group}}$

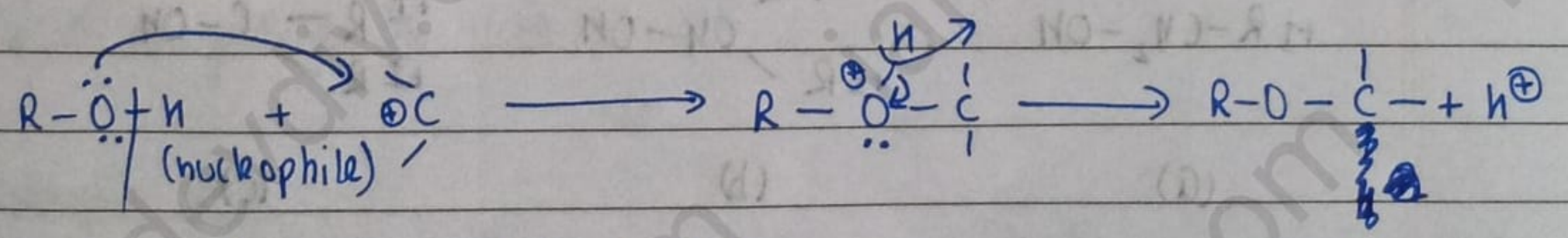
Order of solubility:

Alcohol > Aldehyde/Ketone > Ether > Alkane

☆ **CHEMICAL PROPERTIES OF ALCOHOL**

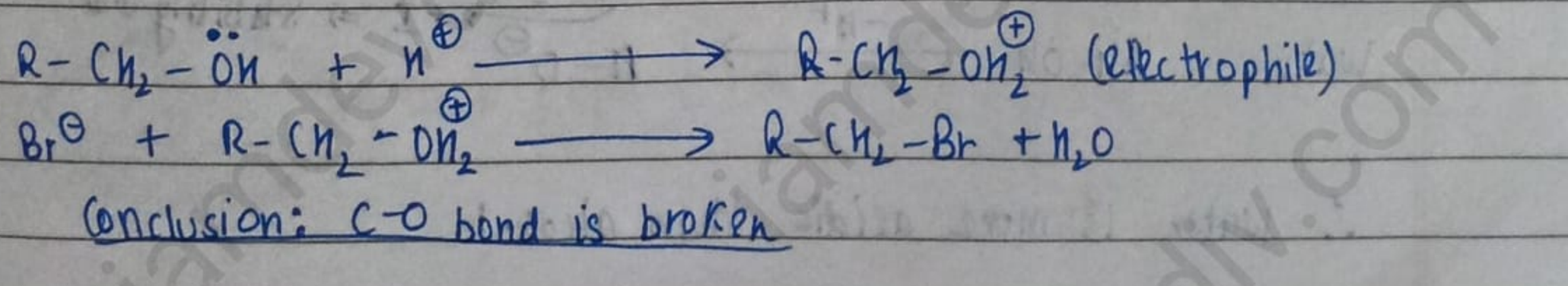
Alcohol behaves as both electrophile and nucleophile

Alcohol as nucleophile



Conclusion: O-H bond is broken

Alcohol as electrophile



Conclusion: C-O bond is broken

* Chemical properties when O-H bond is broken
(i) Acidity of Alcohol and Phenol
(ii) Esterification

* Chemical properties when C-O bond is broken
(i) Lucas reagent
(ii) PX_3
(iii) Dehydration
(iv) Oxidation

- ACIDITY OF ALCOHOL [redacted]

$$R-O(H \xrightarrow{-H^{\oplus}} R-O^{\ominus}$$
anion

Stability of alcohol depends upon stability of anion

Stability of alcohol $\propto$ anion $\propto$ -I $\propto$ -M $\propto \frac{1}{+I} \propto \frac{1}{+M}$

Q Write the order of stability of alcohol.

(a) $+I\ R-CH_2-OH$

(b) $R_{+I}-CH(R_{+I})-OH$

(c) $R_{+I}-C(R_{+I})(R_{+I})-OH$

Sol. Order : a > b > c

Q Which is more acidic : Alcohol or H_2O?

Sol. Alcohol $R-OH \xrightarrow{-H^+} R-O^{\ominus}$ ($+I \Rightarrow$ Stability ↓↓)

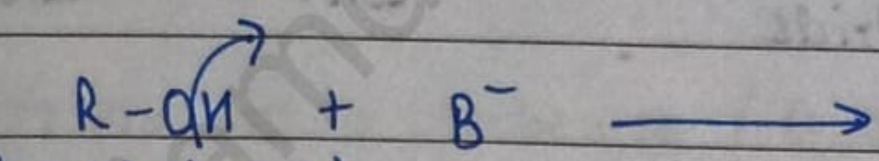
Water $H-OH \xrightarrow{-H^+} H-O^{\ominus}$

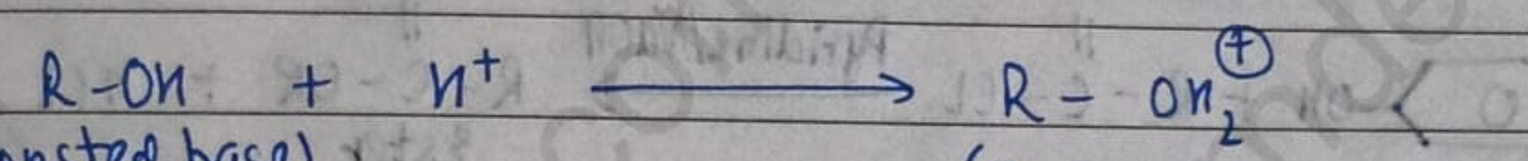
∴ Water is more acidic than alcohol

* **BRONSTED ACID/BASE**

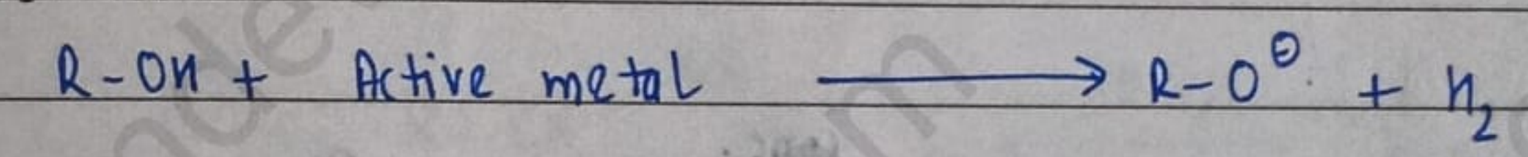
Alcohol acts as <u>bronsted acid</u> as well as <u>bronsted base</u>

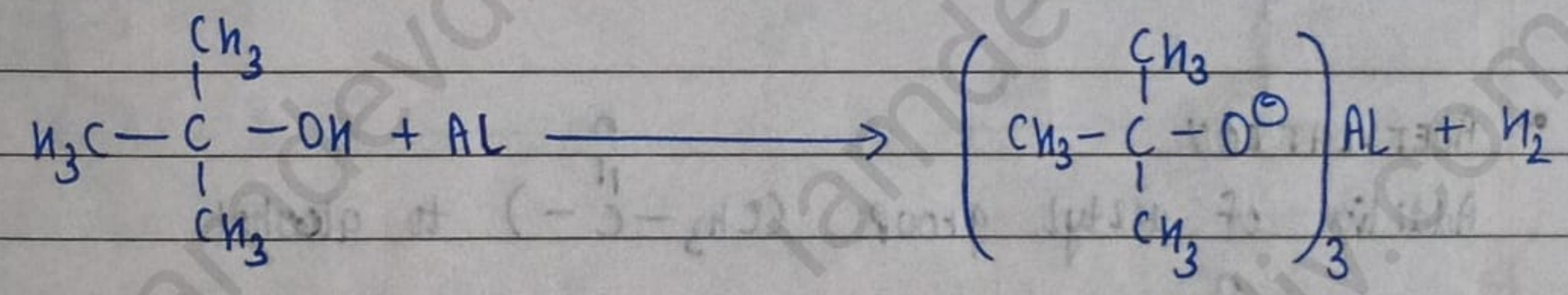
(H^+ donor) (H^+ acceptor)





- **REACTION OF METALS**



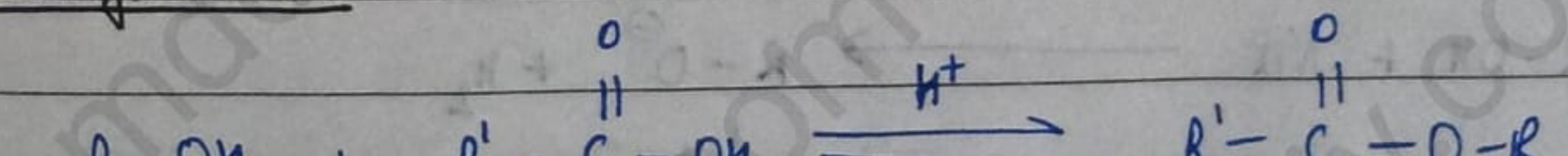


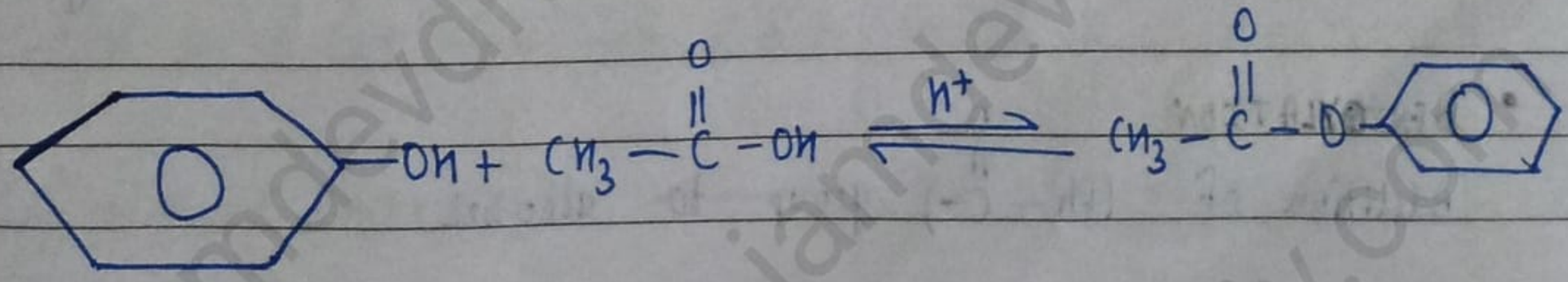
- **ESTERIFICATION**

Alcohol ⟶ Ester

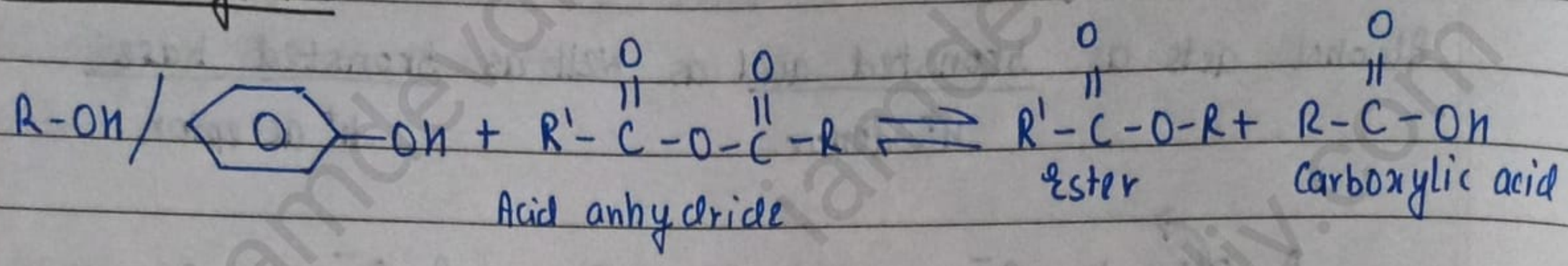
It can be produced by reacting alcohol either by carboxylic acid or acid anhydride or acid chloride.

<u>Carboxylic acid</u>

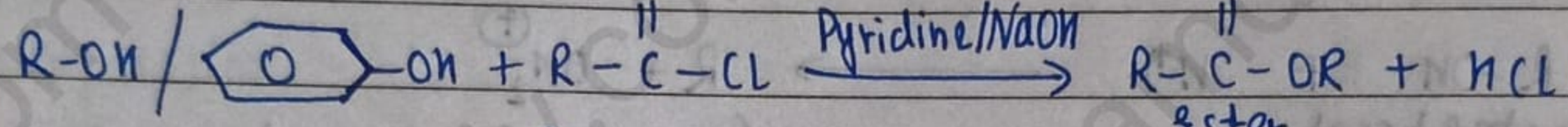




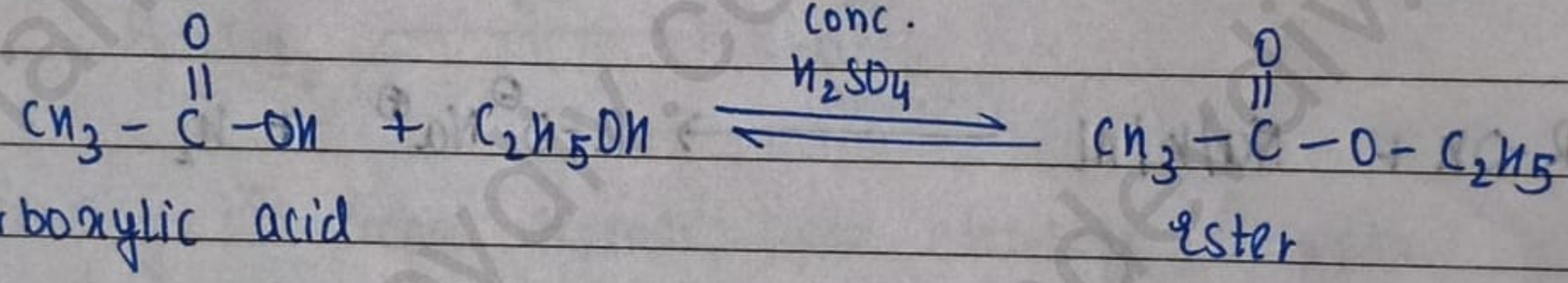
Acid anhydride



Acid chloride

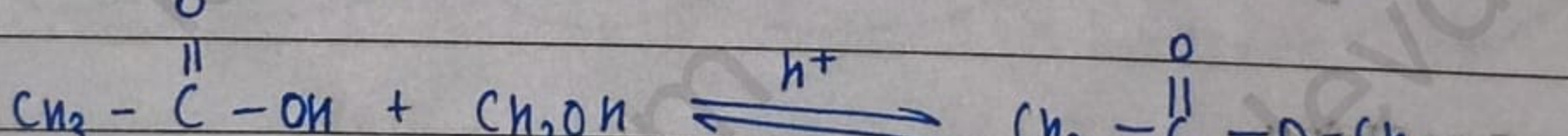


Example



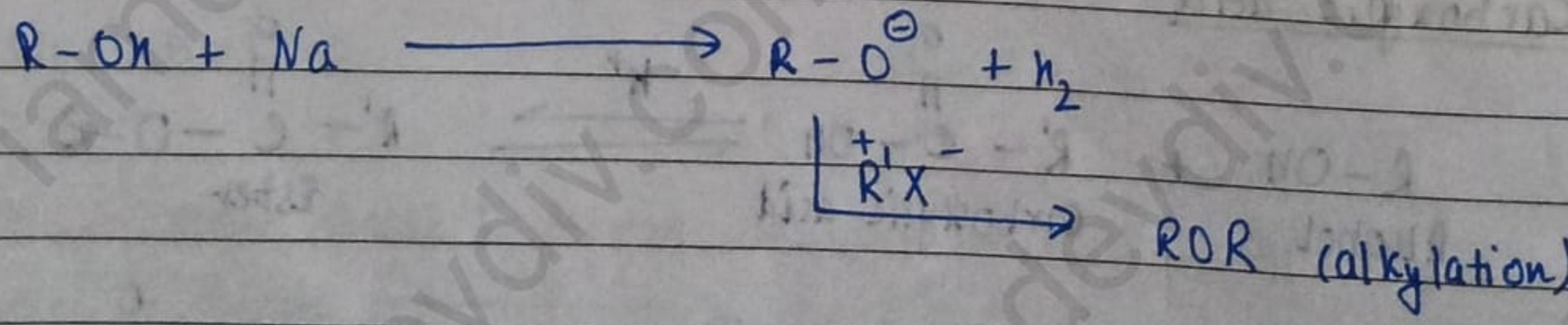
- **ACETYLATION**

Addition of acetyl group ($CH_3-\overset{O}{\overset{\|}{C}}-$) to alcohol



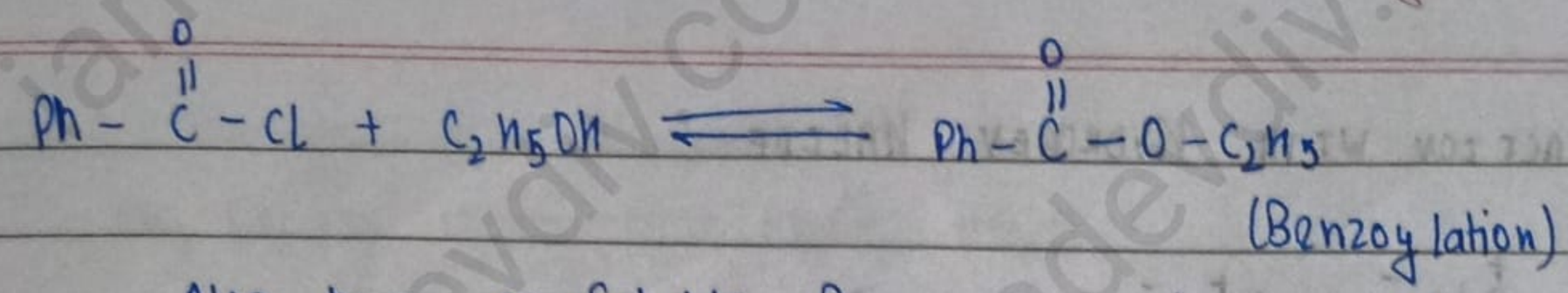
- **ALKYLATION**

Addition of alkyl group to alcohol



- **BENZOYLATION**

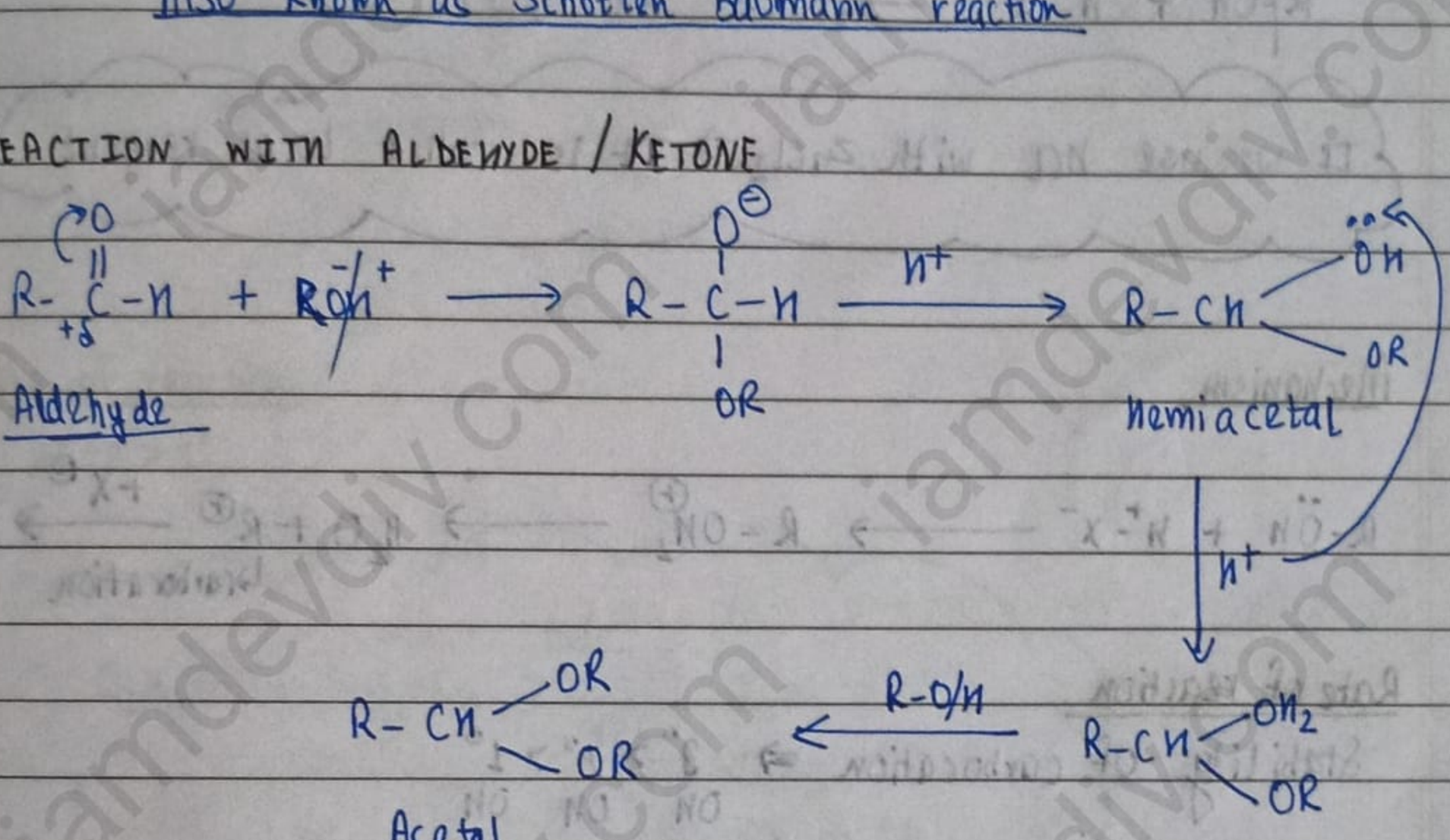
Addition of ($Ph-\overset{O}{\overset{\|}{C}}-$) group to alcohol



(Benzoylation)

Also known as Schotten Baumann reaction

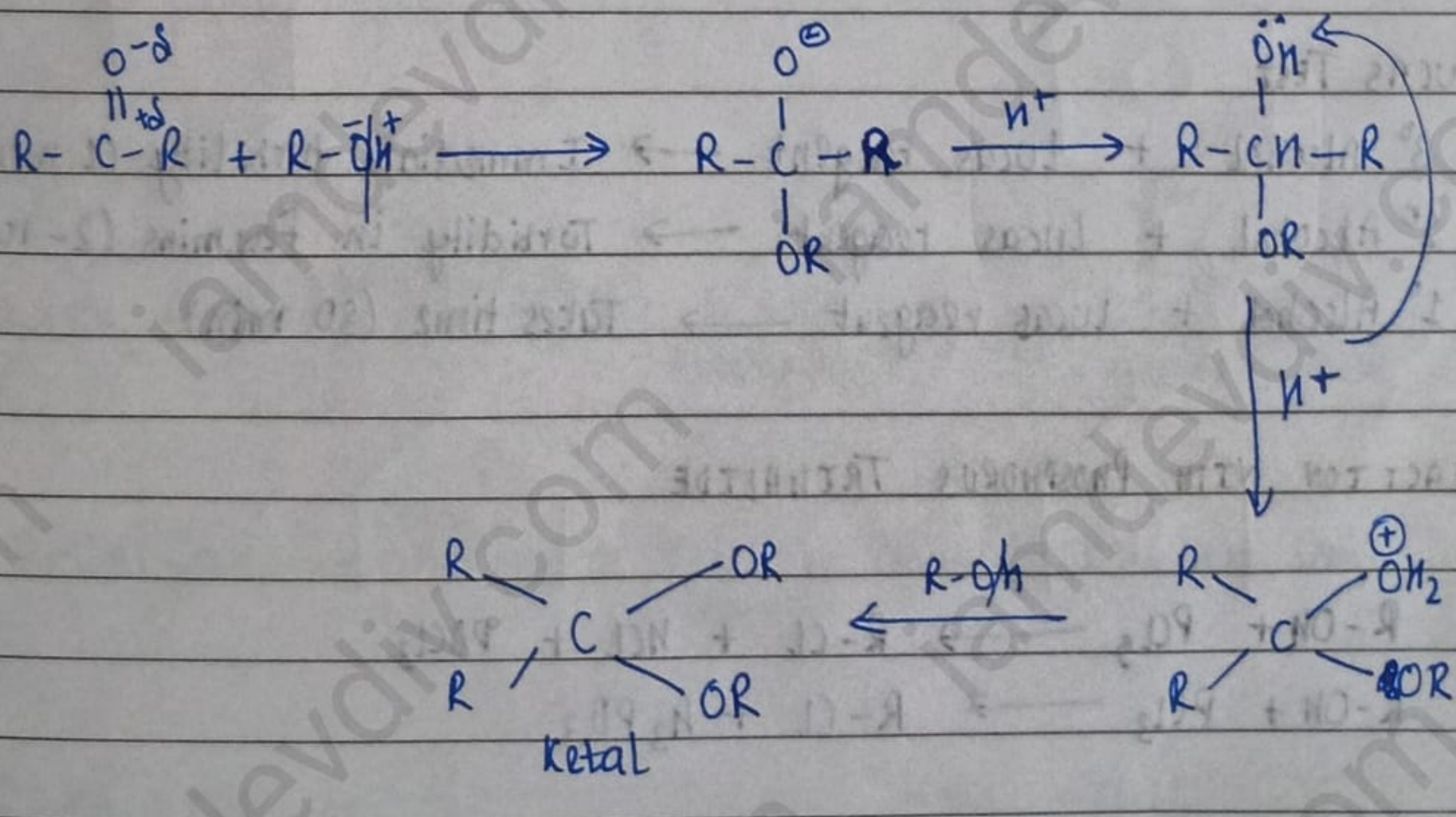
- REACTION WITH ALDEHYDE / KETONE



Aldehyde

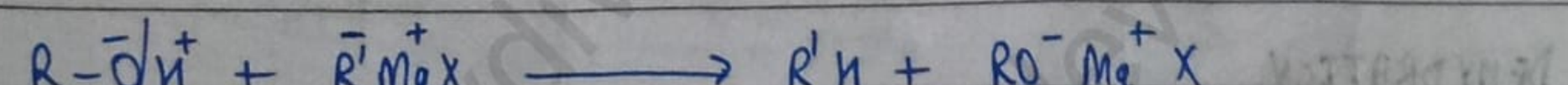
Hemiacetal

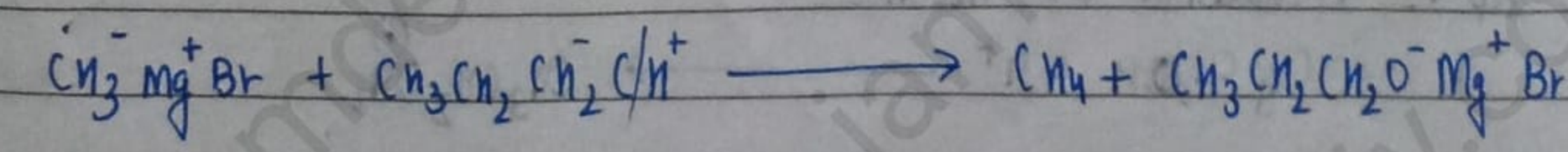
Acetal



Ketal

- REACTION WITH GRIGNARD REAGENT





- REACTION WITH HYDROGEN HALIDE

$$R\overset{+}{-}O\overset{-}{H} + H^+X^- \longrightarrow RX + H_2O$$

If we use HCl with $ZnCl_2$ ⇒ It is called Lucas reagent

Mechanism

$$R-\ddot{O}H + H^+-X^- \longrightarrow R-OH_2^{\oplus} \longrightarrow H_2O + R^{\oplus} \xrightarrow{+X^{\ominus}} R-X + H_2O$$

(carboration)

Rate of reaction

Stability of carbocation ⇒ $\underset{OH}{3^\circ} > \underset{OH}{2^\circ} > \underset{OH}{1^\circ}$

- LUCAS TEST

3° Alcohol + Lucas reagent ⟶ Immediate turbility (1 min)
2° Alcohol + Lucas reagent ⟶ Turbidity in Few mins (2-10 mins)
1° Alcohol + Lucas reagent ⟶ Takes time (30 min)

- REACTION WITH PHOSPHORUS TRIHALIDE

$$R-OH + PCl_5 \longrightarrow R-Cl + HCl + POCl_3$$
$$R-OH + PCl_3 \longrightarrow R-Cl + H_3PO_3$$

- REACTION WITH THIONYL CHLORIDE

$$R-OH + SOCl_2 \longrightarrow R-Cl + HCl + SO_2$$

- DEHYDRATION

Step-1 Protonation of Alcohol

$$CH_3CH_2\ddot{O}H + H^+ \longrightarrow CH_3CH_2O\overset{\oplus}{H}_2$$

Step-2 Formation of carbocation

$$CH_3CH_2\overset{\oplus}{O}H_2 \longrightarrow CH_3\overset{\oplus}{C}H_2 + H_2O$$

Step-3

$$CH_3\overset{\oplus}{C}H_2 \rightleftharpoons CH_2=CH_2 + H^+$$

Alkene

Rate of reaction

$3^\circ > 2^\circ > 1^\circ$

$$C_2H_5OH + \underset{\text{conc.}}{H_2SO_4} \xrightarrow{100^\circ C} C_2H_5-HSO_4$$

$$\xrightarrow{140^\circ C} C_2H_5-O-C_2H_5$$

$$\xrightarrow{170^\circ C} CH_2=CH_2$$

- OXIDATION

$$R-CH_2-OH \xrightarrow{KMnO_4/K_2Cr_2O_7} \underset{\text{Aldehyde}}{RCHO} \longrightarrow \underset{\text{Carboxylic acid}}{RCOOH}$$

$$R-CH_2-OH \xrightarrow{CrO_3} \underset{\text{Aldehyde}}{R-CHO}$$ (good yield is not seen)

$$R-CH_2-OH \xrightarrow{PCC} R-CHO$$ (good yield)

2° Alcohol $\longrightarrow$ ketone

high temp^r $\longrightarrow$ ketone $\longrightarrow$ RCOOH

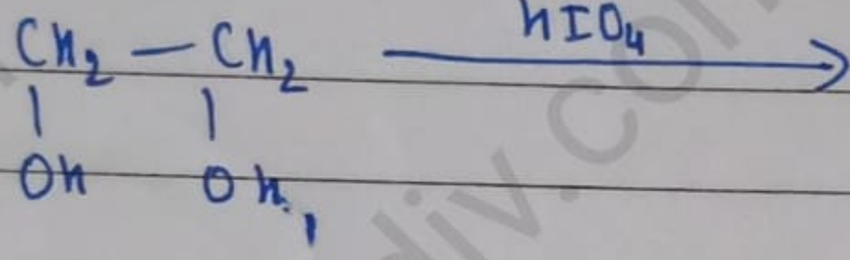
- REACTION WITH $Cu/300^\circ C$

1° Alcohol ⟶ Aldehyde

2° Alcohol ⟶ Ketone

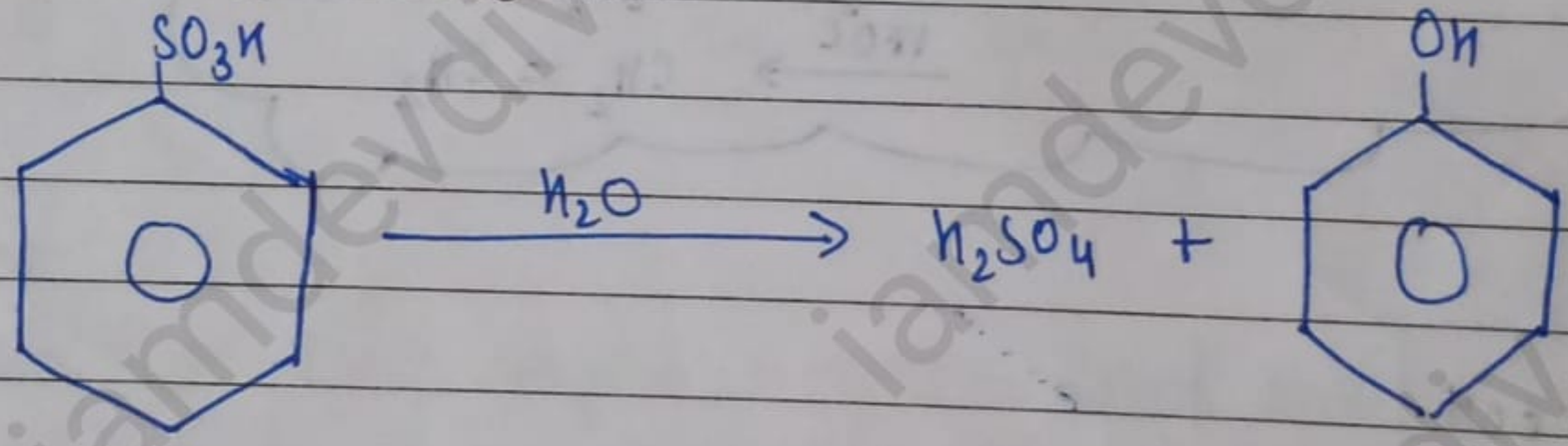
3° Alcohol ⟶ Alkene

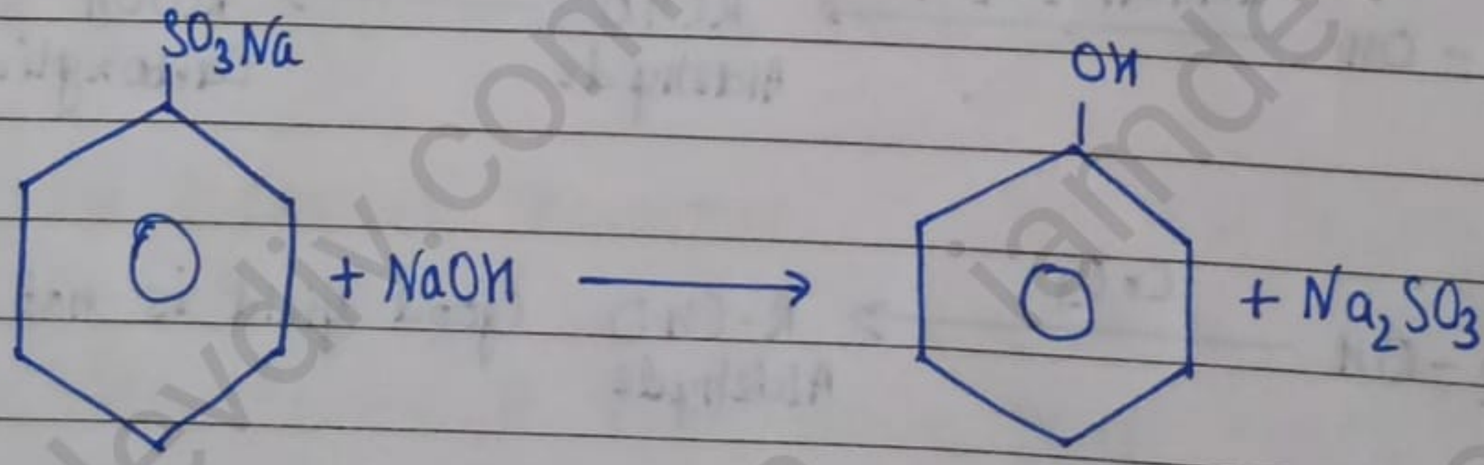
- REACTION WITH HIO_4



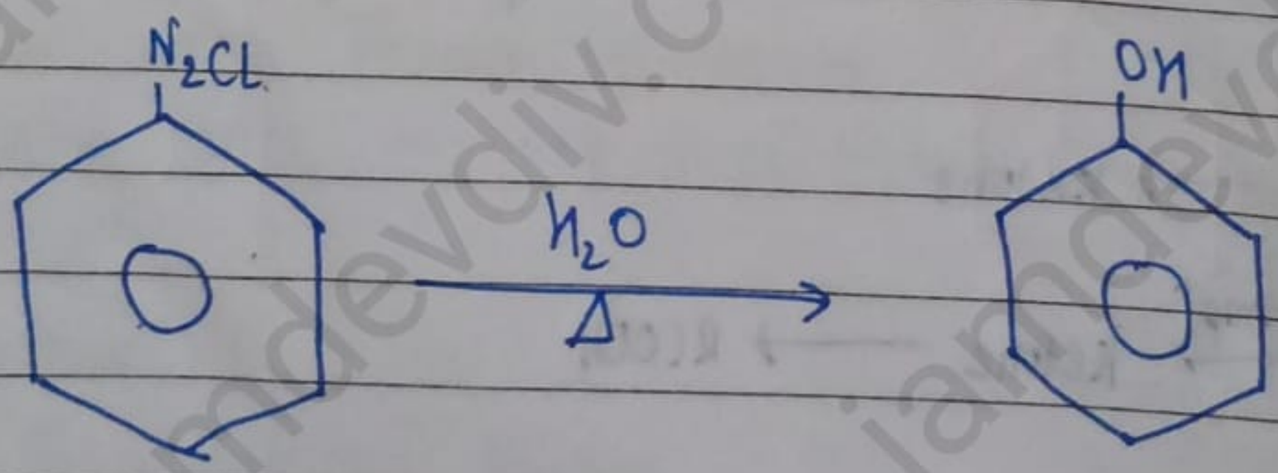
★ METHODS OF PREPARATION OF PHENOL

- FROM BENZENE SULPHURIC ACID

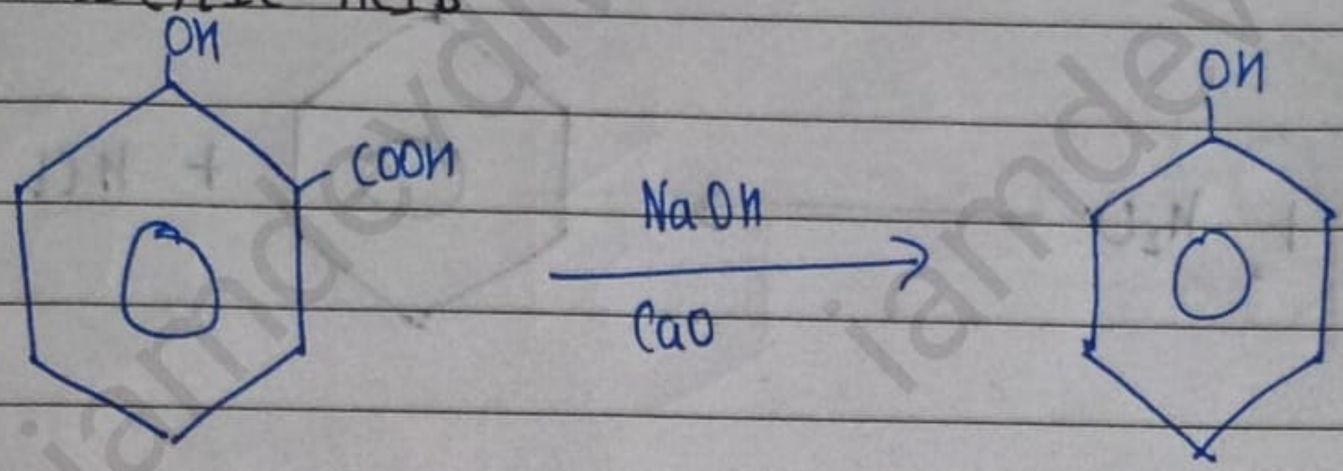




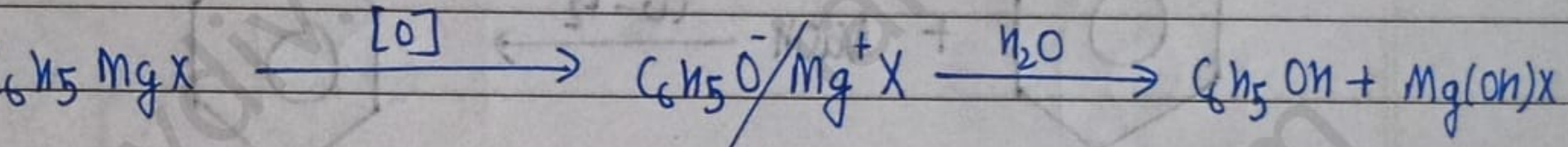
- FROM DIAZONIUM SALT



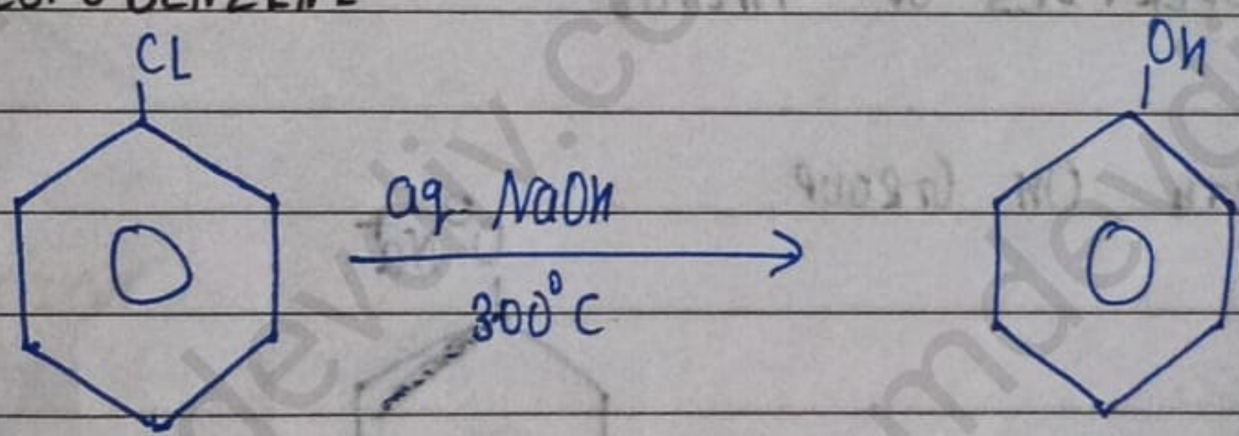
- FROM SALICYLIC ACID



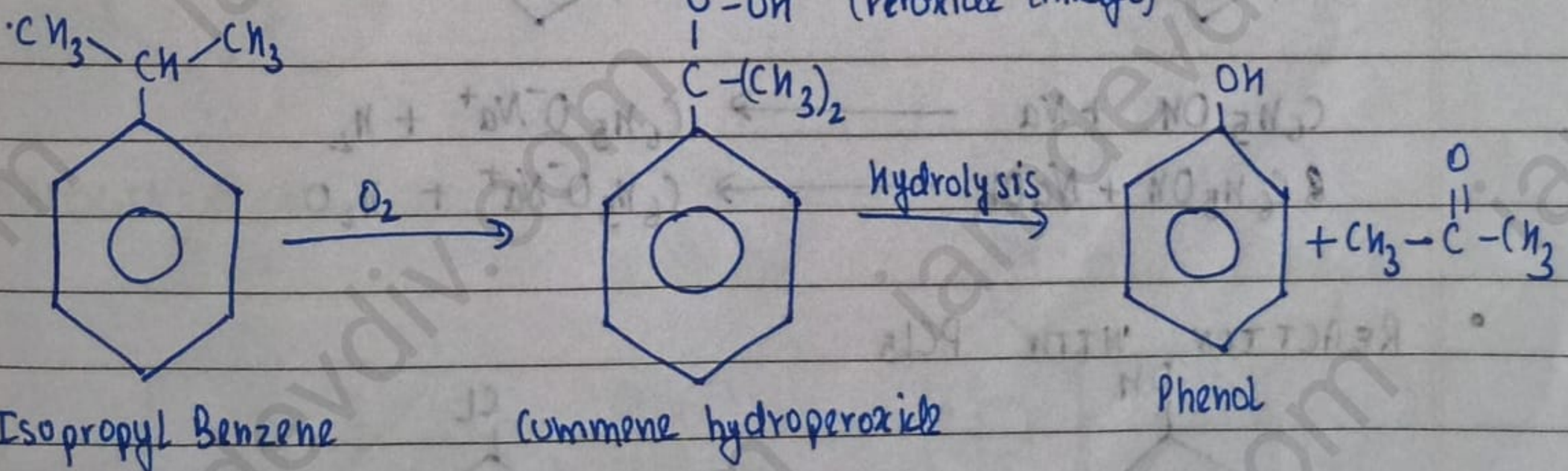
- FROM GRIGNARD REAGENT



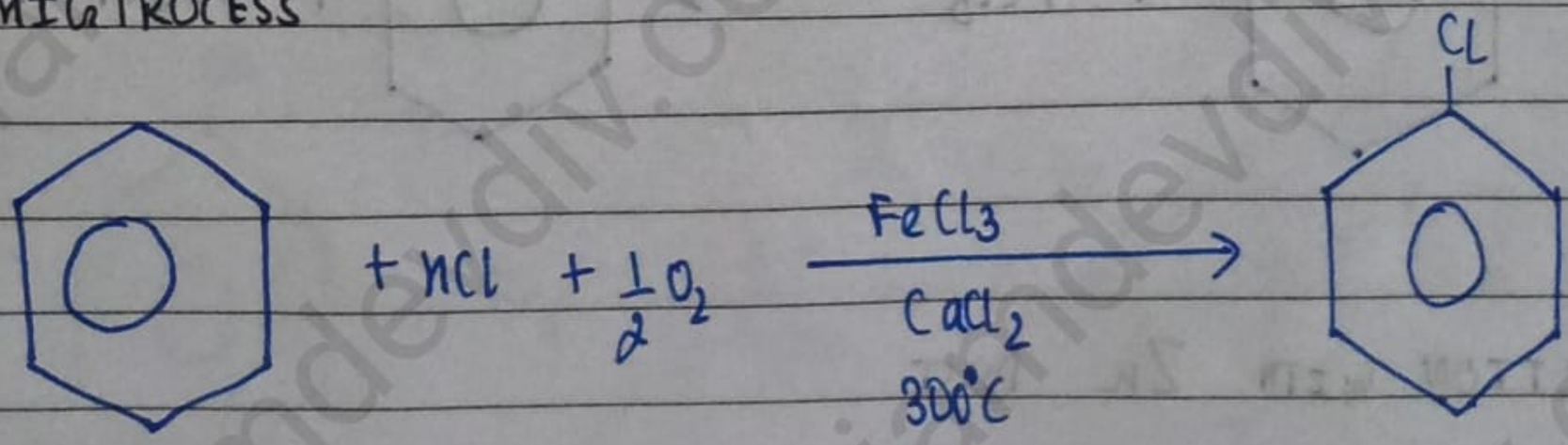
- FROM CHLOROBENZENE

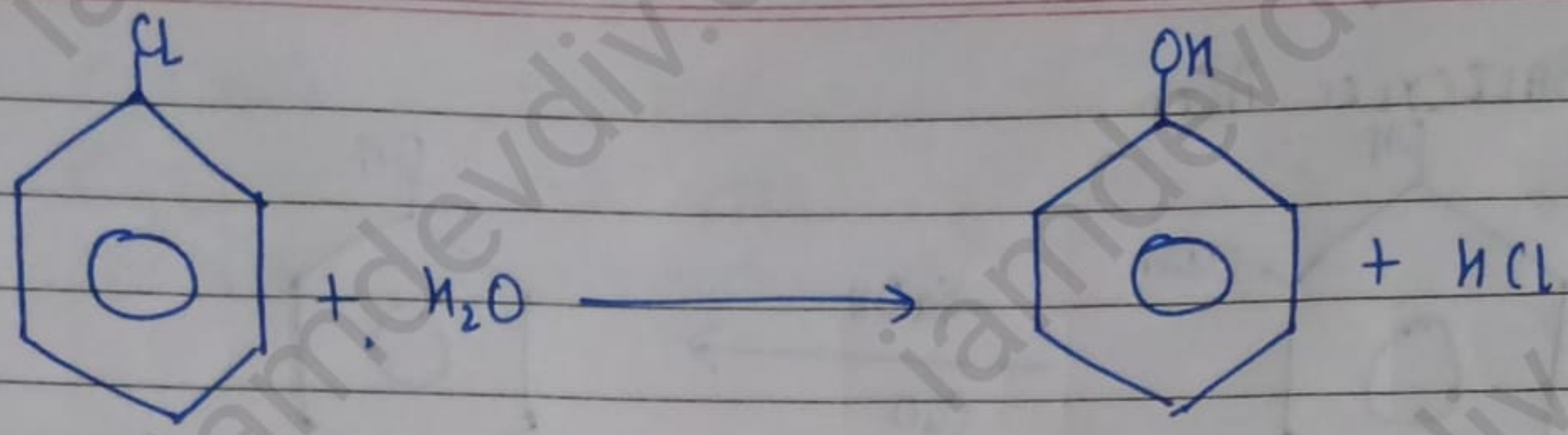


- FROM CUMMENE

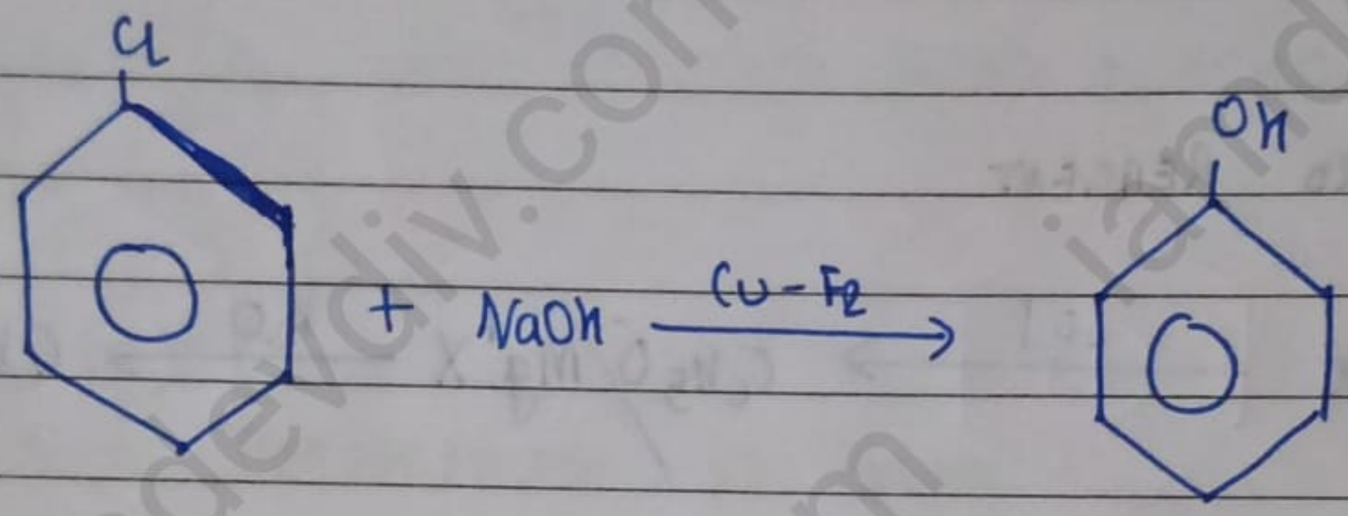


- RASCHIG PROCESS



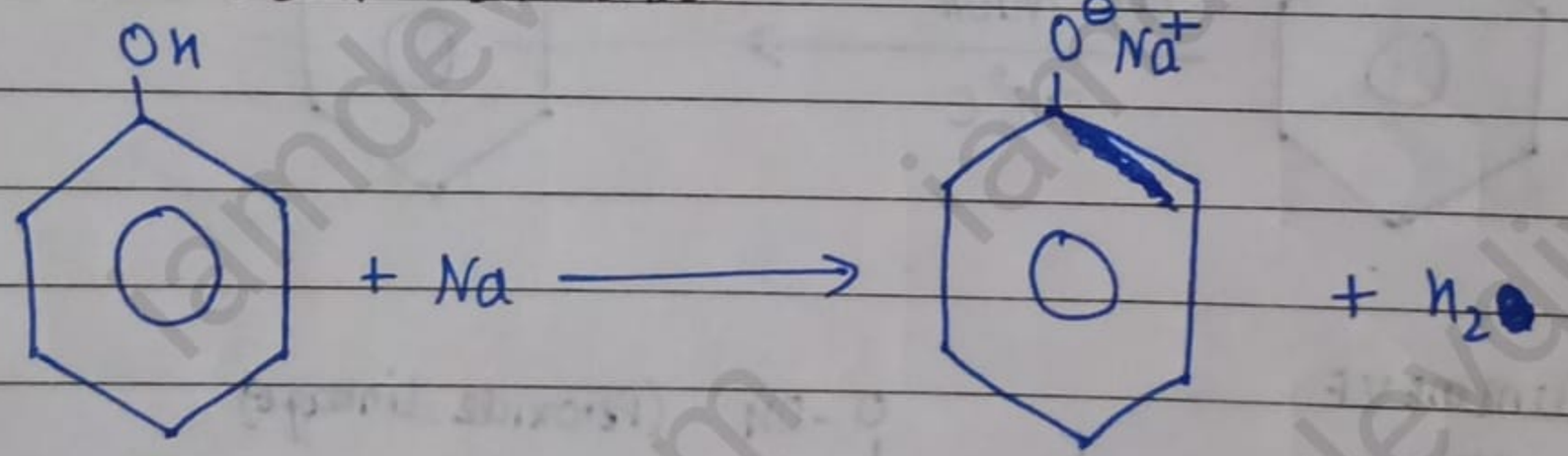


- DOWS PROCESS



☆ CHEMICAL PROPERTIES OF PHENOL

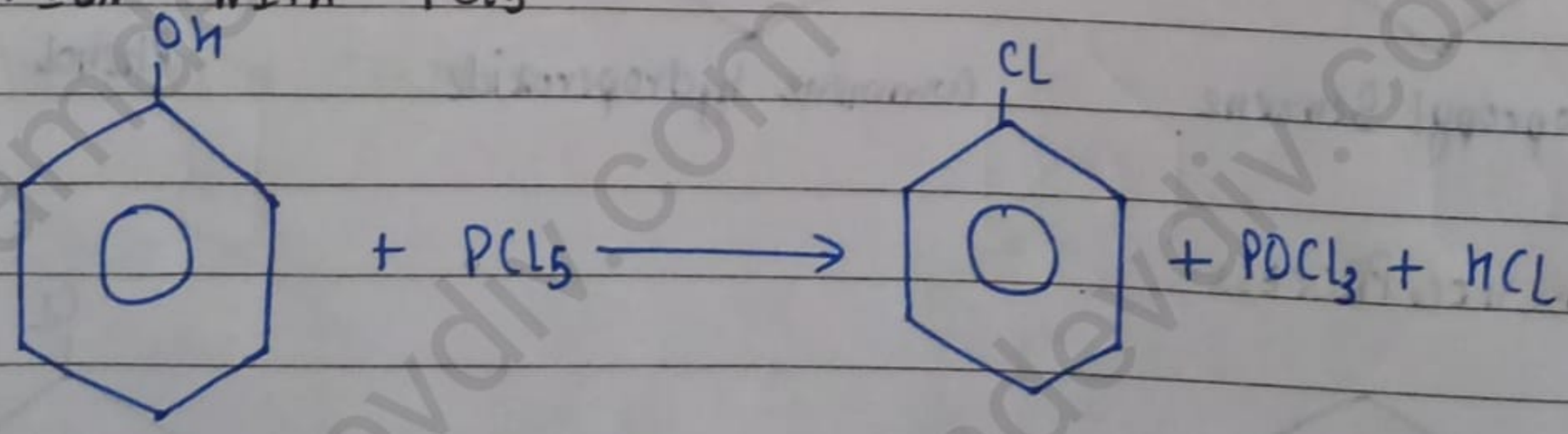
- REACTION WITH OH GROUP



$C_6H_5OH + Na \longrightarrow C_6H_5O^-Na^+ + H_2$

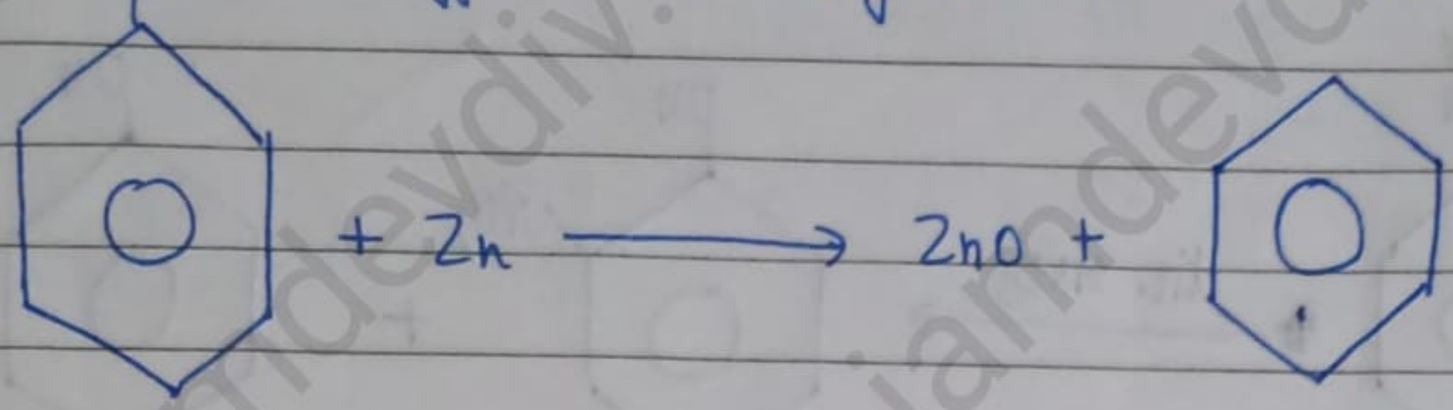
$C_6H_5OH + NaOH \longrightarrow C_6H_5O^-Na^+ + H_2O$

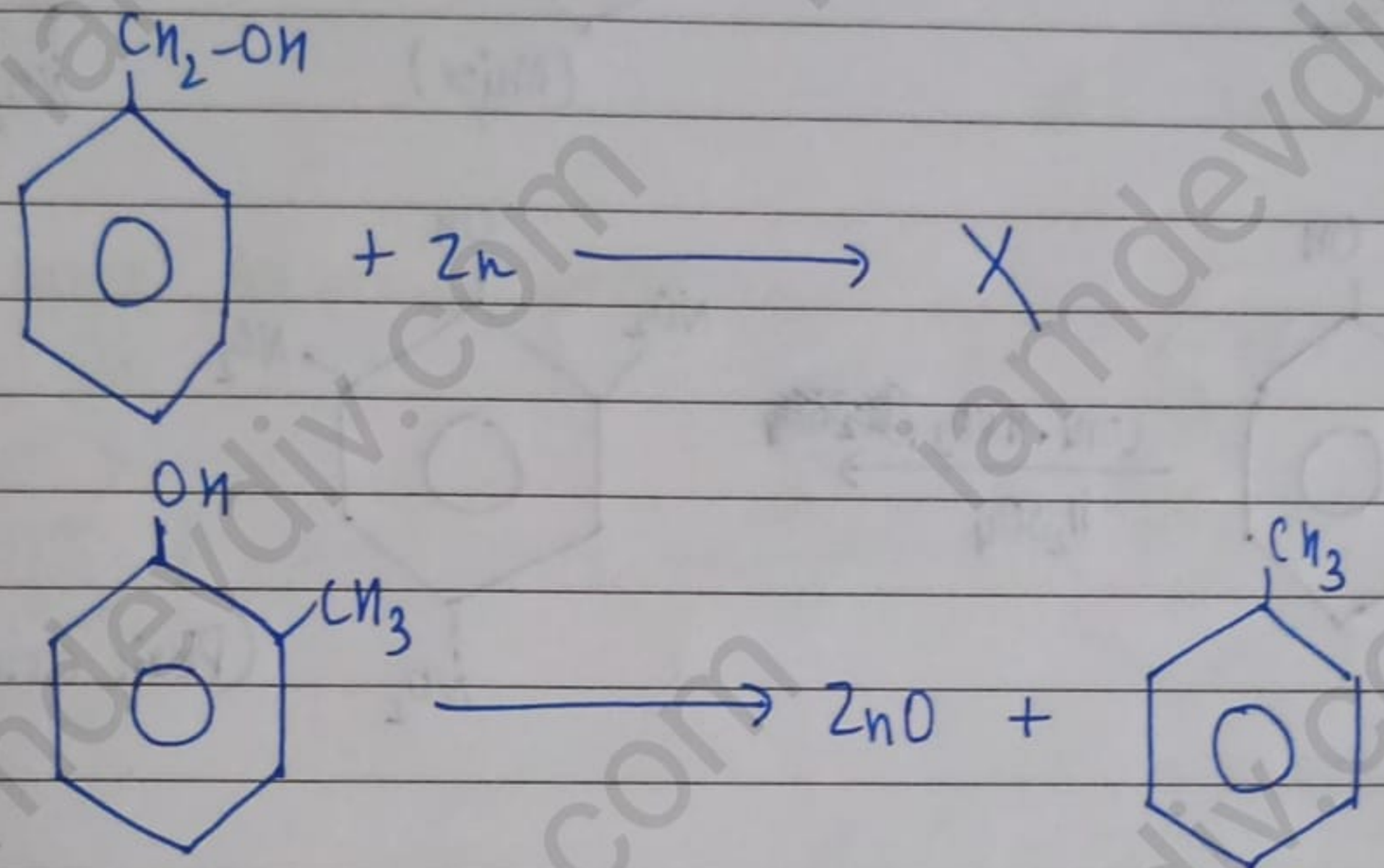
- REACTION WITH PCl_5



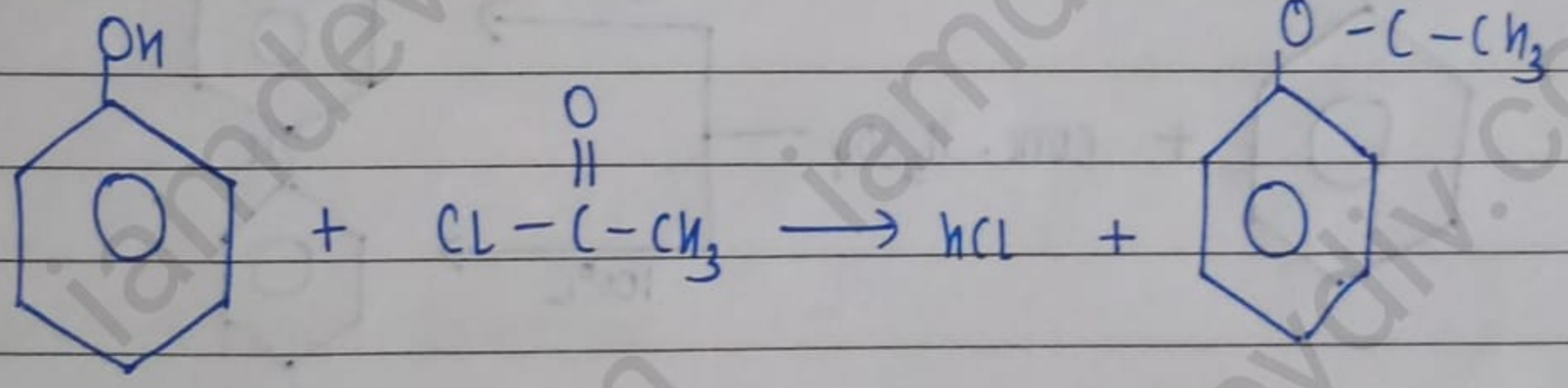
- REACTION WITH Zn DUST

OH → Oxygen should directly be bonded with Benzene

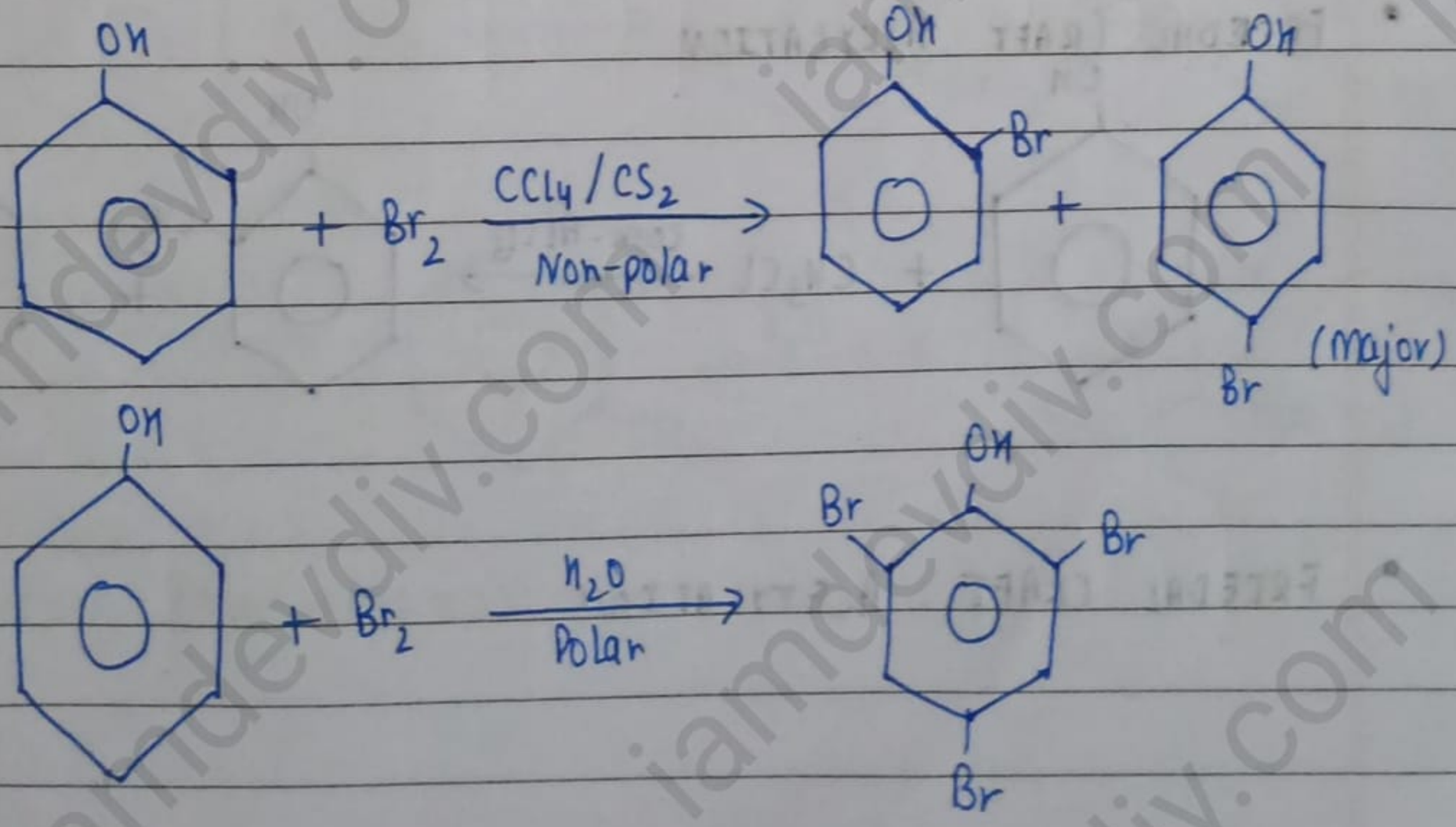




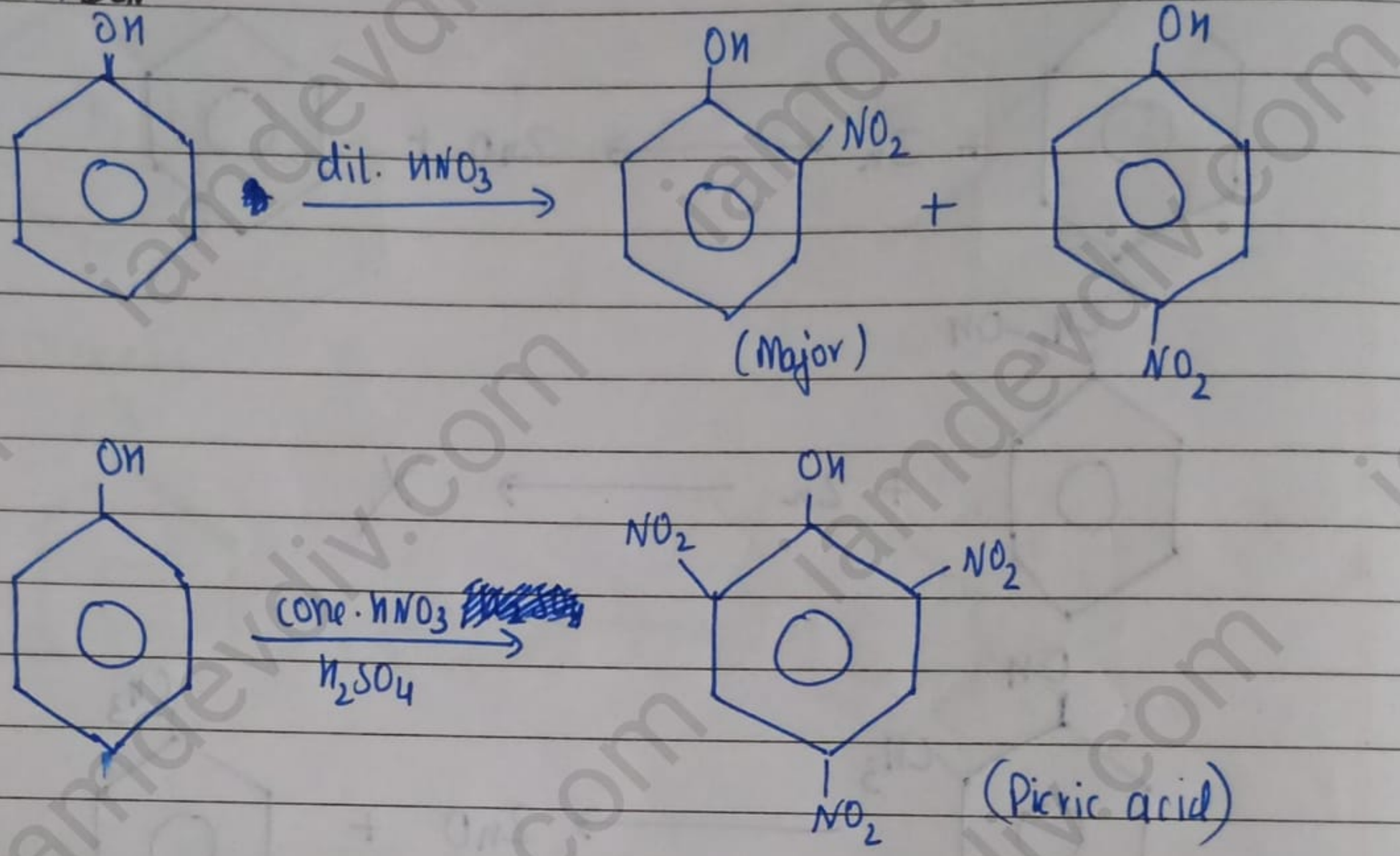
- ACETYLATION



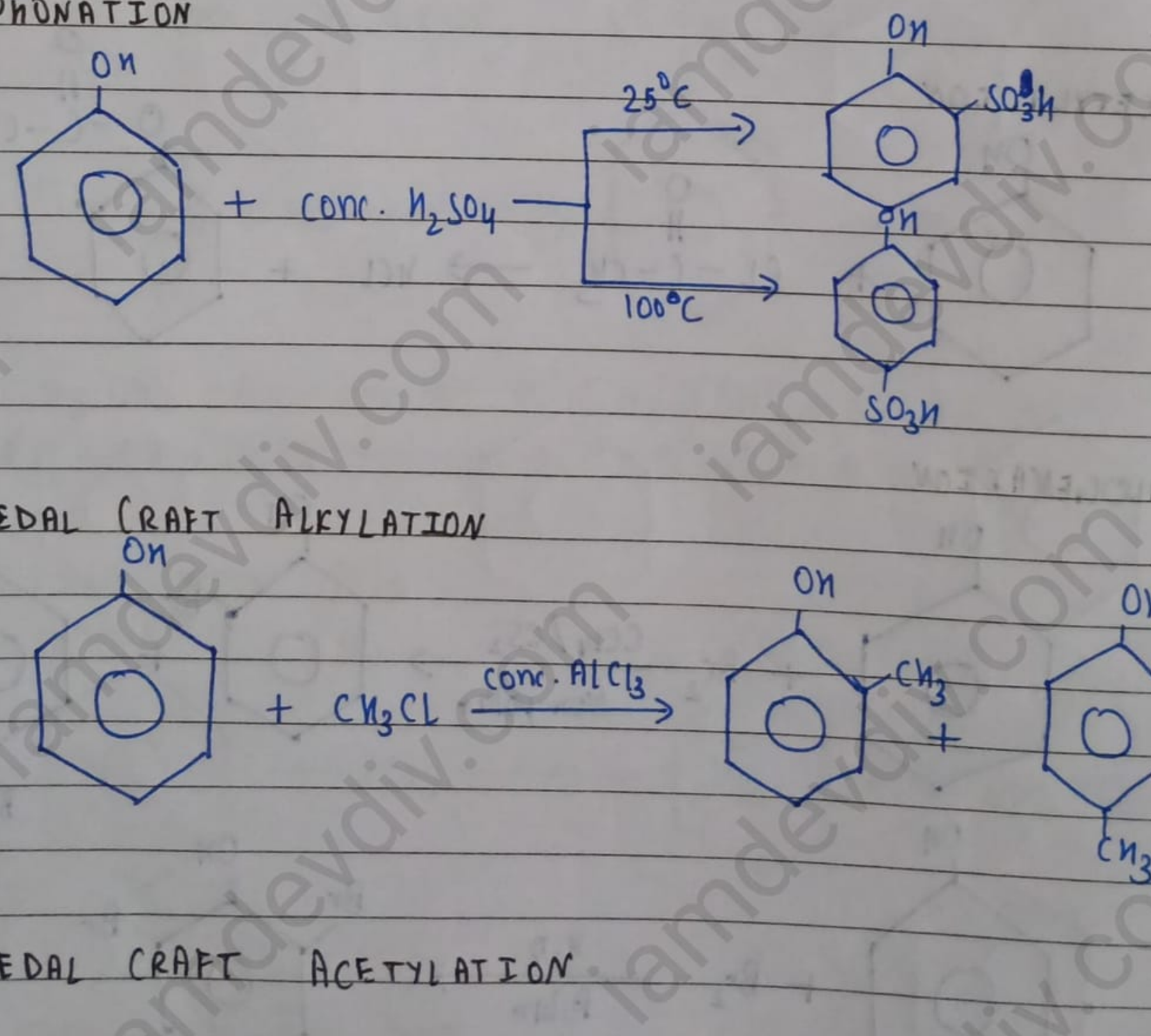
- HALOGENATION



- NITRATION

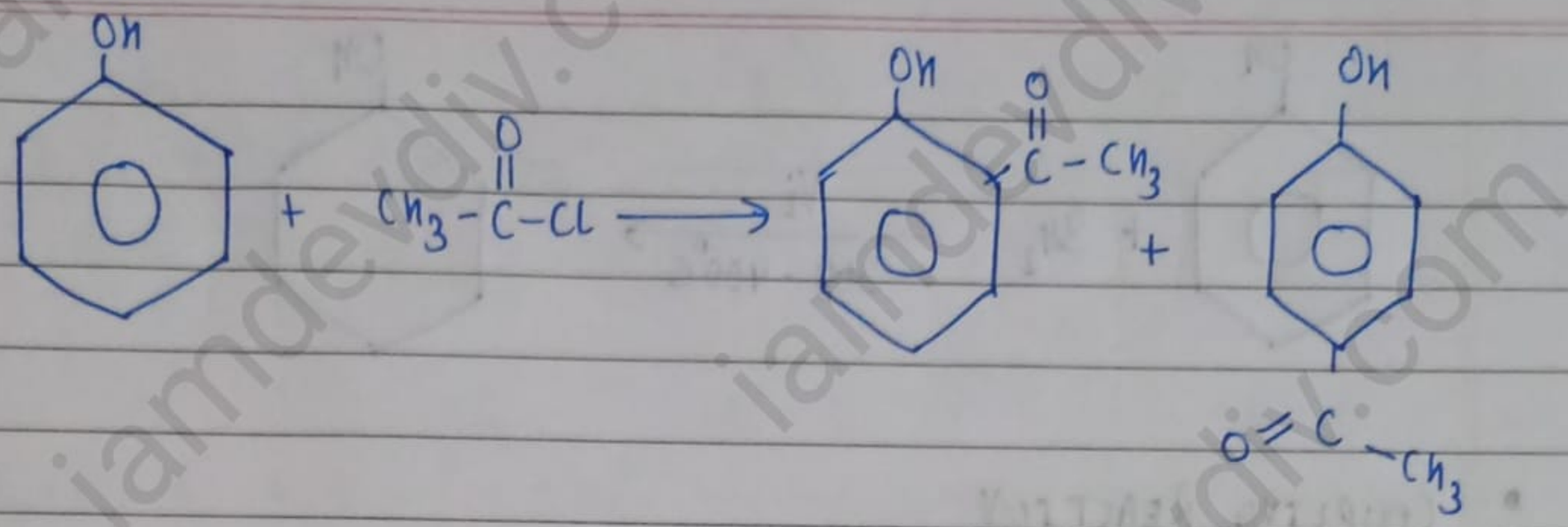


- SULPHONATION

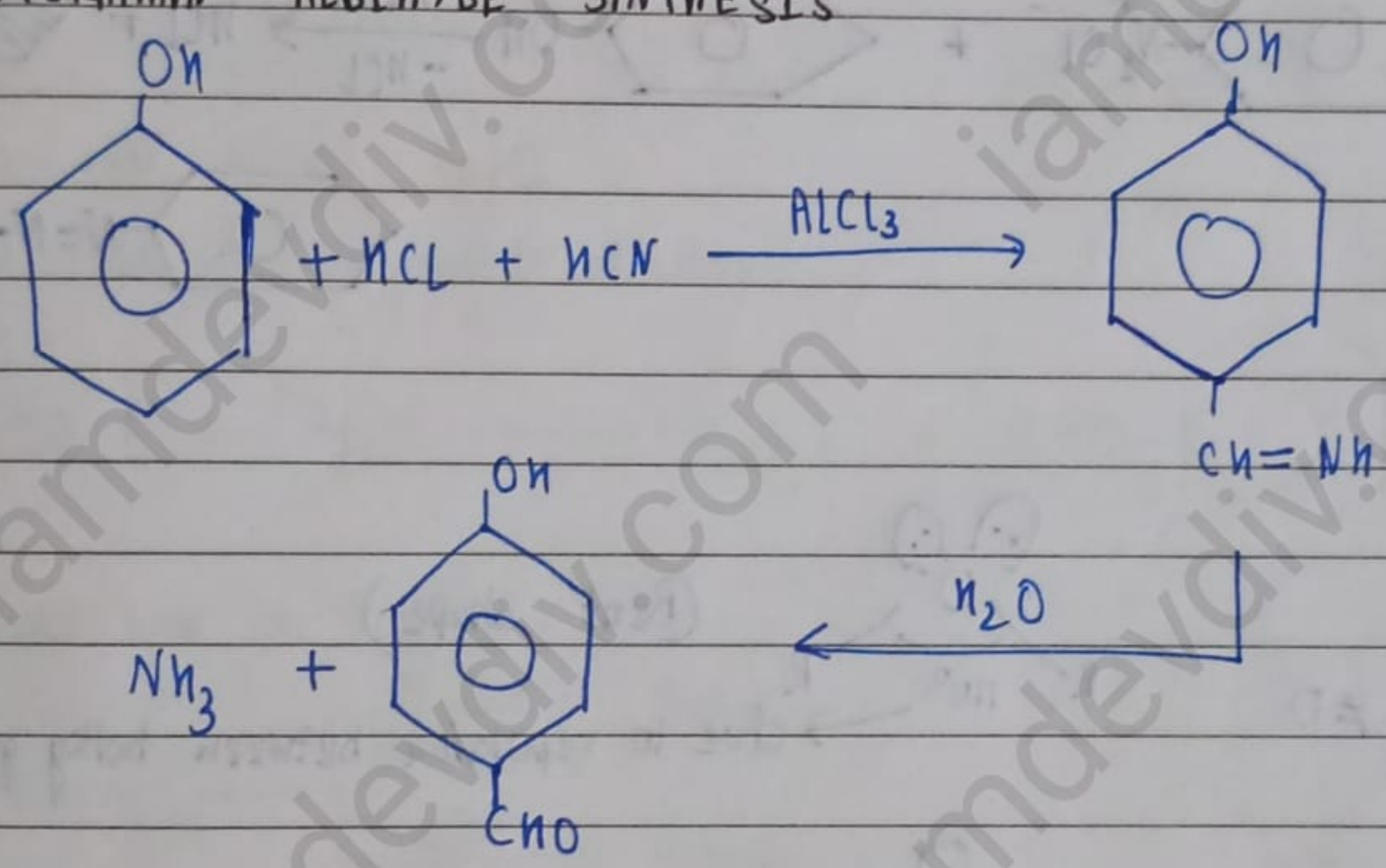


- FRIEDAL CRAFT ALKYLATION

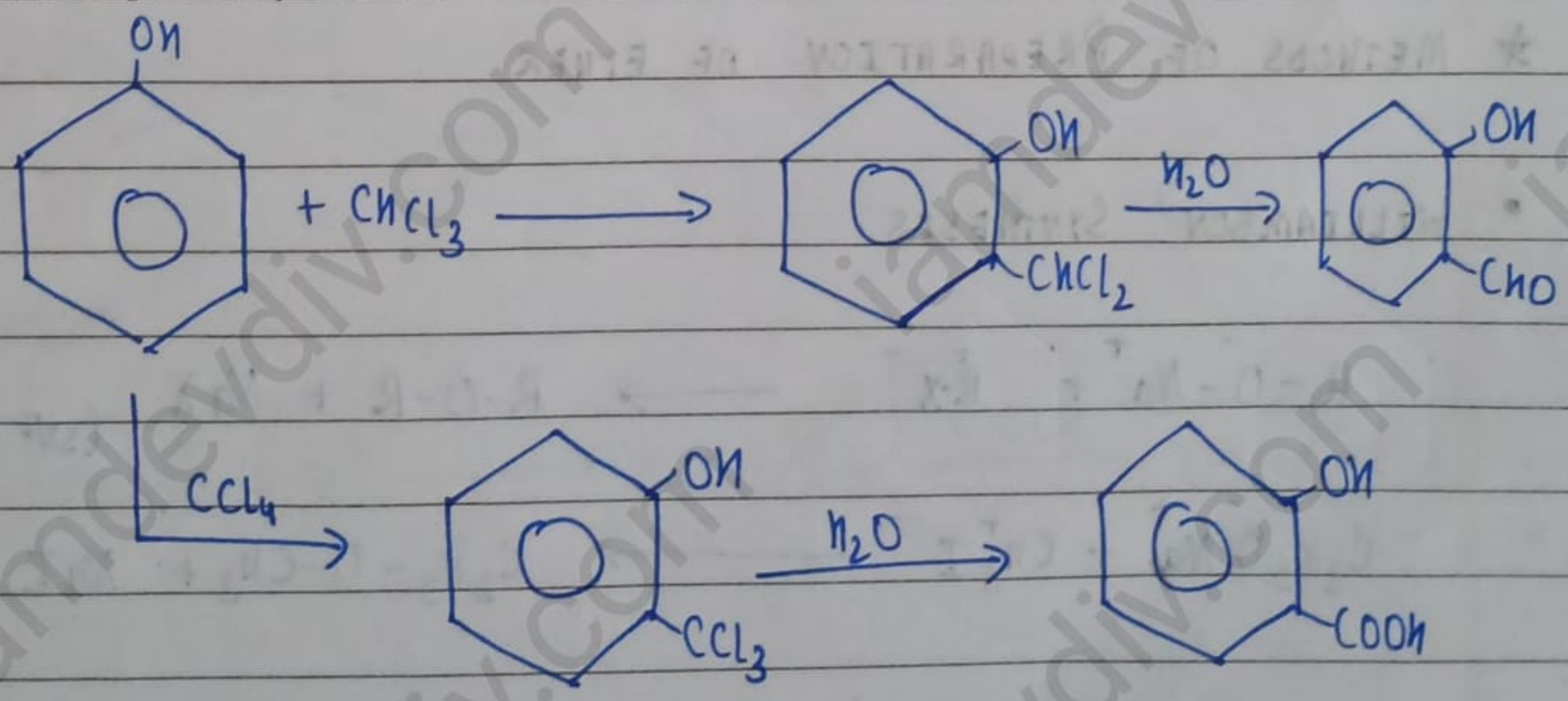
- FRIEDAL CRAFT ACETYLATION



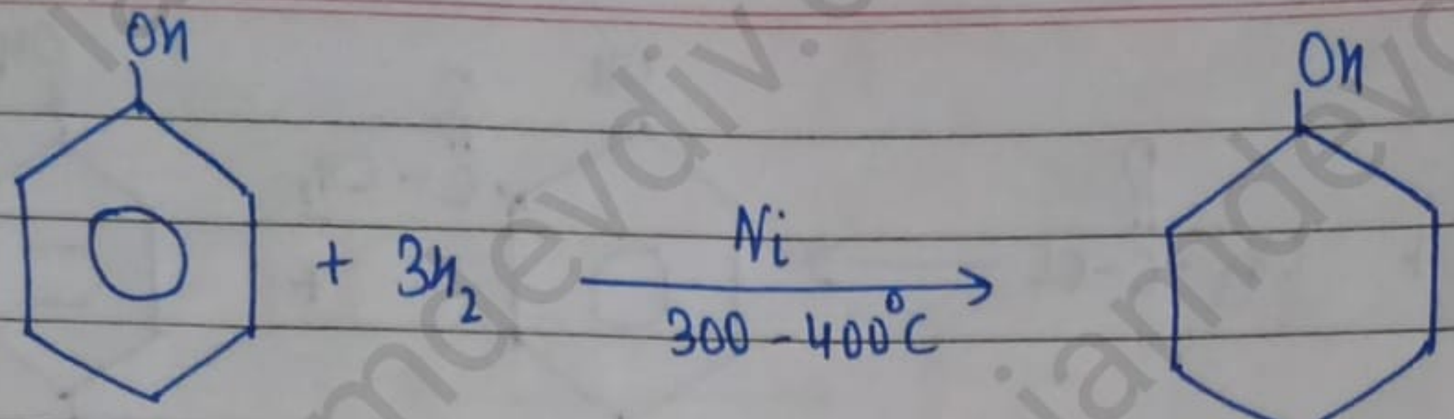
- GATTERMANN ALDEHYDE SYNTHESIS



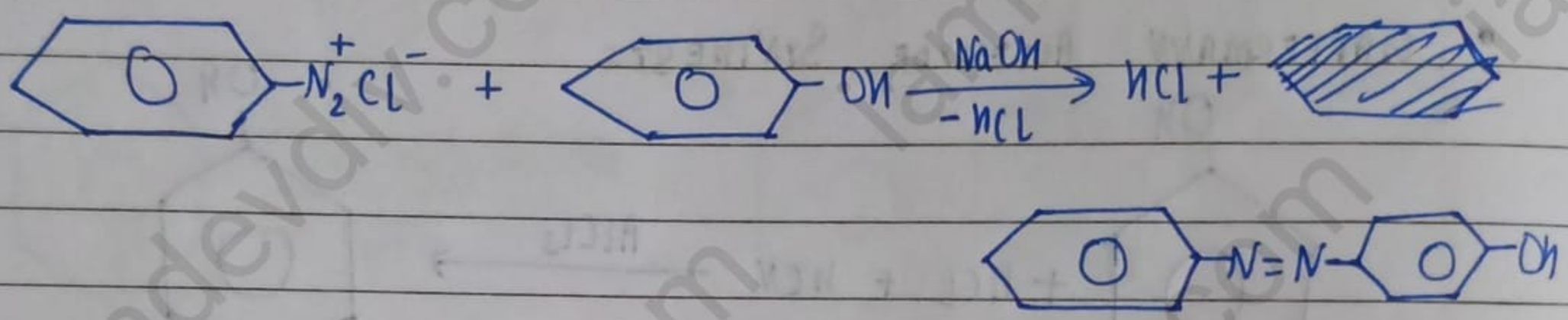
- REIMER - TIEMANN REACTION



- CATALYTIC HYDROGENATION



- COUPLING REACTION



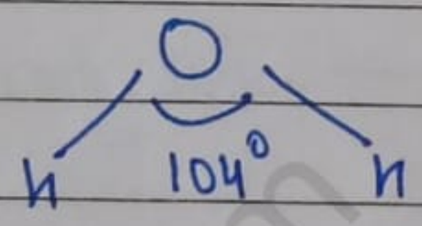
★ ETHER

(Bent shape)

$\mu \neq 0$

Dipole moment

→ due to repulsion between bulky groups



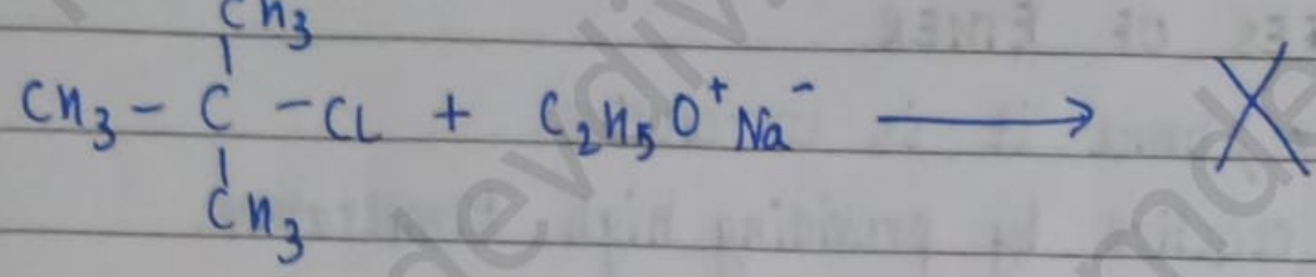
★ METHODS OF PREPARATION OF ETHER

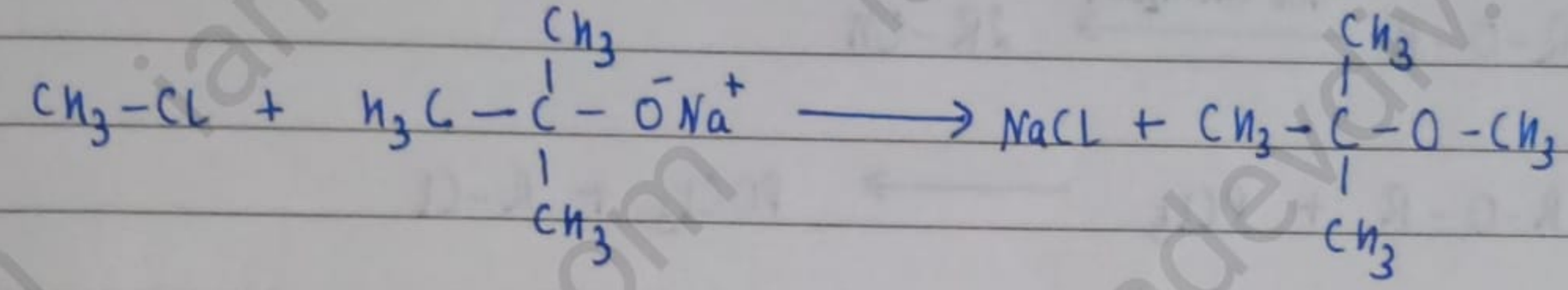
- WILLIAMSON SYNTHESIS

$$R-\overset{-}{O}-Na^{+} + R^{+}X^{-} \longrightarrow R-O-R + NaX \quad (SN^2 \text{ mechanism})$$

$$C_2H_5O^{-}Na^{+} + CH_3^{+}I^{-} \longrightarrow C_2H_5-O-CH_3 + NaI$$

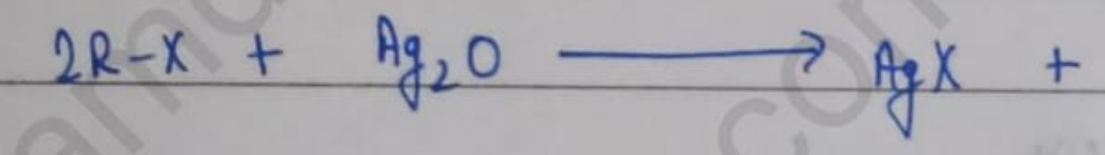
Williamson synthesis is not seen in 3° Alkyl halide because they don't follow SN^2 mechanism



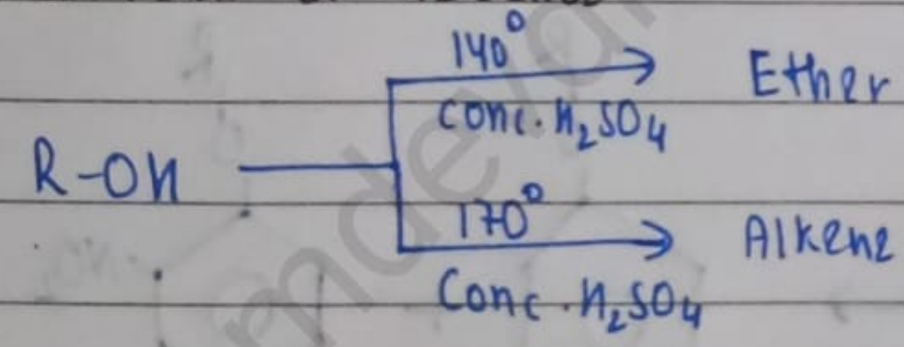


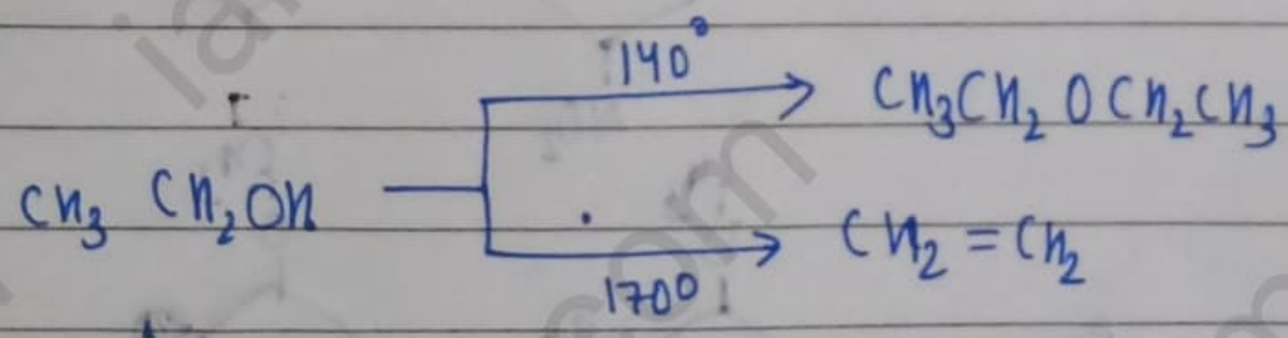
- REACTION WITH Ag_2O

→ Produces symmetrical ether

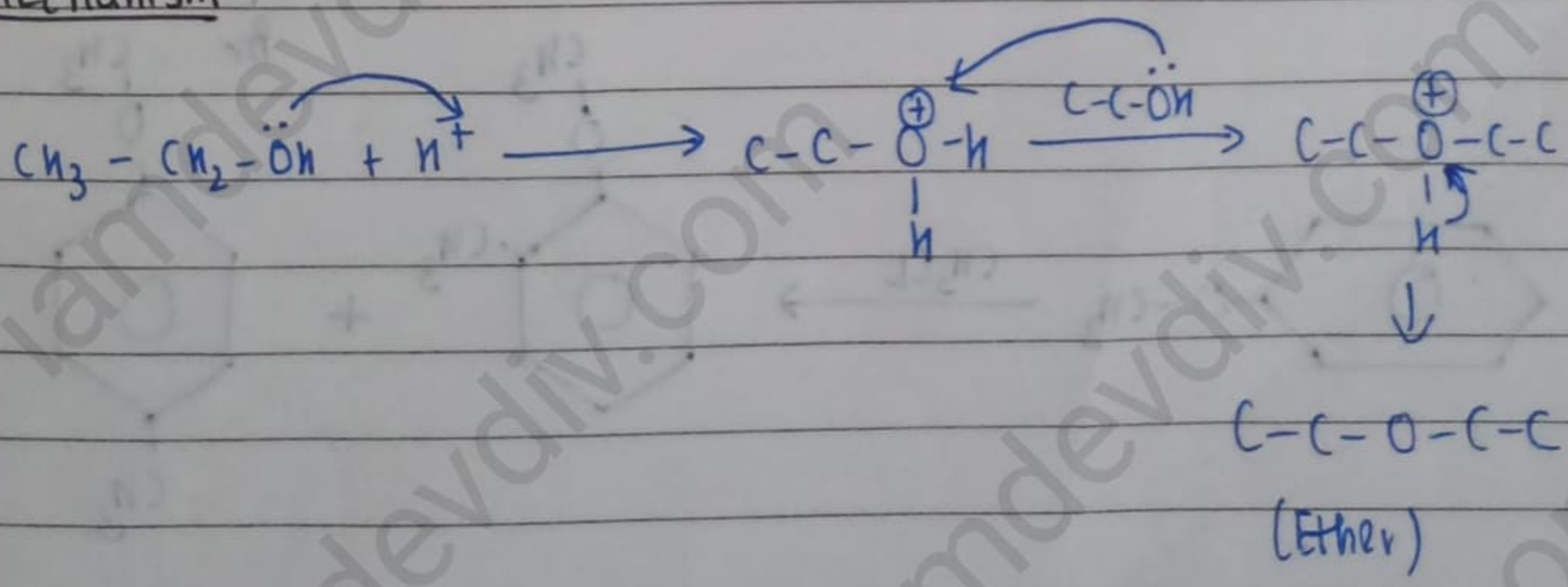


- DEHYDRATION OF ALCOHOL





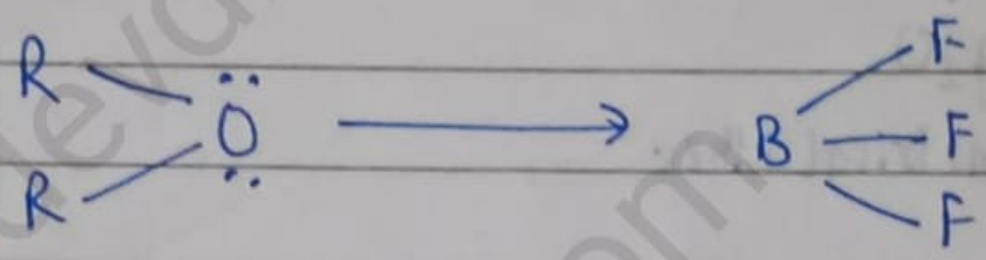
Mechanism

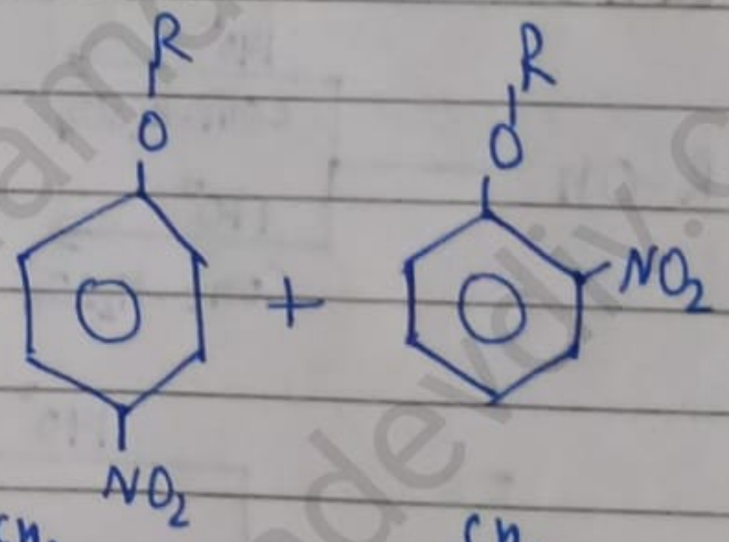
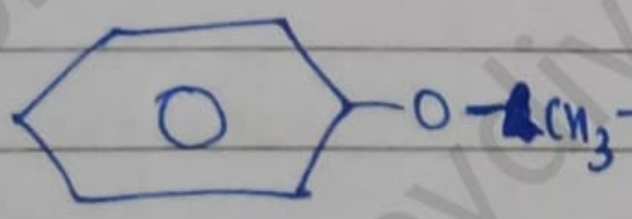
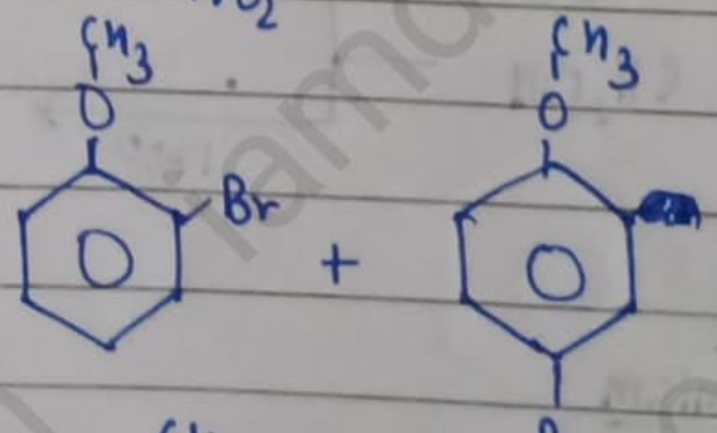
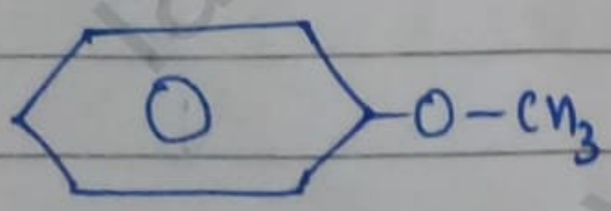


★ CHEMICAL PROPERTIES OF ETHER

As it is less polar, hence it is unreactive.
It can be made reactive by providing high temperature.

- $R-O-R \xrightarrow{\text{hot dil. } H_2SO_4} 2R-OH$
- $R-O-R + PCl_5 \longrightarrow POCl_3 + R-Cl$
- Ether forms coordinate bond with lewis acid because oxygen has lp



- $R-O-R \xrightarrow{\text{limited } HX} R-OH$
- $R-O-R \xrightarrow{\text{Excess } HX} R-X$
-  $\xrightarrow{conc.\ HNO_3}$ 
-  $\xrightarrow{Br_2}$ 
-  $\xrightarrow{CH_3Cl}$