MIND MAP FOR JEE ASPIRANTS

Organic Chemistry

ALCOHOLS, PHENOLS AND ETHERS

By- Yogesh Jain (YJ) Sir

Today's Targets

1. ALCOHOLS, PHENOLS AND ETHERS

MOP of Alcohol

① From Hydrocarbon

Acid catalyzed Hydration

* M w R ✓
* Int → $C^{\oplus}$
* Rearr. ✓

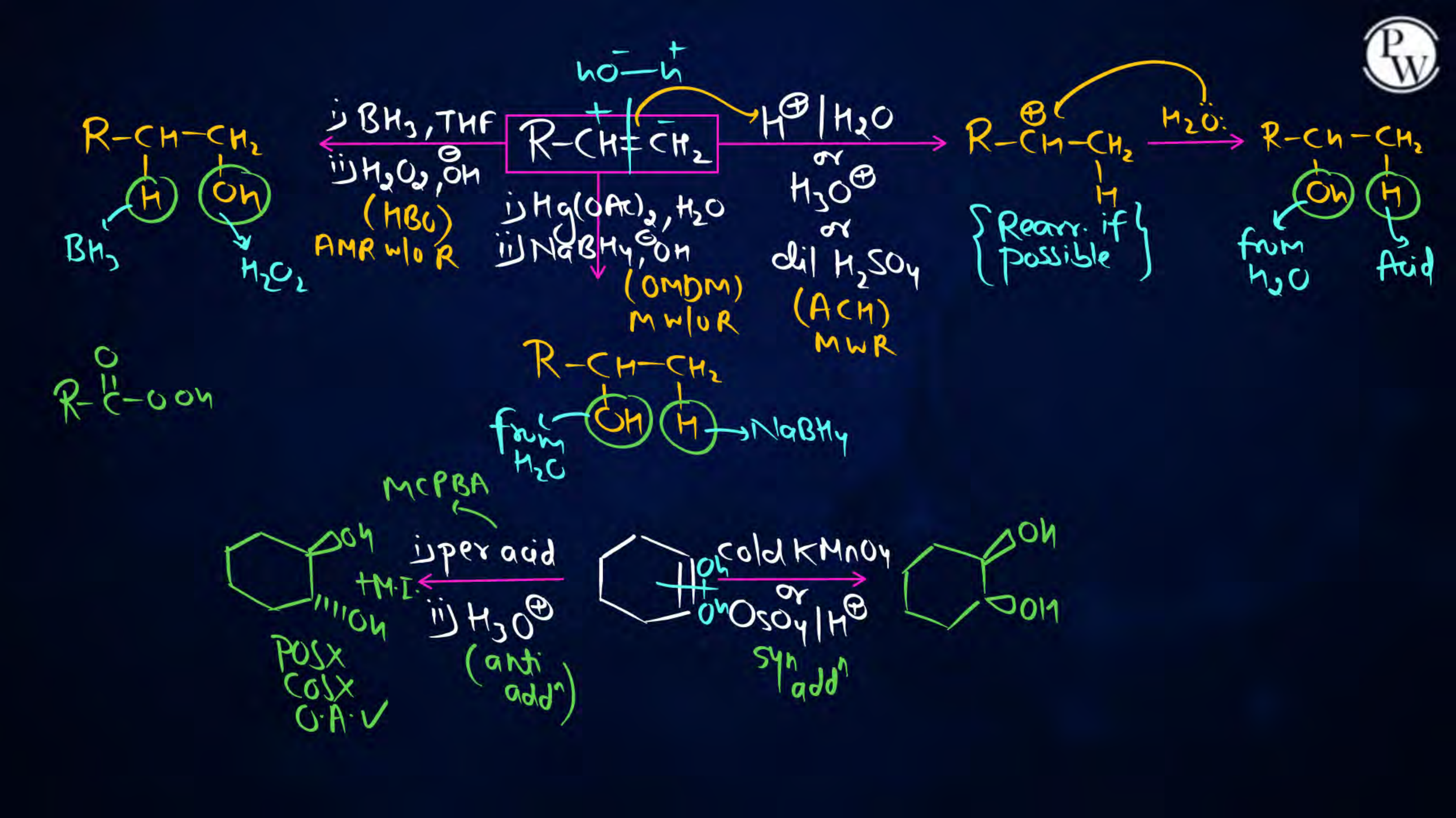
OMDM

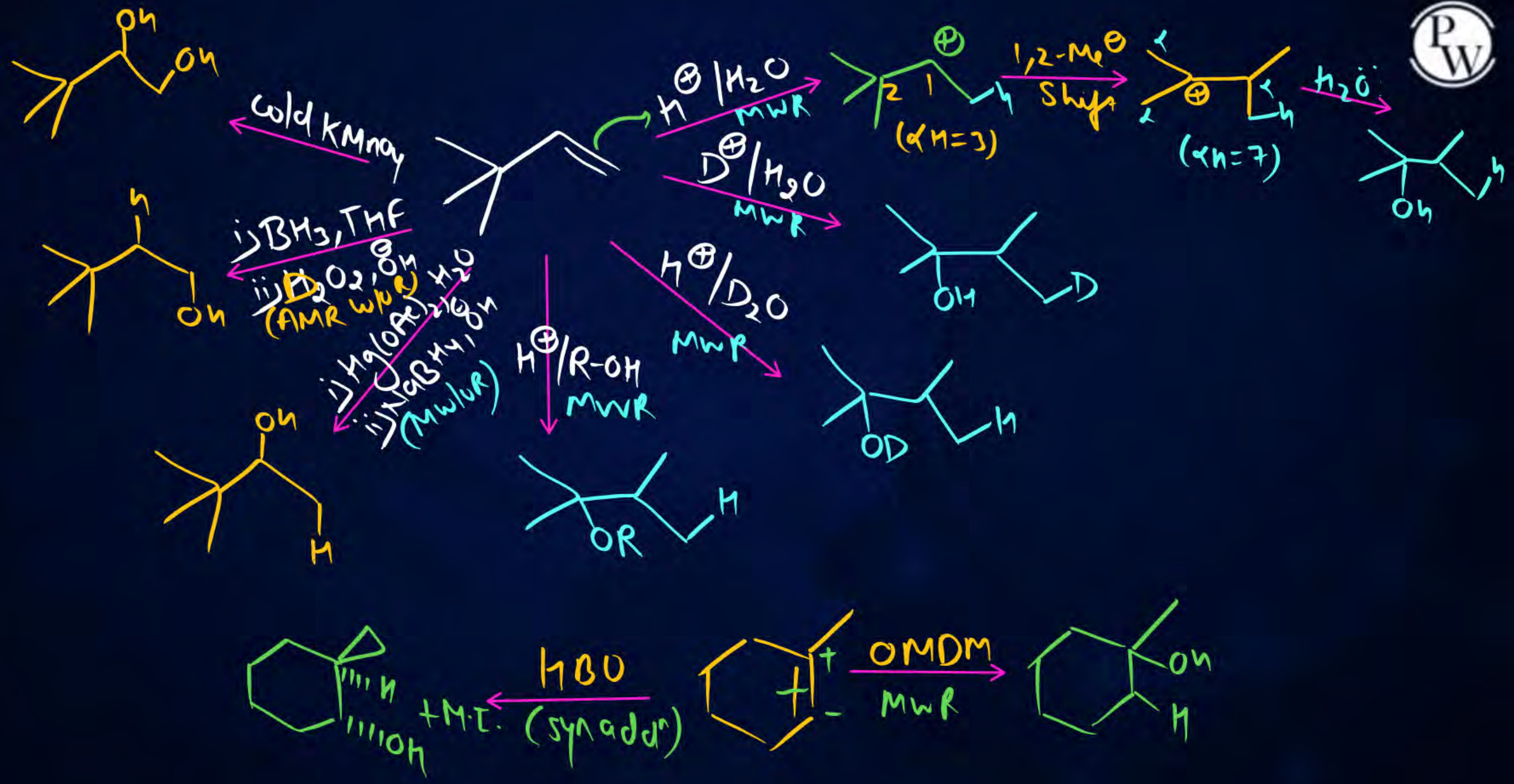
* M w/o R
* Int. → $NCC^{\oplus}$
* Rearr. X

HBO

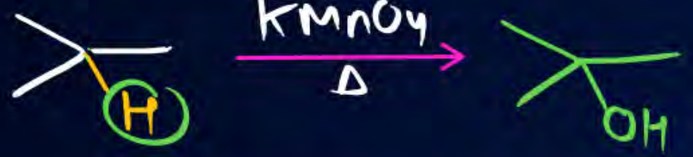
* AMR w/o R
* Int. X T.S. ✓
* Rearr. X
* Syn add^{n} ✓

prepr^{n} of vicinal diol


R–CH–CH2
H
OH
BH3
H2O2
i) BH3, THF
ii) H2O2, ⊖OH
(HBO)
AMR w/o R
R–CH=CH2
HO⁻ H⁺
i) Hg(OAc)2, H2O
ii) NaBH4, ⊖OH
(OMDM)
M w/o R
H⊕ / H2O
or
H3O⊕
or
dil H2SO4
(ACH)
MWR
R–C(⊕)H–CH2
H
{Rearr. if possible}
H2O:
R–CH–CH2
OH
H
from H2O
Acid
R–C(=O)–OOH
R–CH–CH2
from H2O
OH
H
NaBH4
MCPBA
peracid
i)
ii) H3O⊕
(anti addn)
+M·I·
OH
POSX
COSX
O·A·✓
cold KMnO4
or
OsO4 / H⊕
syn addn
OH
OH

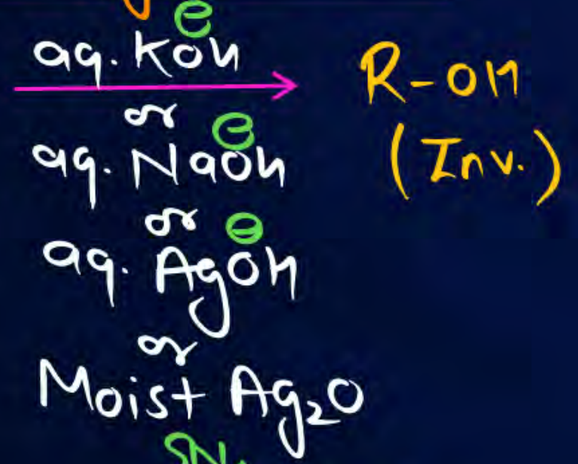

Cold KMnO4
i) BH3, THF
ii) H2O2, OH⊖
(ASR w/r)
i) Hg(OAc)2, H2O
ii) NaBH4, OH⊖
(MwIR)
H⊕/H2O
MWR
D⊕/H2O
MWR
H⊕/D2O
MWR
H⊕/R-OH
MWR
1,2-Me⊖ Shift
(α H=3)
(α H=7)
H2O
OH
D
OD
OR
HBO
+M.I. (syn addn)
OMDM
MwR

② From Alkane



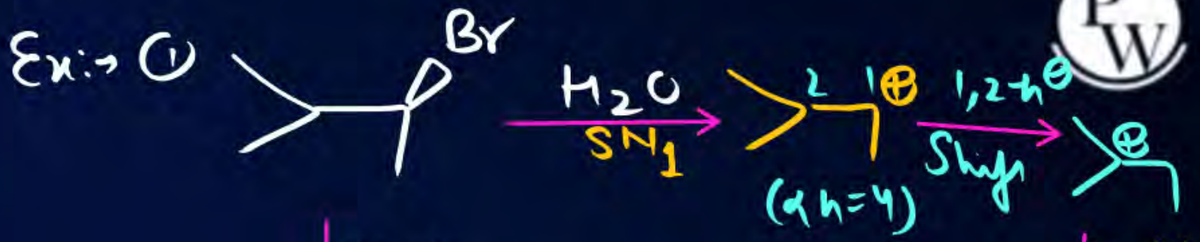
③ From Alkyl Halide

i) R-X (CH3 | 1° | 2°)

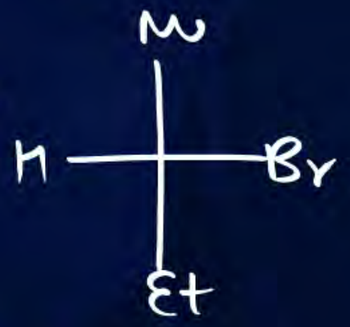


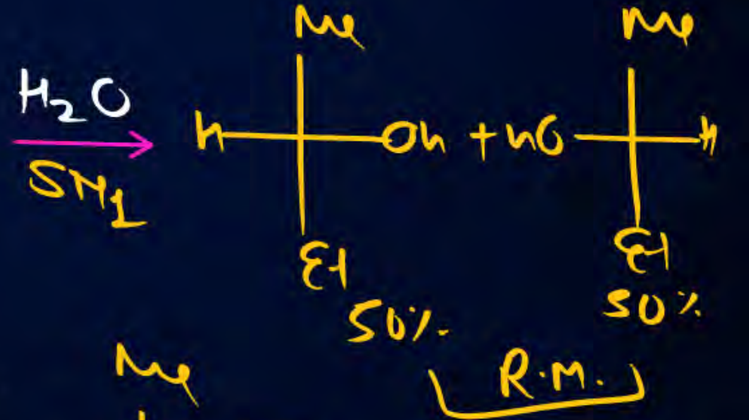
ii) R-X (2° | 3°)

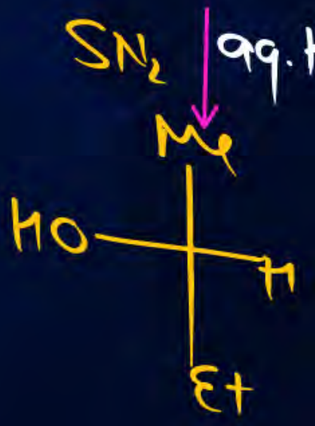
Ex:- ①



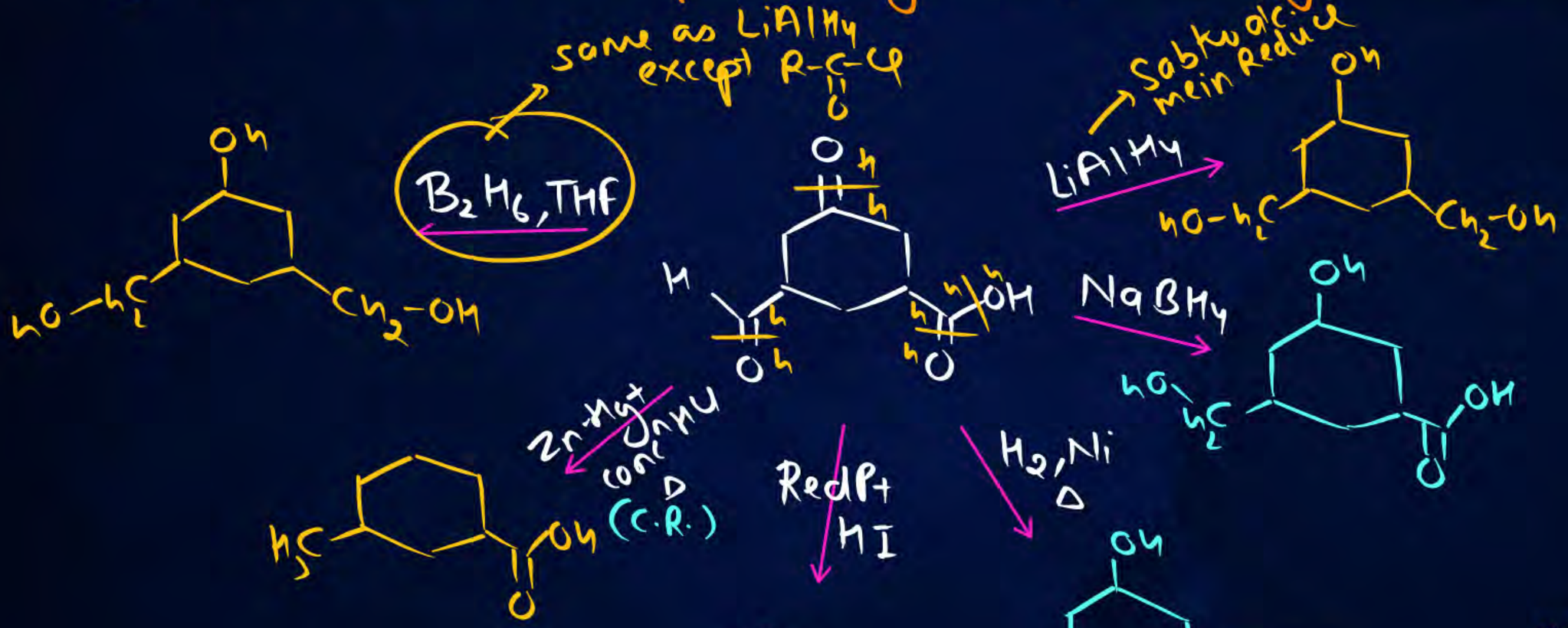
②







③ From Reduction of Carbonyl Compd, Carboxylic acid & Ester:-



④ From Grignard Reagent $\overset{\ominus}{R}MgX$

i) $H-\underset{\delta+}{C}(=O)-H \xrightarrow[ii)\ H_2O]{i)\ \overset{\ominus}{R}MgX} R-CH_2-OH$ 1° alc.

ii) $R-\underset{\delta+}{C}(=O)-H \xrightarrow[ii)\ H_2O]{i)\ \overset{\ominus}{R}MgX} R_2CH-OH$ 2° alc.

iii) $R-\underset{\delta+}{C}(=O)-R \xrightarrow[ii)\ H_2O]{i)\ \overset{\ominus}{R}MgX} R_3C-OH$ 3° alc.

L.Grp. $-X$, $-OR$, $-O-\overset{O}{\overset{\|}{C}}-R$

iv) $R-\underset{\delta+}{C}(=O)-L.G. \xrightarrow[ii)\ H_2O]{i)\ RMgX\ (2\ mole)} R_2C(OH)-R$ 3° alc.

v) $L.G.-\underset{\delta+}{C}(=O)-L.G. \xrightarrow[ii)\ H_2O]{i)\ RMgX\ (3\ mole)} R_3C-OH$ 3° alc.

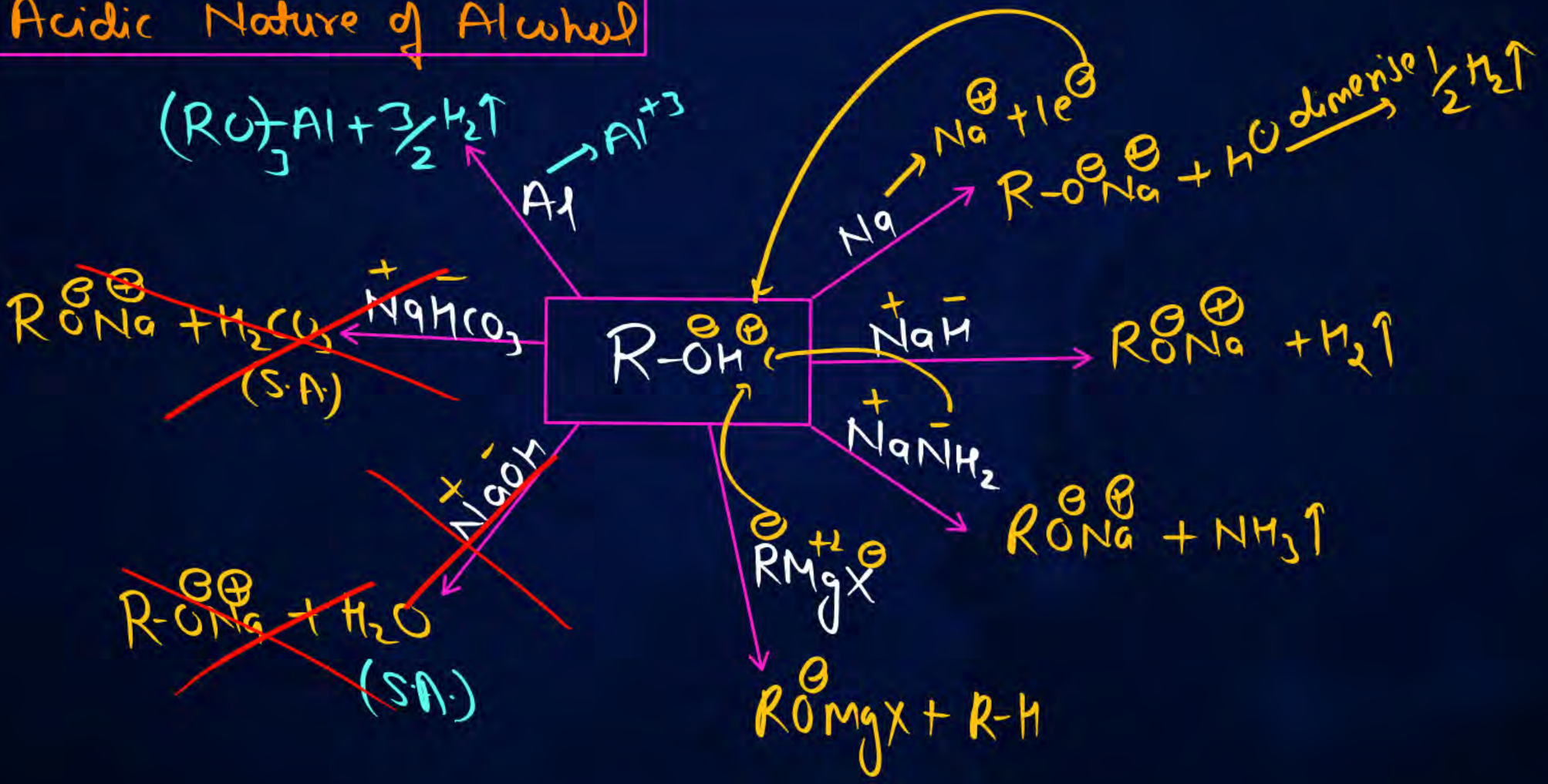
vi) $\overset{\ominus}{R}MgX \xrightarrow[ii)\ H_2O]{i)\ \frac{1}{2}O_2} R-OH$

Gehri Baat :- ① G.R. ke R ko $\overset{\delta+}{C}$ ke α par jode

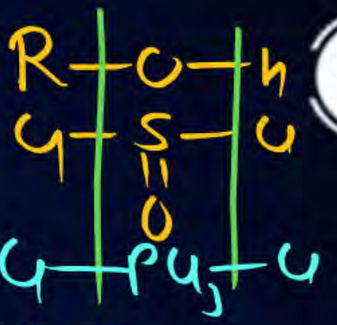
② L.G. ko R replace karega aur 1 mole khayega

Chemical properties of Alcohol

① Acidic Nature of Alcohol



② Rxn. of R-OH with $SOCl_2$ (Δ) | PCl_5 (Δ) | PCl_3 (Δ)



R-OH + $SOCl_2$ (Δ, SN_i) → R-Cl + $SO_2\uparrow$ + HCl↑ (Ret.)

R-OH + $SOCl_2$, Py (Δ, SN_2) → R-Cl + $SO_2\uparrow$ + HCl↑ (Inv.)

R-OH + PCl_5 (Δ, SN_i) → R-Cl + $POCl_3$ + HCl↑

R-OH + HCl + $ZnCl_2$ (Δ, SN_1) → $R^{\oplus}$ (Rearr. if possible) → $R-Cl$ (white turbidity)

R-OH + PCl_3, Δ → R-Cl + H_3PO_3 (SN_i)

R-OH + P + Cl_2 (Δ, SN_2) → R-Cl + H_3PO_3

Lucas Test — White turbidity

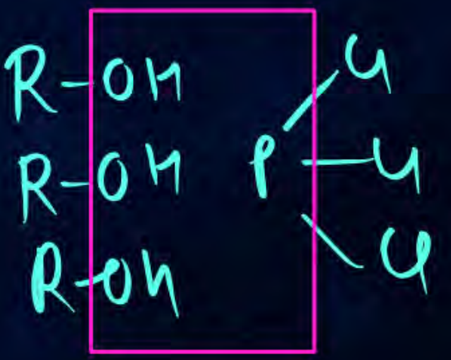
3° R-OH $\xrightarrow{L.R}$ Immediate

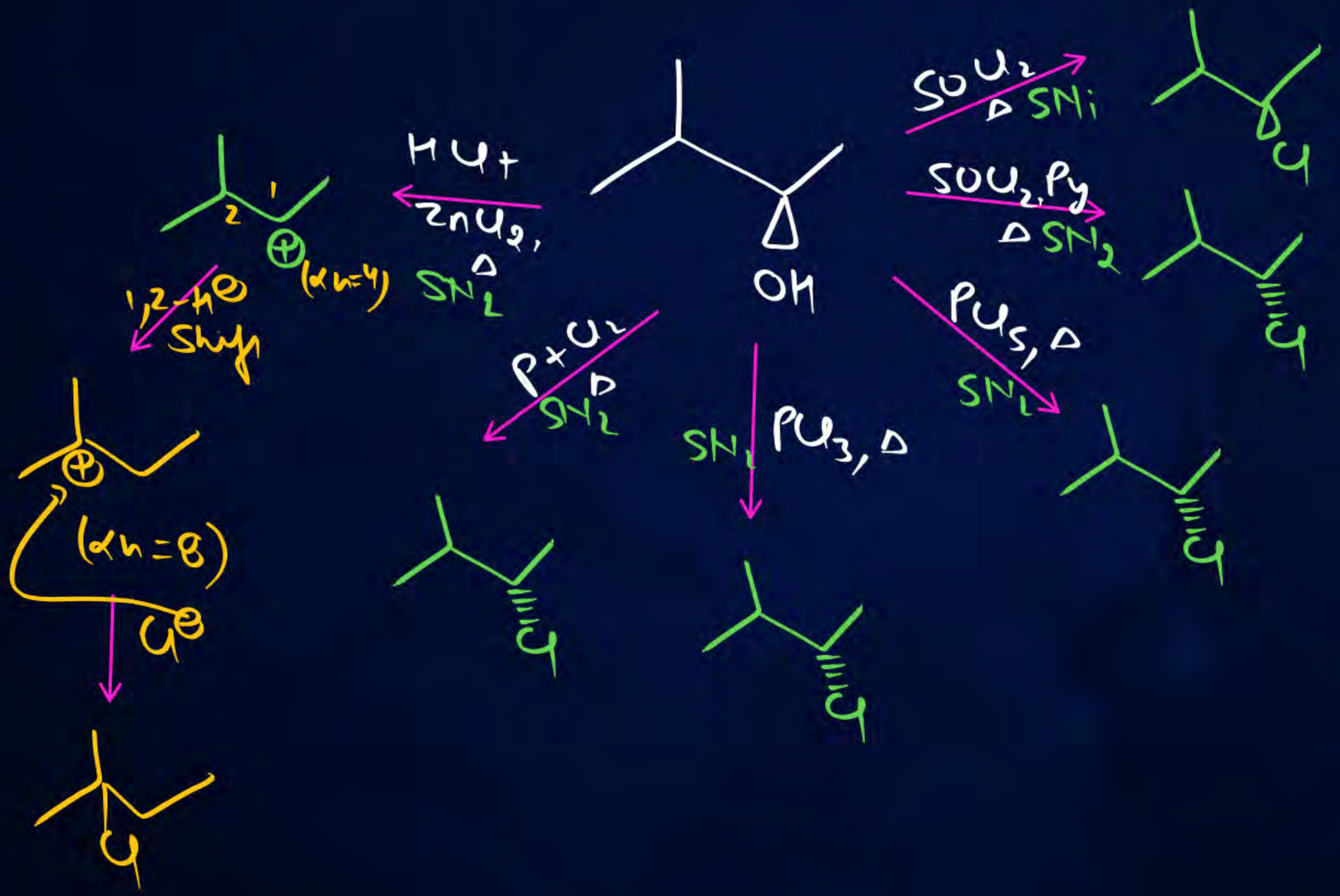
2° R-OH $\xrightarrow{L.R}$ 5-8 min.

1° R-OH $\xrightarrow{L.R}$ > 30 min on heating

×

Lucas Reagent → conc^ HCl + anhyd. $ZnCl_2$




HCl + ZnCl2, Δ SN2
SOCl2, Δ SNi
SOCl2, Py, Δ SN2
PCl5, Δ SN1
P + Cl2, Δ SN2
SN1 PCl3, Δ
1,2-H⊖ Shift
(4°)
(3°)
OH
Cl

③ Victor Meyer Test

Observation → R B C → 1° 2° 3°

Reagents:-
① $P + I_2$
② $AgNO_2$
③ HNO_2
④ NaOH

1° R-OH

$R-CH_2-OH$

$\downarrow SN$ $P + I_2$

$R-CH_2-I$

$\downarrow SN$ $AgNO_2$

$R-CH_2-N(=O)-O$

$\downarrow O=N-OH$

$R-C(=N-OH)-NO_2$ Nitrolic acid

$\downarrow NaOH$

Red colour

2° R-OH

R_2CH-OH

$\downarrow SN$ $P + I_2$

R_2CH-I

$\downarrow SN$ $AgNO_2$

$R_2C(-NO_2)-N(=O)-O$

$\downarrow OH-N=O$

$R_2C(-NO_2)-N=O$ (pseudo nitrol)

$\downarrow NaOH$

(Blue colour)

3° R-OH

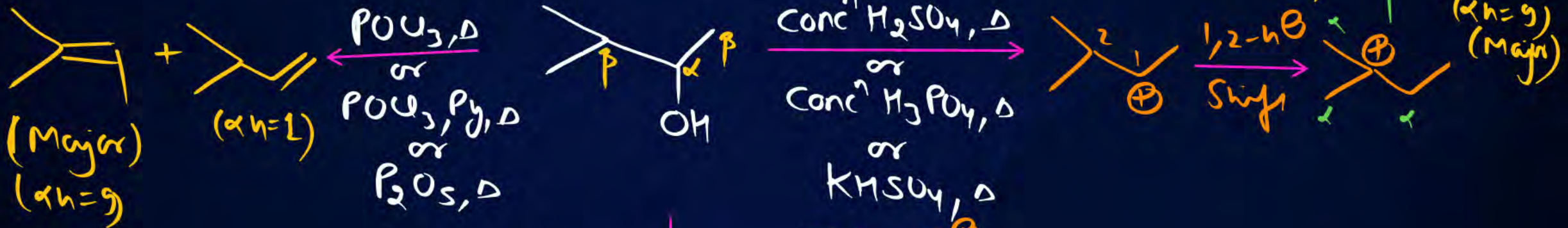
R_3C-OH

$\downarrow P + I_2$

X

Colourless

⊕ Elimination Rxn. {Dehydration of R-OH}



Int → ✗

Rearr → ✗

Major product → Stable alkene

Gehri Baat → α-se OH β-se H nikal k alkene banaye

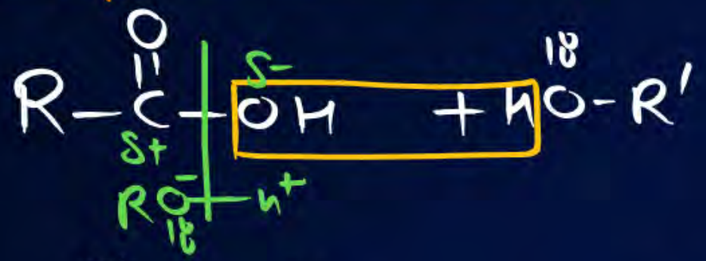
Int → C⊕

Rearr → ✓

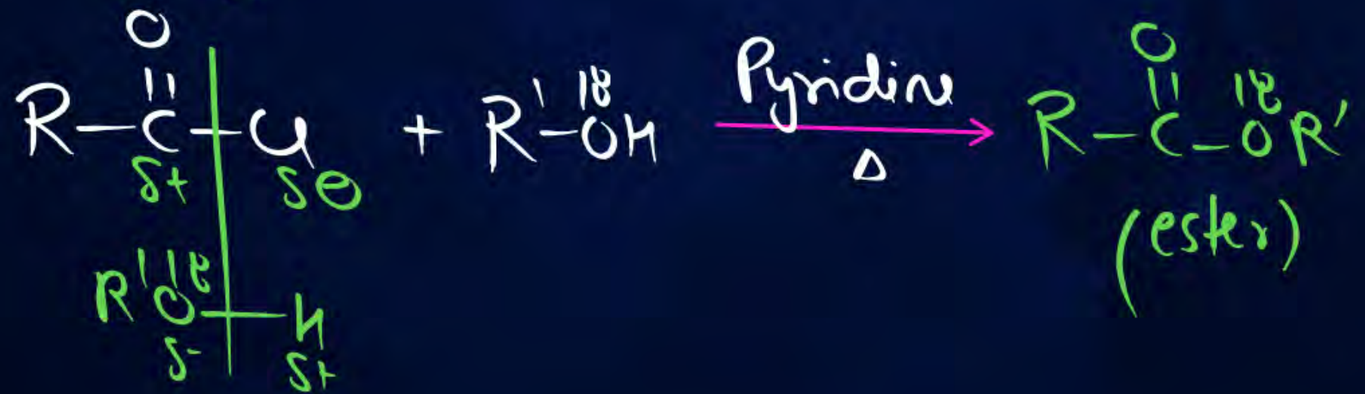
Major product → Stable alkene

Gehri Baat → −OH hatao ⊕ banao rearrange karao Fir α-H nikalke alkene banado

(5) Esterification Rxn :-

i) 

ii) 

iii) 

(6) Oxidation of Alcohol

1° alc. $R-CH_2-OH \xrightarrow[\text{Mild}]{[O]} R-CH=O \xrightarrow[\text{Strong}]{[O]} R-\overset{O}{\overset{\|}{C}}-OH$

2° alc. $R-\underset{OH}{\underset{|}{CH}}-R \xrightarrow[\text{Mild or Strong}]{[O]} R-\overset{O}{\overset{\|}{C}}-R$

$CH_3-OH \xrightarrow[\text{Mild}]{[O]} H-\overset{O}{\overset{\|}{C}}-H \xrightarrow{[O]} H-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[\text{Strong}]{[O]} (CO_2)$

3° alc. $R-\overset{R}{\underset{R}{\overset{|}{\underset{|}{C}}}}-OH \xrightarrow[\text{Mild or Strong}]{[O]} \times$

$R-\overset{R}{\overset{|}{\underset{\beta}{C}}}-\underset{\alpha}{OH} \xrightarrow[\text{or } Ag,\Delta]{Cu,\Delta \rightarrow 300^\circ} R-\overset{R}{\overset{|}{C}}=CH_2$

Oxidising Agent	1° R-OH	2° R-OH	3° R-OH
① $KMnO_4/H^{\oplus}$	Strong O.A. → CARBOXYLIC ACID	KETONE	X
② $K_2Cr_2O_7/H^{\oplus}$			X
③ Jone's Reagent {$CrO_3+H_2SO_4$ or CrO_3+H_2O or H_2CrO_4}			X
④ Conc^{n} HNO_3			X
⑤ PCC {Pyridinium chloro chromate}	Mild O.A. → ALDEHYDE		X
⑥ PDC {Pyridinium dichromate}			X
⑦ CrO_3 + Acetone			X
⑧ Cu, Δ or Ag, Δ → 300°C			Alkene

Special O.A.

MnO_2 → Mild O.A. only oxidise allylic or Benzylic R-OH

1° allylic or Benzylic R-OH → Ald.

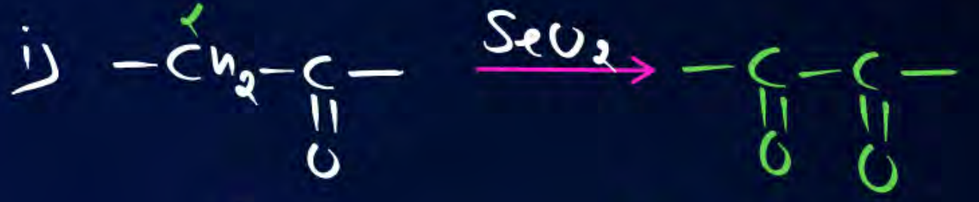
2° allylic or Benzylic R-OH → ketone

3° allylic or Benzylic R-OH → X

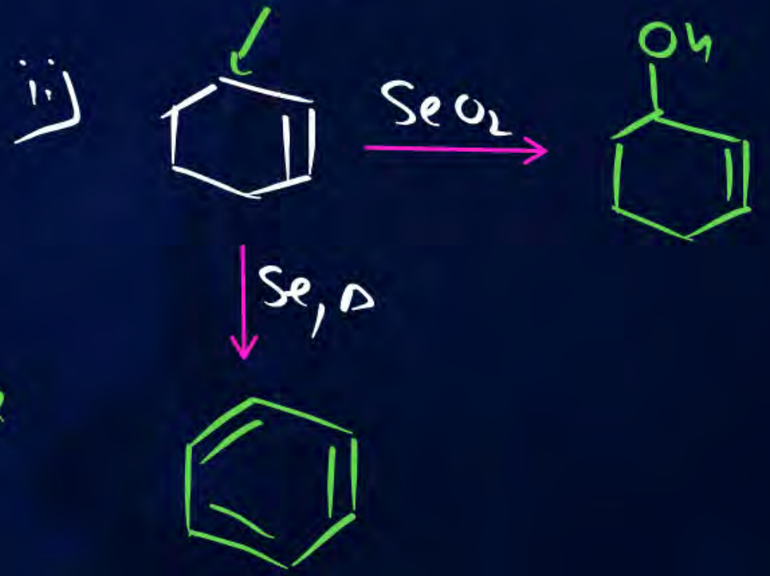
Rxn:-

SeO_2 → Mild O.A.

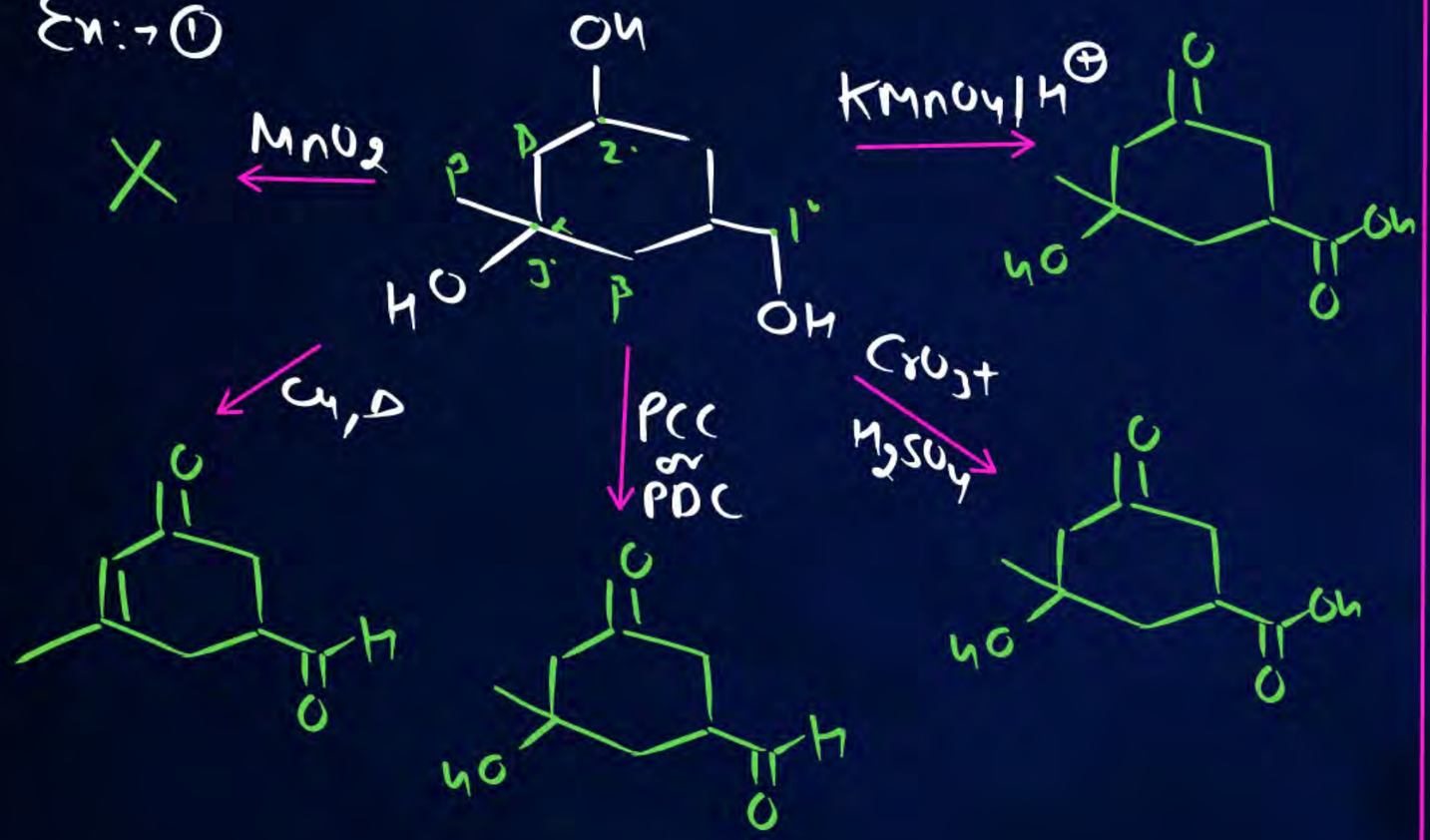
i)



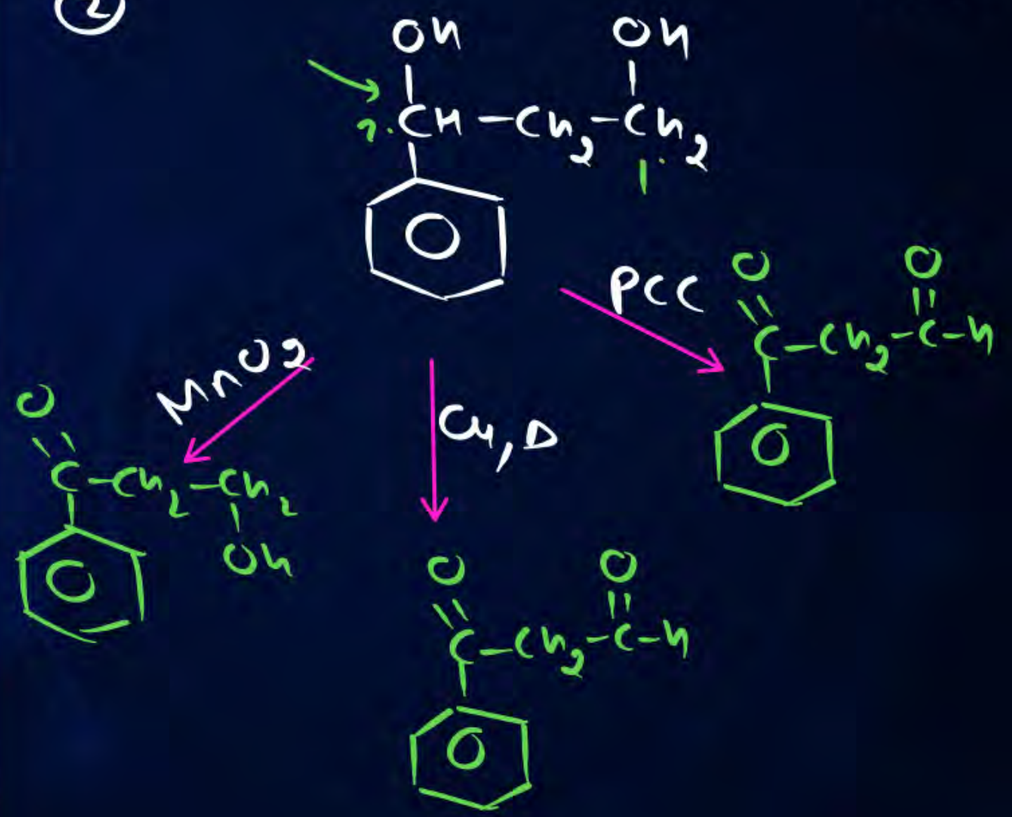
ii)



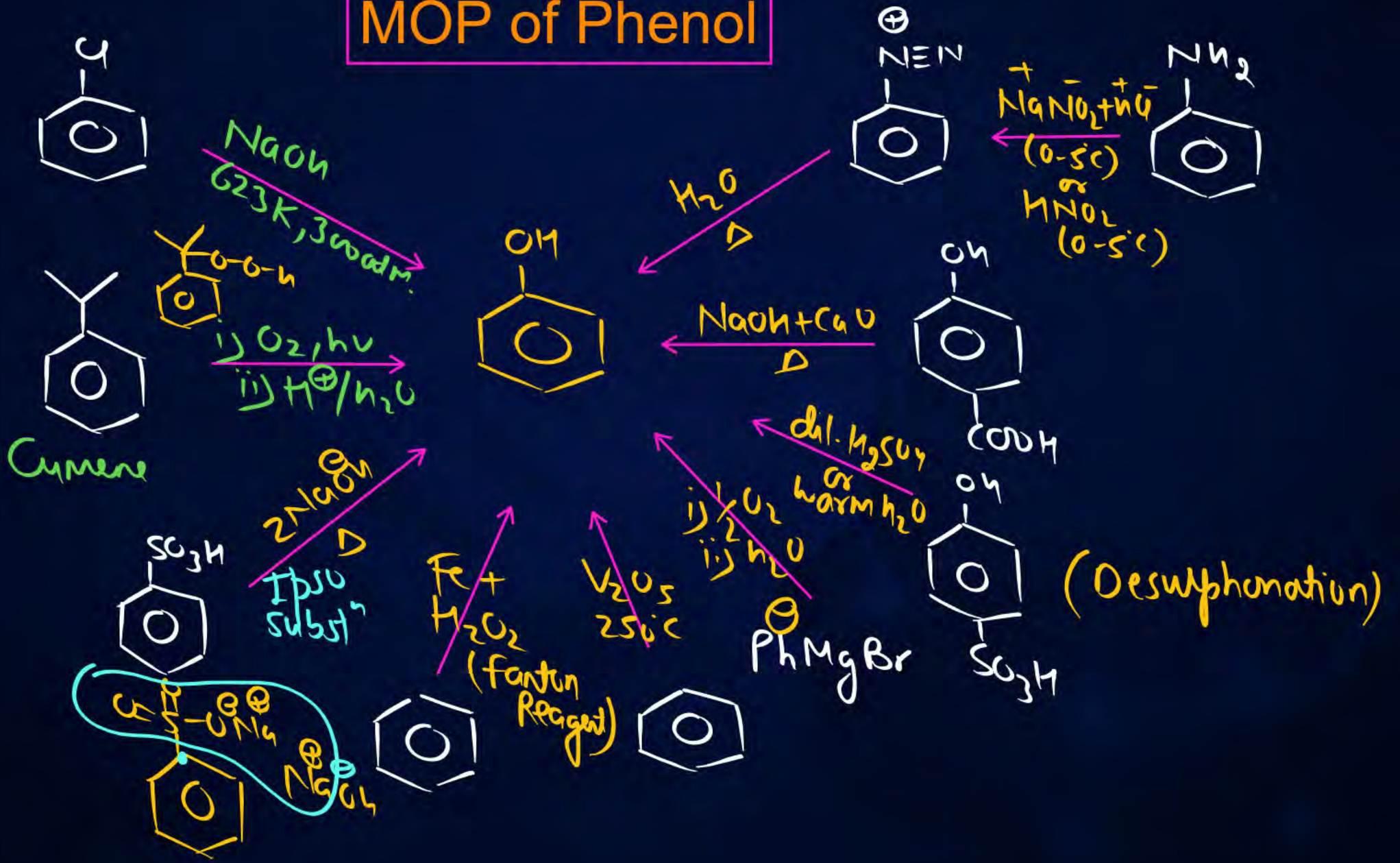
Ex:- ①



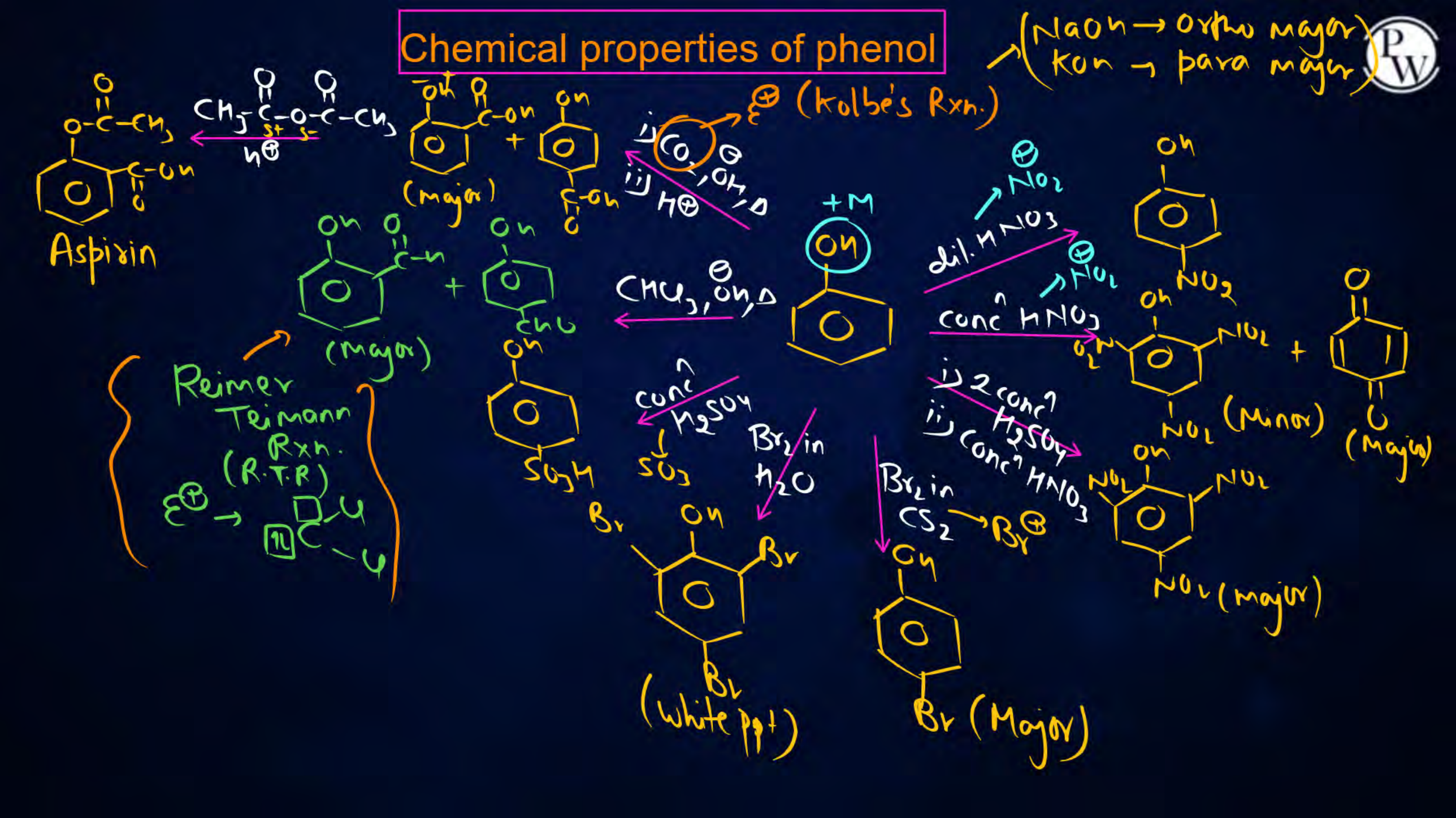
②



MOP of Phenol



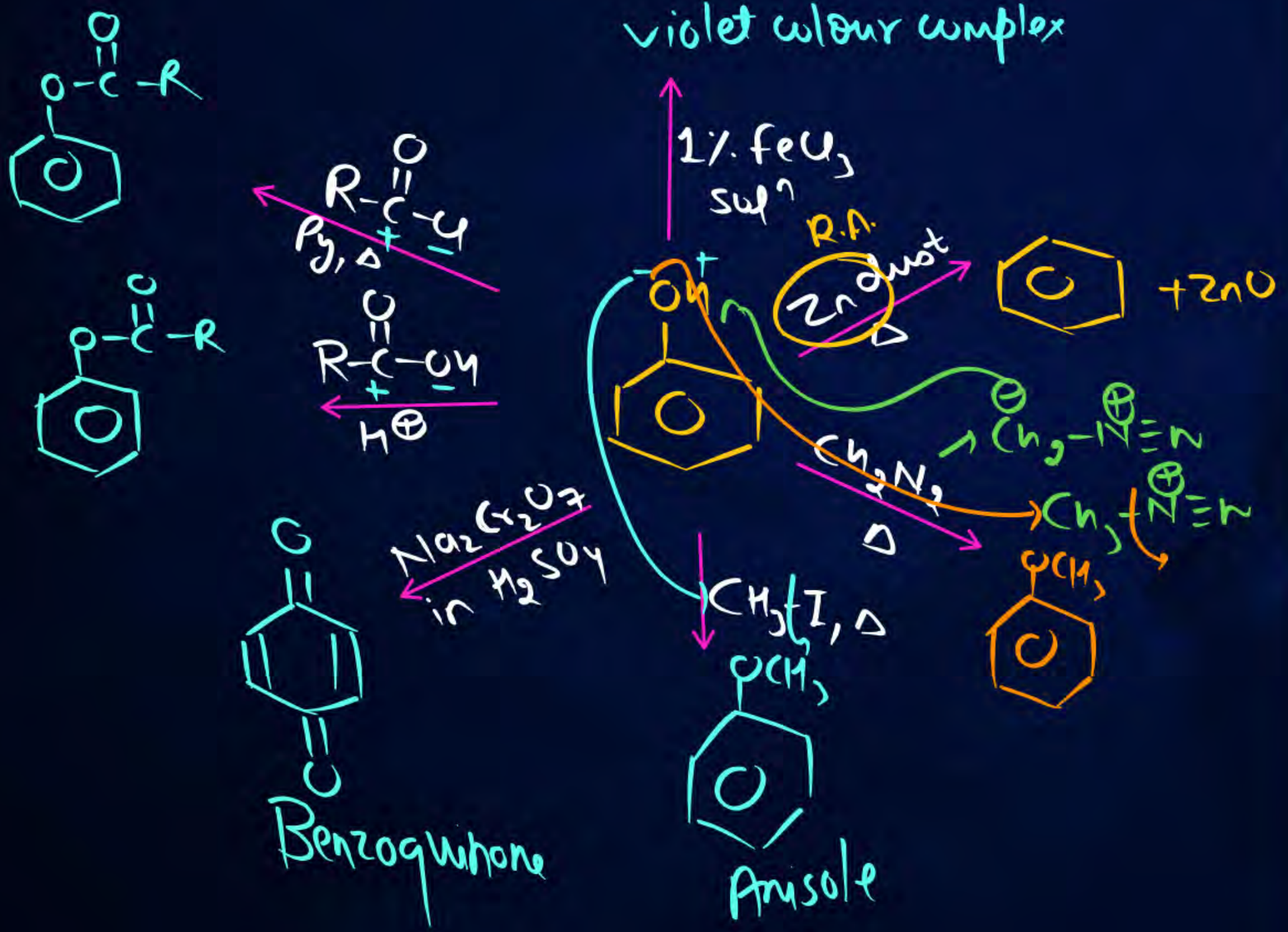
Chemical properties of phenol



Chemical properties of phenol

(GRB)

Libermann Nitroso phenol test



Phenol

↓ HNO_2

(A)

↓ Ph-OH

(B) (green)

↓ H_2SO_4

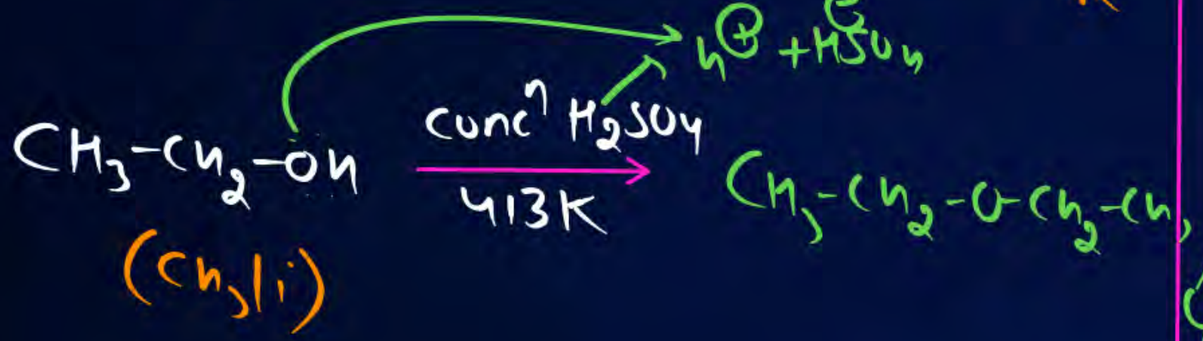
(C) (Red)

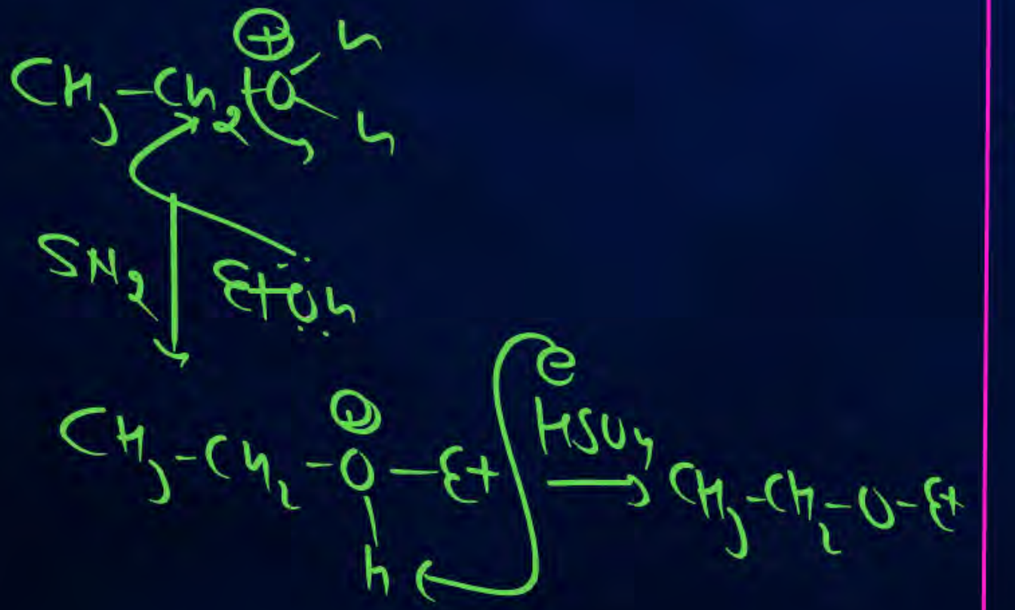
↓ NaOH

(D) (Blue)

MOP of Ether

① Rxn. of R-OH with conc^{n} H_2SO_4 at 413 K



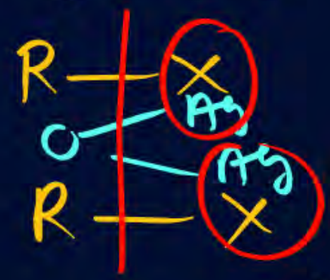


② Rxn. of R-X with dry Ag_2O

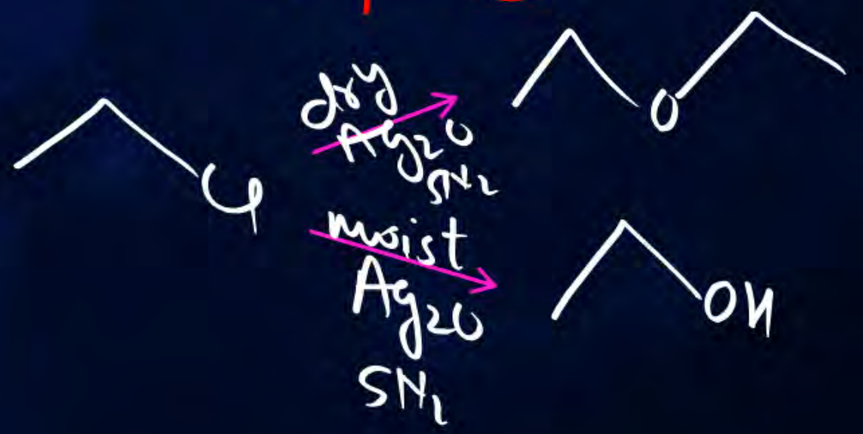
$2R-X \xrightarrow[Ag_2O]{\text{dry}} R-O-R + 2AgX\downarrow$

(CH_3Li)

Short Trick →

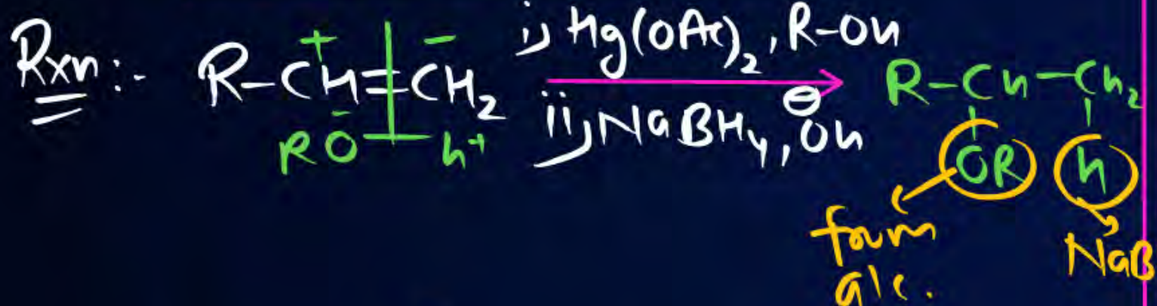


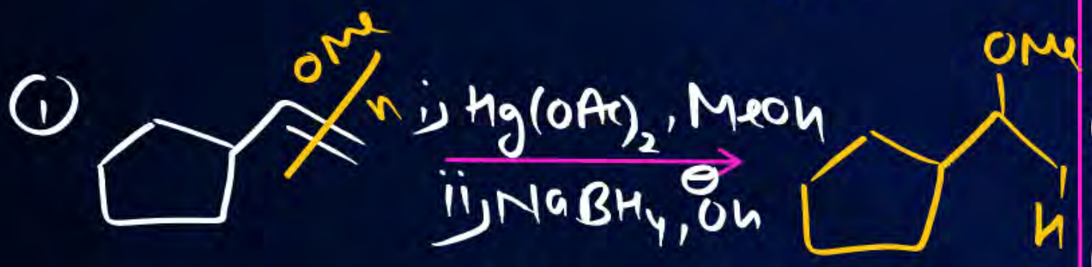
①

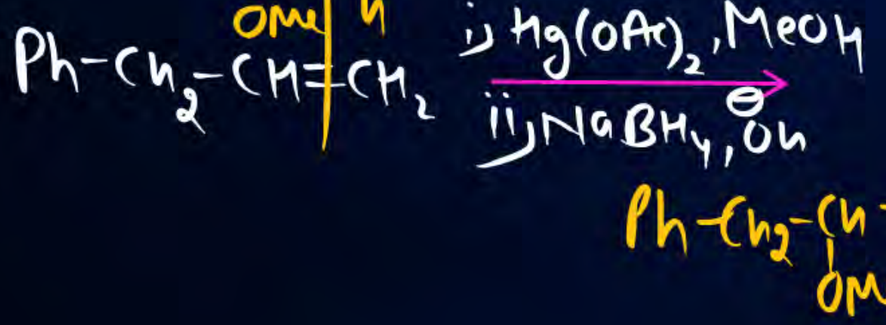


③ Alkoxymercuration-Demercuration (M w/o R)

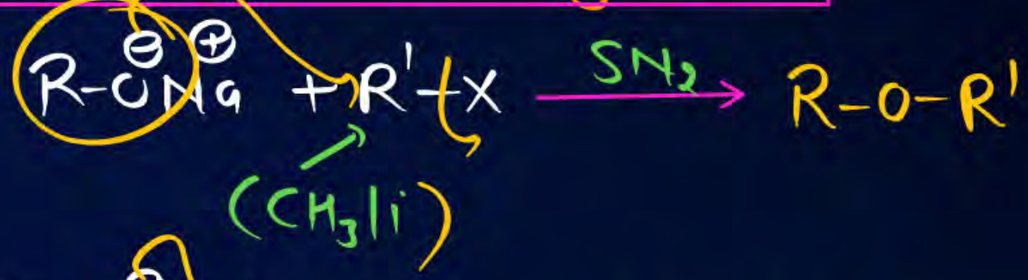
Rxn:-



① 

② 

④ Williamson Ether Synthesis

Rxn:- 

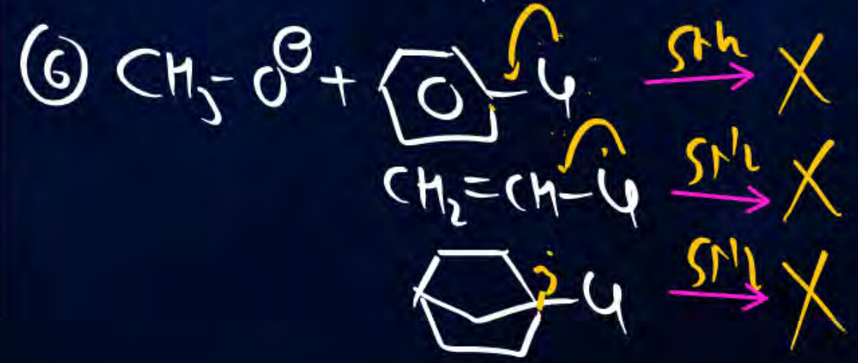
① $CH_3-O^{\ominus} + CH_3-I \longrightarrow CH_3-O-CH_3$

② $CH_3-O^{\ominus} + CH_3-Br \longrightarrow CH_3-O-CH_3$

③ $CH_3-O^{\ominus} + CH_3-CH_2-Br \longrightarrow CH_3-O-CH_2-CH_3$

④ 

⑤ 

⑥ 

Chemical properties of Ether

① Rxn. of Ether with H–X

$R-O-R$ (Symm.)

$H-X$ (Excess) → $2\,R-X + H_2O$

$H-X$ (1 mole) → $R-X + R-OH$

$R-O-R'$ (Unsymm.)

$H-X$ (Excess) → $R-X + R'-X + H_2O$

$H-X$ (1 mole) → depends on mech^{n}

Mech^{n} :-

$R > R'$

Bulky

$R-\ddot{O}-R' \xrightarrow{H-X} R-\overset{\oplus}{O}(H)-R'$

$\overset{\oplus}{O}H$ leaves as H_2O → $R^{\oplus}$ + $R'-OH$

$X^{\ominus}$ attacks $R^{\oplus}$ (SN1) → $R-X + R'-OH$

$X^{\ominus}$ attacks R' (SN2) → $R-OH + R'-X$

Gehri Baat :- YJ²

If alkyl grp is $CH_3/1^\circ$ $\longrightarrow$ SN_2

If alkyl grp is 2° $\xrightarrow{dil.\ HI}$ SN_1

If alkyl grp is 2° $\xrightarrow{conc^n\ HI}$ SN_2

If alkyl grp is 3° $\longrightarrow$ SN_1

If alkyl grp is Back bonding / Reso stabilised $\longrightarrow$ SN_1

If anhyd. HI $\longrightarrow$ Always SN_2
(Not possible in 3°)

① $CH_3-O-CH_2-CH_3$ (1° and 1°)

$\xrightarrow[\text{(excess)}]{H-I} CH_3-I + CH_3-CH_2-I$

$\xrightarrow[\text{(1 mole)}]{H-I} CH_3-I + CH_3-CH_2-OH$ (SN_2)

② $CH_3-CH_2-O-C(CH_3)_3$ (1° and 3°)

$\xrightarrow[\text{(excess)}]{H-I} CH_3-CH_2-I + I-C(CH_3)_3$

$\xrightarrow[\text{(1 mole)}]{H-I} CH_3-CH_2OH + I-C(CH_3)_3$ (SN_2)

③ $Ph-O-CH_3$ (2° and 1°)

$\xrightarrow[\text{(excess)}]{H-I} Ph-OH + CH_3-I$

$\xrightarrow[\text{(1 mole)}]{H-I} Ph-OH + CH_3-I$

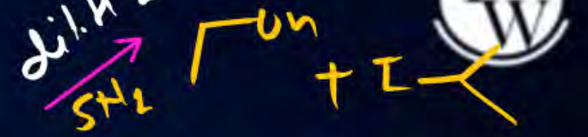
④ $Ph-CH_2-O-CH_2-CH_3$ (1° and 1°)

$Ph-\overset{\oplus}{C}H_2$

$\xrightarrow[\text{(excess)}]{H-I} Ph-CH_2-I + CH_3-CH_2-I$

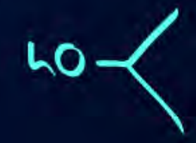
$\xrightarrow[\text{(1 mole)}]{H-I} Ph-CH_2-I + EtOH$ (SN_1)

⑤ 

$\xrightarrow[SN_2]{\text{dil. HI}}$ 

$\xrightarrow[SN_2]{\text{conc}^n\ HI}$

$\downarrow$ anhyd. HI SN_2

CH_3-CH_2-I + 

Gehri Baat :- * 3 or 4 member cyclic ether are unstable due to angle strain ∴ react in both acidic as well as basic medium.

* 5 or 6 member cyclic ether are stable ∴ only react in acidic medium.

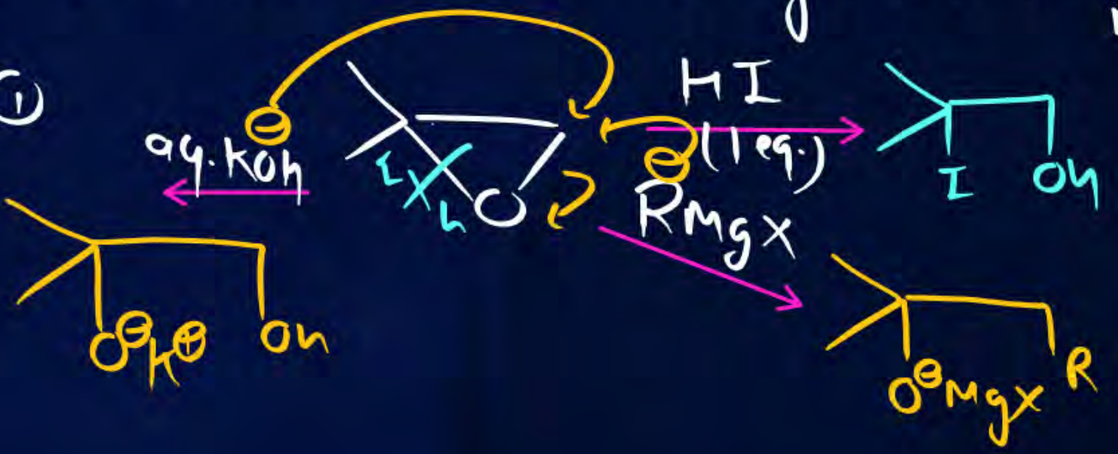
Acidic Medium

Ring open from more steric site

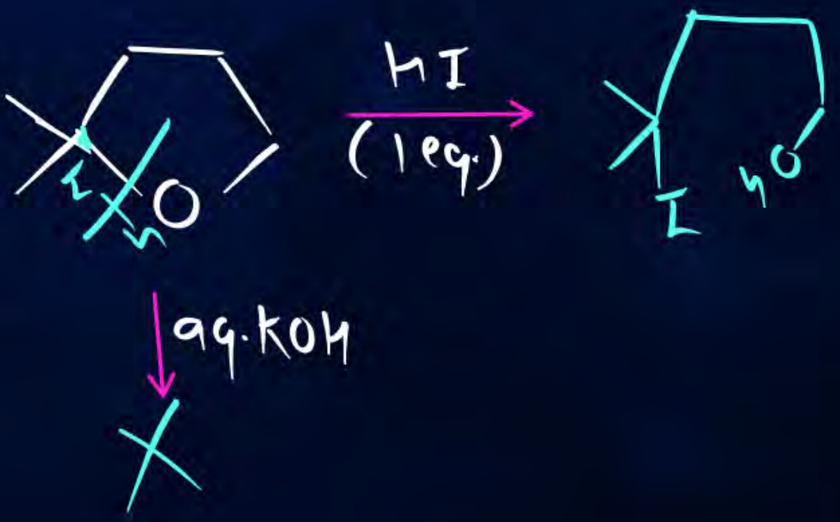
Basic Medium

Ring open from less steric site

Ex:- ①

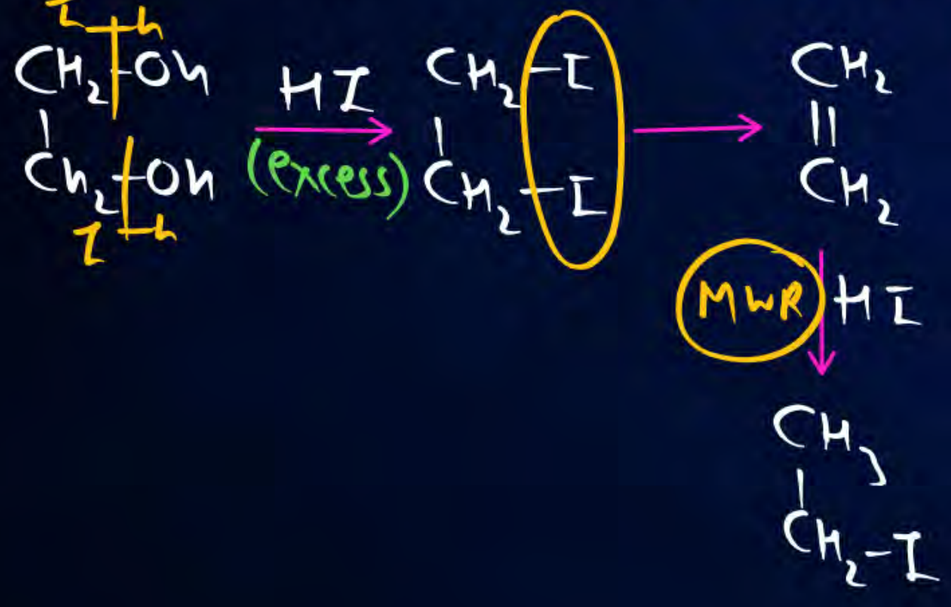


②



Gehri Baat

∴ Vicinal diodide unstable
↓
Remove I_2
↓
Form alkene
↓
1 extra mole reqd. of HI due to EAR. acc. to MR



Qw. Find no. of moles of HI consume if given in excess)?

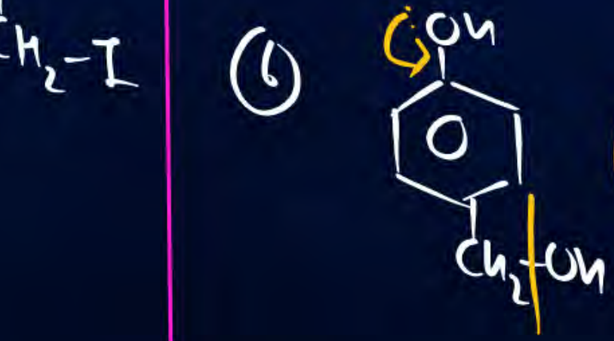
① CH_3-O-CH_3 ②

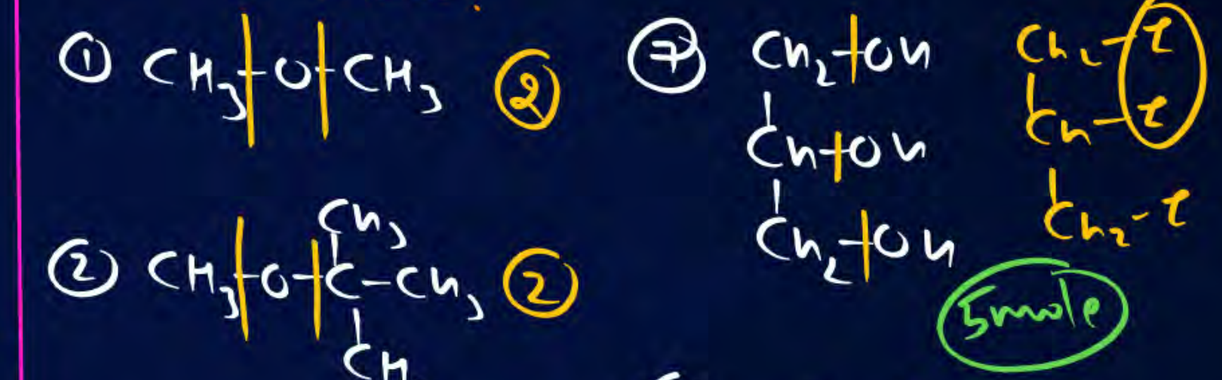
② $CH_3-O-C(CH_3)_2-CH_3$ ②

③ $Ph-O-CH_3$ ①

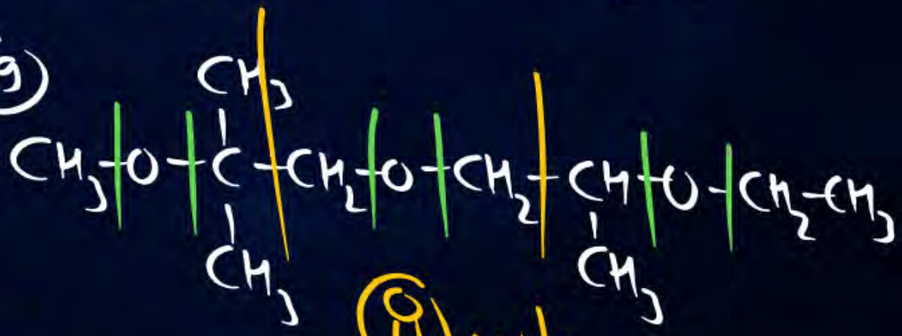
④ $Ph-CH_2-O-CH_3$ ②

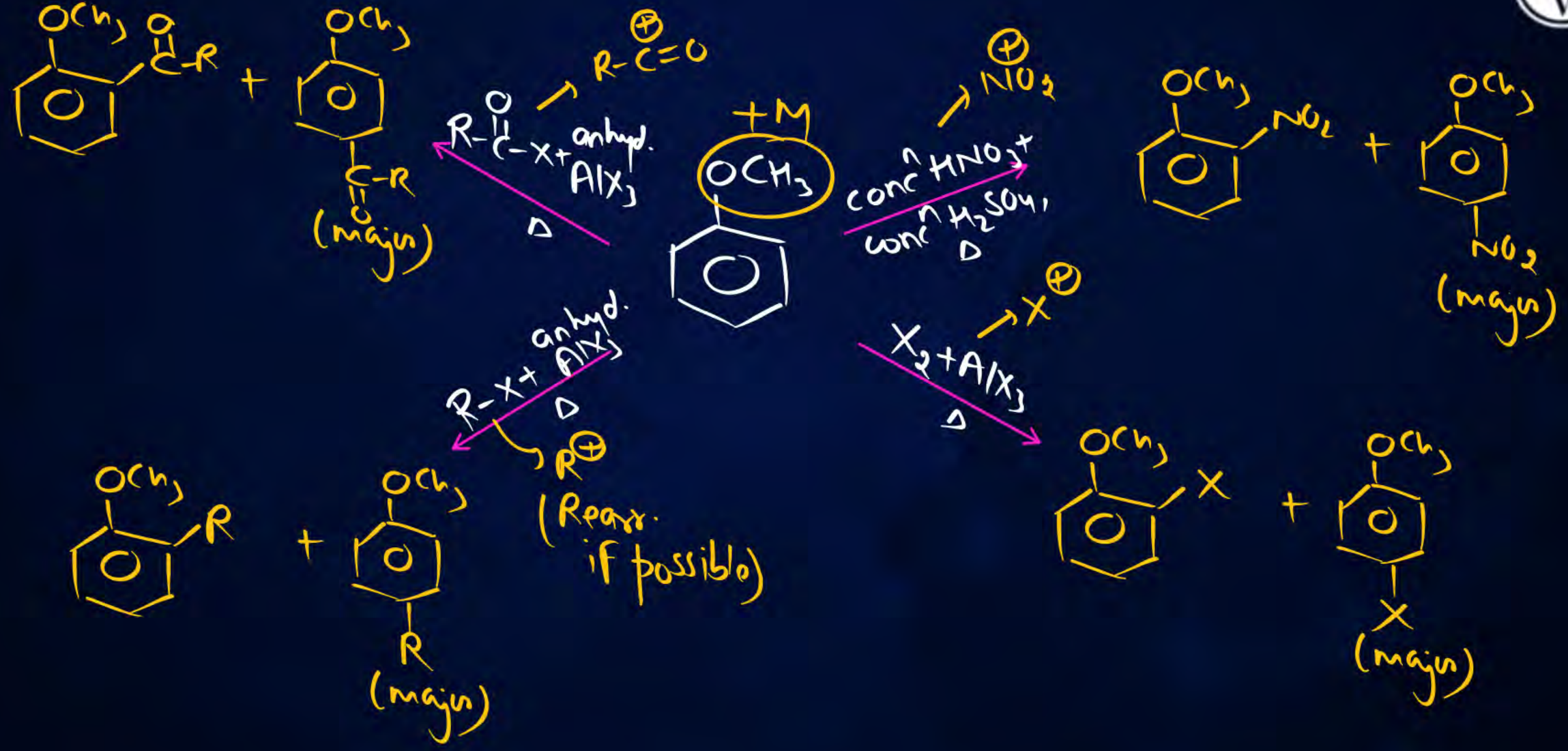
⑤ $Ph-O-Ph$ 0

⑥ 

⑦ 

⑧ 
6 mole

⑨ 
8 mole


OCH3
+M
R-C(=O)-X + anhyd. AlX3
Δ
R-C≡O⊕
conc HNO3 + conc H2SO4, Δ
NO2⊕
R-X + anhyd. AlX3
Δ
R⊕
(Rearr. if possible)
X2 + AlX3
Δ
X⊕
(major)
(major)
(major)
(major)

THANK YOU