

Alkyl halides (Halo alkanes)

MOP:-

I) from Alcohols

1) $\text{HX} / \text{ZnCl}_2 \longrightarrow 3$

2) $\text{NaBr} / \text{H}_2\text{SO}_4 \longrightarrow 3$

3) $\text{PX}_3 \longrightarrow 4$

4) $\text{PCl}_5 \longrightarrow 4$

5) $\text{Red P} / \text{X}_2 \longrightarrow 5$

6) SOCl_2 (Darzen's rxn) $\longrightarrow 5$

II) from Hydrocarbons

A) Alkanes

i) Free radical halogenation $\longrightarrow 6$

B) Alkenes

i) addition of hydrogen halide (HX) $\longrightarrow 7$

ii) addition of halogen ($\text{X}_2 / \text{CCl}_4$) $\longrightarrow 8$

III) Halogen exchange:

a) Finkelstein ($\text{NaI} / \text{acetone}$) $\longrightarrow 9$

b) Swartz ($\text{Inorganic fluoride}$) $\longrightarrow 9$

Chemical reactions :-

1) Nucleophilic substitution

*) SN^1	>	11
*) SN^2	>	12
*) Reagents	>	13
*) Stereochemistry of SN^1	>	14
*) Stereochemistry of SN^2	>	16
*) Energy Profile diagram	>	17
*) SN_1^i	>	25
*) SN_2^i	>	25
*) SN_i	>	26
*) Intramolecular SN_2	>	28
*) NGP	>	29
*) Effect of Solvent	>	34
→ Protic, aprotic		
*) Nucleophilicity	>	36

2) Elimination rxn's> 40

*) E_2 Elimination	>	41
*) E_{1cb}	>	45
*) Elimination v/s Sub	>	47

3) Rxn with metals> 48

- *) Wurtz rxn
- *) Grignard rxn

*) Physical Properties :> 49

→ B.P, Density

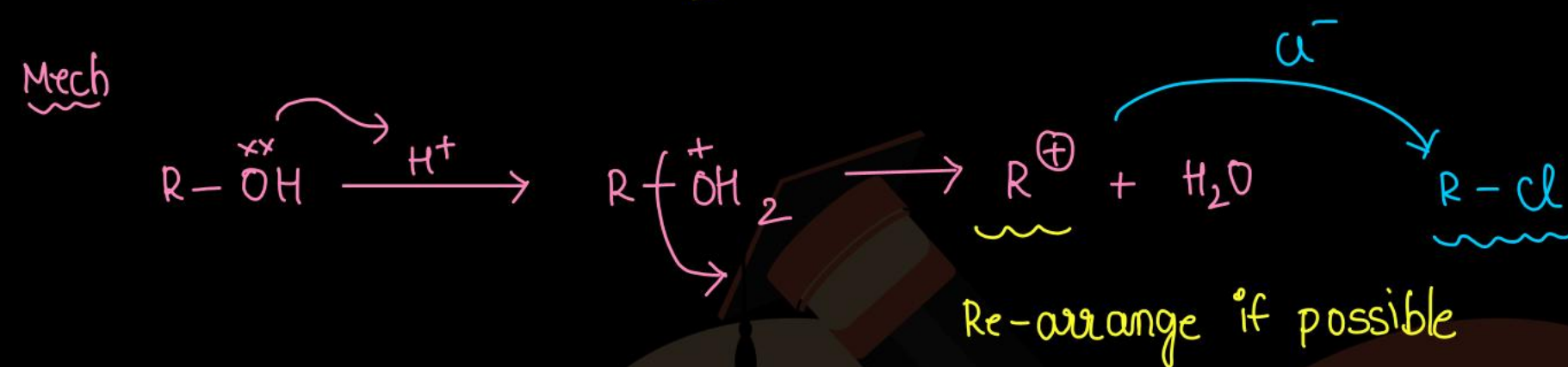
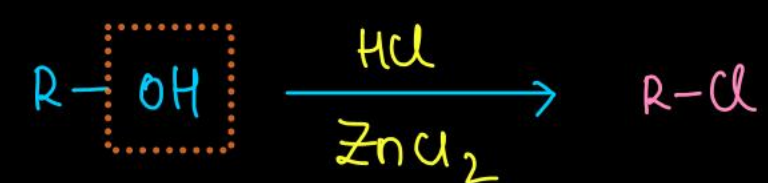
4) Haloforn

→ Preparation	>	50
→ oxid, red	>	
→ rxn with Ag	>	51
→ rxn with HNO_3	>	
*) Carbyl amine	>	52
*) Reimer - Tiemann	>	

*) NCERT points> 53

I) Reaction of ROH with

① $\text{HCl} / \text{ZnCl}_2 \rightarrow \text{catalyst}$



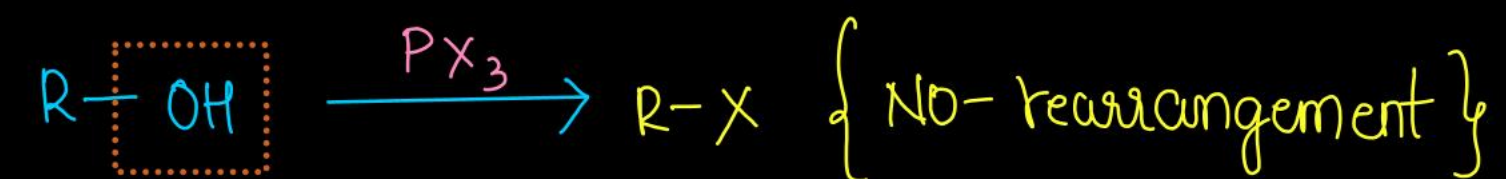
② $\text{NaBr} / \text{H}_2\text{SO}_4$



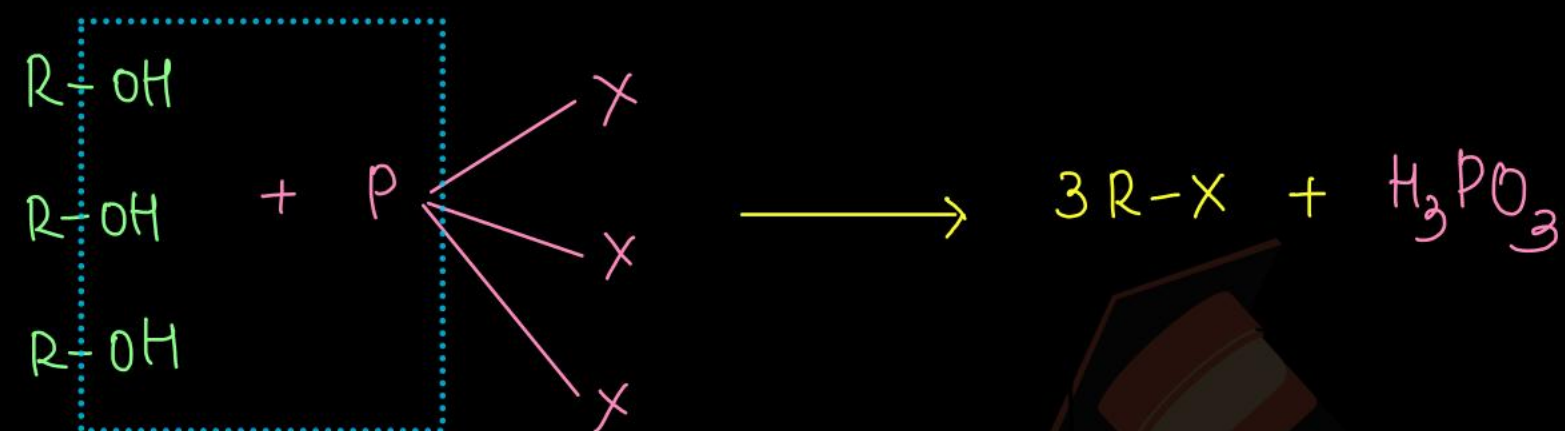
* $3^\circ > 2^\circ > 1^\circ$

* $\text{HI} > \text{HBr} > \text{HCl}$

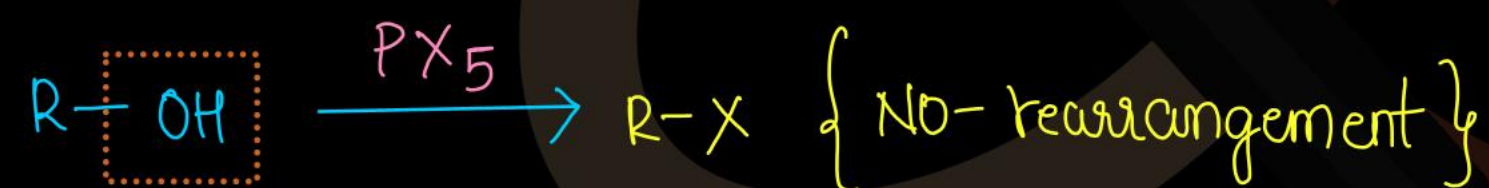
③ PX_3 ($X = Cl, Br$)



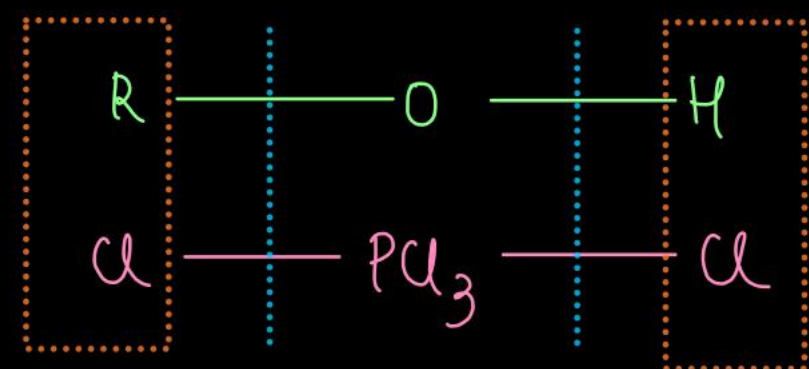
DM:-



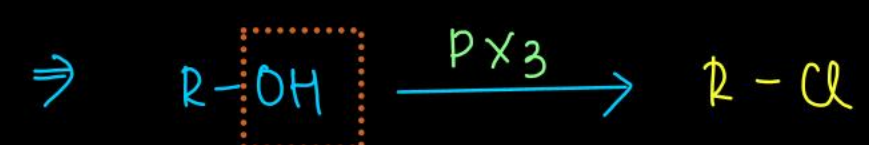
④ PCl_5



DM:-



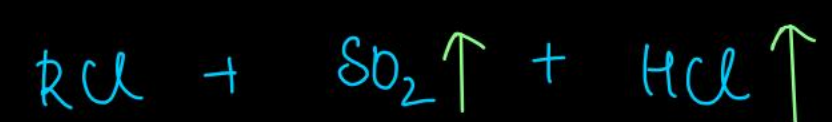
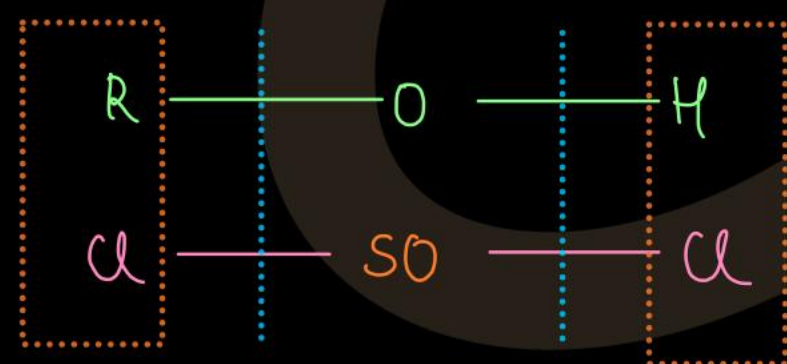
⑤ Red P / X_2 ($X = Br, I$)



* ⑥ $SOCl_2$ (Darzen's rxn's)

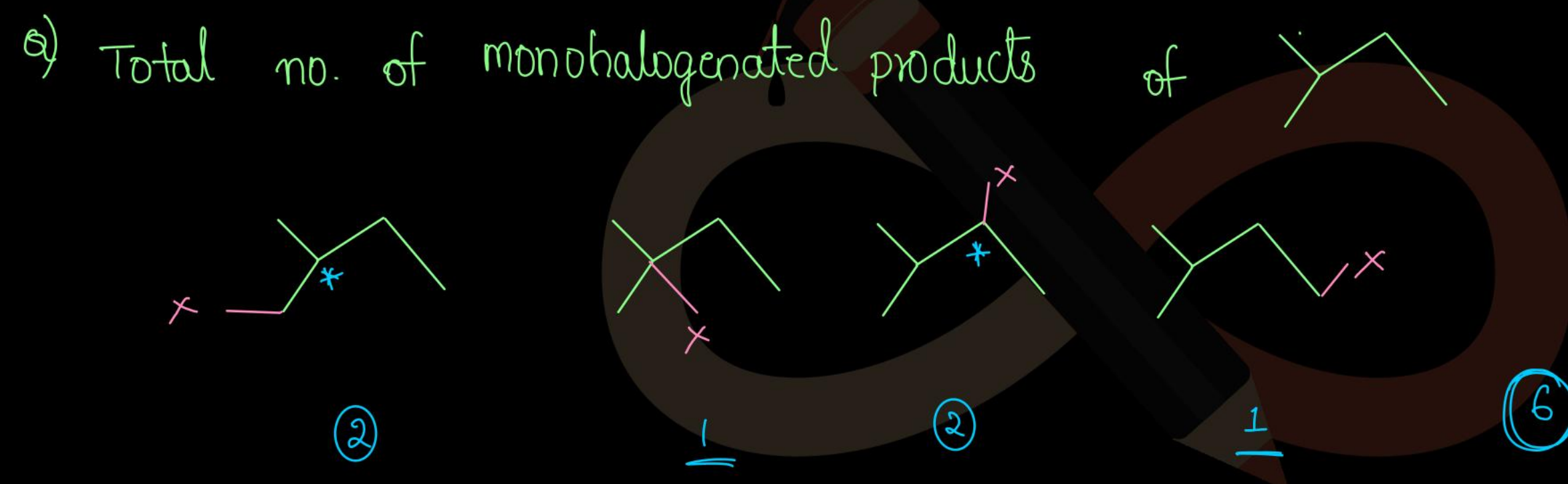
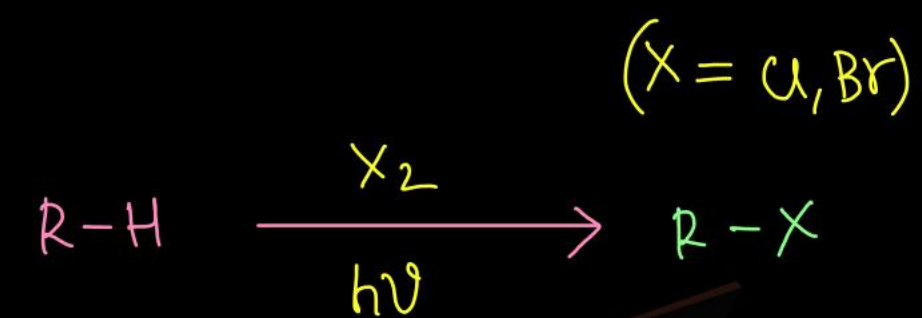


DM :-



II) from Hydro Carbons

1) From alkanes by Free radical halogenation

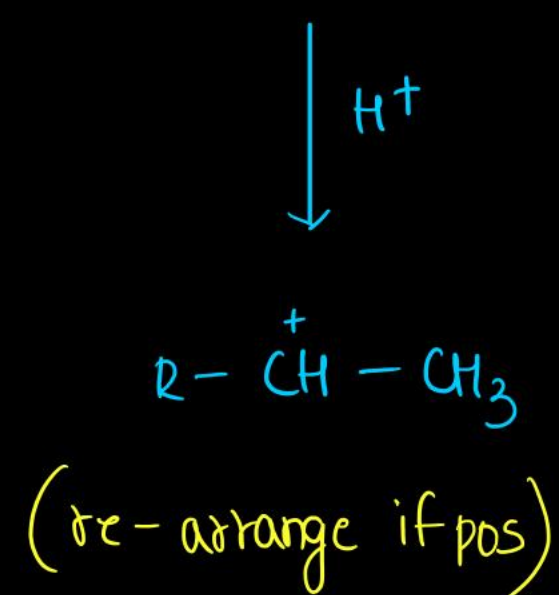
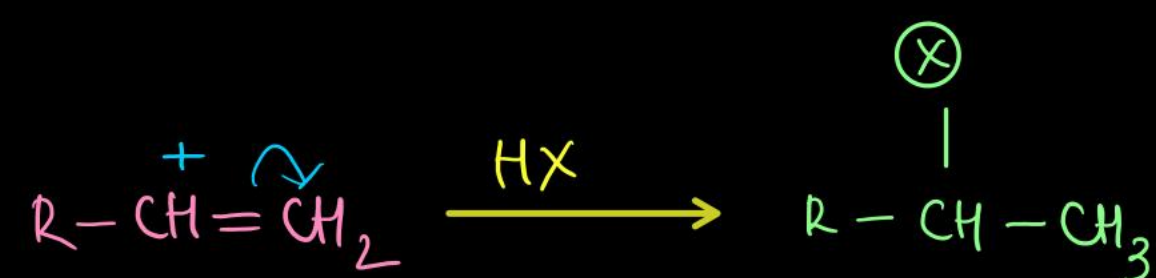


* Chlorination 1 : 3.8 : 5

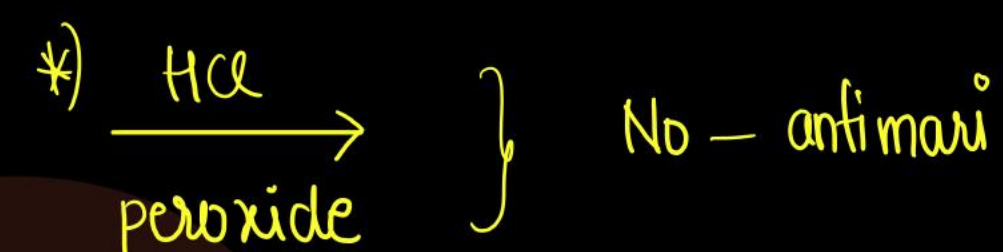
* Bromination ($3^\circ > 2^\circ > 1^\circ$)

② from alkenes

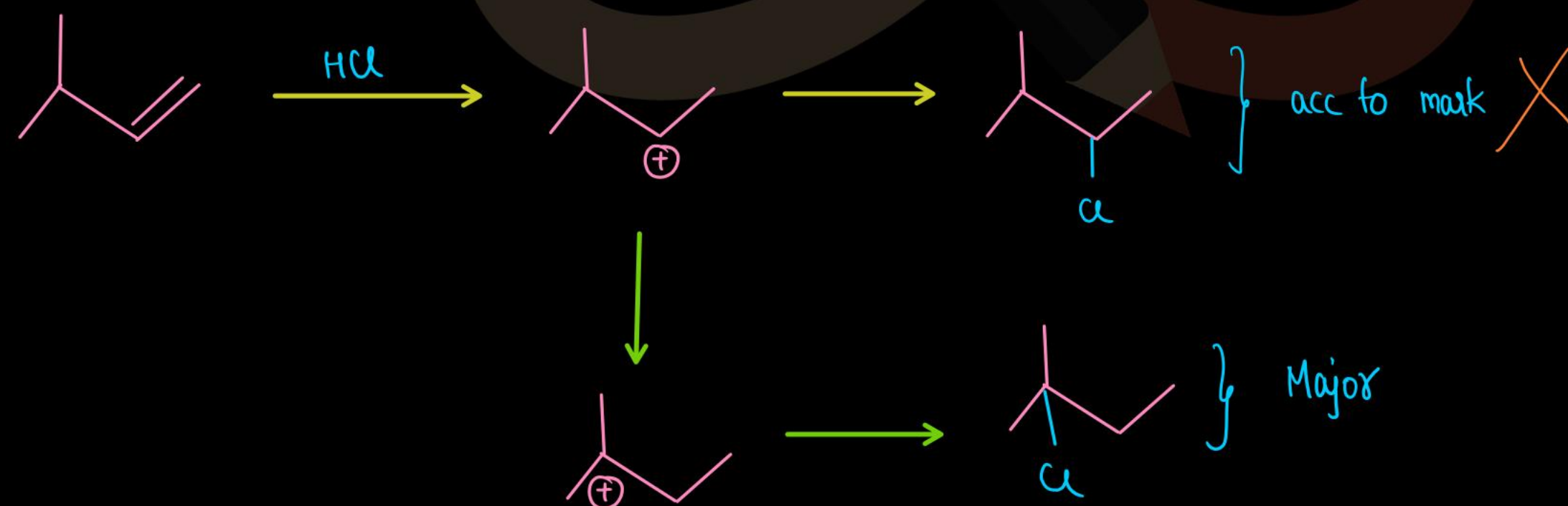
i) HX



(* Don't use markonikov's rule)

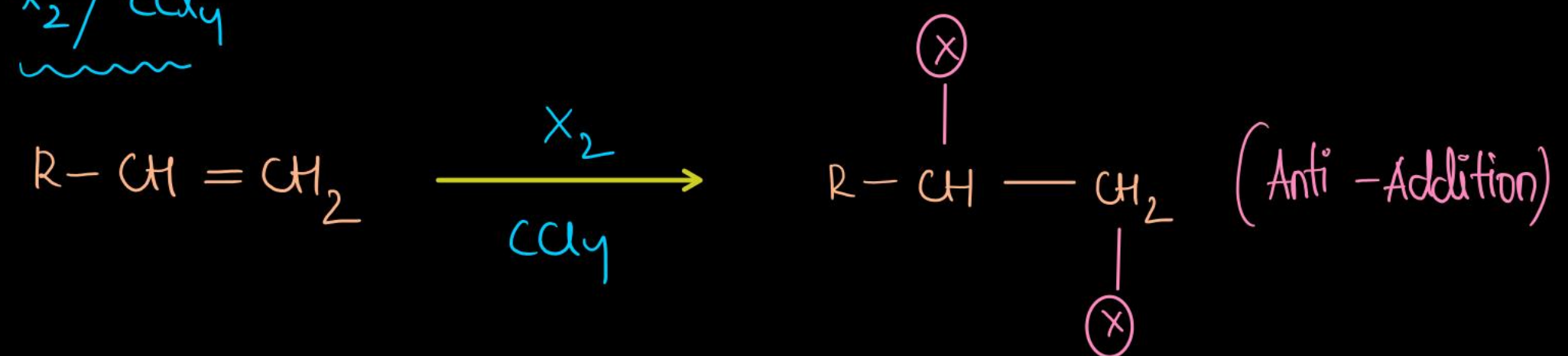


Ex:-

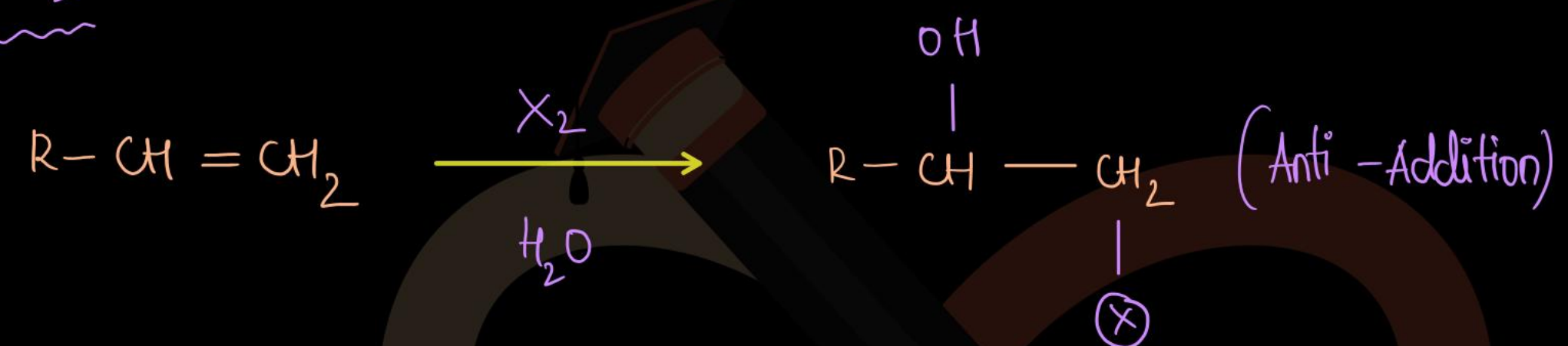


ii)

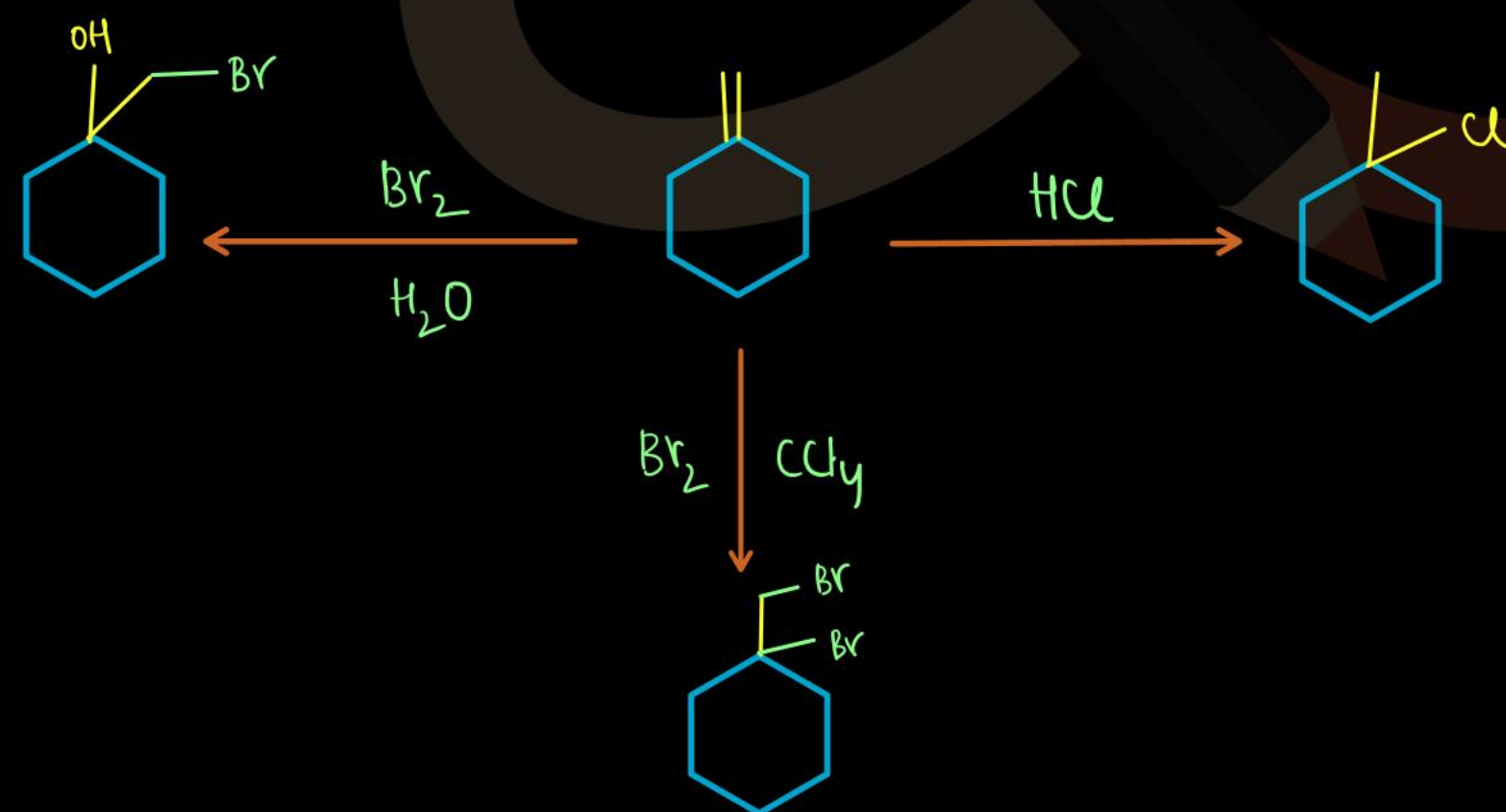
(a) X_2 / CCl_4



(b) X_2 / H_2O

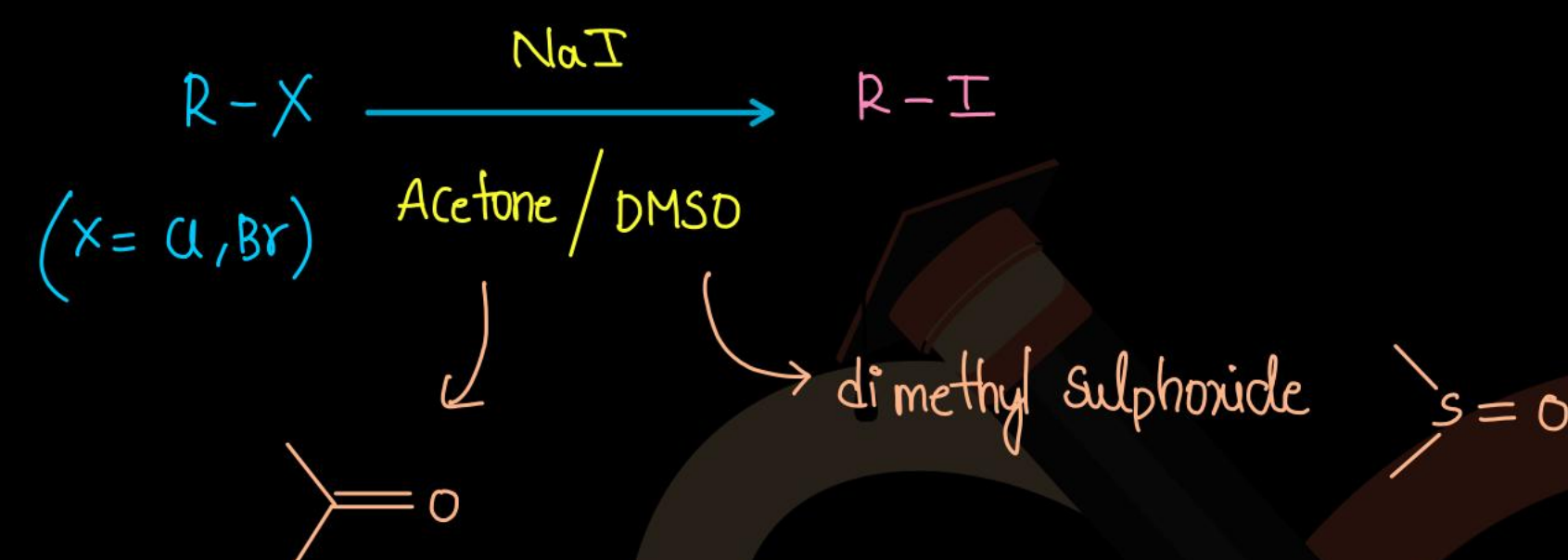


Q)

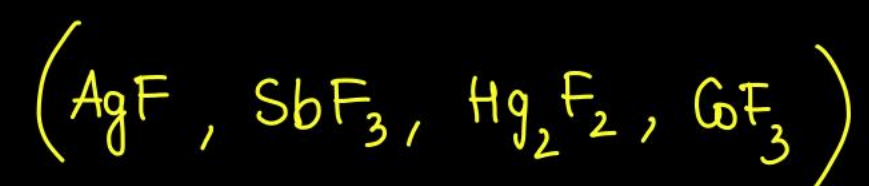
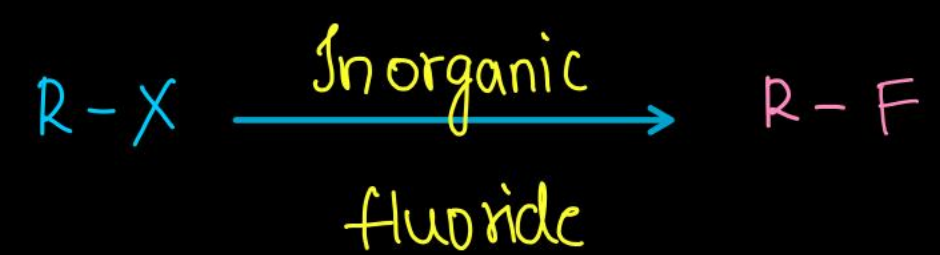


III) Halogen exchange

a) Finkelstein rxn



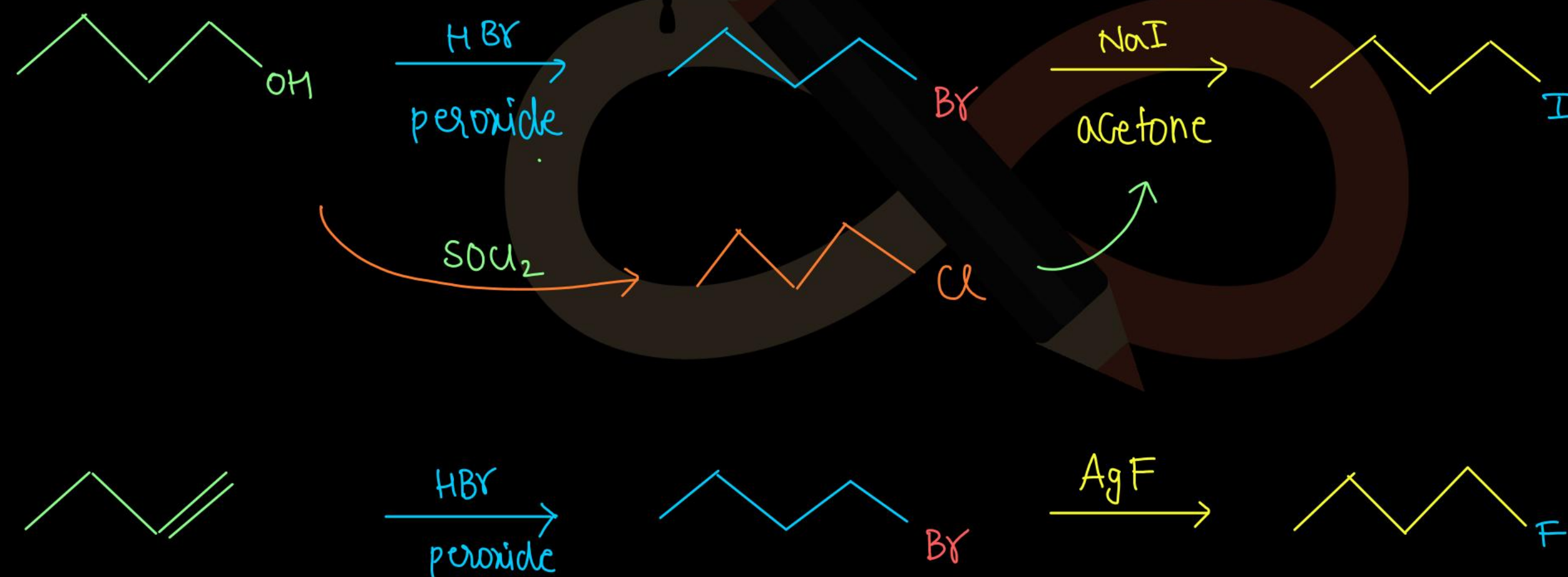
b) Swartz rxn :



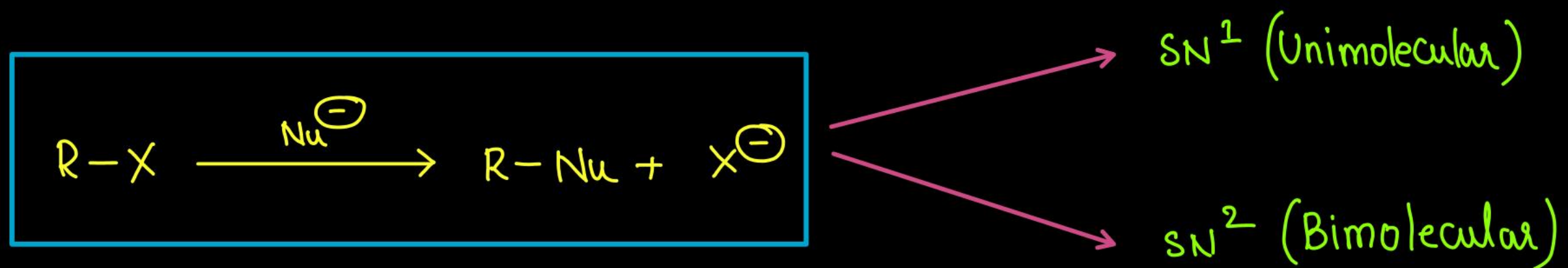
Q) Convert



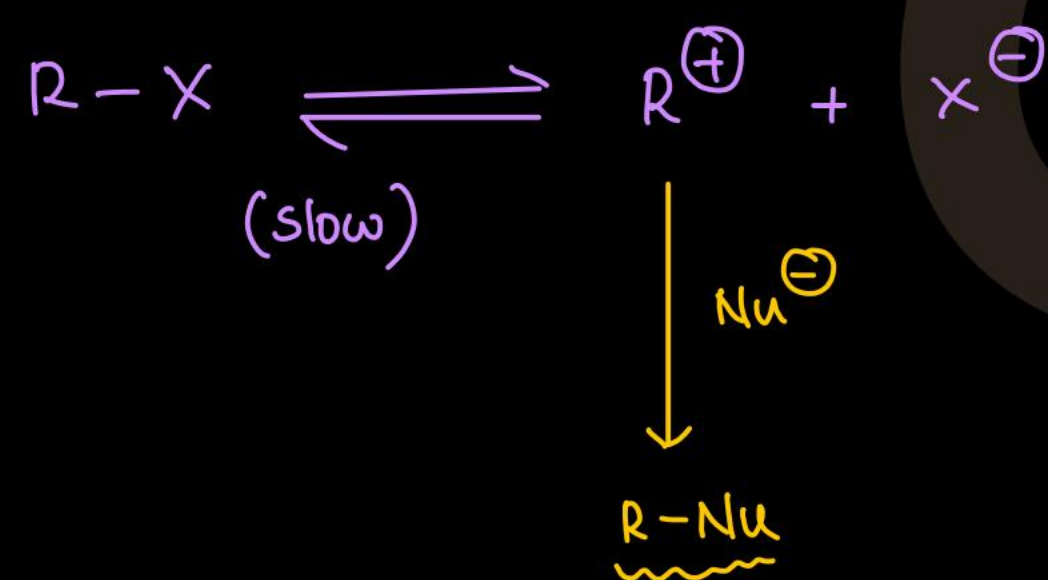
Ans:-



Nucleophilic Substitution Rxn's (NSR) :-



SN^1

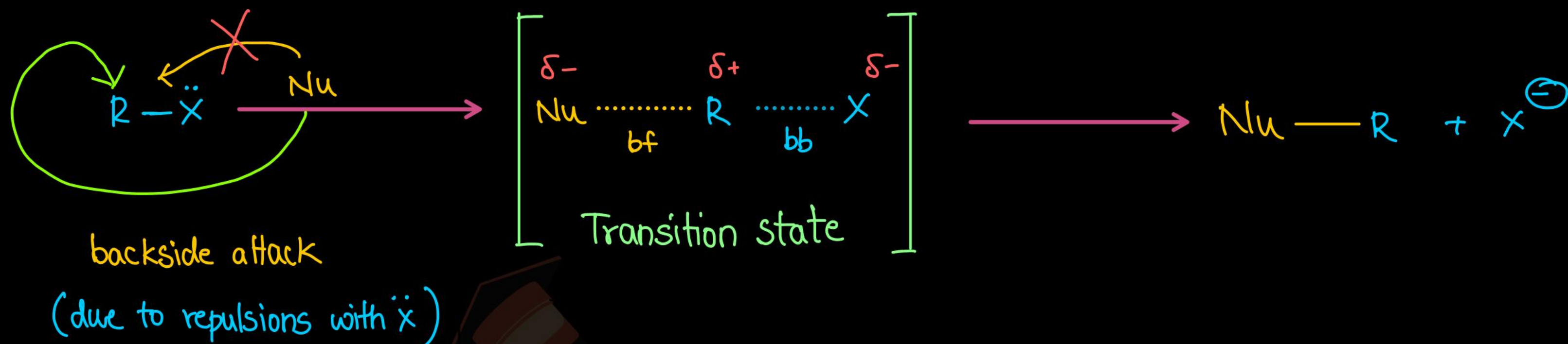


1) 2 step rxn

2) $C^{\oplus}$ is formed

3) Rate = $k[R-X]^1$ $\rightarrow$ order = 1 (not always)
 $\rightarrow$ molecularity = 1

4) ROR of $R-X$: $3^{\circ} > 2^{\circ} > 1^{\circ}$
: $R-I > R-Br > R-Cl$



Note:-

- 1) 1 step rxn
- 2) T.S formed
- 3) Rate = [R-X] [Nu⁻] → order = 2
→ molecularity = 2
- 4) R.O.R of R-X : 3° < 2° < 1° (S.H)
∴ R-I > R-Br > R-Cl

* Polar aprotic solvents favour.

	Reagent	Nu [⊖]	Product
1)	NaOH / KOH	OH ⁻	R-OH
2)	H ₂ O	H ₂ O	R-OH
3)	NaOR	OR ⁻	ROR
4)	NaI	I ⁻	R-I
5)	NH ₃	NH ₃	R-NH ₃
6)	KCN	[⊖] C≡N:	R-CN
7)	AgCN	Ag-CN:	R-NC
8)	KNO ₂	O=N-O	R-ONO
9)	AgNO ₂	Ag- ^{••} O-N=O	R-NO ₂
10)	LiAlH ₄	H	R-H

*) Ambient Nu[⊖] : (more than 2 donors)

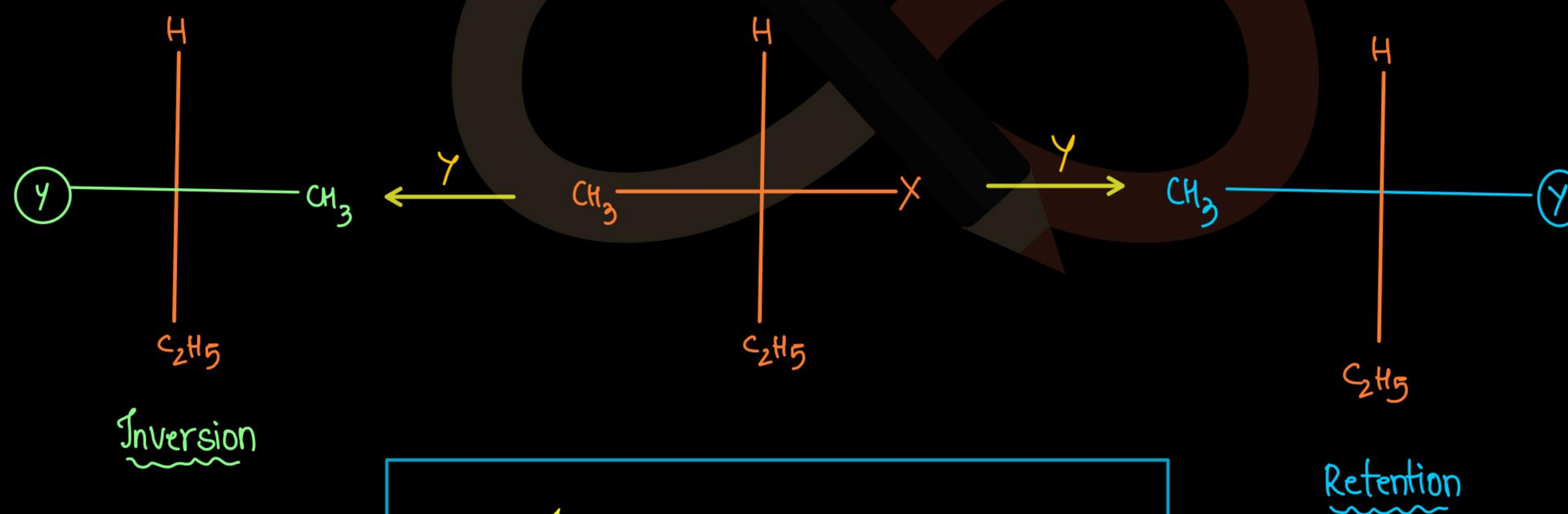
*) $\ominus \text{C} \equiv \text{N}:$ (alkyl Cyanide)

*) $:\text{C} \equiv \text{N}^{\ominus}$ (iso cyanides)

*) $\ominus \text{O}-\text{N}=\text{O}$ (alkyl Nitrite)

*) $\ominus \text{NO}_2$ (Nitro alkane)

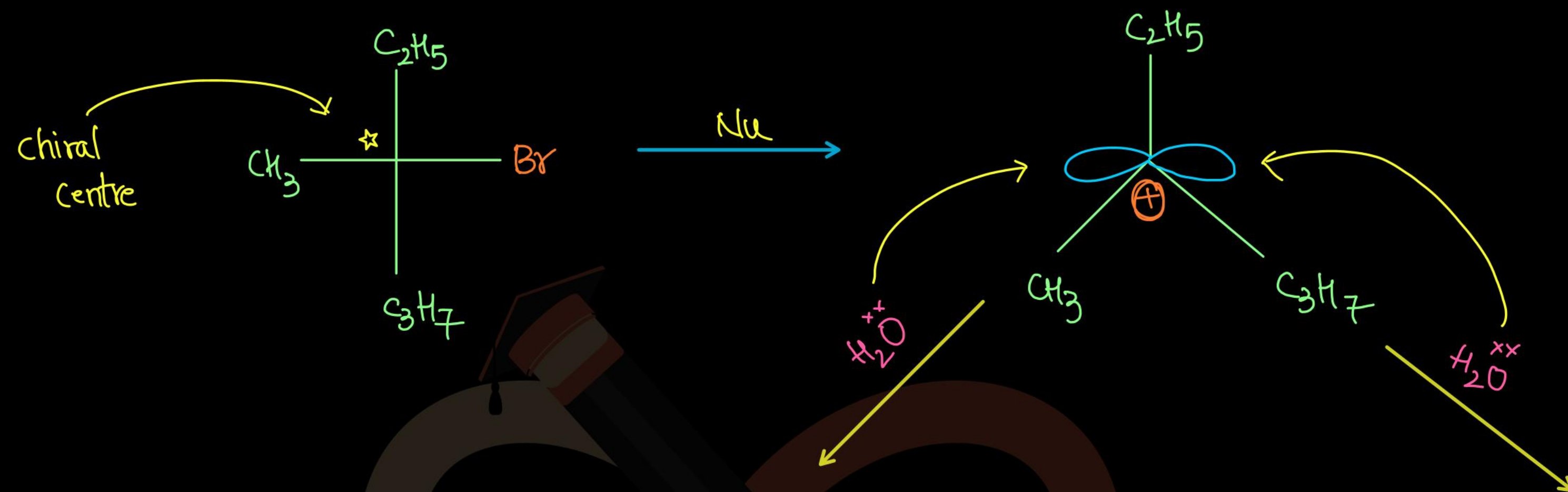
Stereochemistry of SNR :



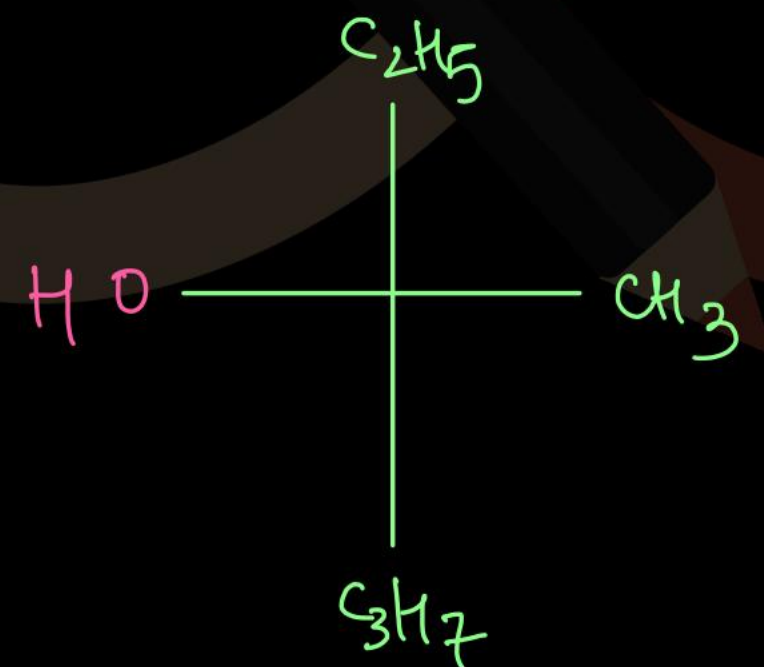
*) SN^1 : A+B = Racemic mixture

*) SN^2 : B = only Inversion

Stereochemistry of S_N1

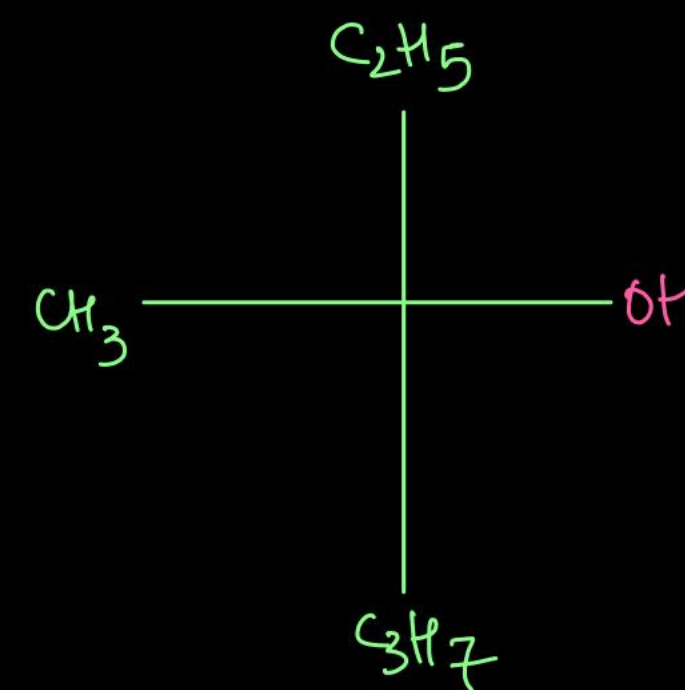


$$\% \text{ back side attack} = \left[\begin{array}{l} \% \text{ inversion product} \\ + \frac{1}{2} \% \text{ racemic product} \end{array} \right]$$



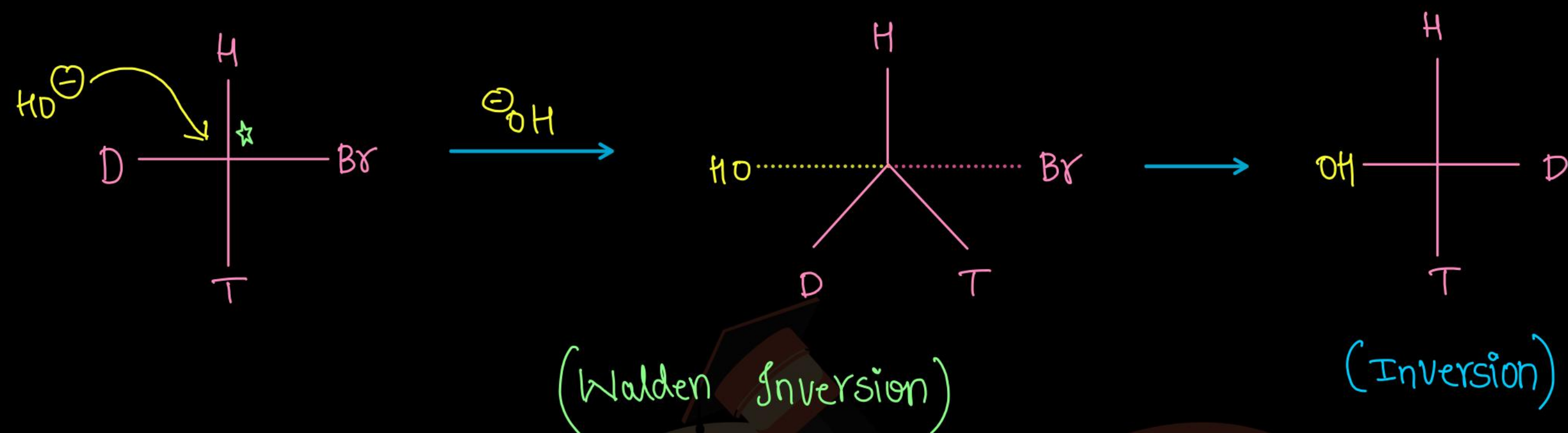
Inversion (50%)

(Racemisation)



Retention (50%)

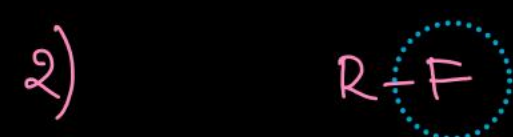
Stereochemistry of S_N2



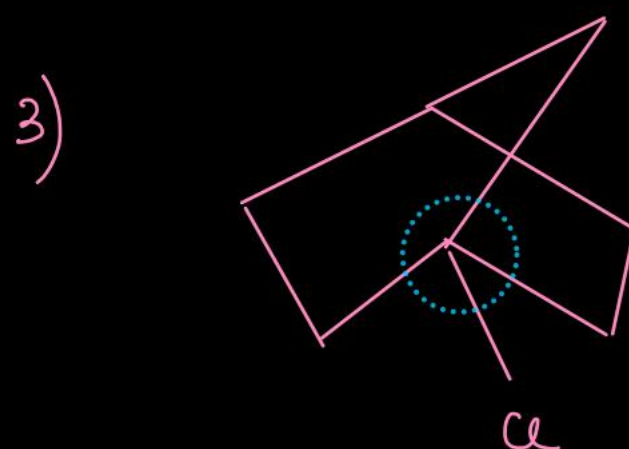
Note:- following Compounds do not give S_N1 & S_N2



— due to partial double bond character

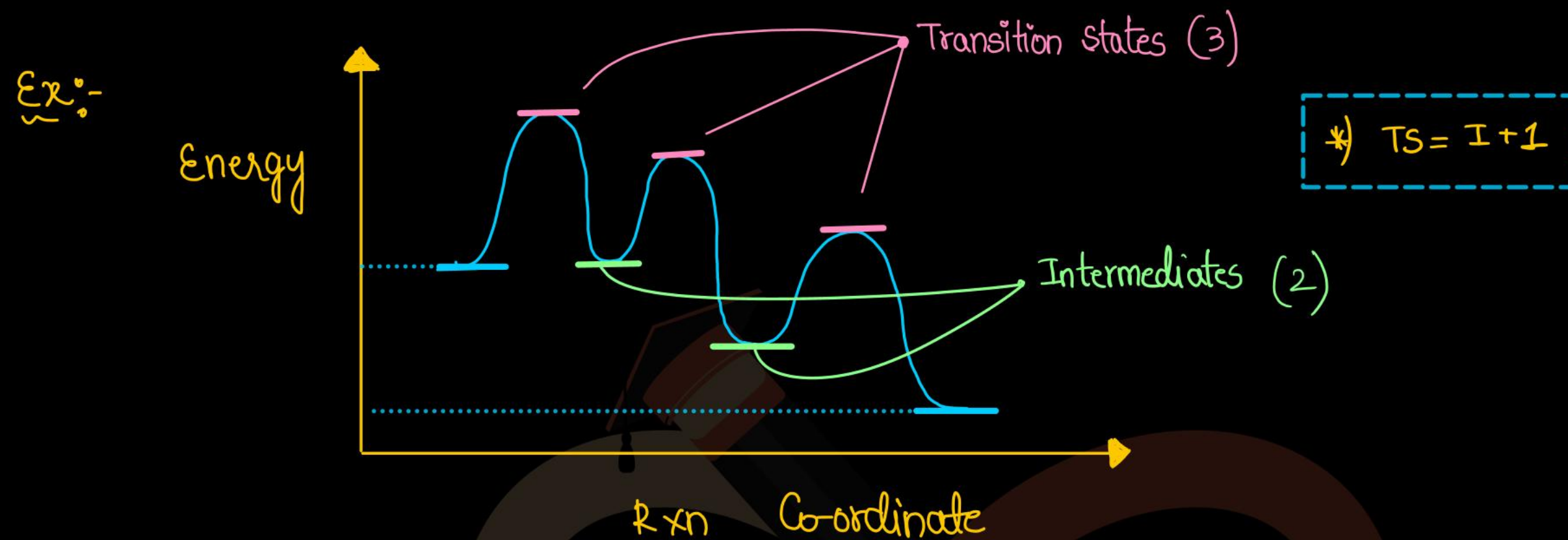


— F^- is a poor leaving group

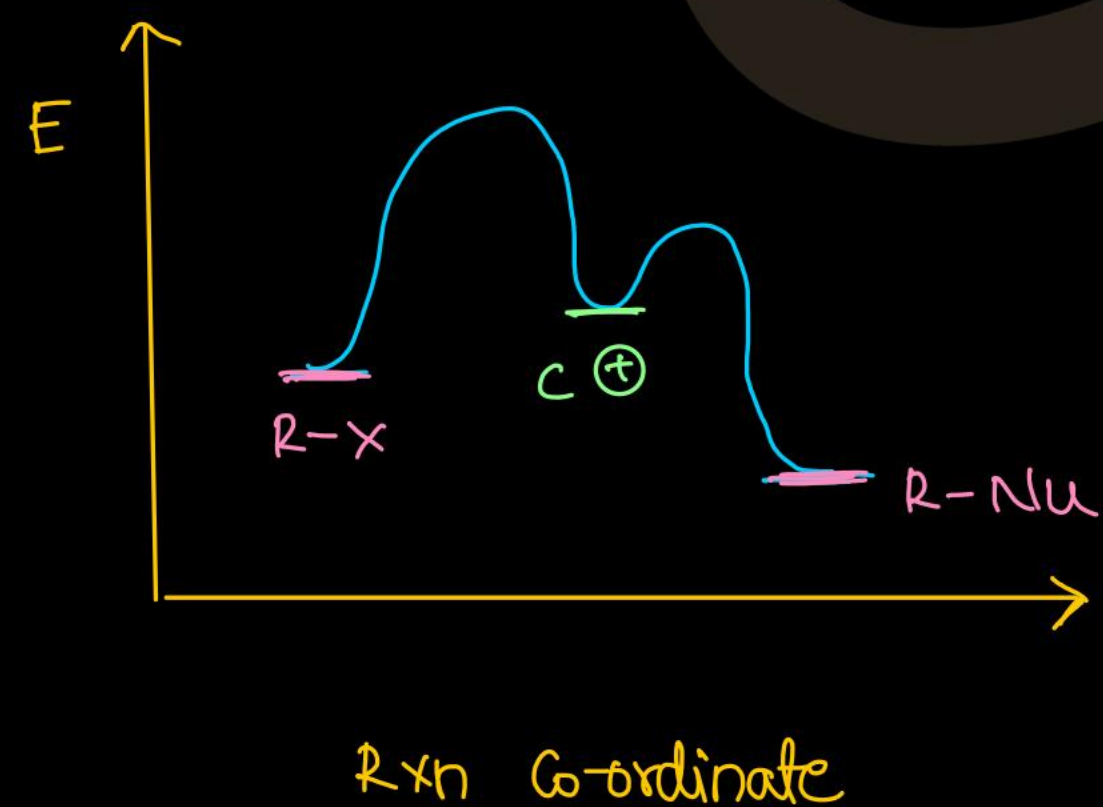


— Bredt's rule
(Bridged carbon — C^+)

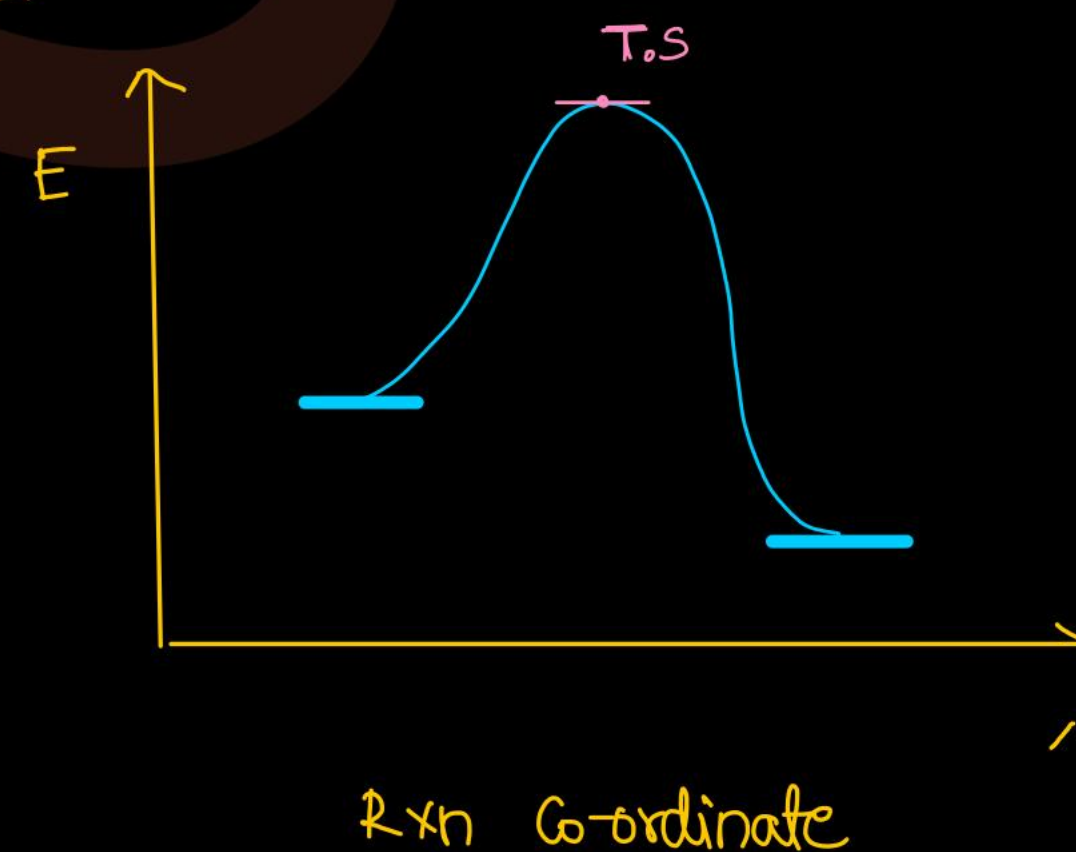
Energy profile diagram :-

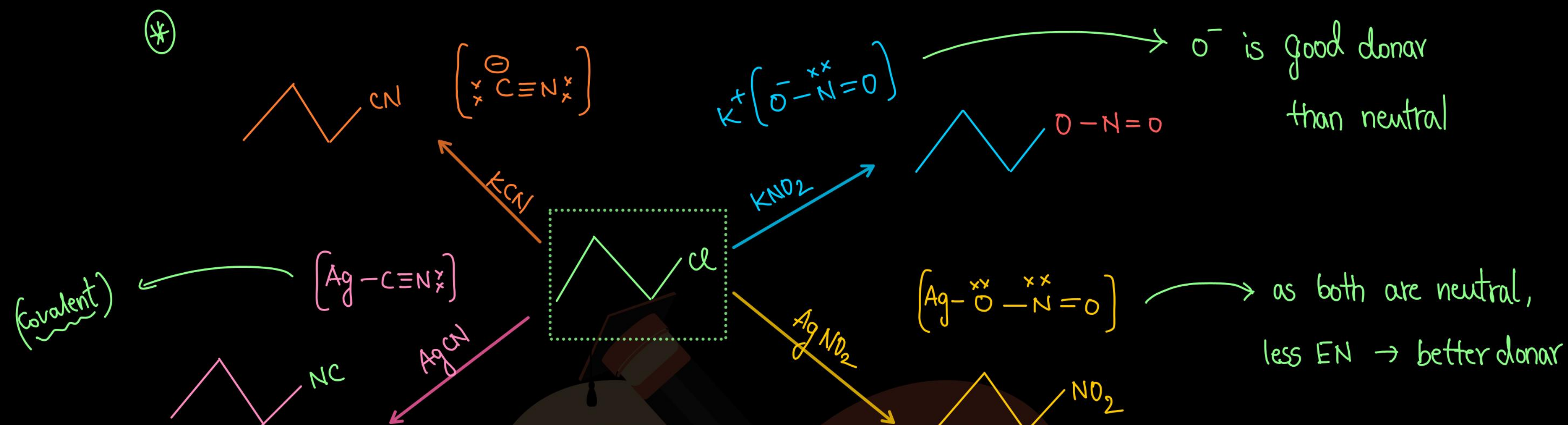


① SN¹

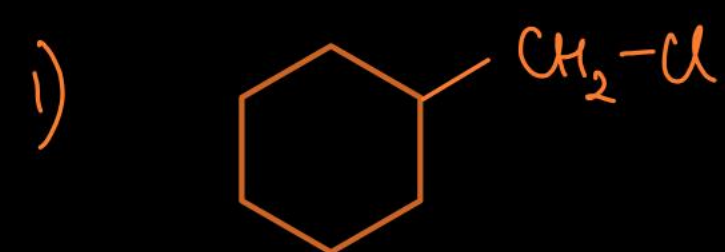


② SN²





Practice: Compare ROR towards $\text{S}_{\text{N}}2$

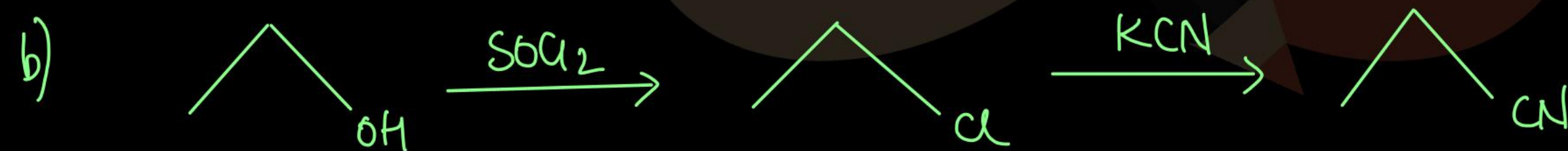
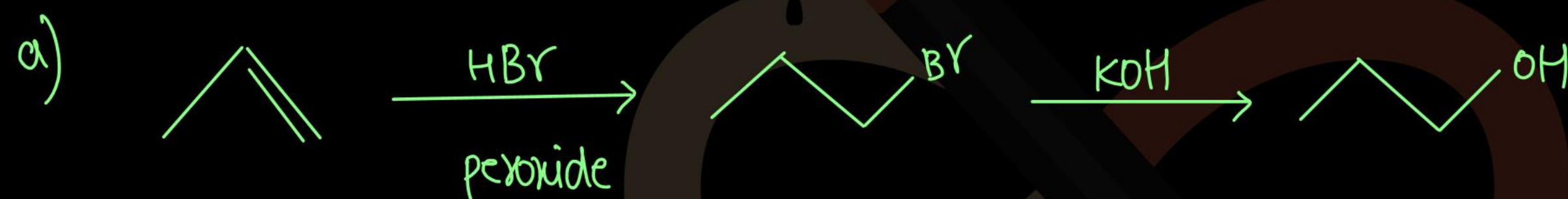
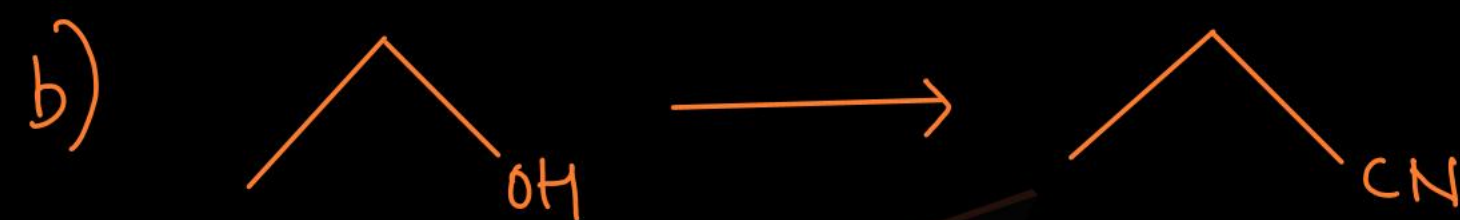


$A > B$ ($1^\circ > 2^\circ$)



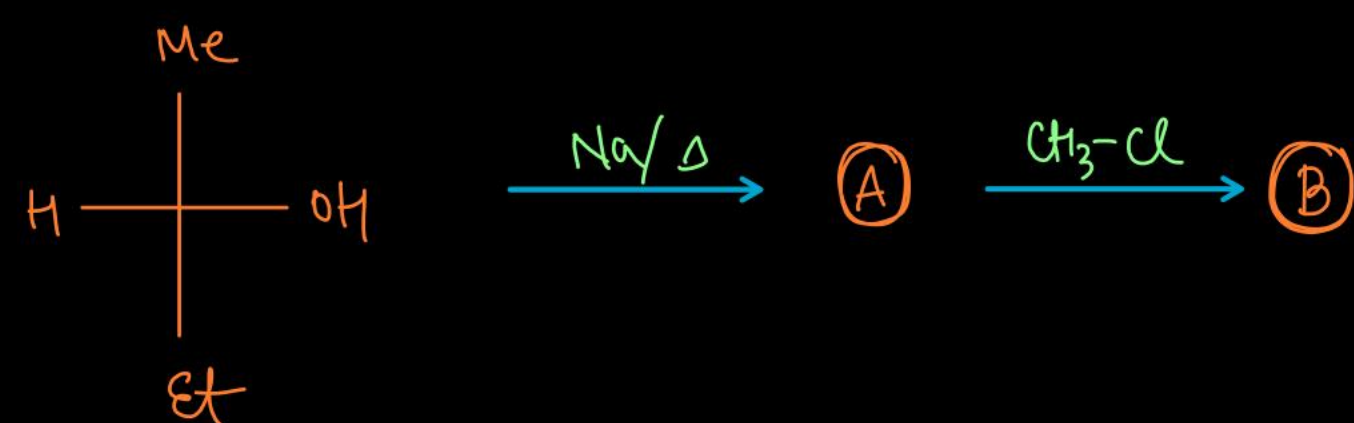
$A > B$ (leaving ability)

2) Convert

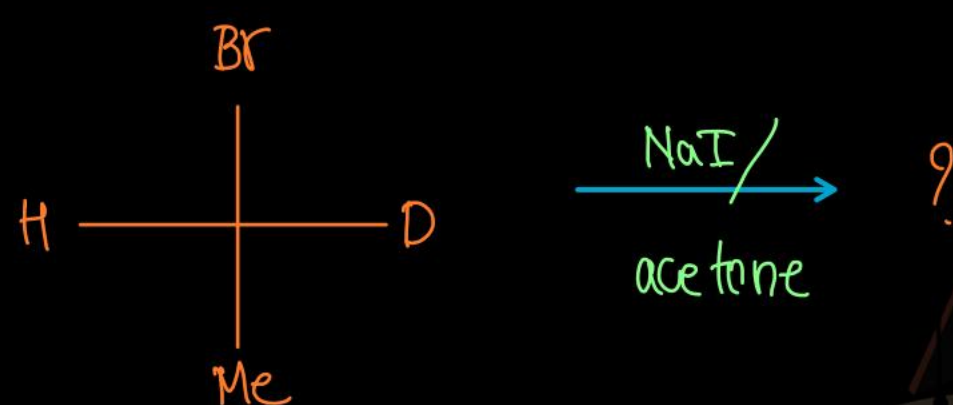


3

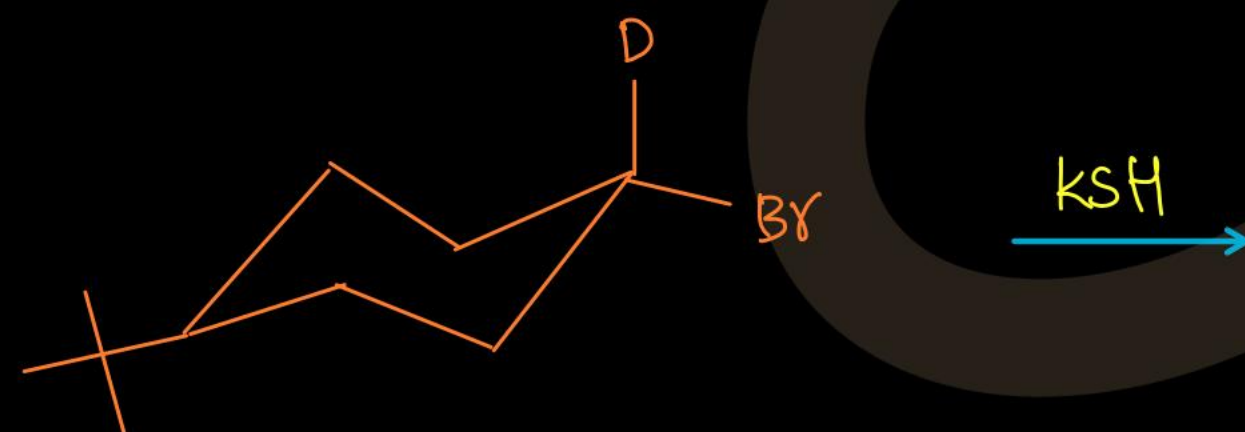
1a)



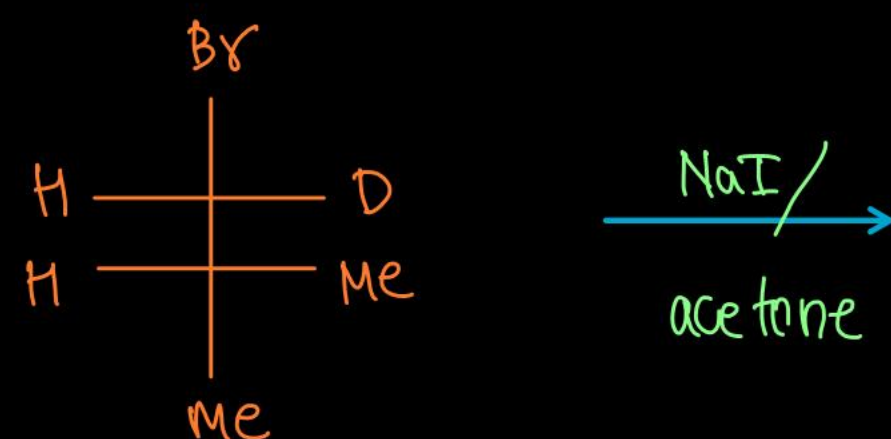
2a)



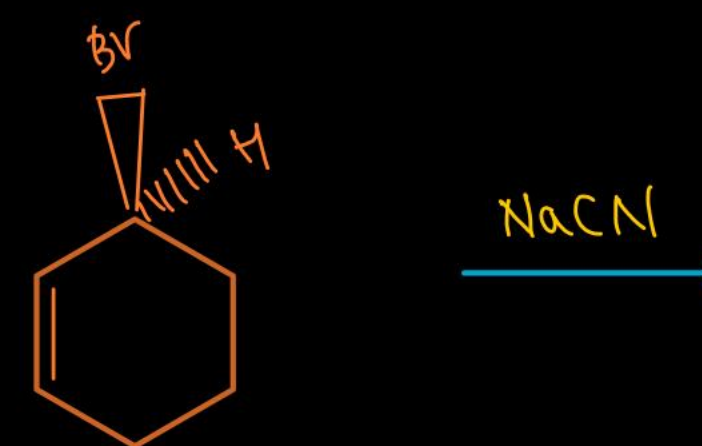
3a)



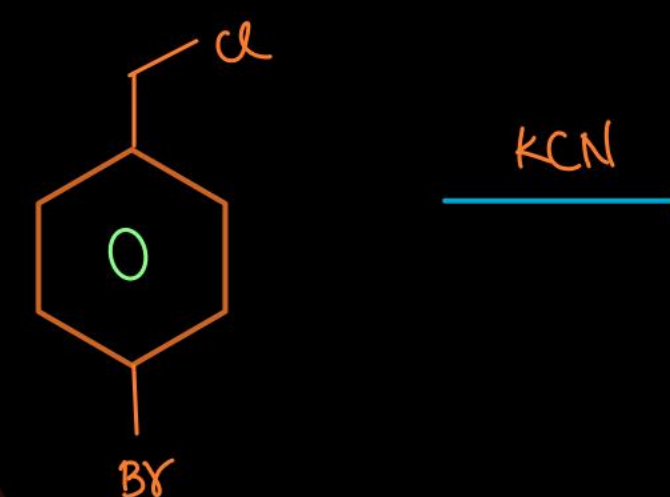
4a)



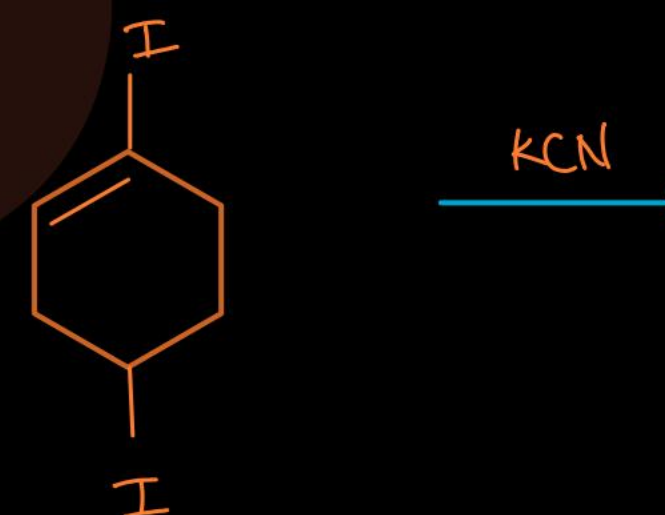
5a)



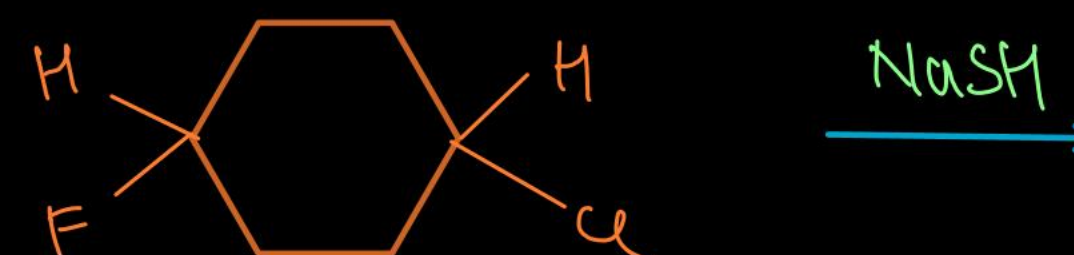
6a)

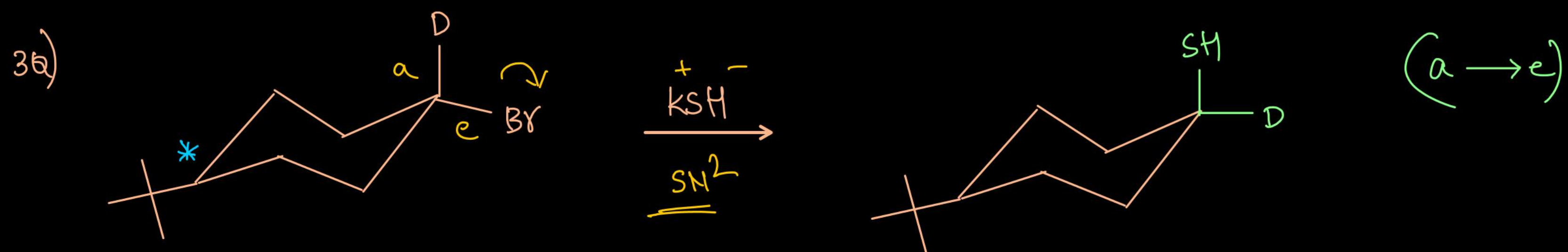
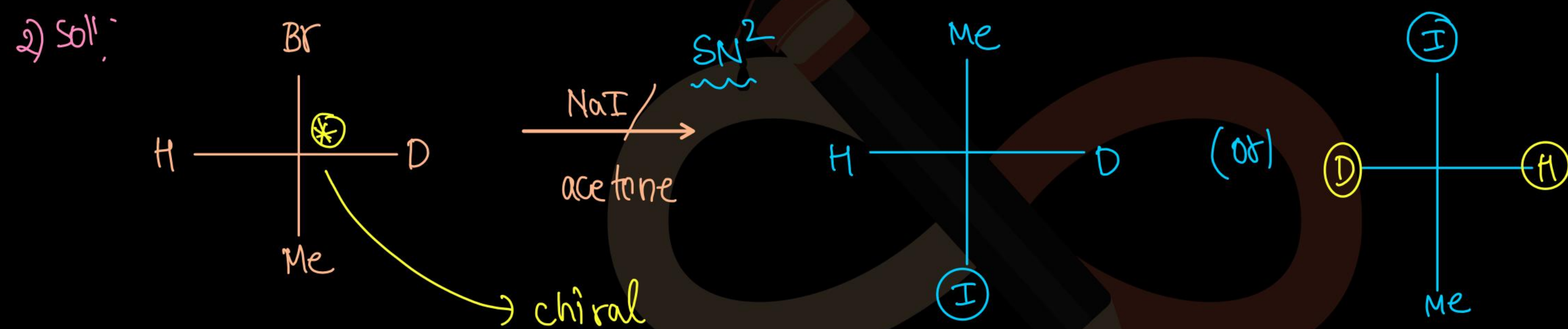
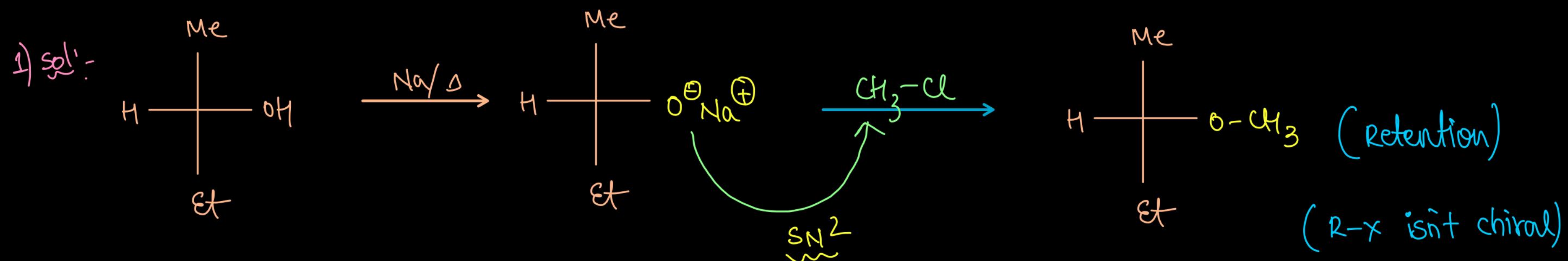


7a)

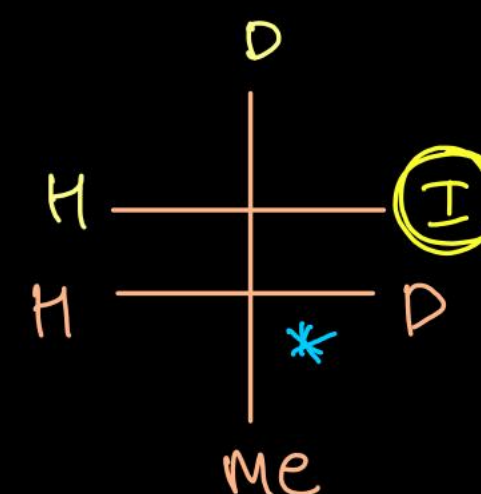
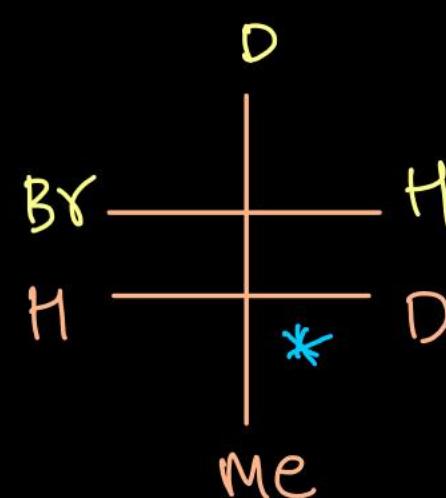
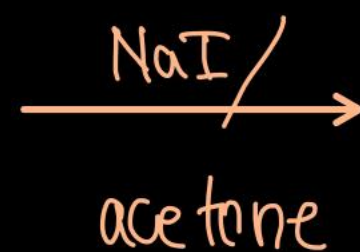
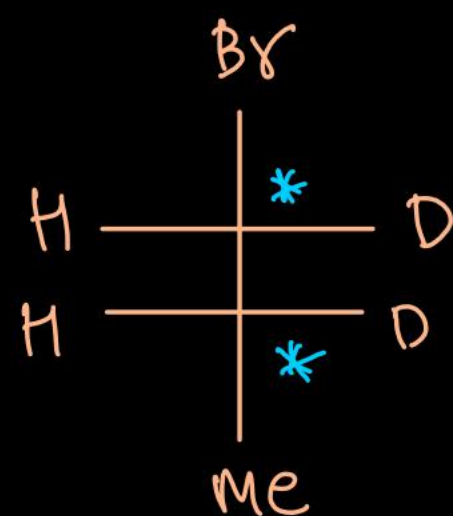


8a)



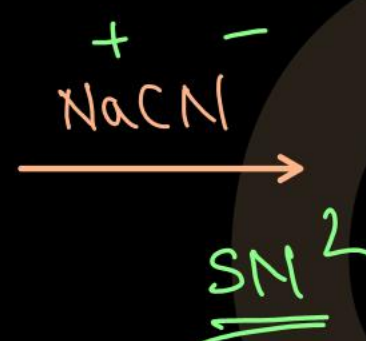


4b)

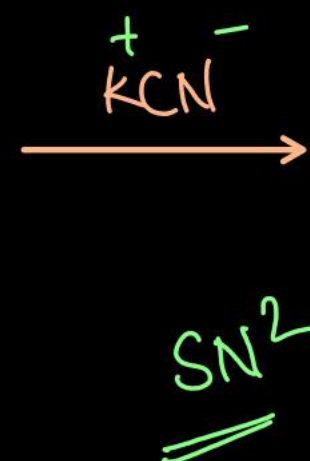


even changes

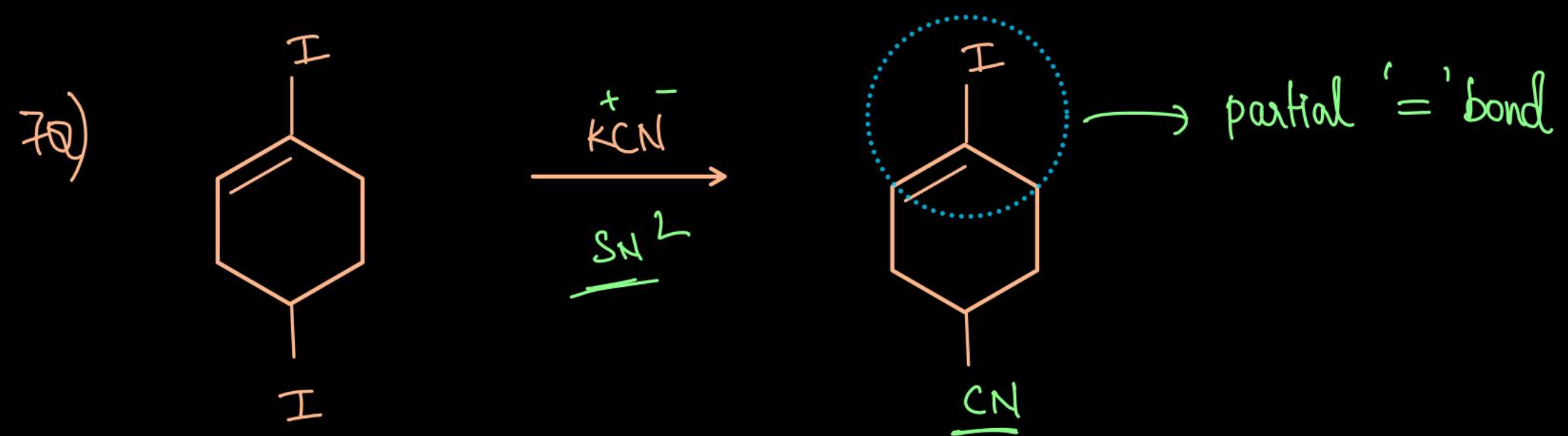
5b)



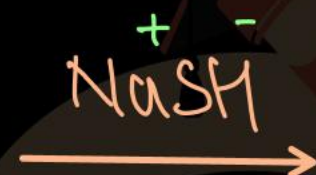
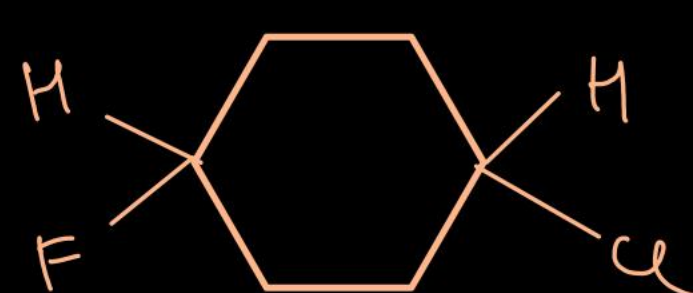
6b)



} partial double bond character



8a)



R.O.R
 $(\text{R-Cl} > \text{R-F})$

④

Compounds

S_N1

S_N2



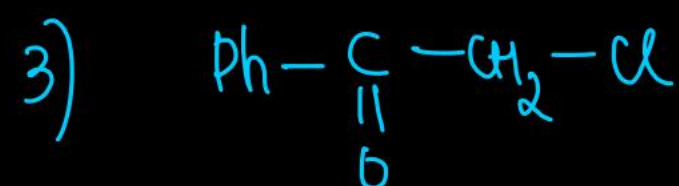
✓ ($W Nu^\ominus$)

✓ ($S Nu^\ominus$)



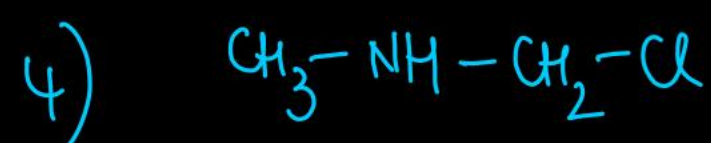
✗

✗



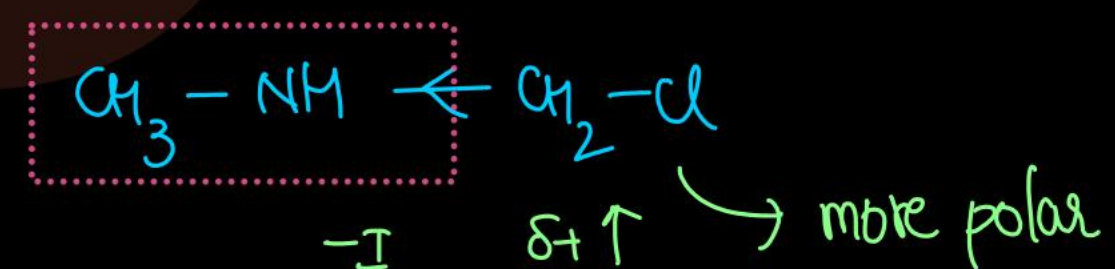
✗

✓ (Not stabilised by resonance)



✓ (BBS)

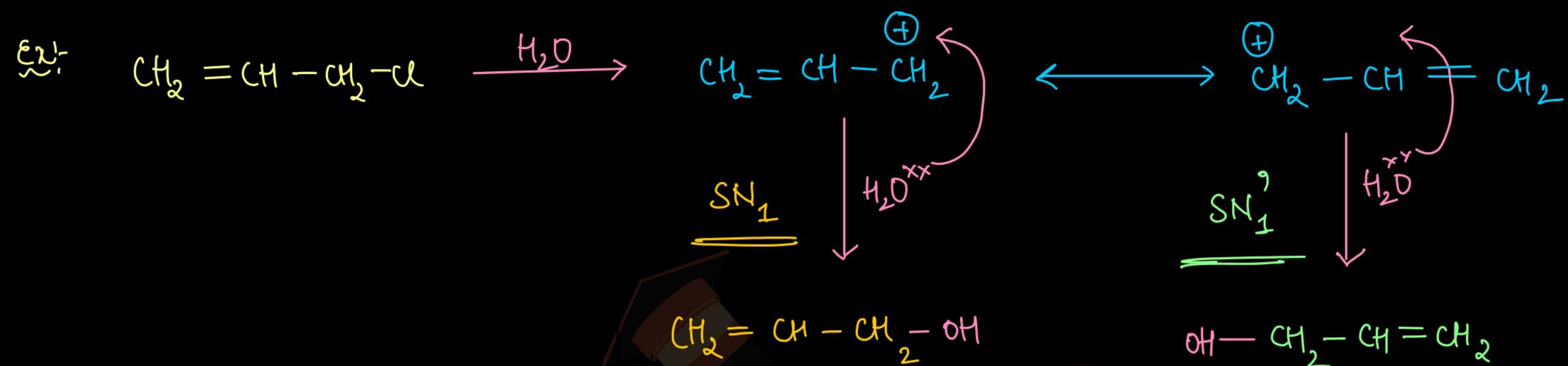
✓



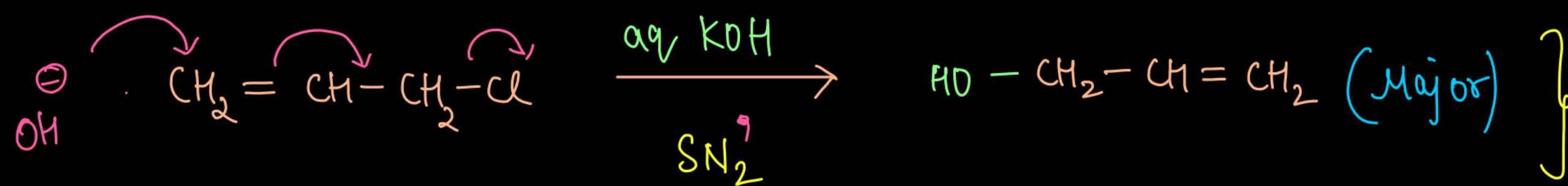
✓ ($W Nu$)

✓ ($S Nu$)

* SN_1 : $\rightarrow$ Carbocation is re-arranged due to resonance/shifting ...

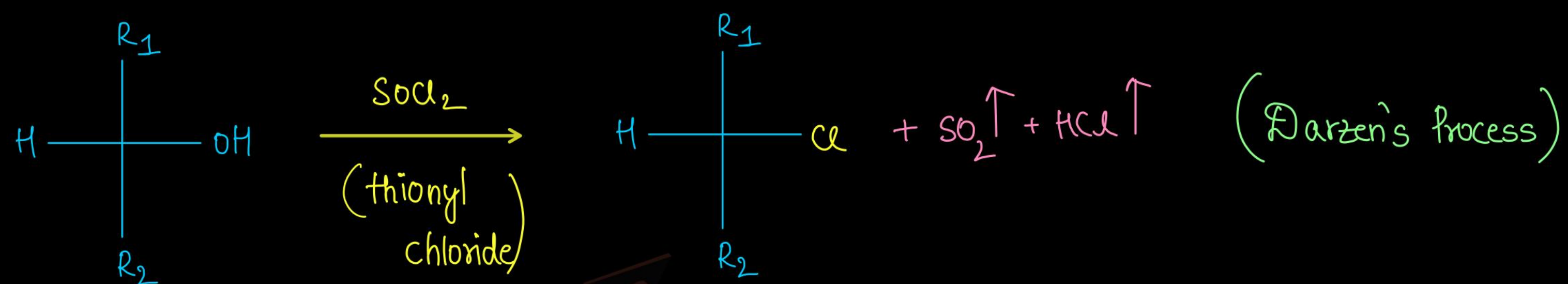


* SN_2^* :

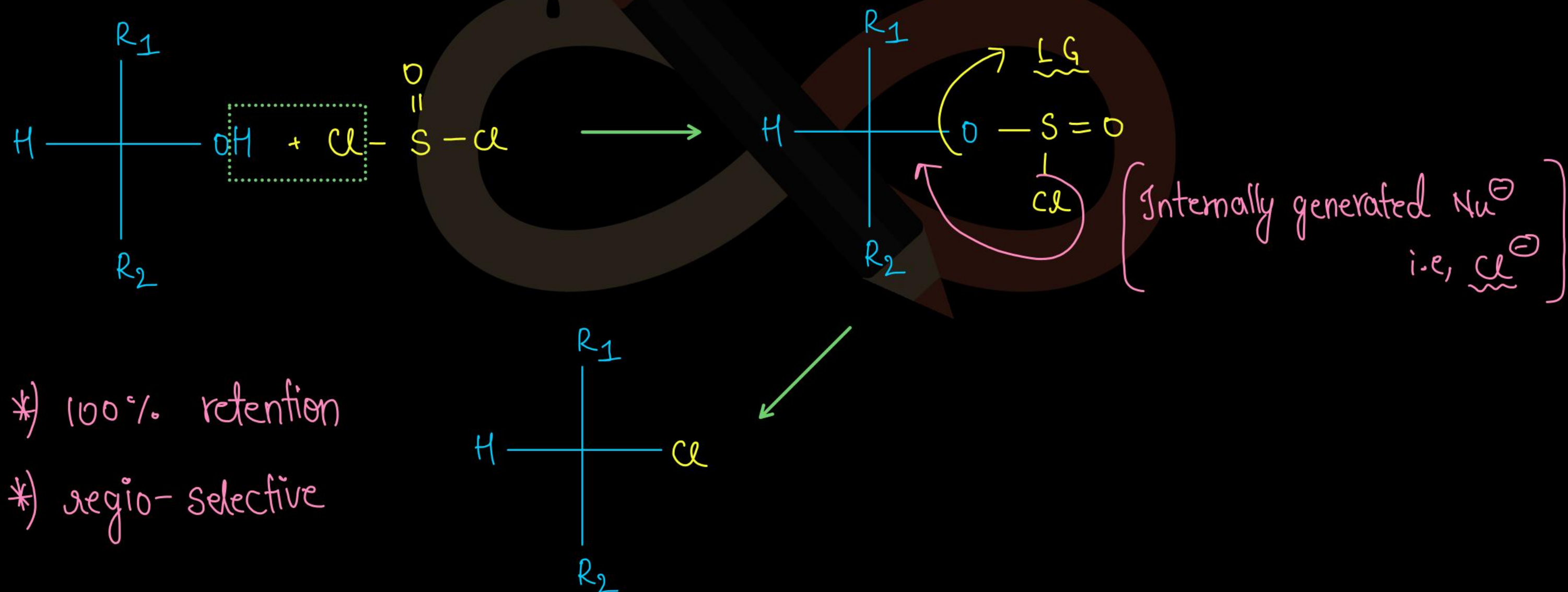


} due to less
Hindrance on
attack.

* SN_i: (Subs Nucleophilic Internal)

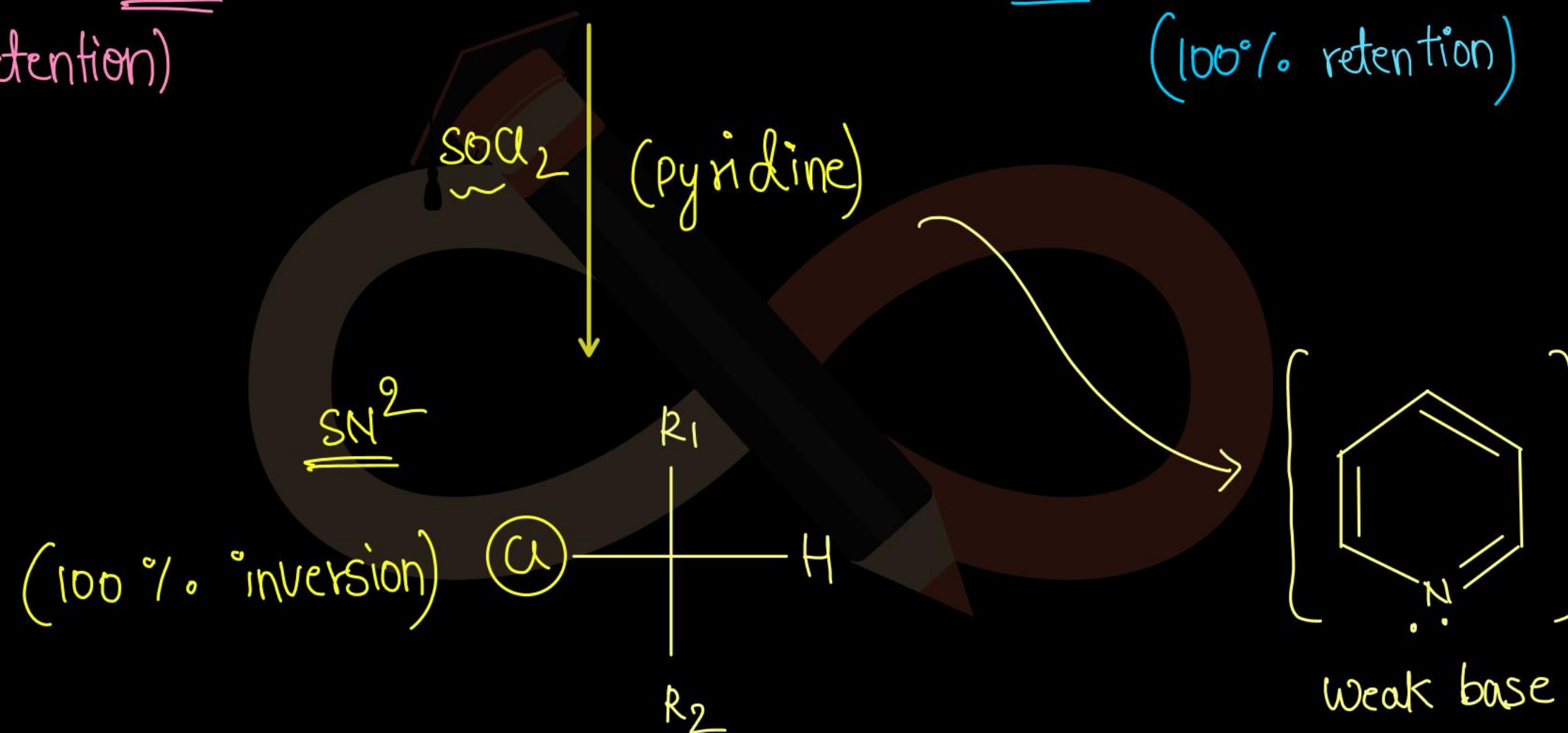
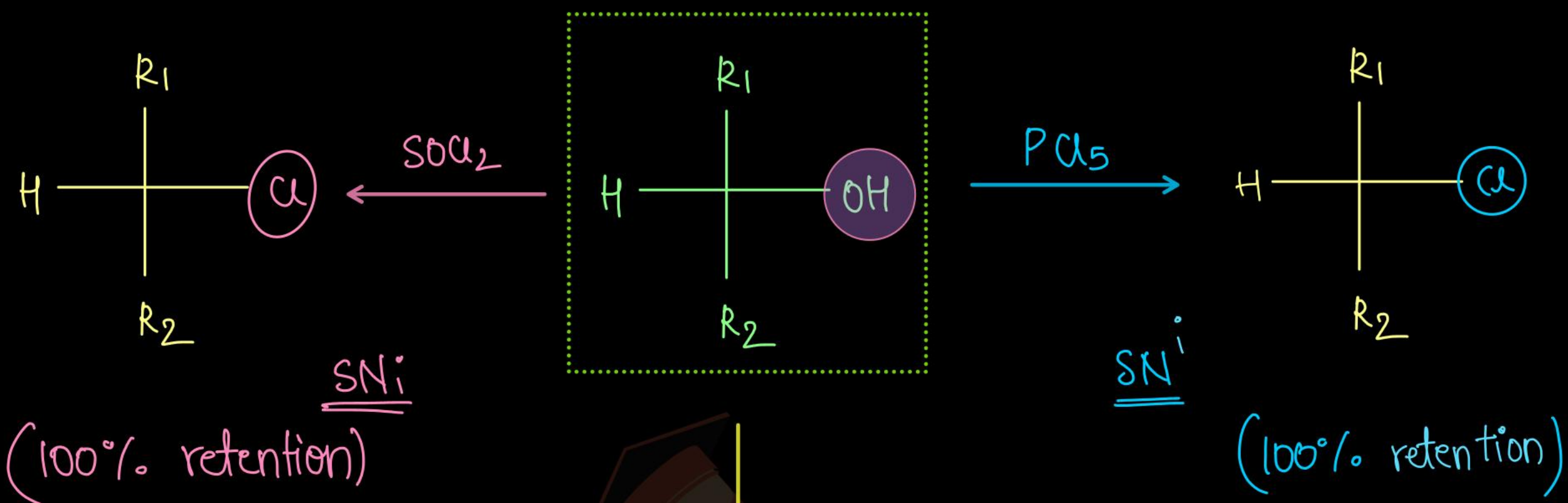


Mech:-



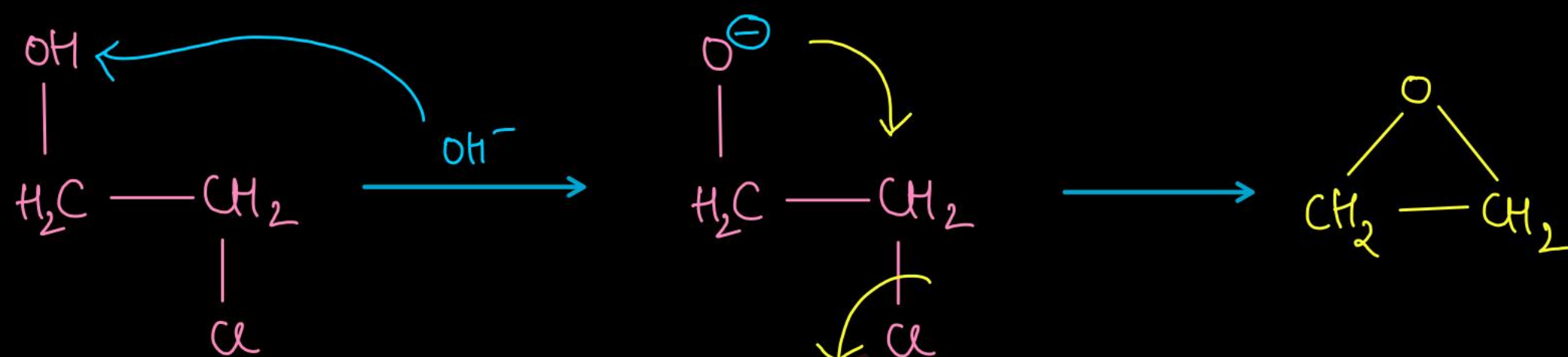
(*)

Ex:-

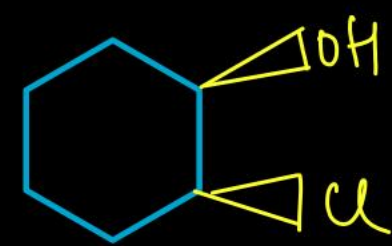


Intramolecular S_N2 rxn :-

Ex:-

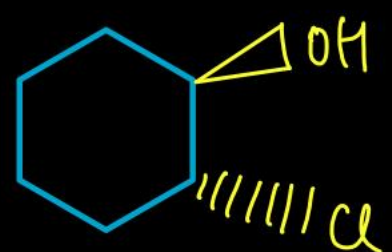


Ex:-

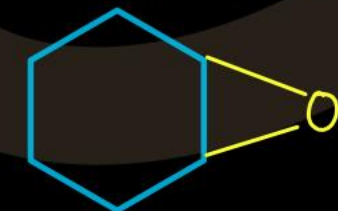


NaOH

No epoxide formation



NaOH



*) Both leaving grp & incoming grp must be opposite

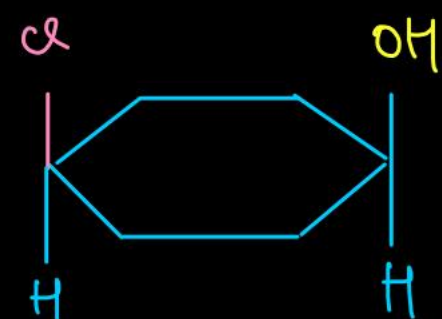
Ex:-



NaOH



Ex:-



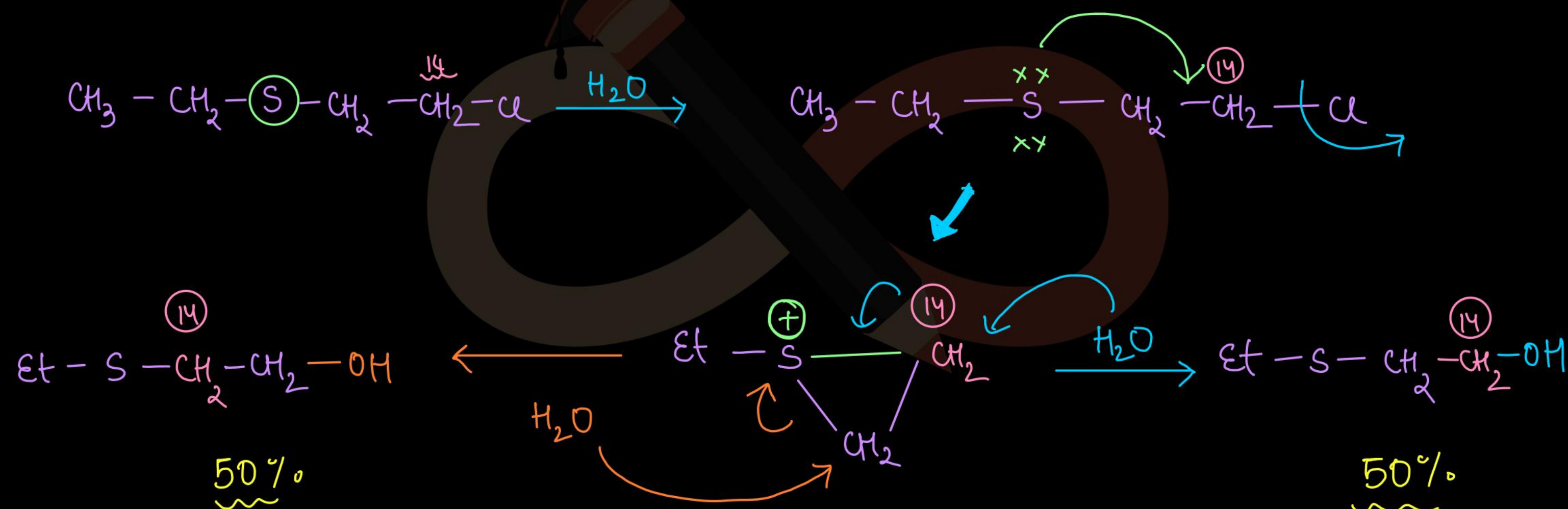
NaOH

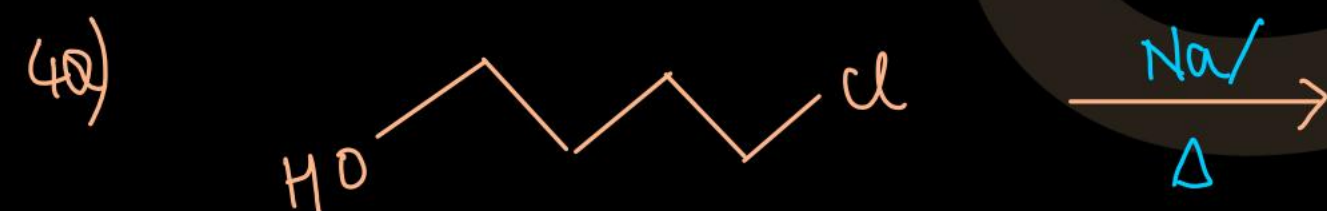
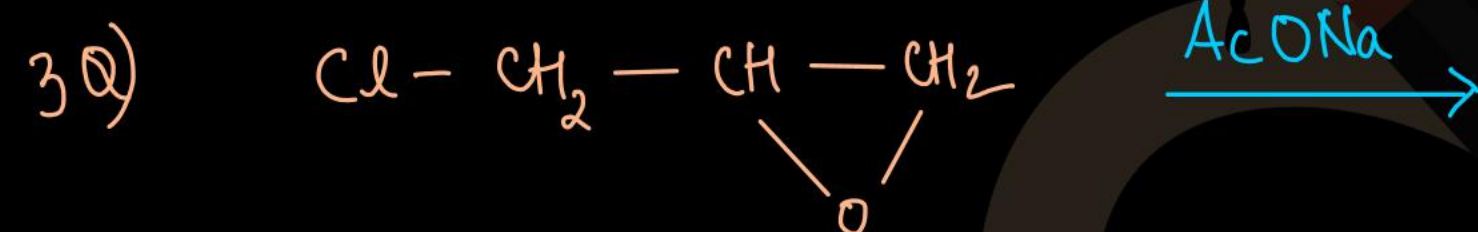
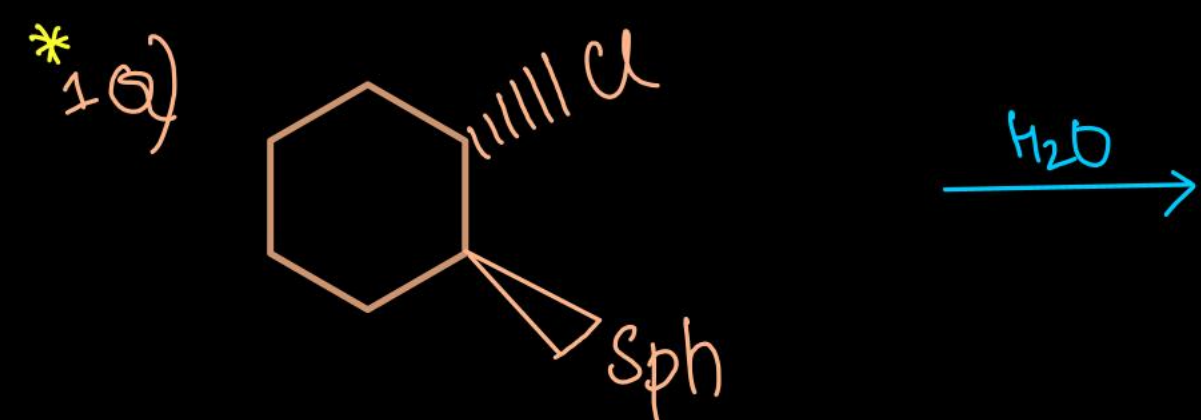


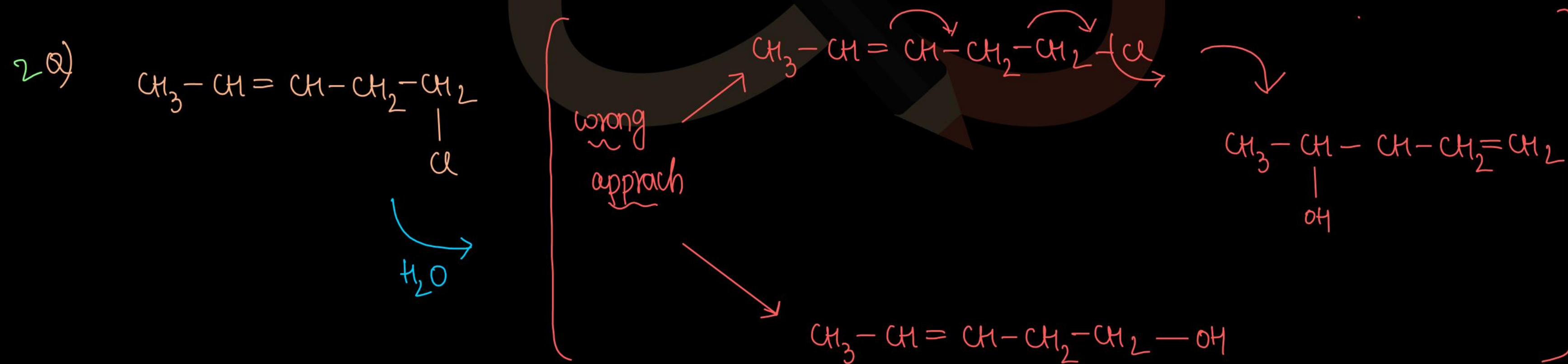
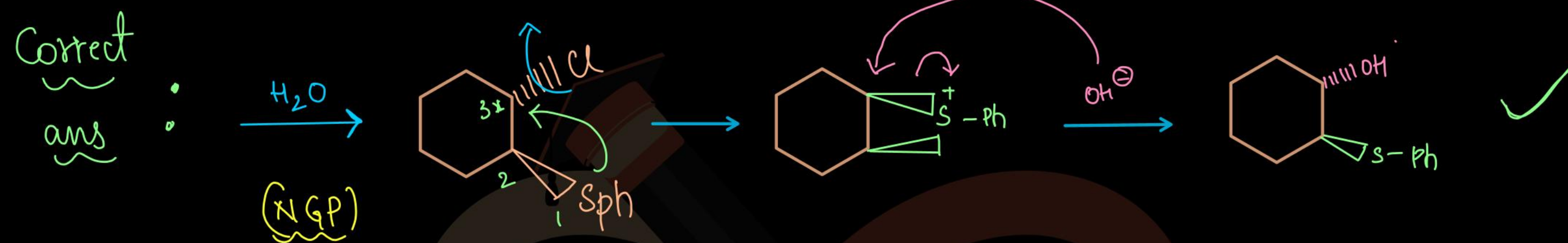
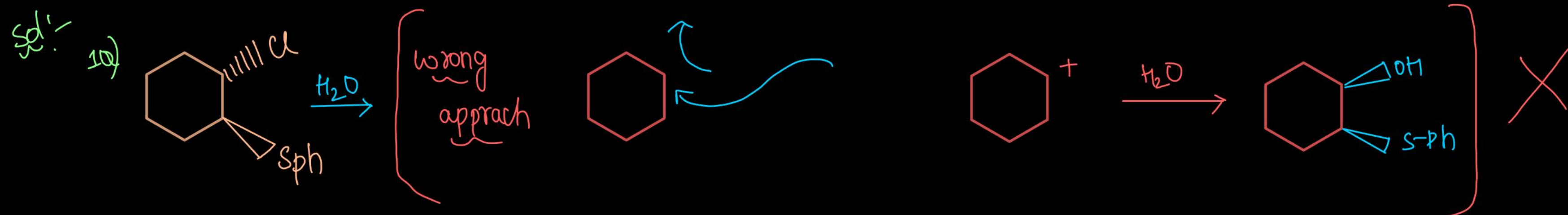
* NGP (Neighbouring Group Participation)

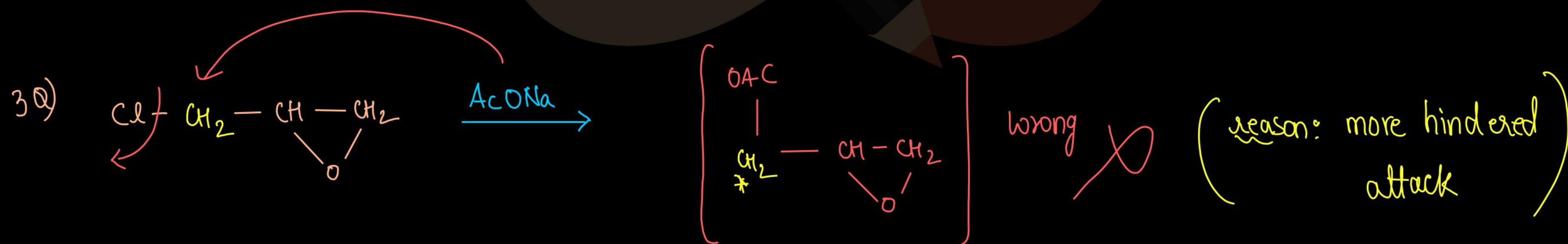
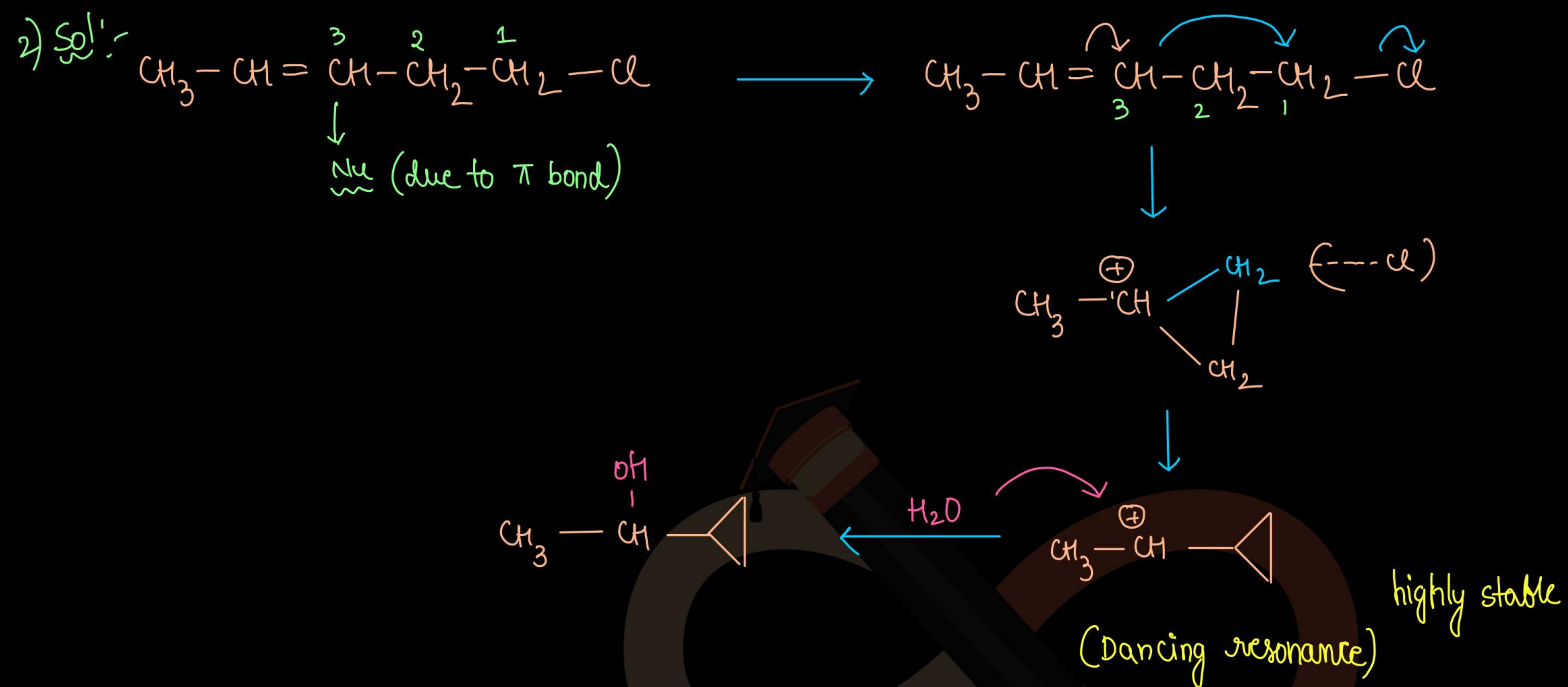
- i) When $\text{Nu}^\ominus$ is present at 3rd, 5th, 6th position from leaving Group
- ii) special case of Intramolecular $\text{S}_\text{N}2$ rxn
- iii) Intramolecular > Inter molecular (rate)

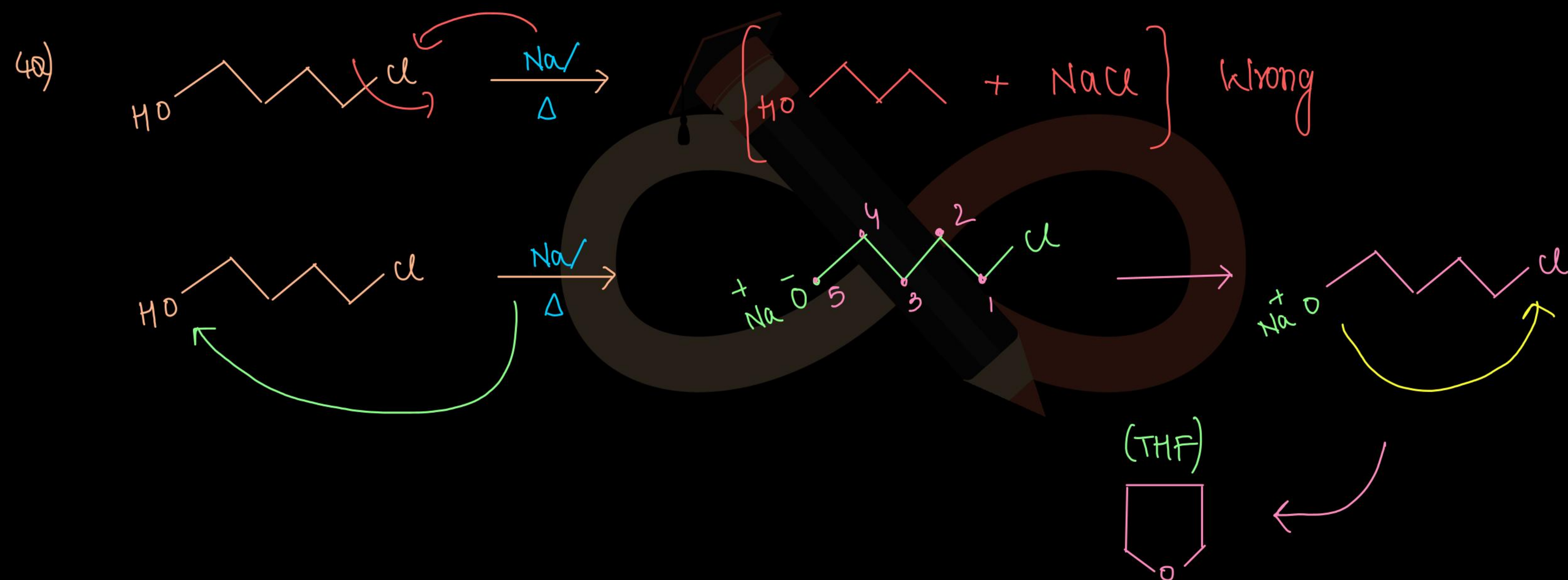
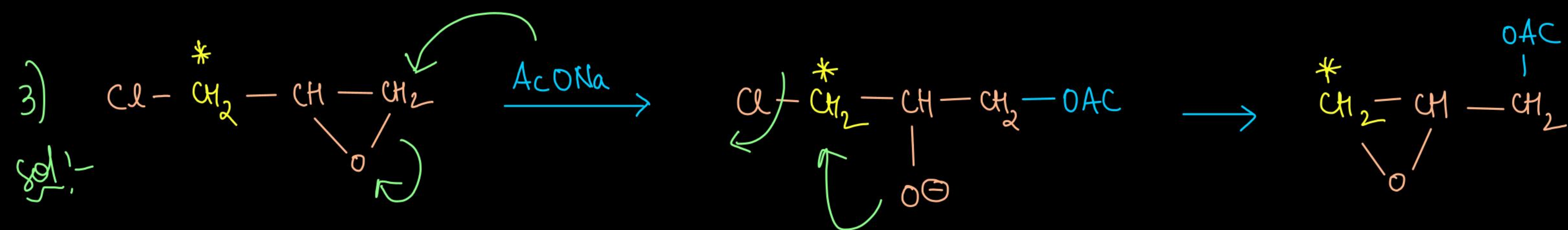
Ex¹



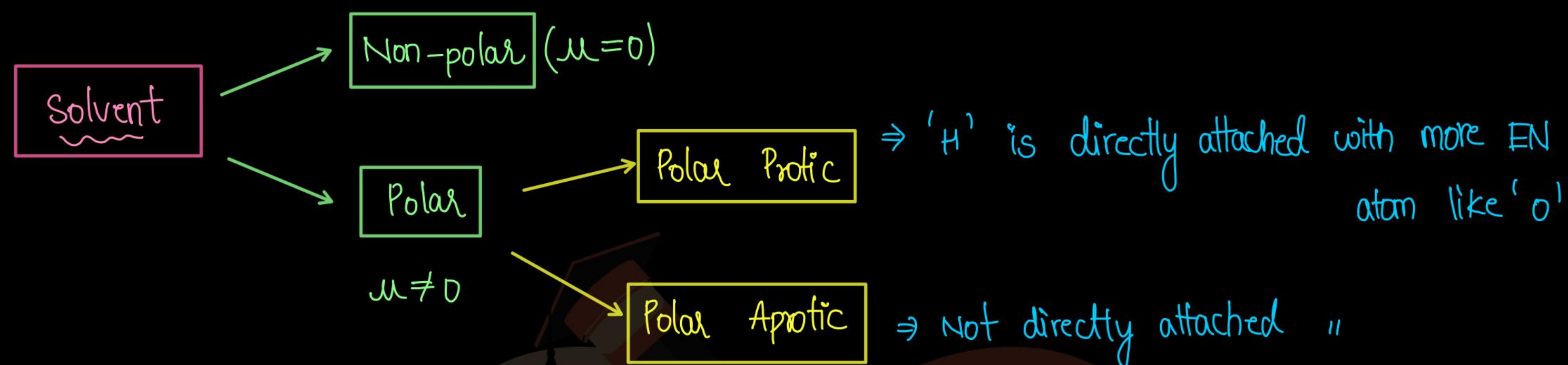








Effect of Solvent in NSR (SN^1 & SN^2)



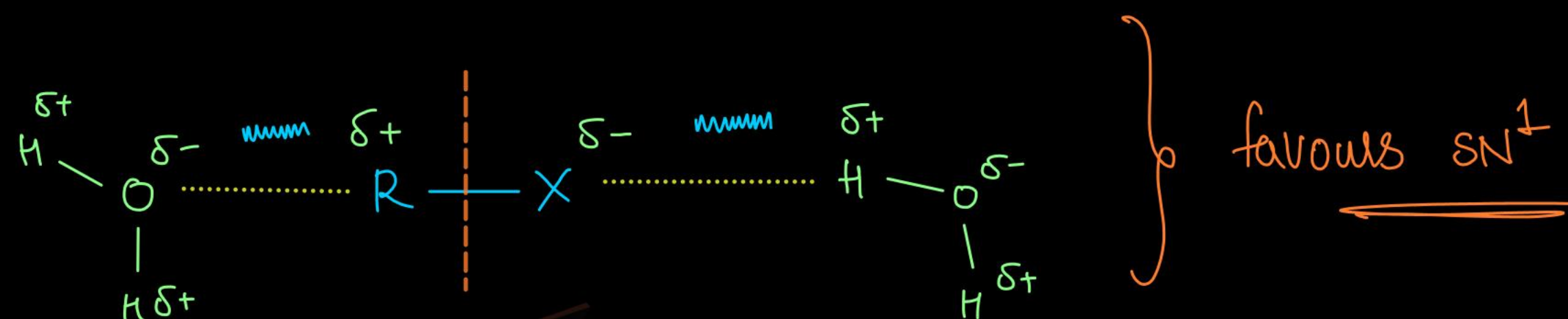
Ex:-

Polar protic : H_2O , ROH , $RCOOH$ --- etc } favours SN^1

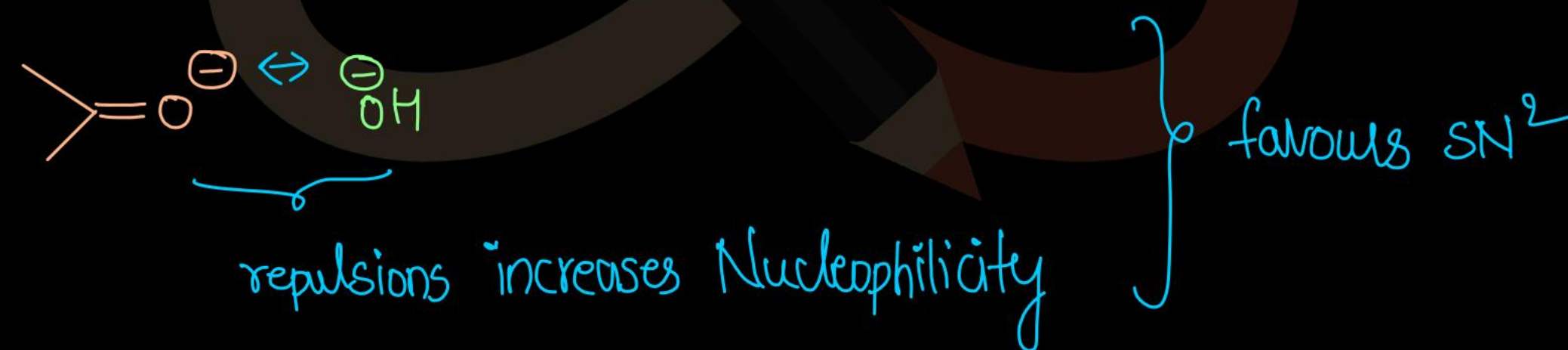
Polar aprotic : $DMSO$ (dimethyl Sulphoxide)
 DMF (dimethyl formamide)
acetone, ether } favours SN^2

Note:-

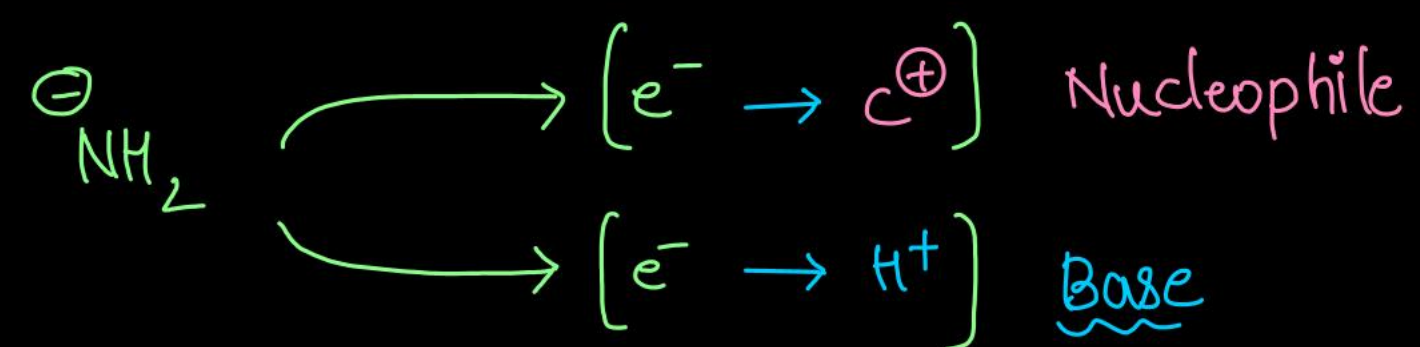
In polar protic solvents :



In Polar aprotic solvents



Nucleophilicity :-



* strength of $\text{Nu}^- \propto \frac{1}{\text{EN of donor}}$

$\Rightarrow$ In Polar protic Solvents

① -vely charged atom is more nucleophilic than its corres. neutral atom



② If $\text{Nu}^\ominus$ atom is same / belongs to same group then ; $\text{Nu}^\ominus$ || Basicity

Ex:-



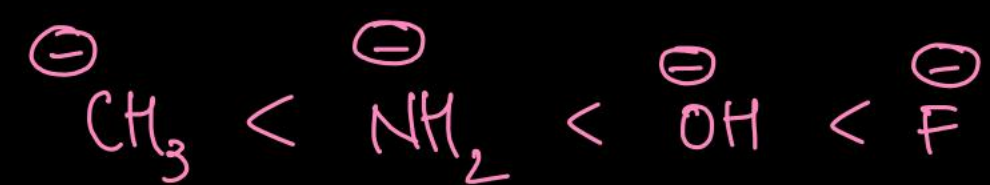
③ Top to bottom $\text{Nu}^\ominus$ city $\uparrow$

Ex:-

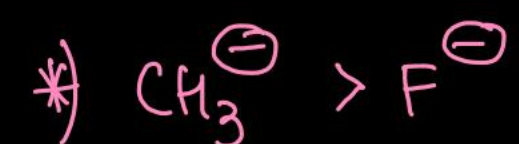


Case-II > In Polar aprotic Solvents

① In period (left to right)

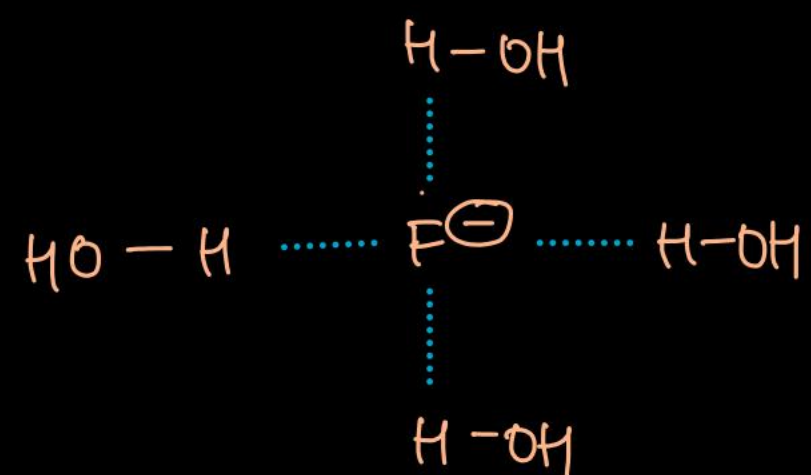


Polar protic



Solvation

⇒ size ↓ charge density ↑
Solvation ↑ $\text{Nu}^{\ominus}$ ↓

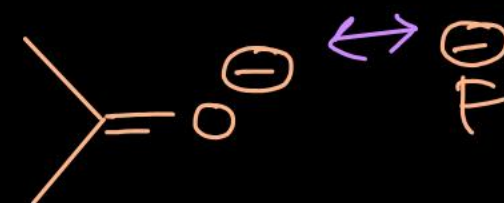


Polar aprotic

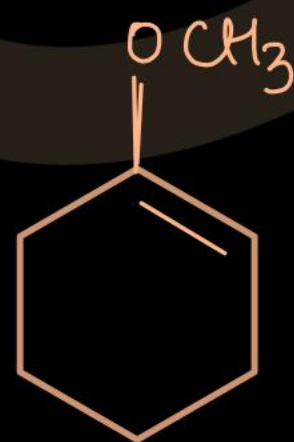
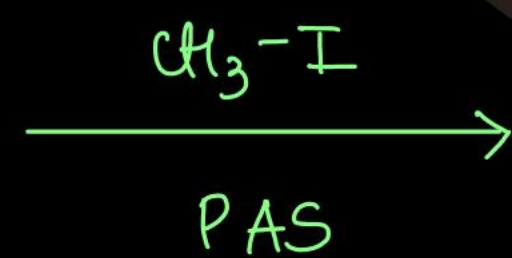
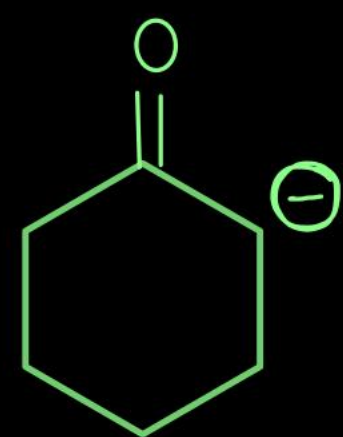
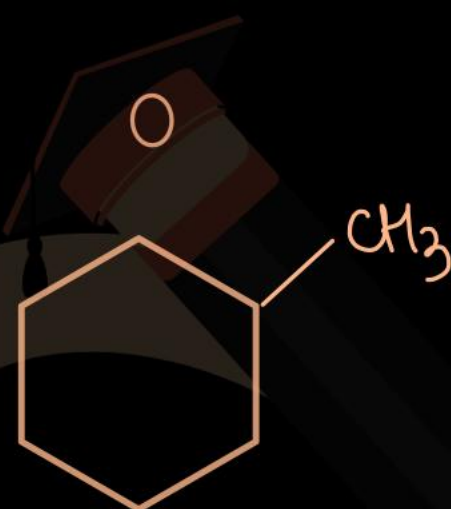
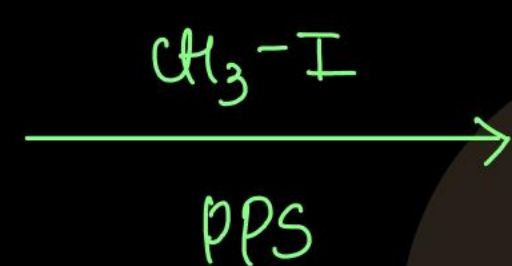
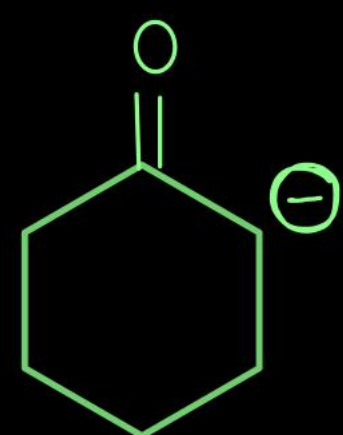


Repulsion

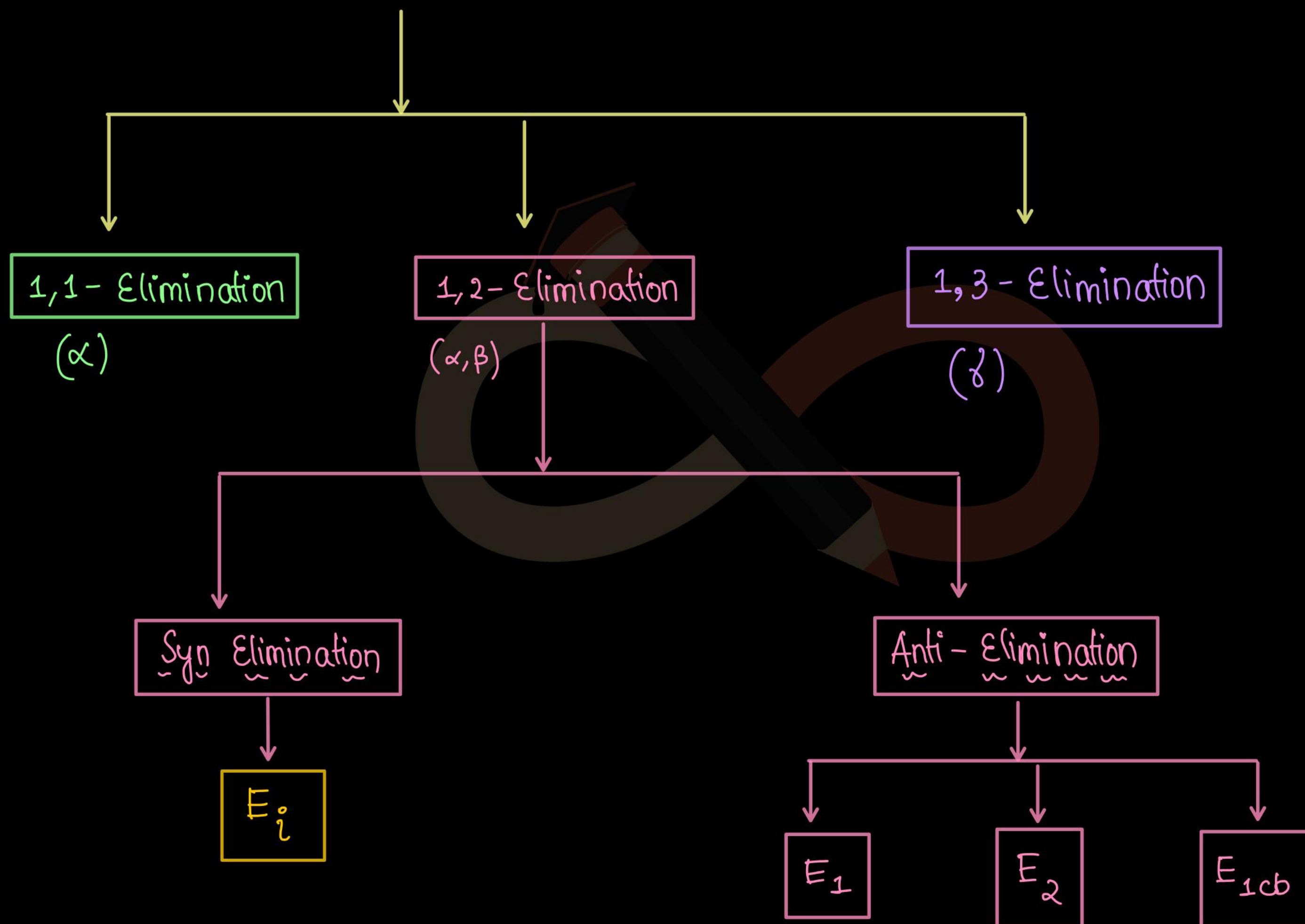
⇒ size ↓ charge density ↑
repulsion ↑ $\text{Nu}^{\ominus}$ ↑



② In group (top to bottom)



Elimination rxn's :-



E₂ Elimination :- (α - Elimination / α, β Elimination)

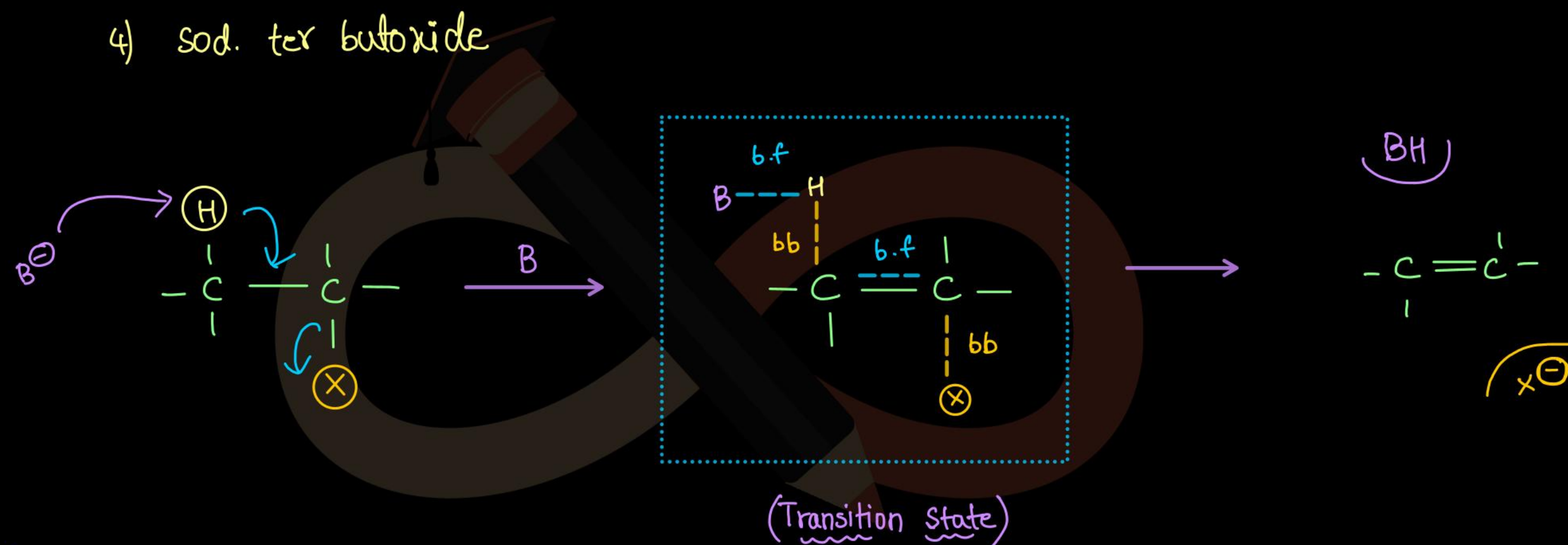
Reagents :- 1) Alc. KOH (ROH + KOH)

2) NaNH₂

3) tBuO[⊖]K[⊕]

4) sod. ter butoxide

Mech :-



Imp points :-

1) No Intermediate, only TS

2) one step rxn

3) rate = k[R-X][Nu[⊖]]

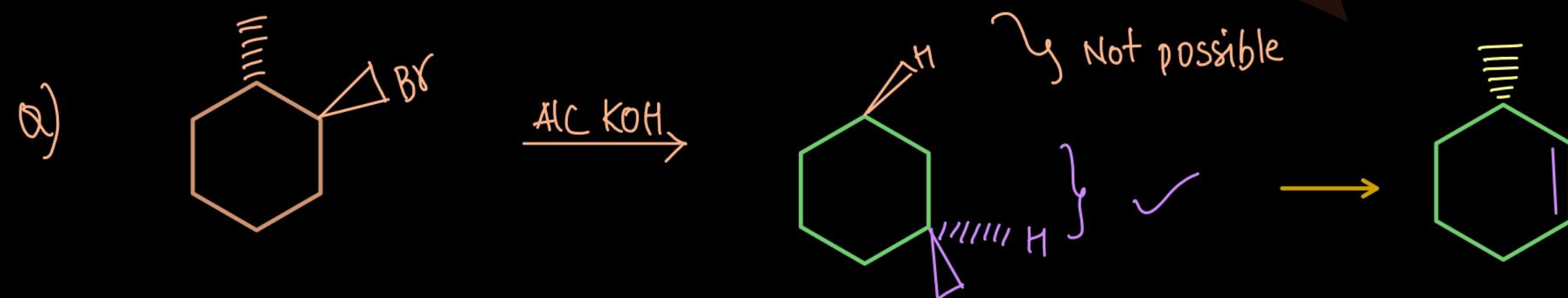
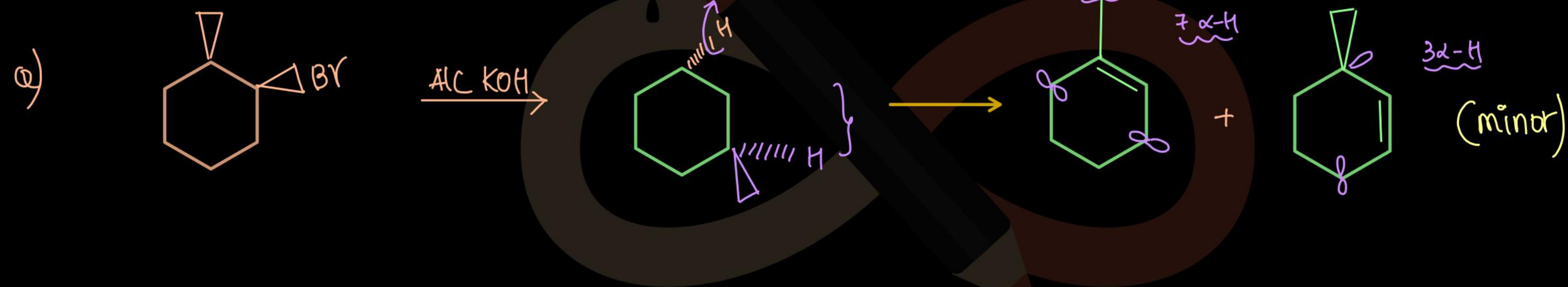
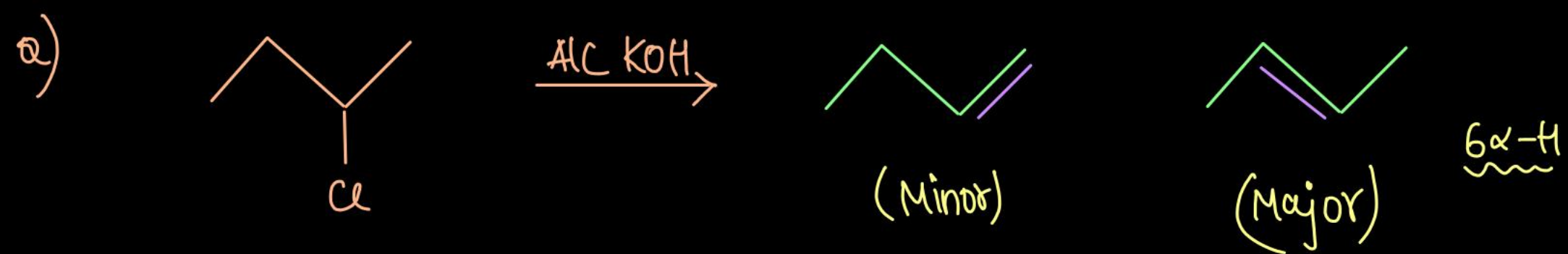
4) More stable alkene is major product

5) Anti Elimination

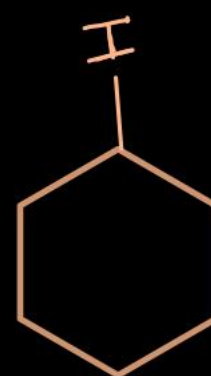
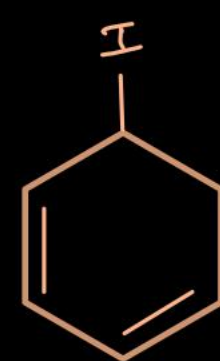
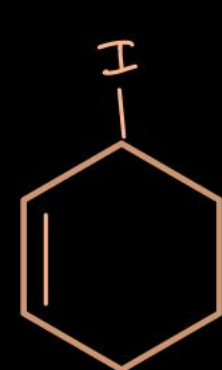
*) Stereo specific

*) regioselective

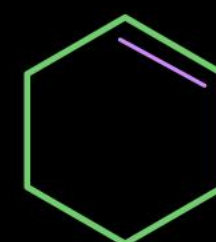
*) Primary kinetic isotopic effect $k_H > k_D$



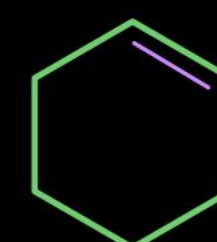
1a) Compare R.O.R towards E_2 :



$2 > 1 > 3$



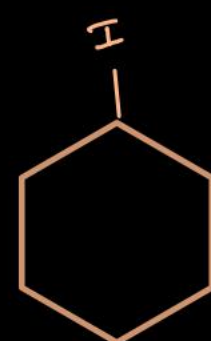
Conjugated



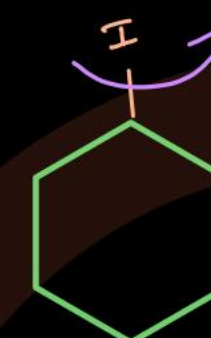
(Ar)



2a)



$1 > 2 > 3$



$I > Br > Cl$ (leaving ability)

3a)



A/c KOH

r_1

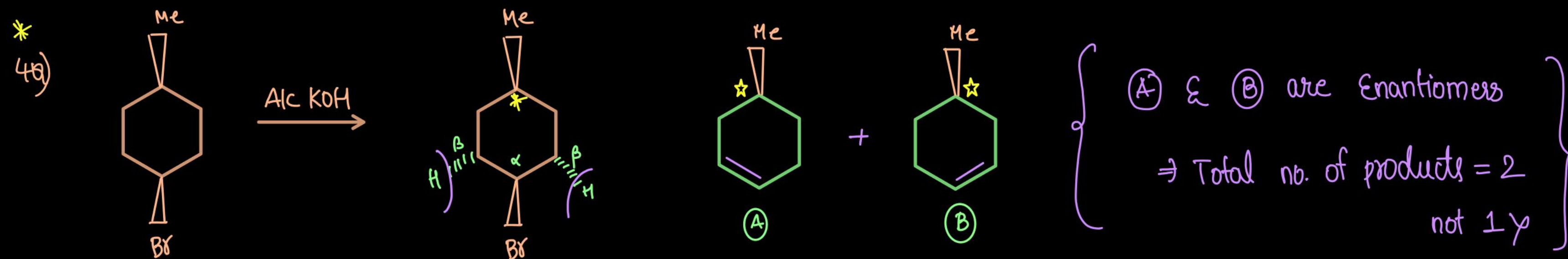
$NaNH_2$

r_2

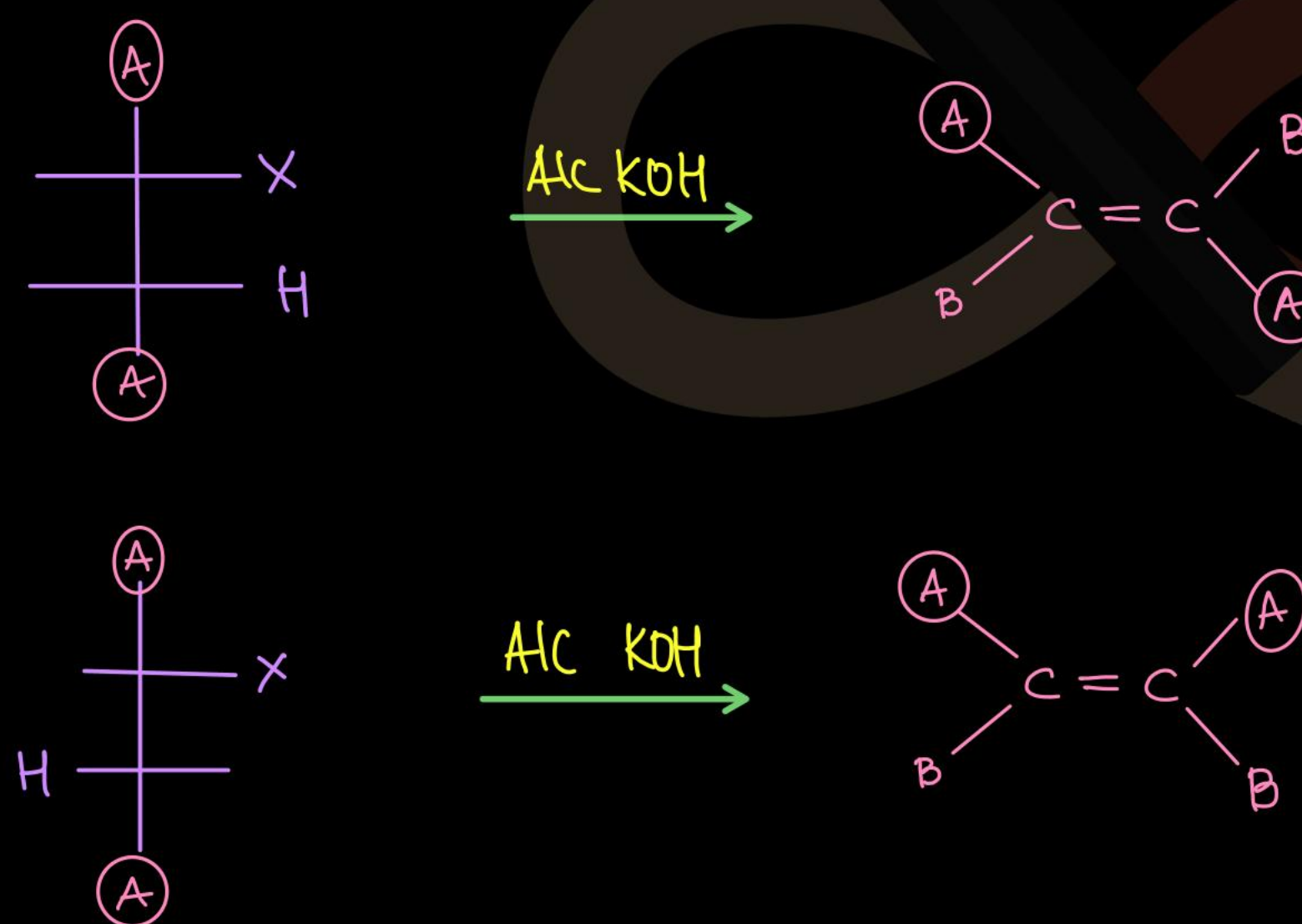
$* r_2 > r_1$

$NaNH_2 > KOH$ (basicity)

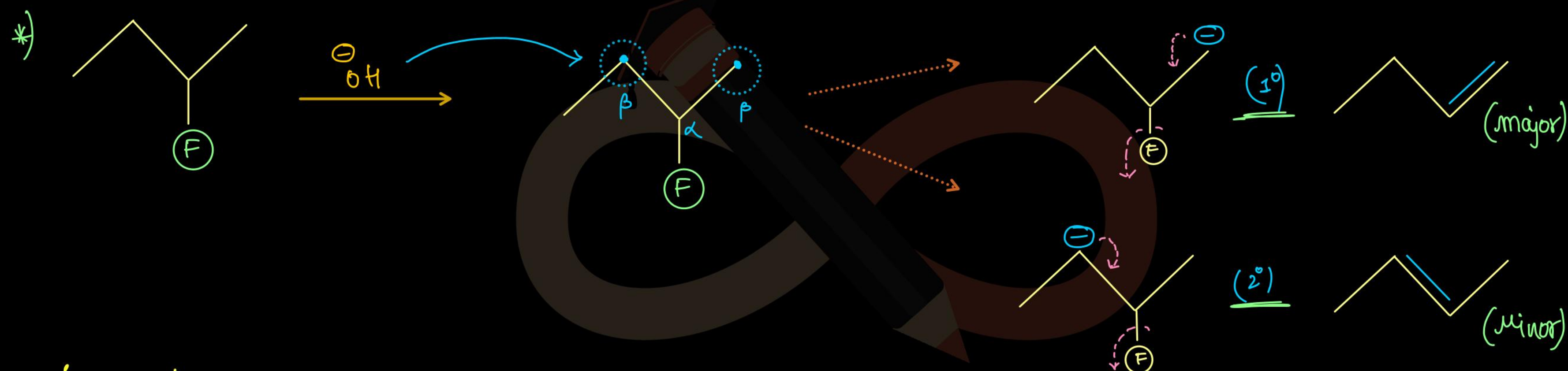
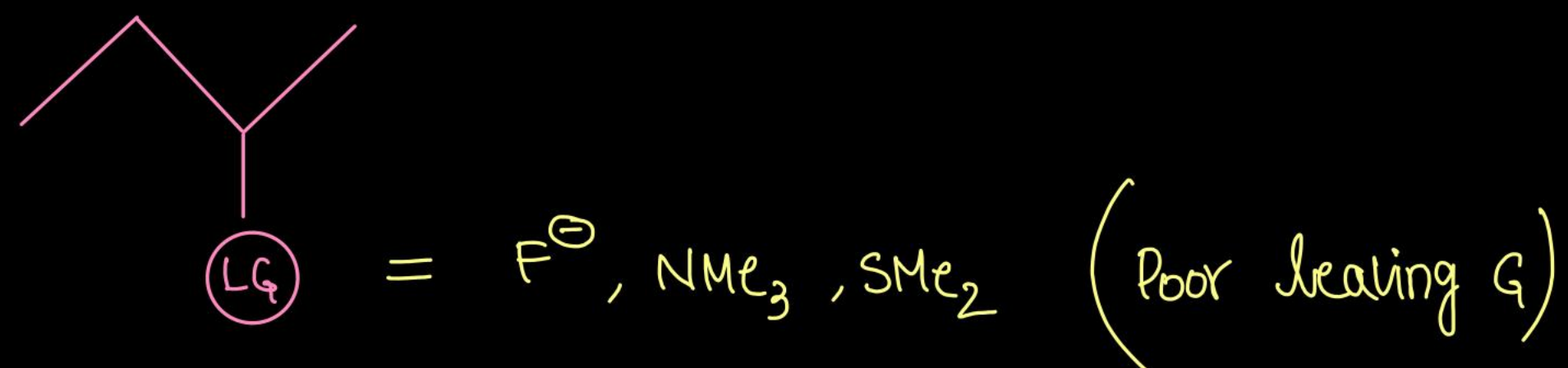
Compare r_1 & r_2



Trick

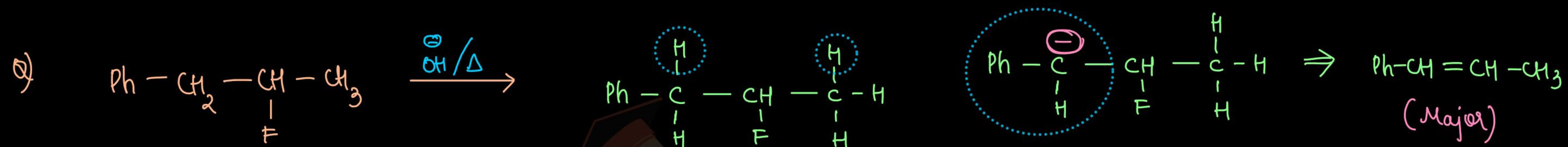
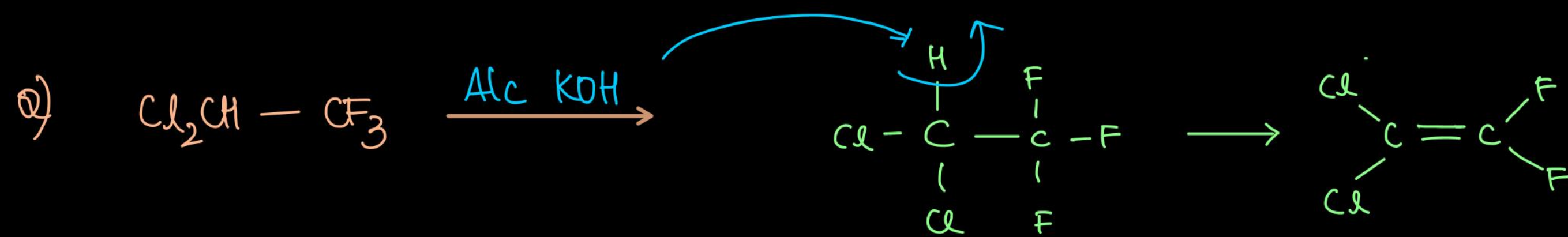


E_{1cb} → (Conjugate base) :-



Imp points :-

- 1) Carbanion - Intermediate
- 2) More stable $\text{C}^\ominus$ will decide major product
- 3) Anti Elimination



Substitution v/s Elimination

SN₁

→ Solvolysis (H₂O, EtOH...)

→ 2°/3°

*) moist Ag₂O

*) AgNO₃

*) CH2=CH-CH2-X → Allylic cation

SN₂

→ 1°/2°

→ strong Nu[⊖]

→ Polar aprotic
(DMF, DMSO)

E₁

→ Dehydration of alc (H⁺, Δ)

→ Pinacol

→ heating, Δ

E₂

→ strong base

→ Alc KOH

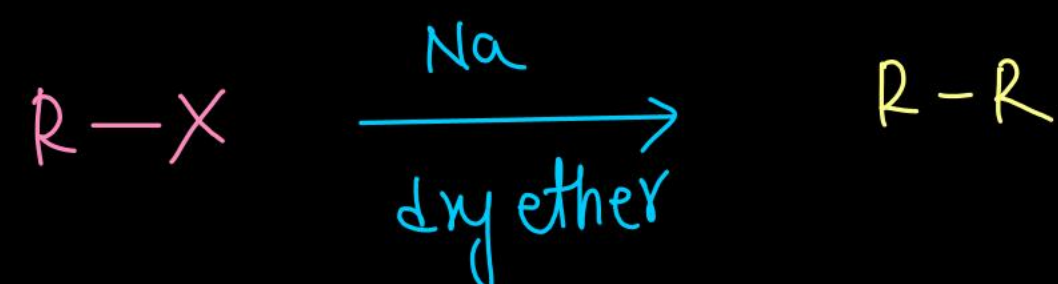
→ NaNH₂

*) As bulkyness of substrate ↑, Elimination ↑

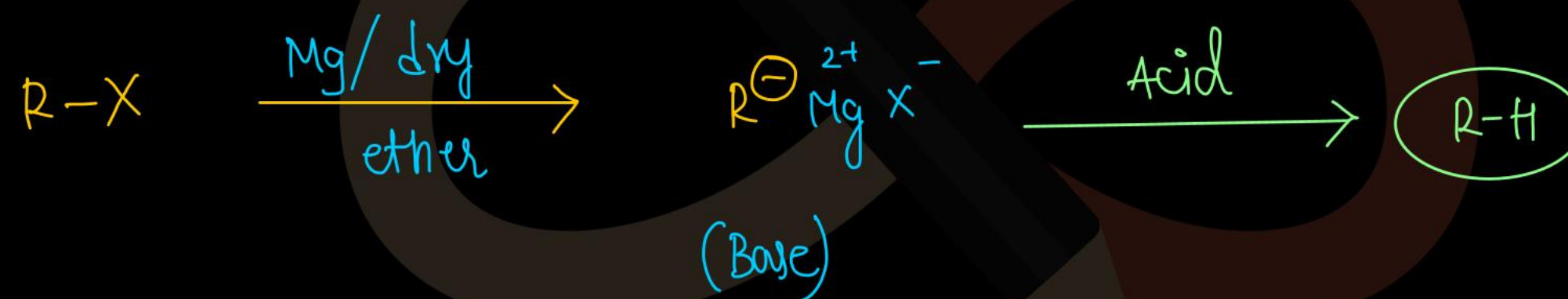
*) As the basic strength of rea ↑, " ↑

Rxn with metals :-

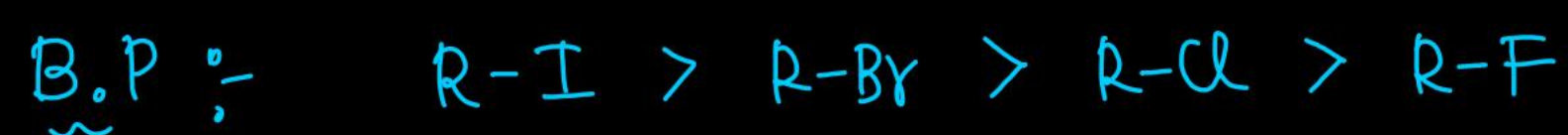
1) Wurtz rxn



2) Grignard Reaction :-



Physical Properties :



Density :-



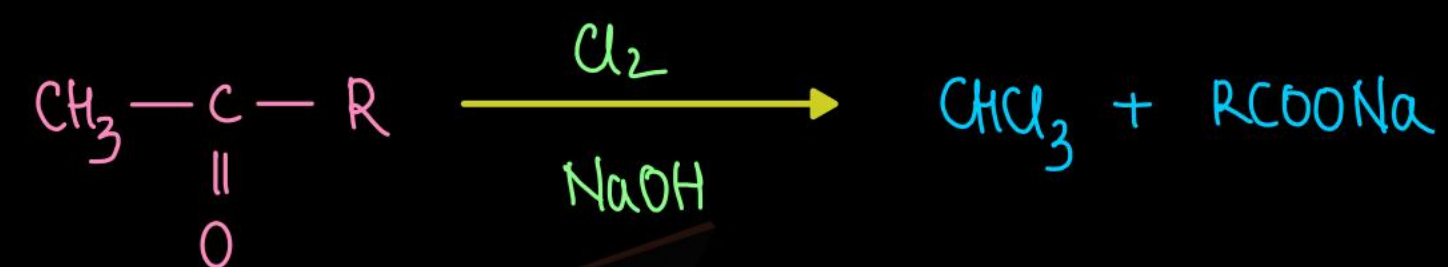
$\propto$ atomic of X

$\propto$ No. of carbons, halogens

Solubility :- Halo-alkanes are very slightly soluble in water.

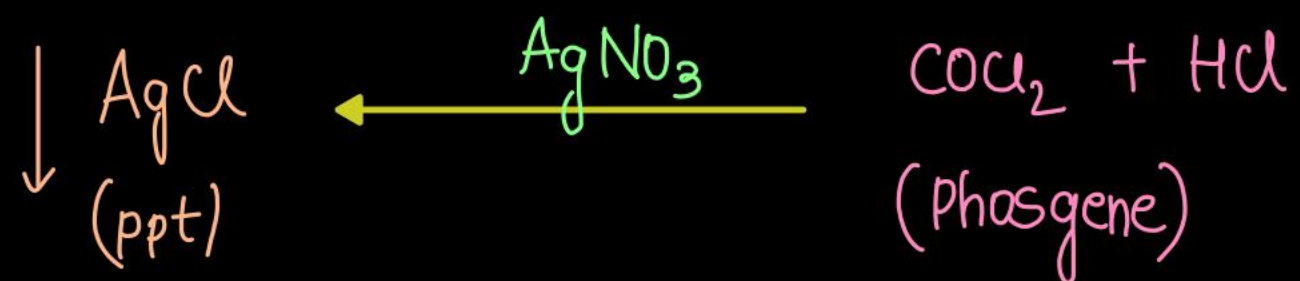
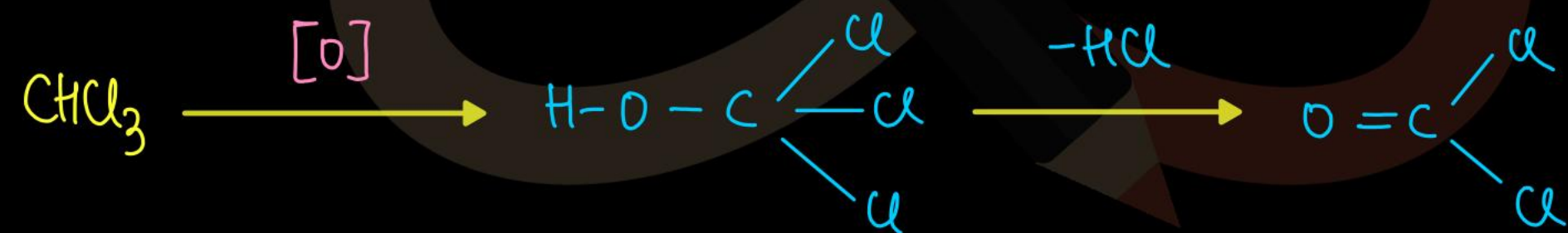
Chloroform (CHCl_3) :-

Prep: Haloform rxn :

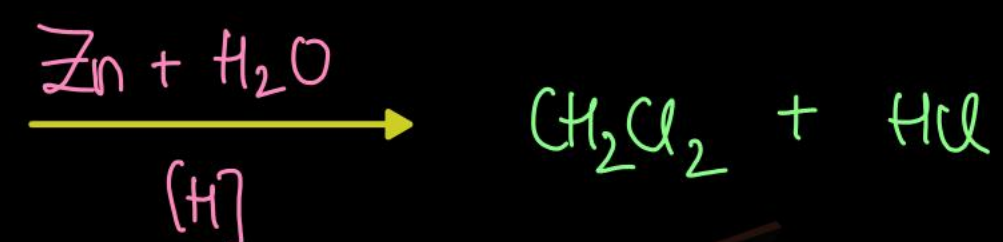
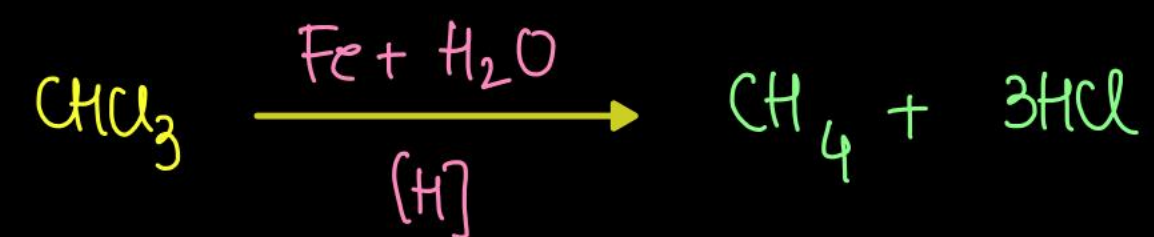


Properties :

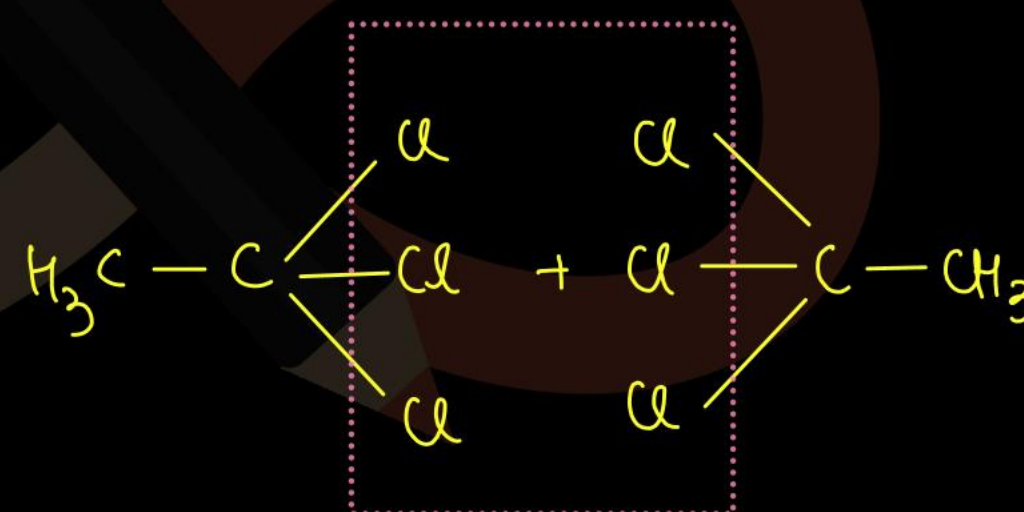
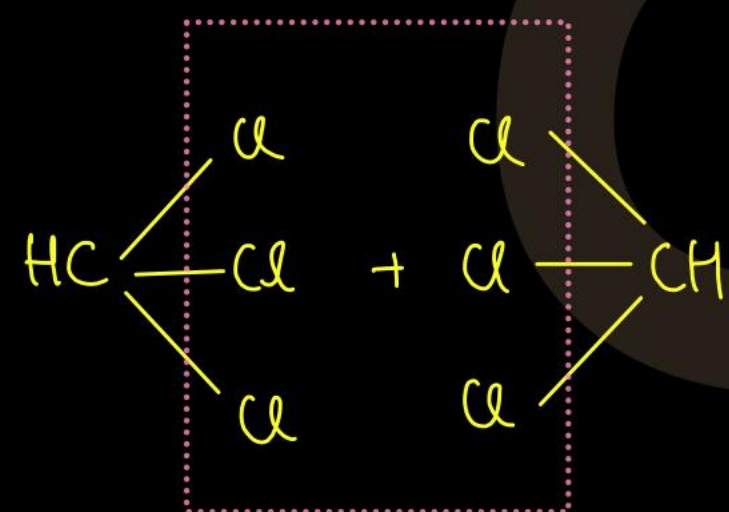
i) Oxidation



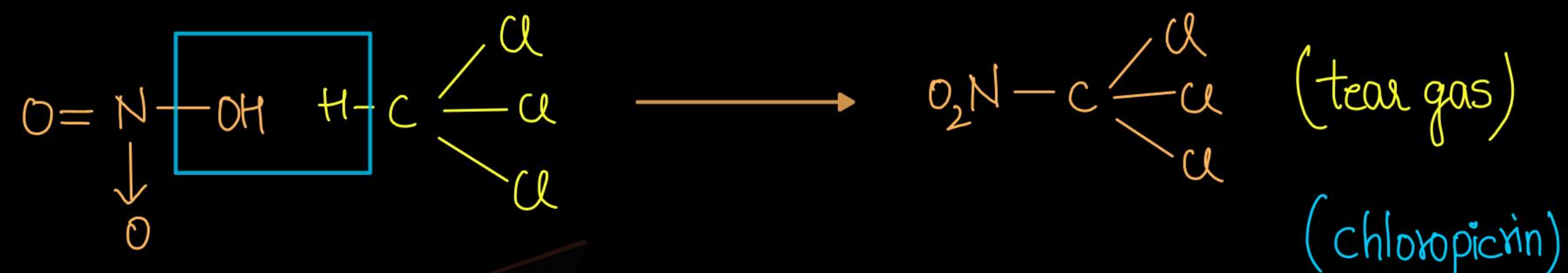
ii) Reduction



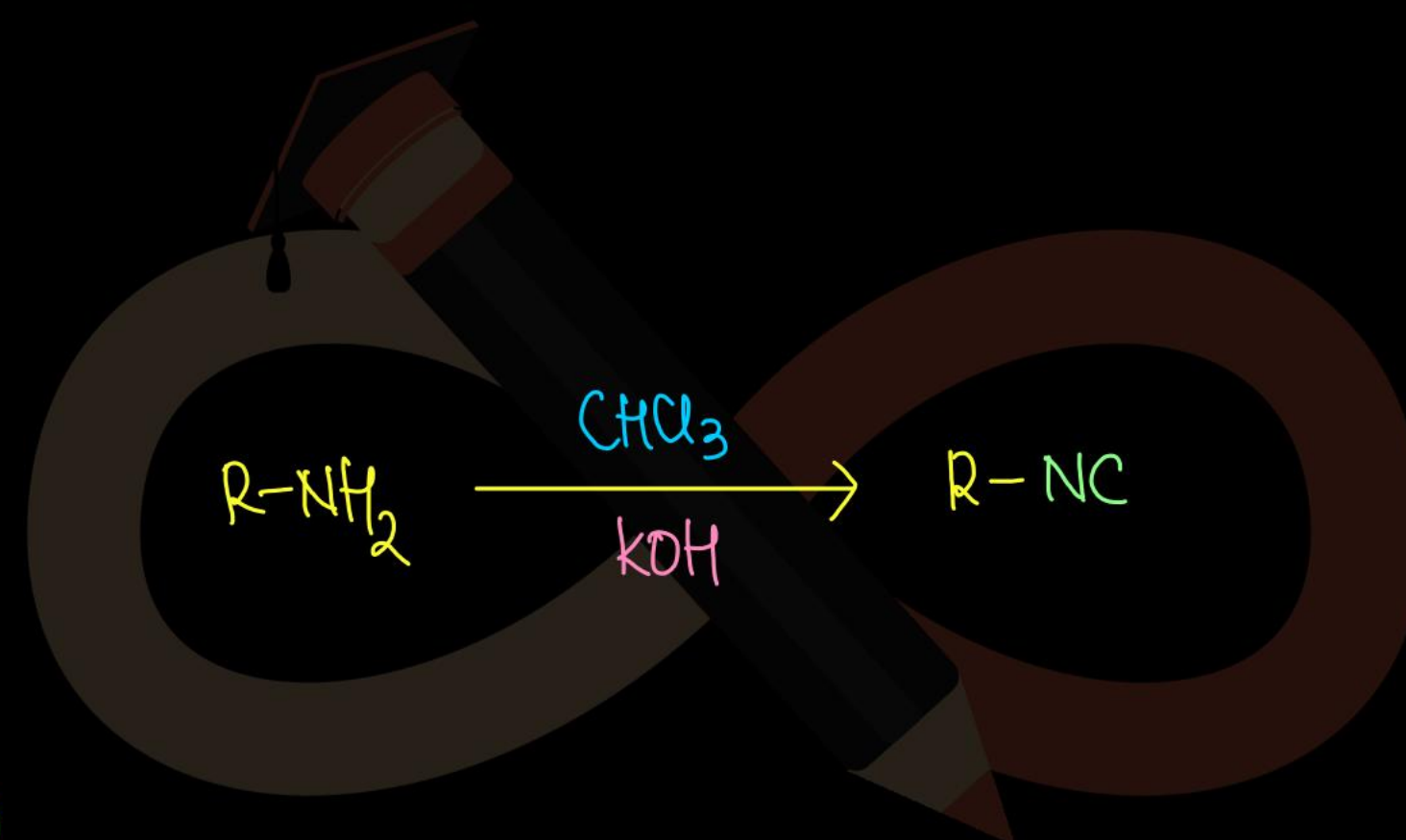
iii) Rxn with Ag



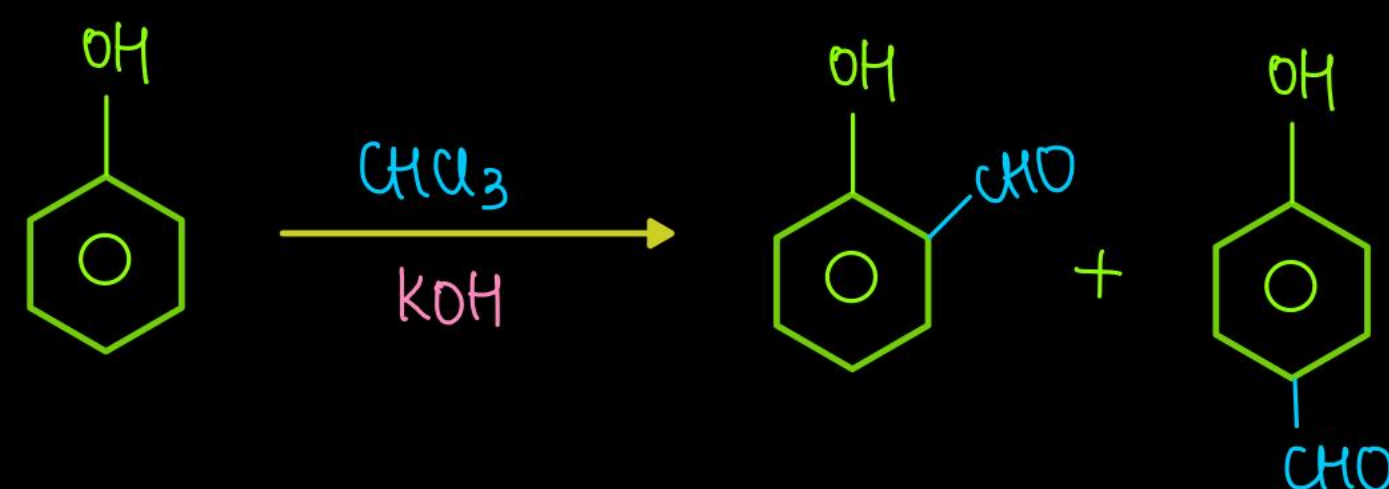
iv) Rxn with HNO_3 :



v) Rxn with 1° -amine
(carbylamine test)



vi) Reimer-Tiemann's rxn

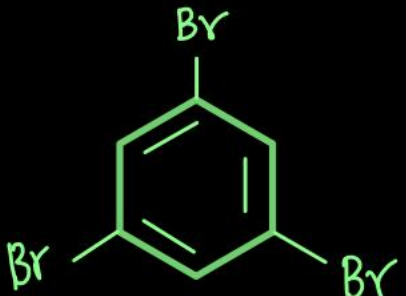


NCERT :-

*) Chloromphenicol $\rightarrow$ antibiotic for typhoid fever.

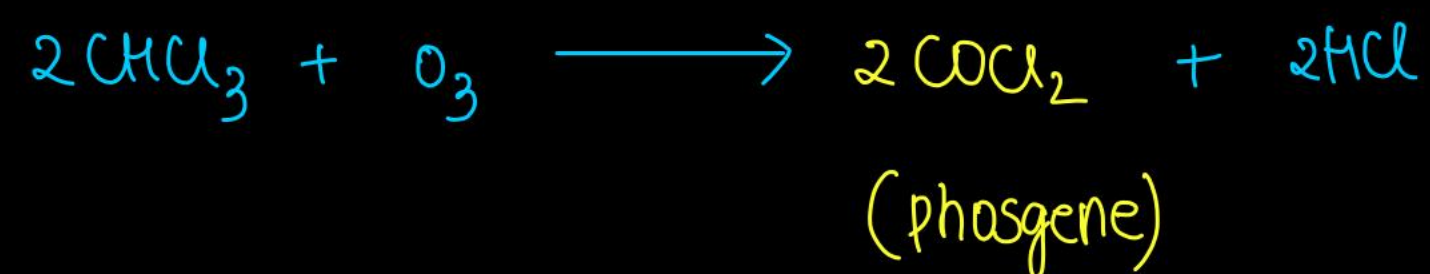
*) chloroquine $\rightarrow$ treatment of malaria

*) Halothane $\rightarrow$ anaesthetic during surgery

*)  $\rightarrow$ Sym - Tribromobenzene

*) CH_2Cl_2 (dichloromethane) $\rightarrow$ can be used as solvent as paint remover
(methylene chloride) $\rightarrow$ as a propellant in aerosols.
 $\rightarrow$ metal cleaning & finishing solvent

*) CHCl_3 (chloroform) $\rightarrow$ used in the production of freon refrigerant R-22
(tri-chloro methane)



*) chloral (CCl_3CHO)

*) Gammaxene ($\text{C}_6\text{H}_6\text{Cl}_6$)

*) chloropicrin ($\text{CCl}_3\text{-NO}_2$)

*) Freon - 12 (CF_2Cl_2)

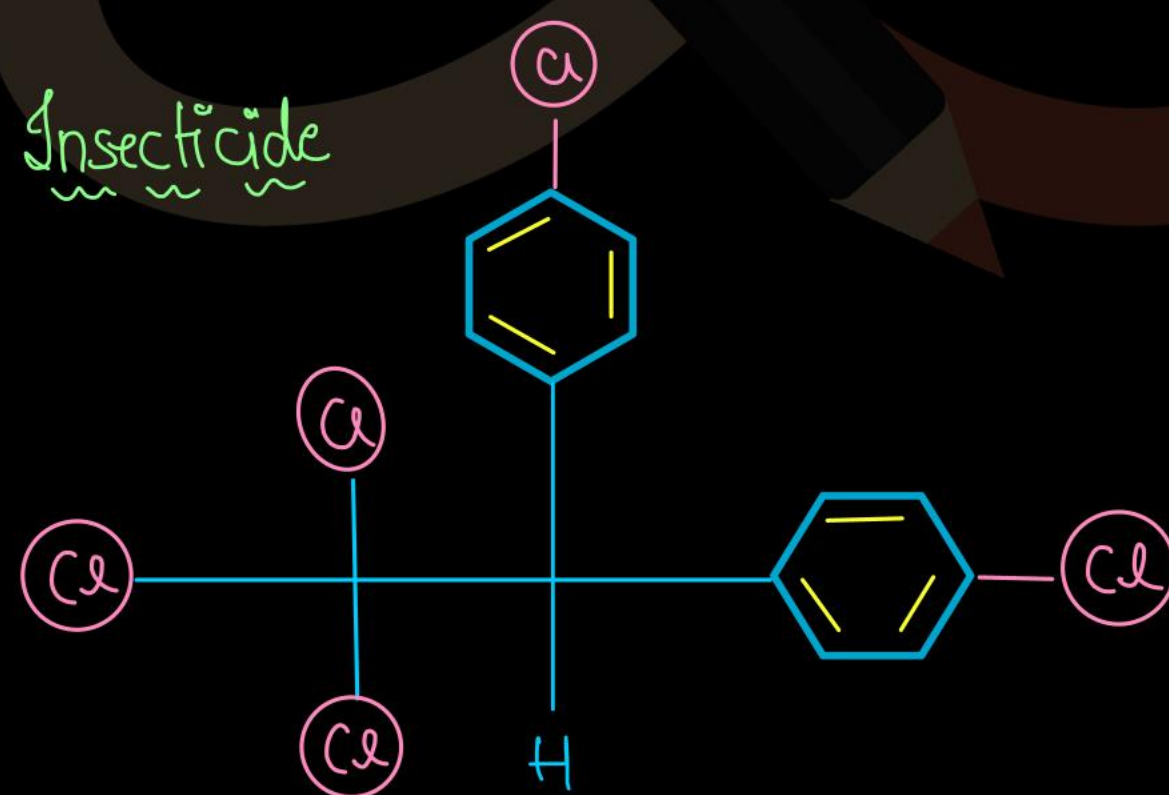
* CHI_3 (Iodoform) $\rightarrow$ used as an antiseptic due to liberation of free Iodine and not due to iodoform itself.

* CCl_4 (carbon tetra chloride) $\rightarrow$ degreasing agent (spot remover)
 $\rightarrow$ used as fire extinguisher
 $\rightarrow$ depletes ozone layer

* Freons $\rightarrow$ chlorofluoro Carbons (of methane & ethane)
 $\rightarrow$ ex: CCl_2F_2 (Freon-12)

* DDT $\rightarrow$ Insecticide

(dichloro diphenyl trichloro ethane)



(Structure of DDT)