

Carbonyl Compounds

MOP :-

- 1) from Oxidation of Alcohols▶ 3
- 2) Reductive ozonolysis▶ 4
- 3) Kuchexov rxn▶ 4
- 4) From $\text{Ca}^{+2}/\text{Ba}^{+2}$ salts of COOH ▶ 5
- 5) From Carboxylic acid▶ 6
- * 6) Malaprade rxn (HIO_4)▶ 7

MOP of Ketone :

- 1) from acid chloride▶ 17
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- 3) from F.C Acylation▶ 18
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MOP of aldehydes :

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1) Rxn with HCN> 29

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MOP:-

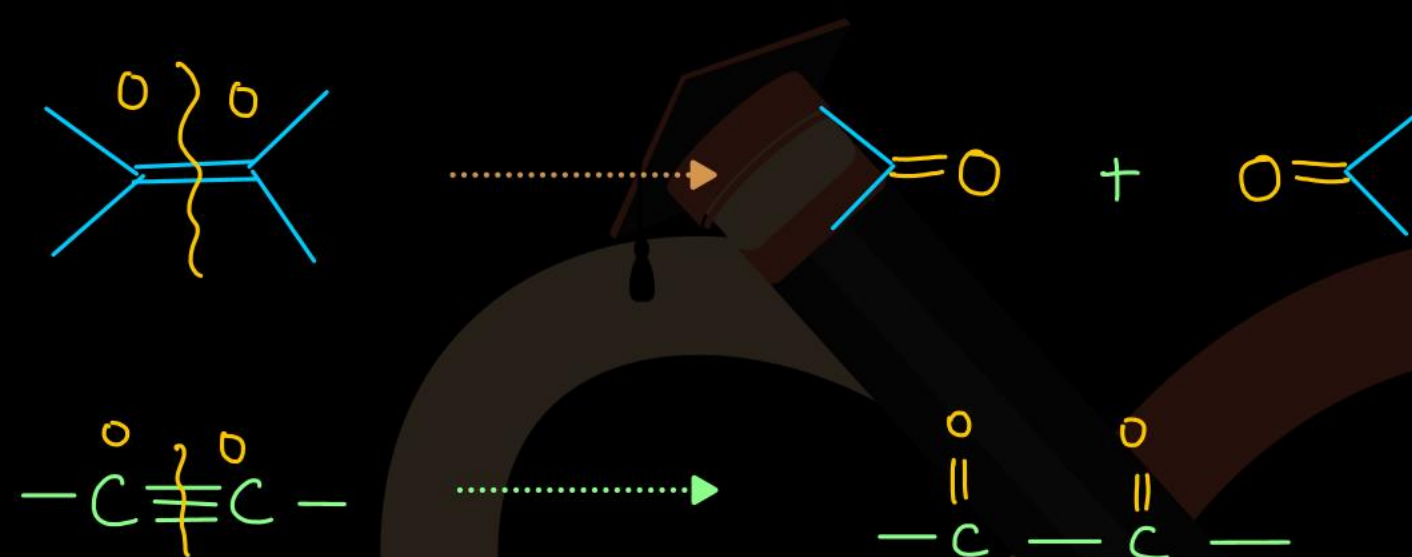
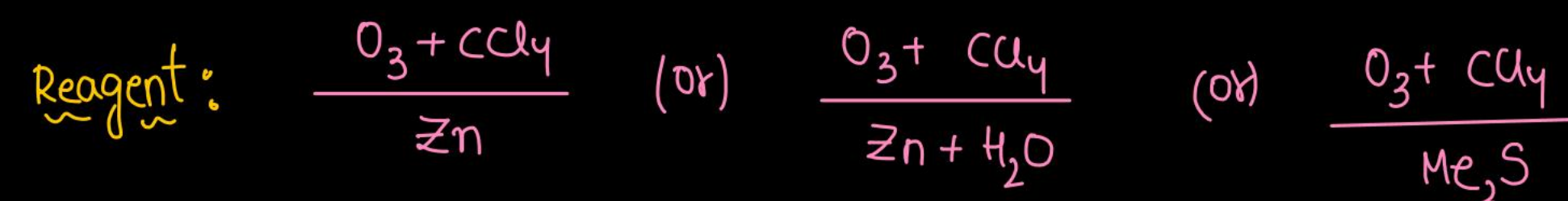
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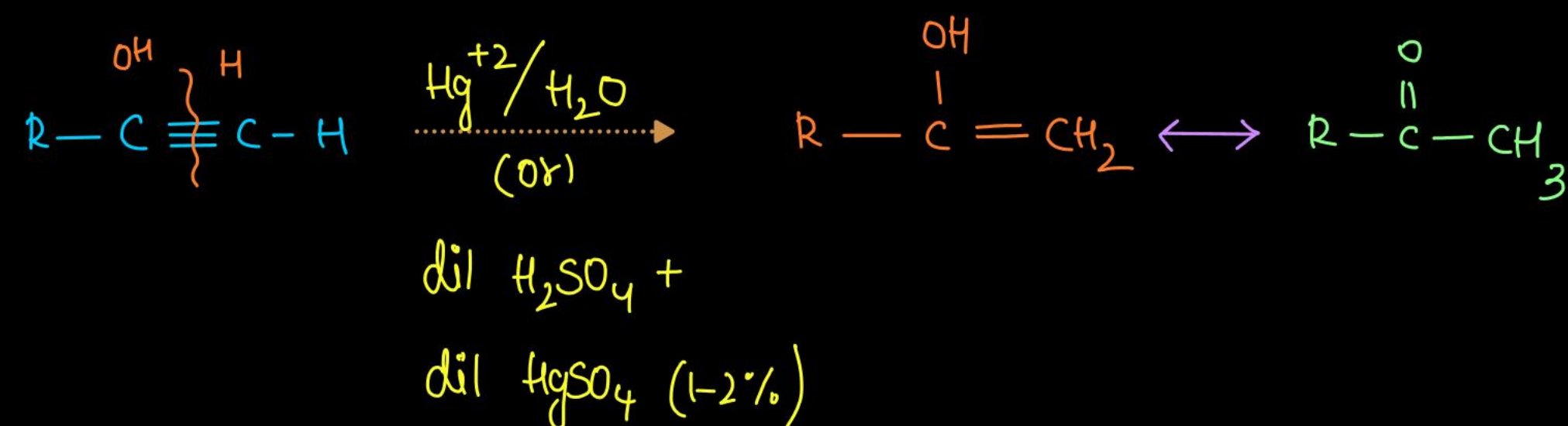
Mild O.A :

- 1) PCC
- 2) PDC
- 3) Collins reagent
- 4) Jones reagent
- 5) $\text{Cr}/300^\circ\text{C}$ (* $3^\circ \rightarrow$ alkene)
- 6) MnO_2 (for benzylic, allylic ROH)

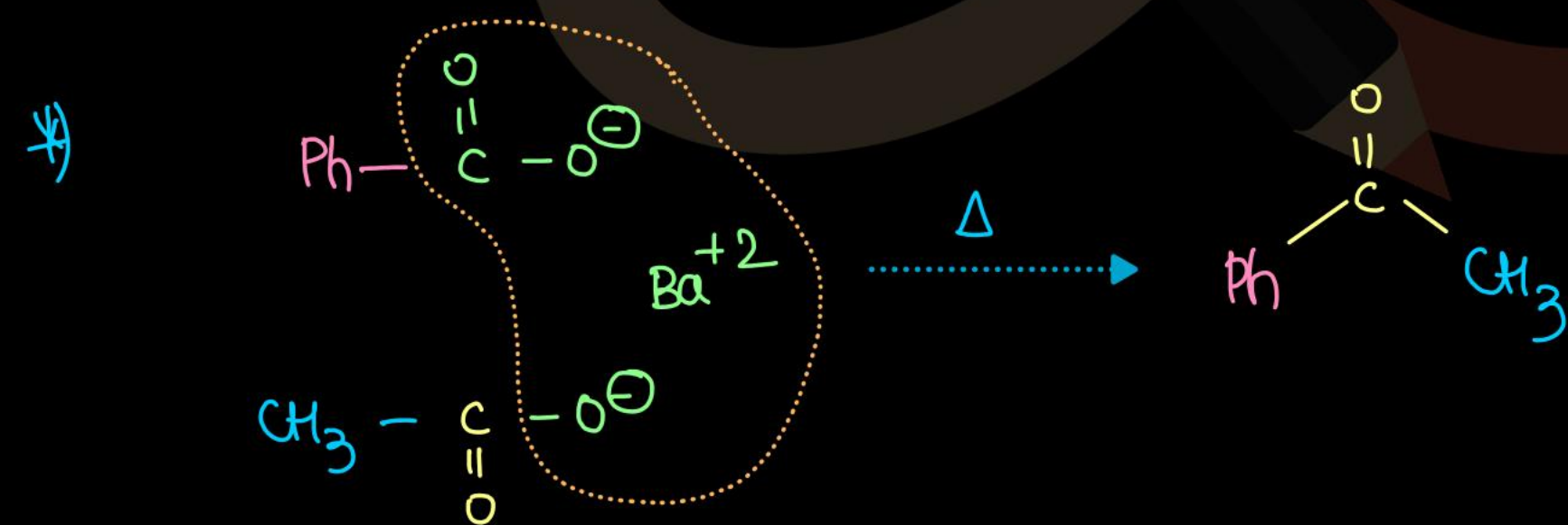
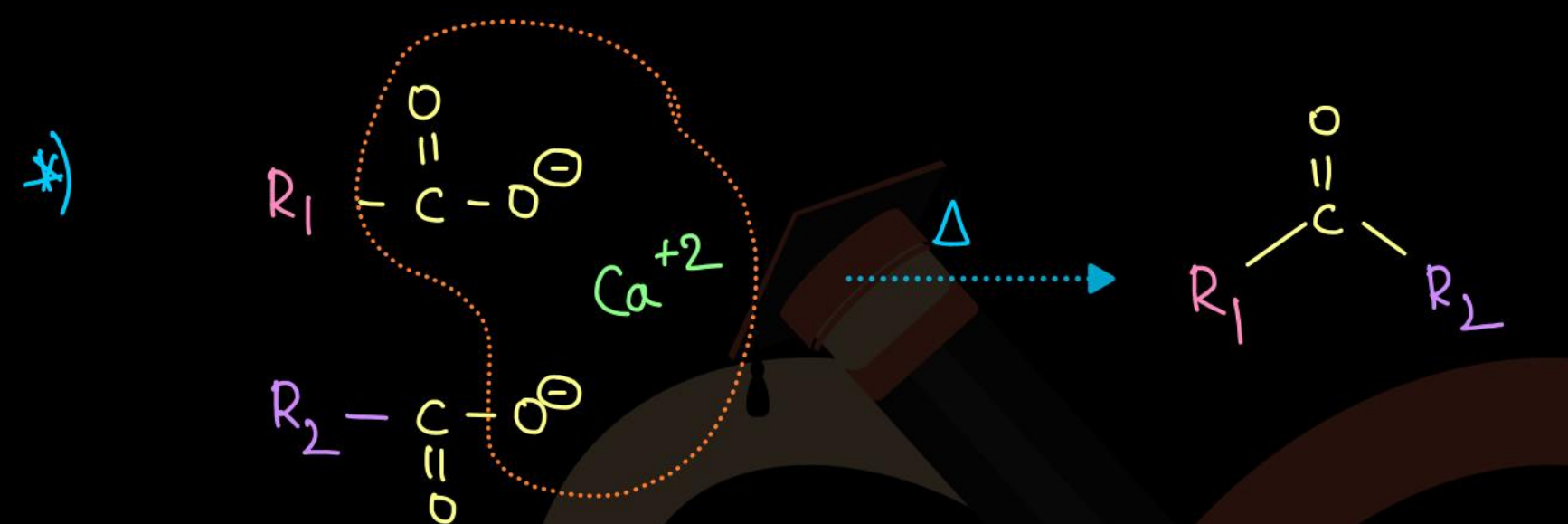
2) Reductive Ozonolysis :



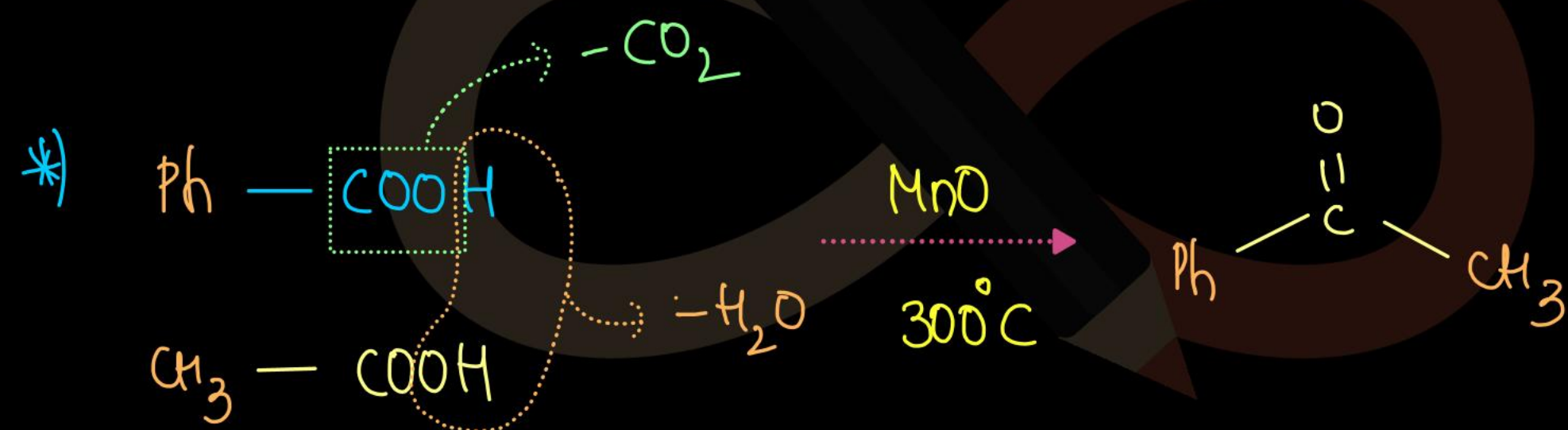
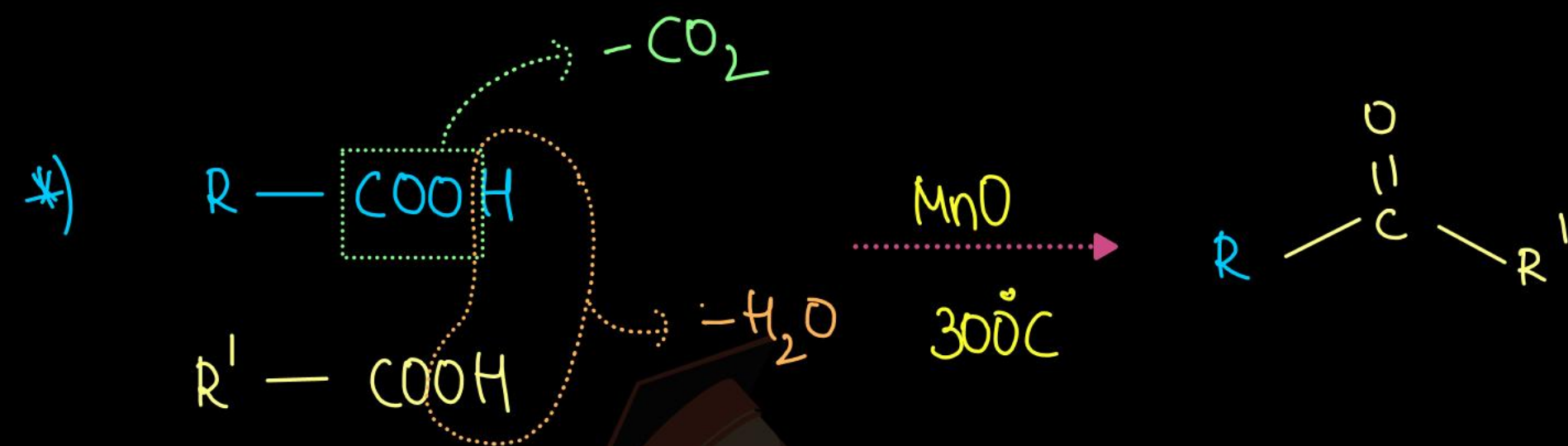
3) Kucherov Rxn



4) From Ca/Ba salt of Carboxylic acid (dry distillation)

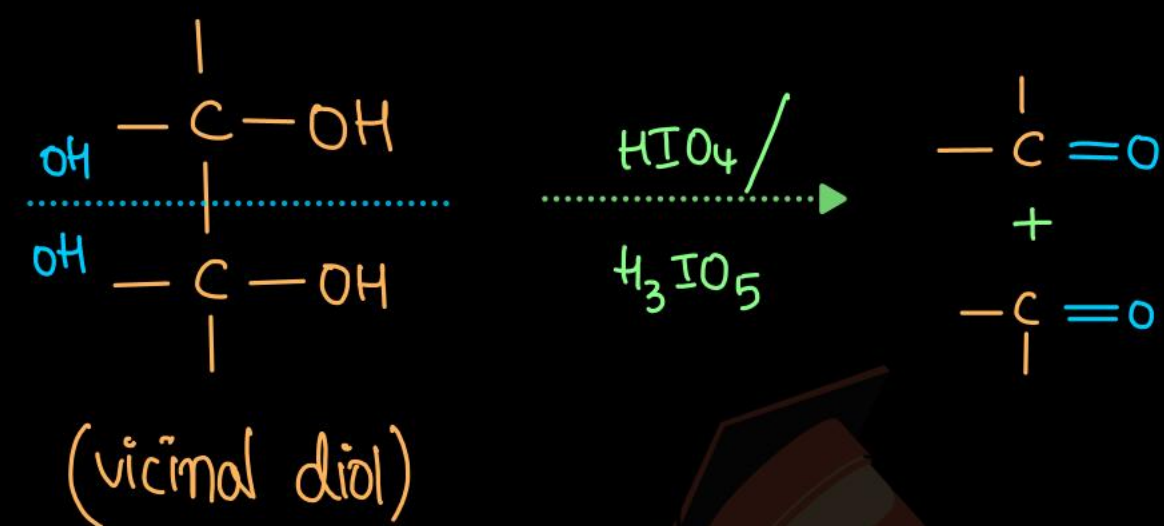


⑤ From Carboxylic acid :-

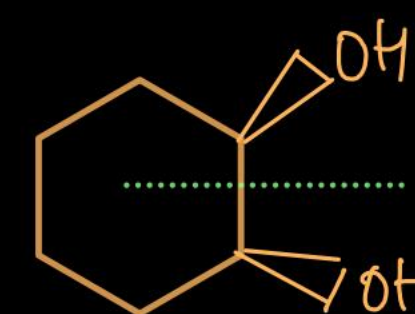
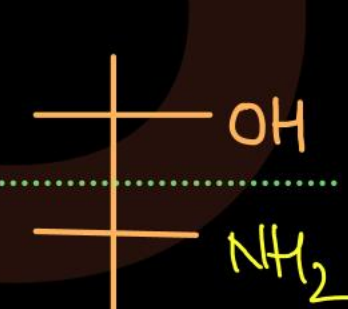
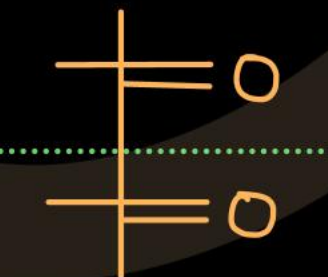
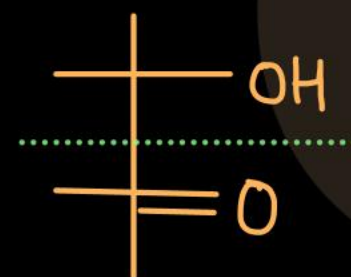
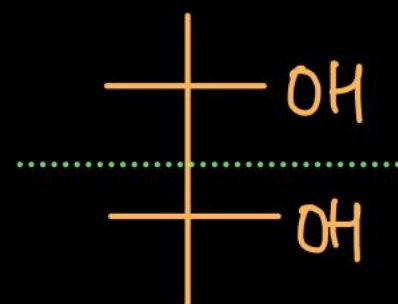


⑥ Malaprade Rxn :

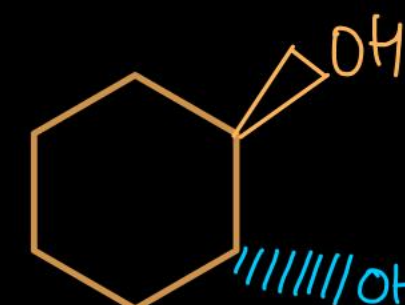
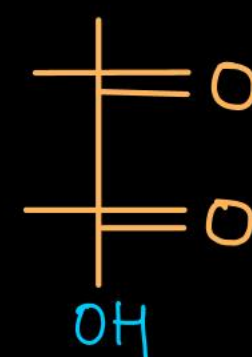
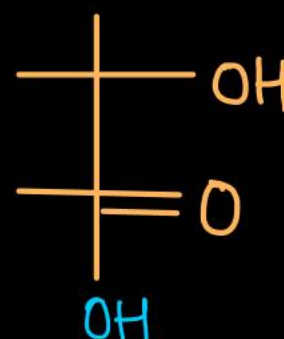
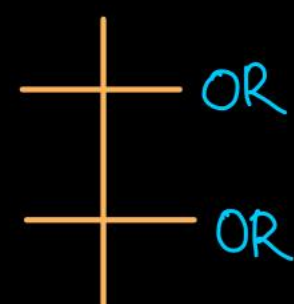
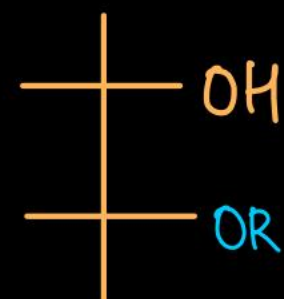
→ Oxidation by HIO_4 ($\text{Pb}(\text{OAc})_4$ or NaIO_4)



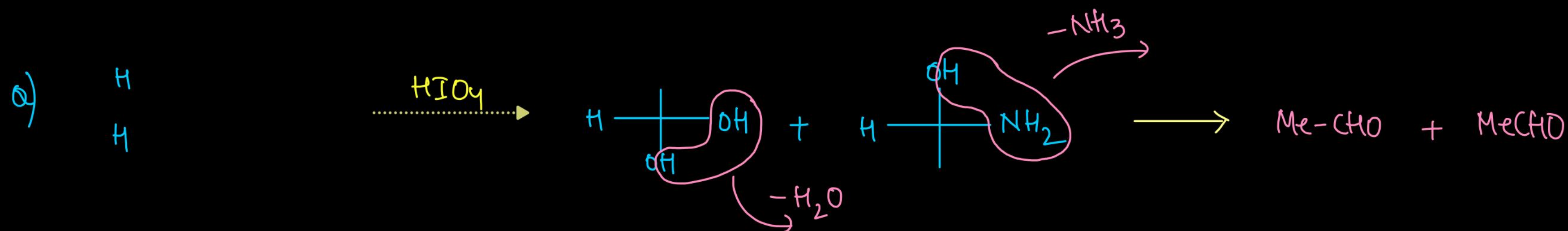
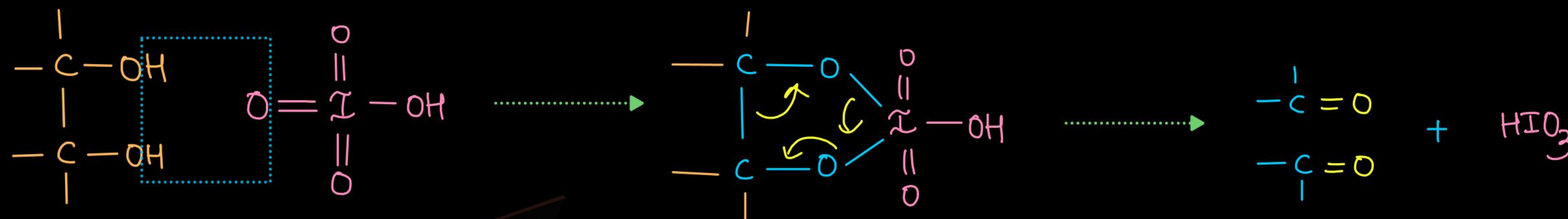
Oxidised by HIO_4

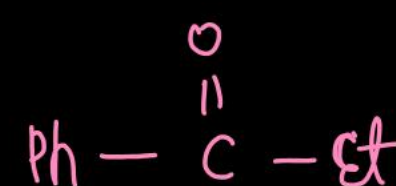
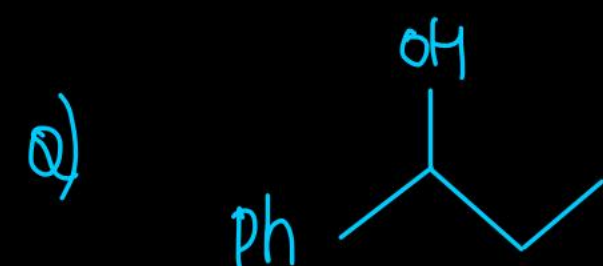
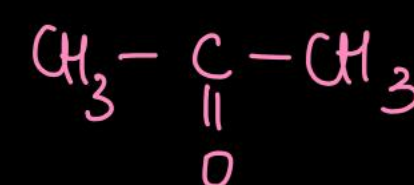
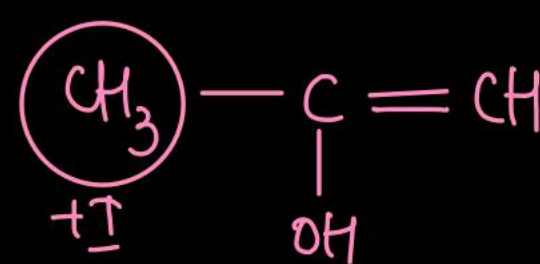
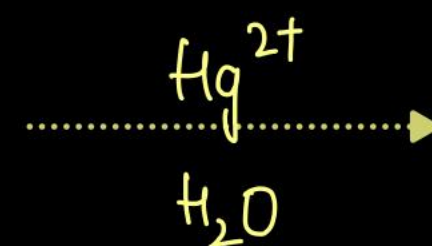
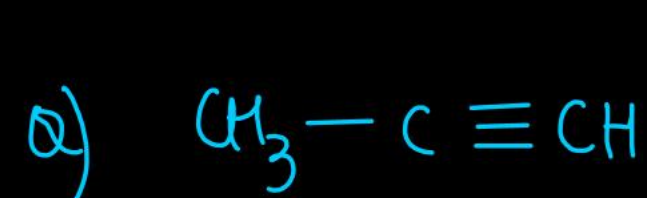
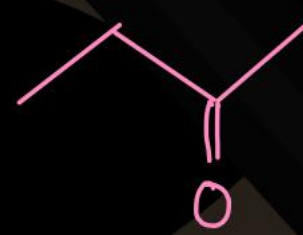
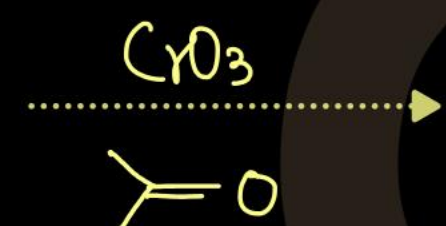
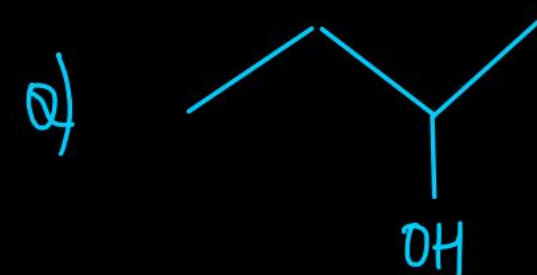
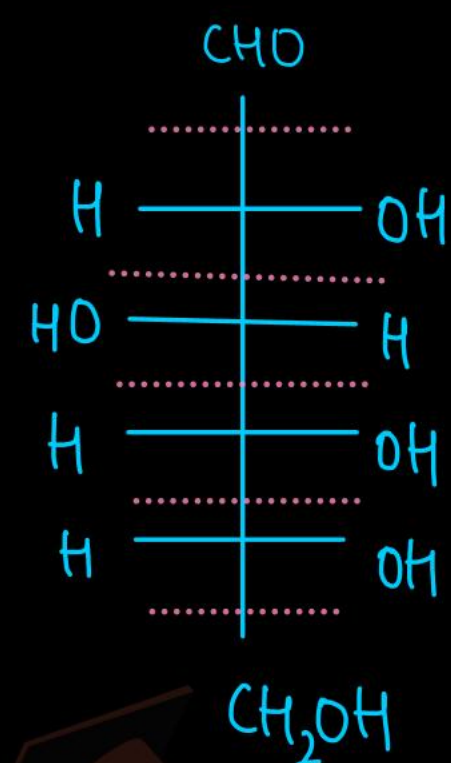
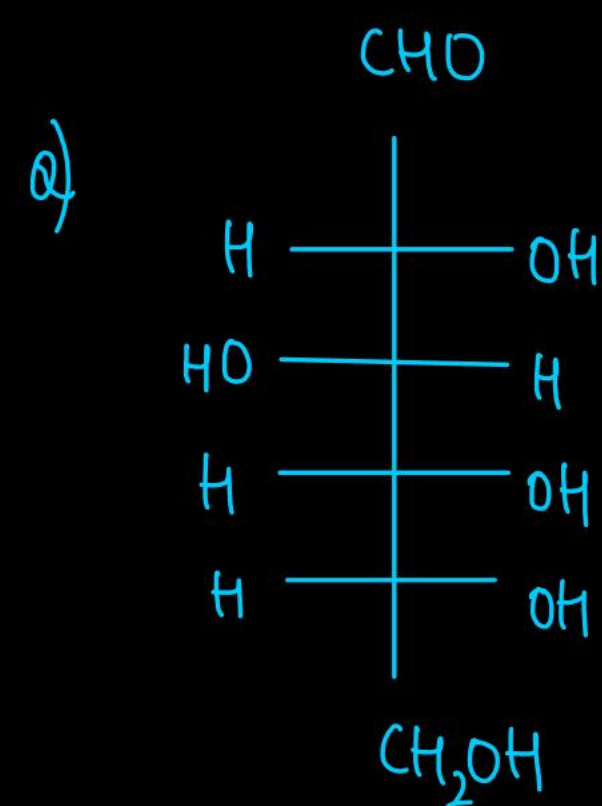


Not oxidised by HIO_4 :



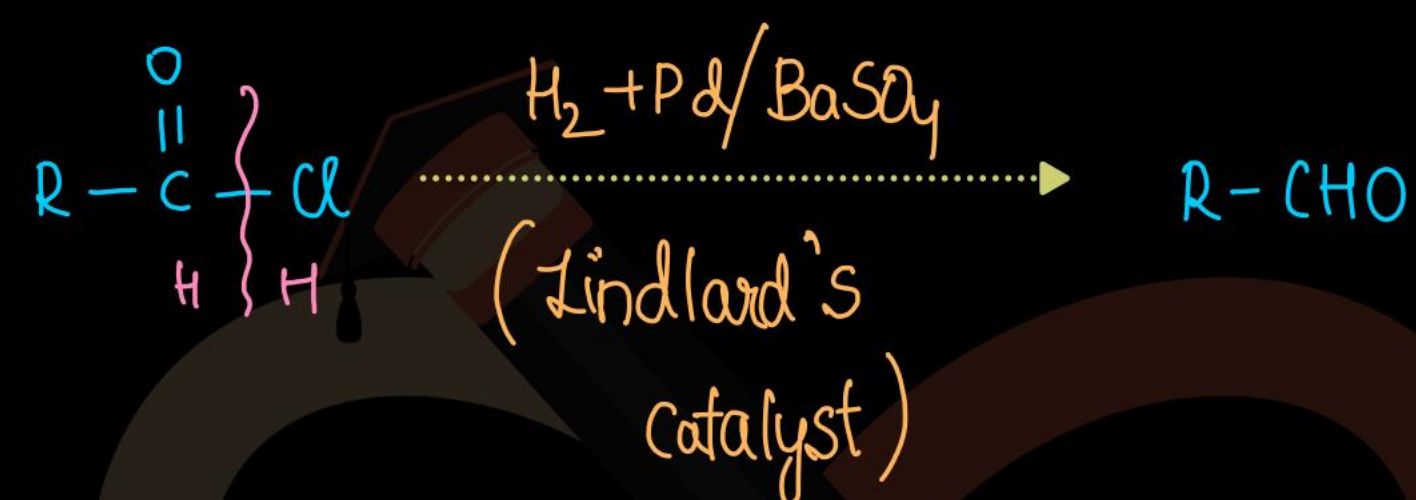
Mechanism :-



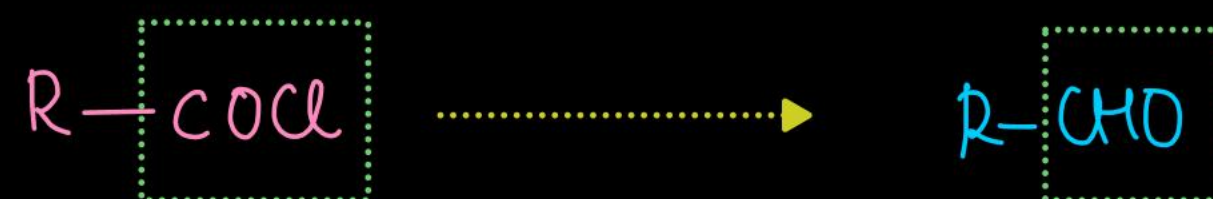


MOP of Aldehydes :-

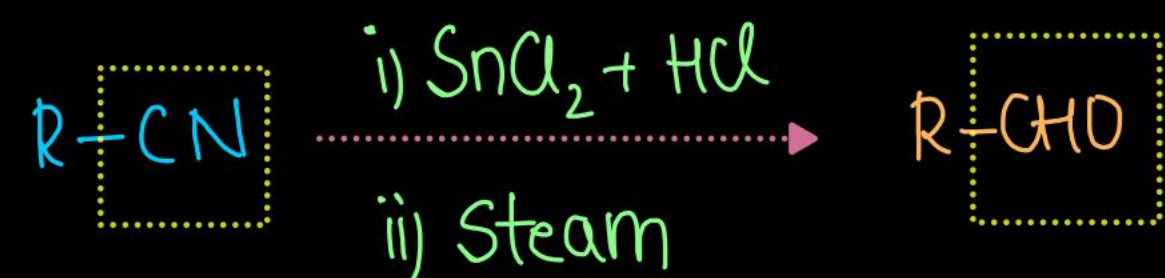
1) Rosendmund's Reduction



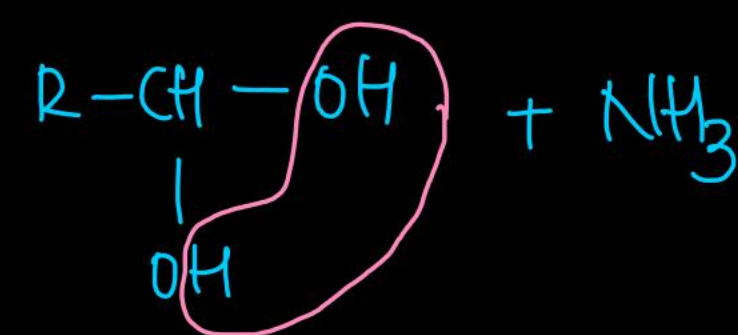
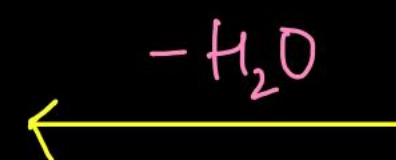
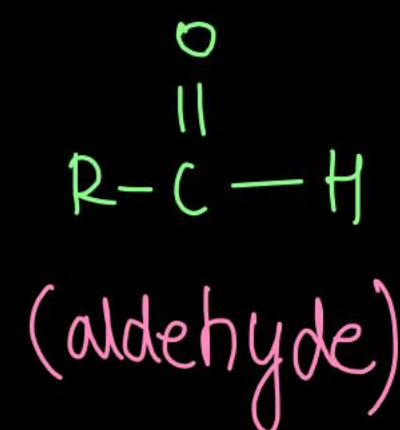
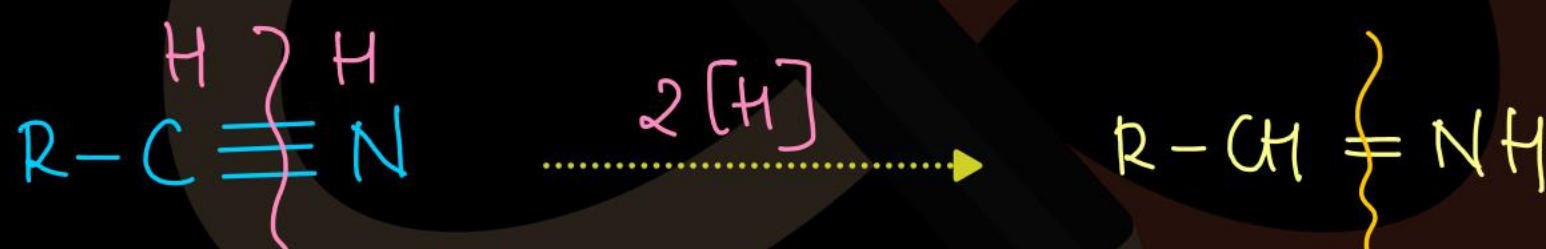
* DM :-



2) Stephan's reduction :-

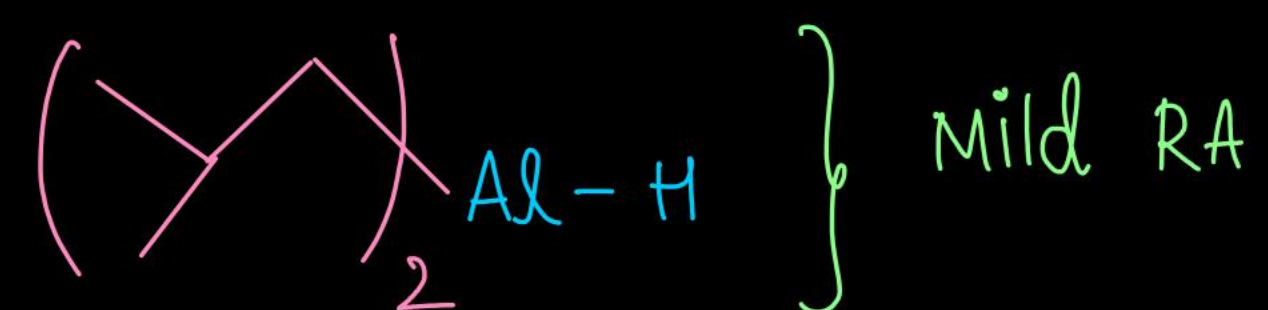


Mech:-

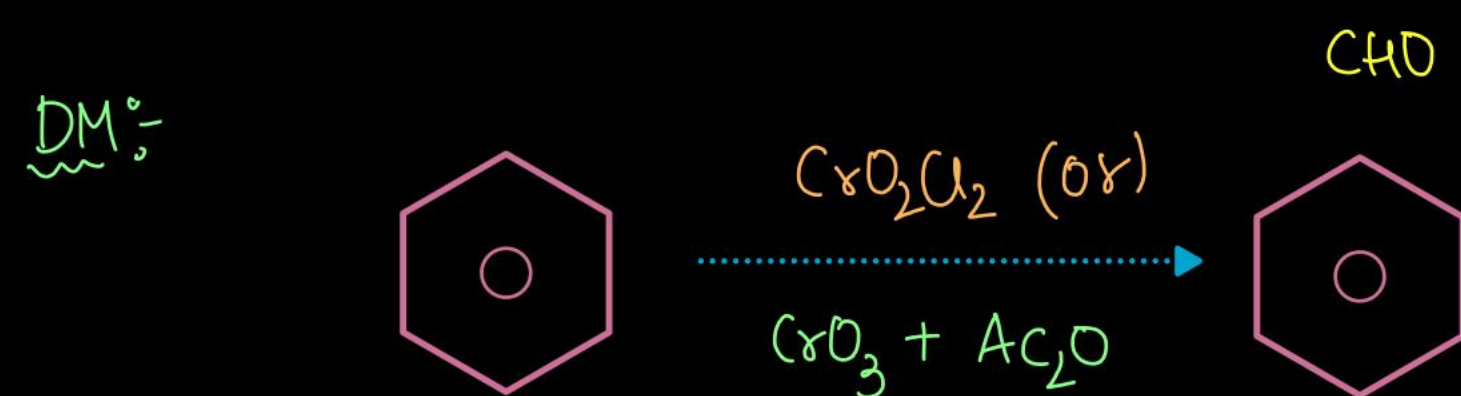
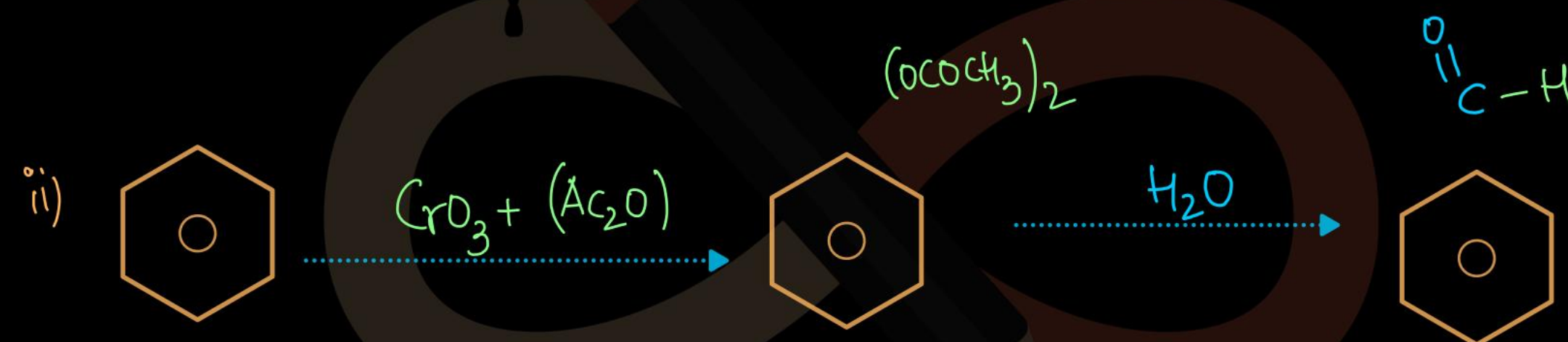
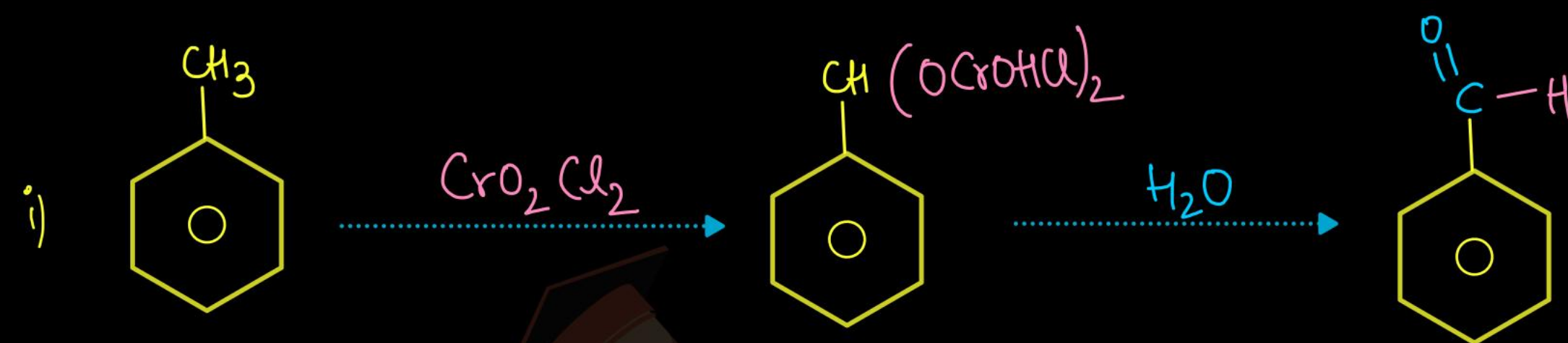


③ Reduction by DIBAL-H

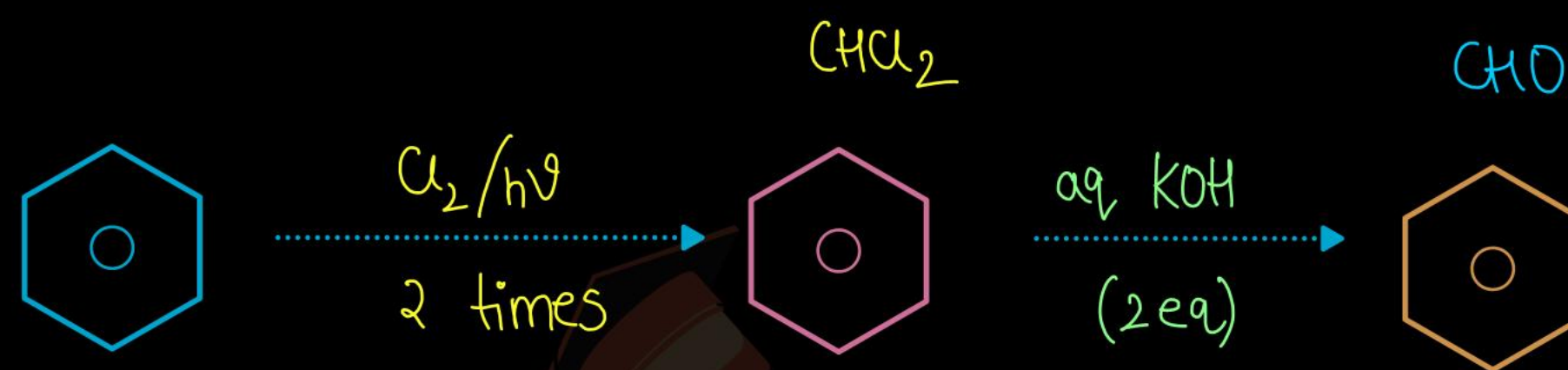
(di-isobutyl aluminium hydride)



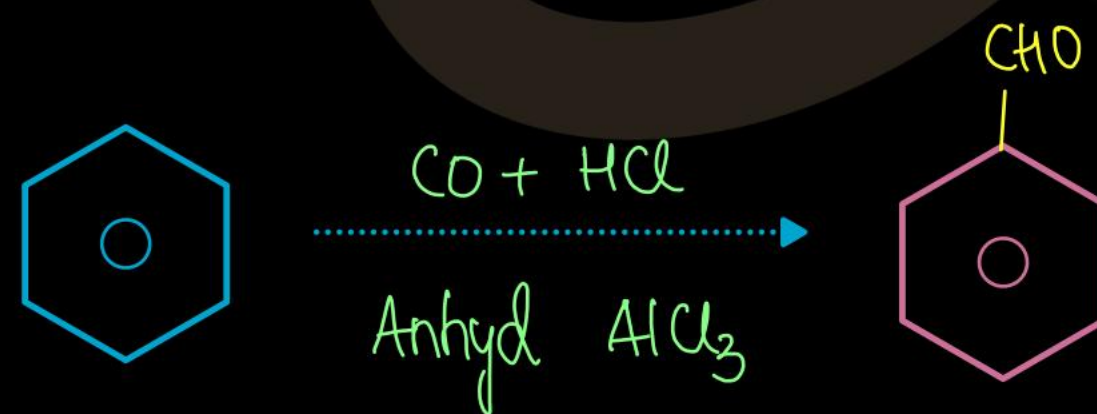
4) Etard reduction :-



5) Side chain Oxidation :-

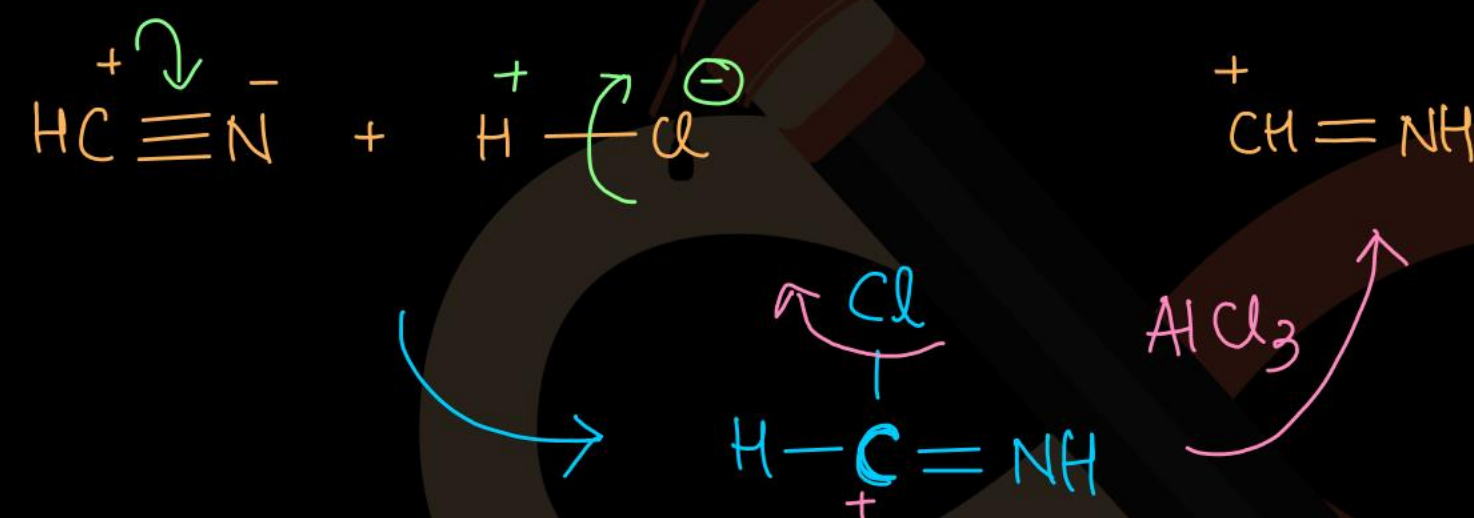
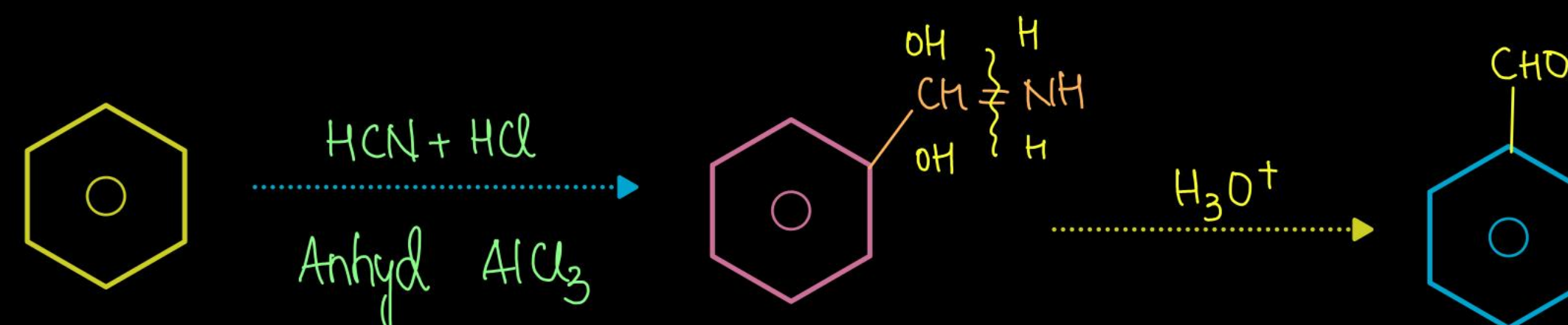


6) Gatterman Koch rxn :

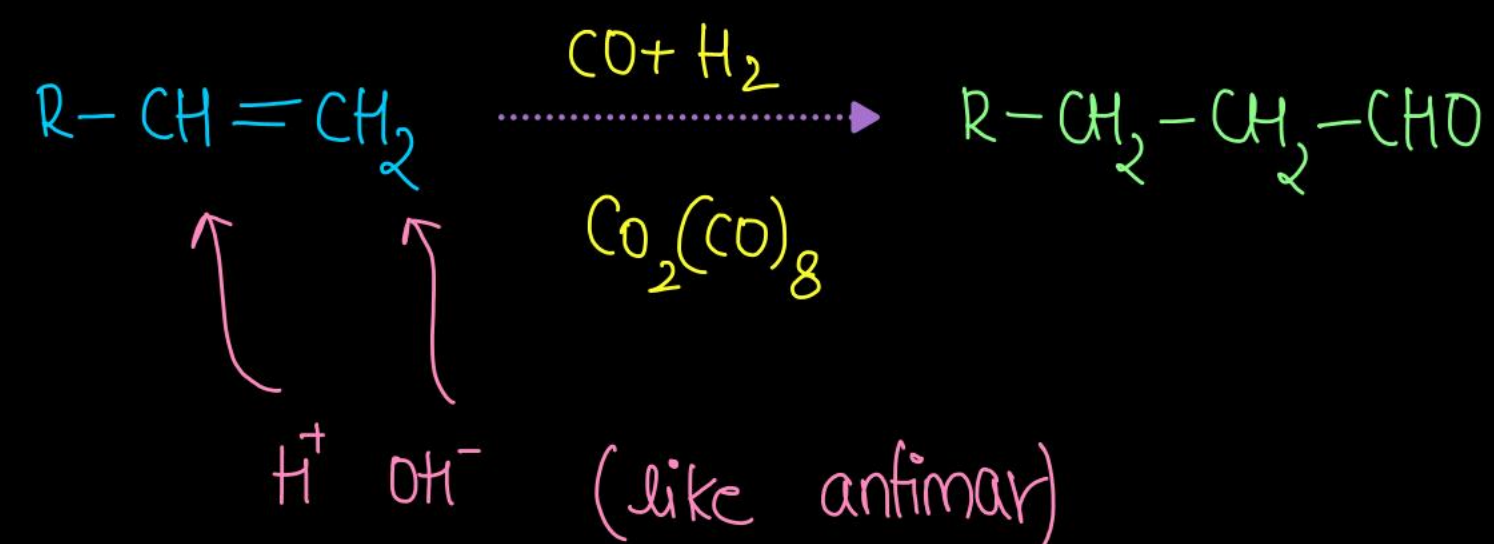


↪ *) EAS

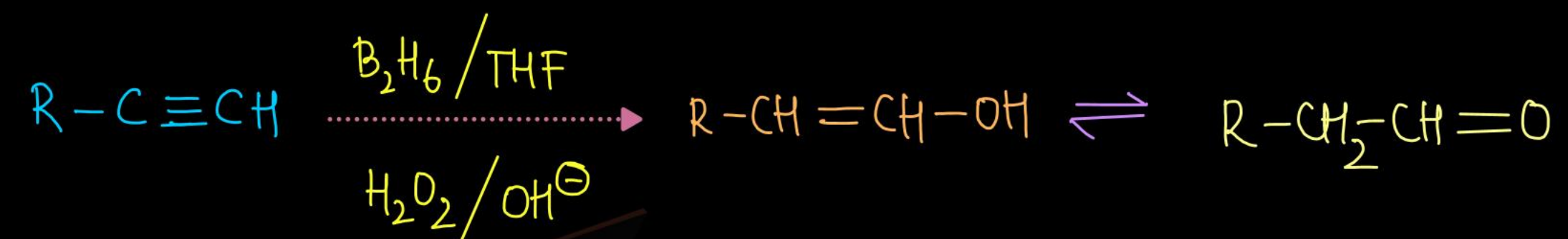
7) Gatterman Ald Rxn :



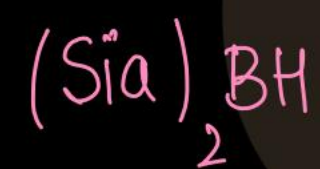
8) OXO Process :-



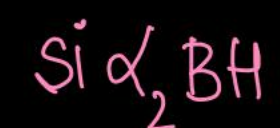
9) HBO of alkyne :-



☆) Disiamylborane can also be used

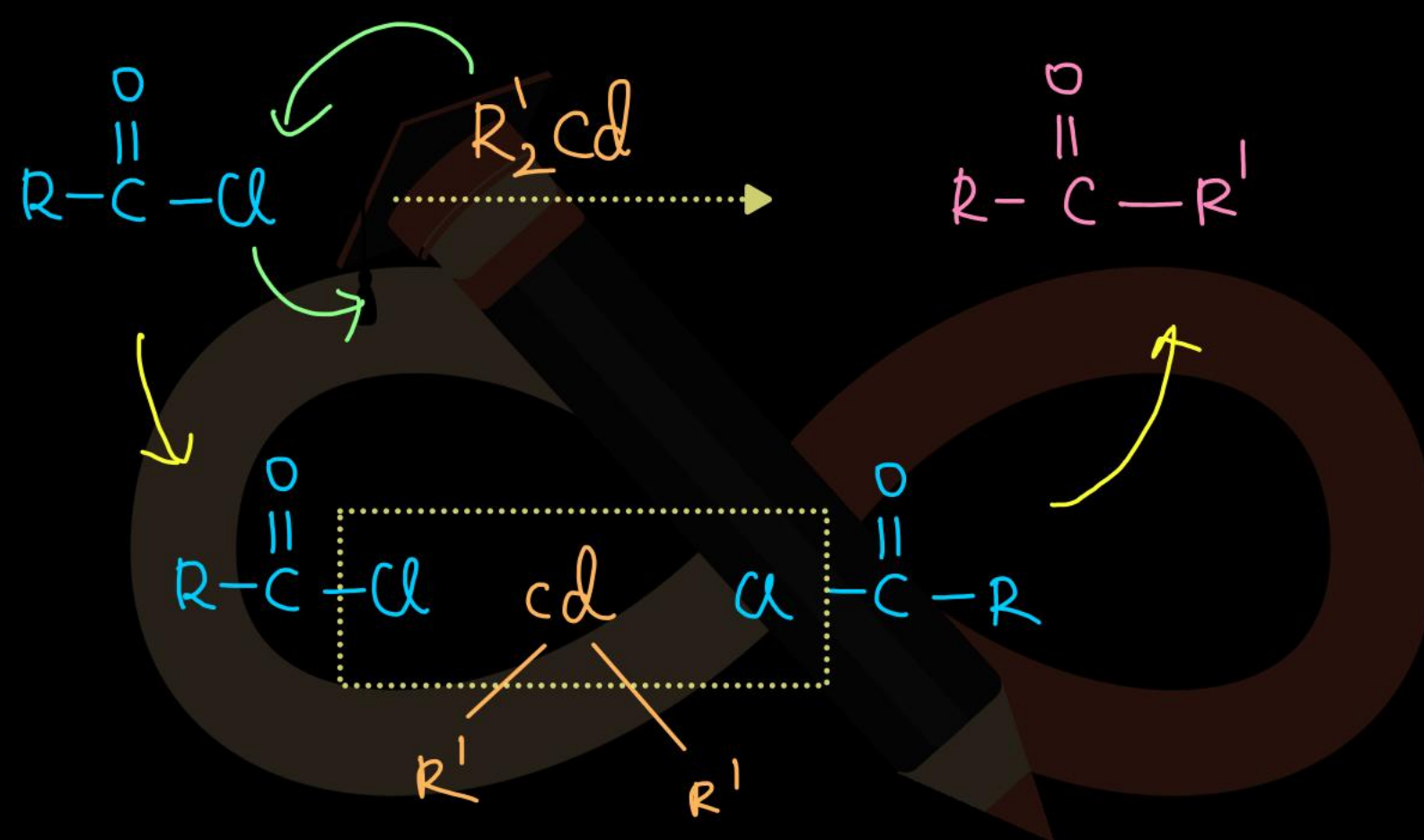


(or)

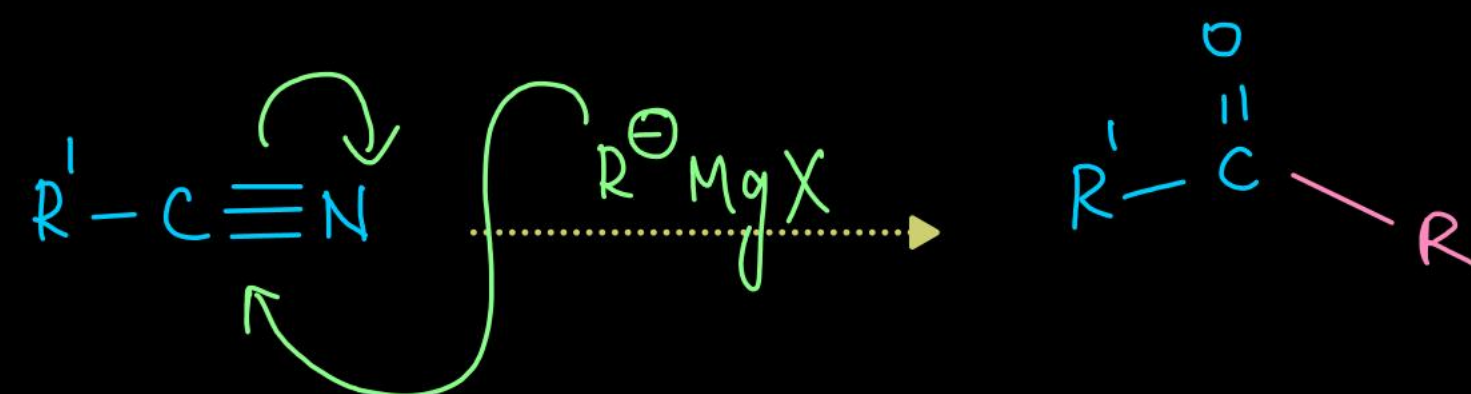


MOP of ketone :-

1) from acid chloride



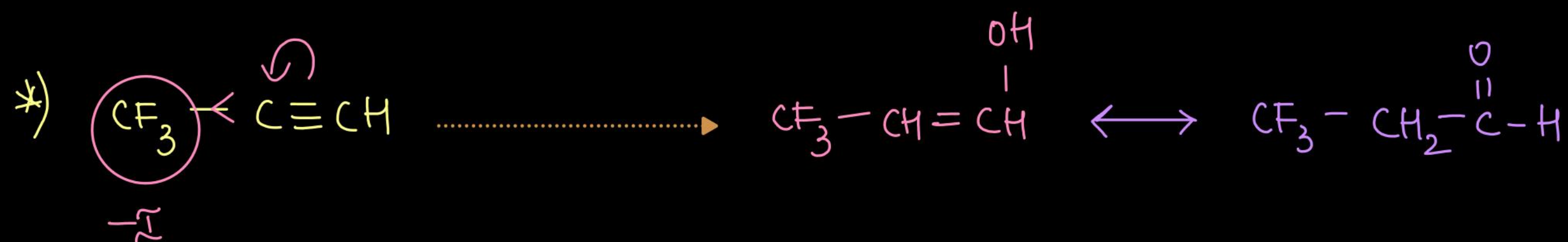
2) From nitrile with GR :



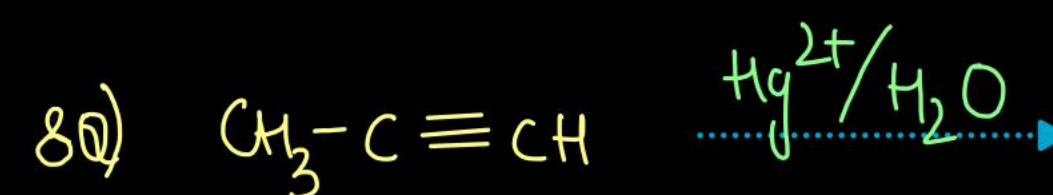
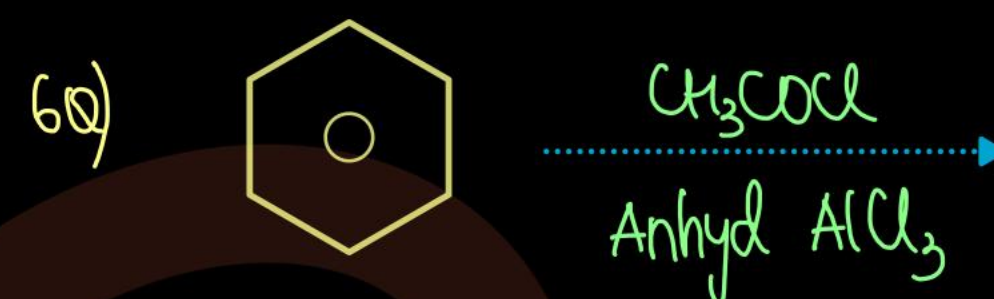
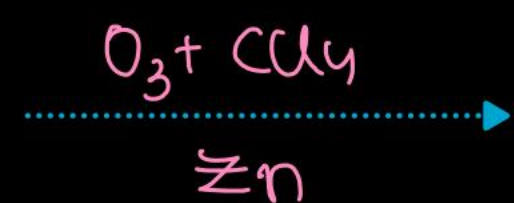
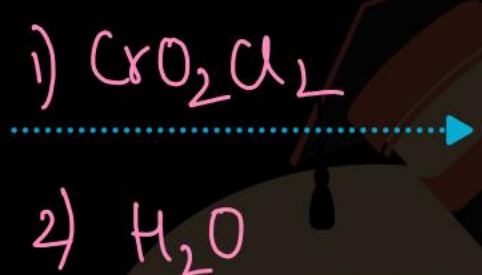
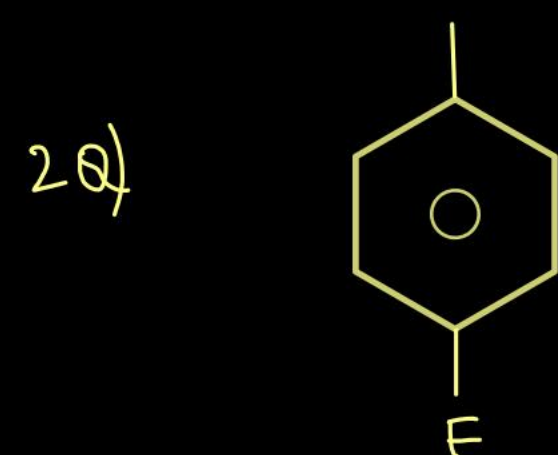
3) from Friedel Crafts acylation :

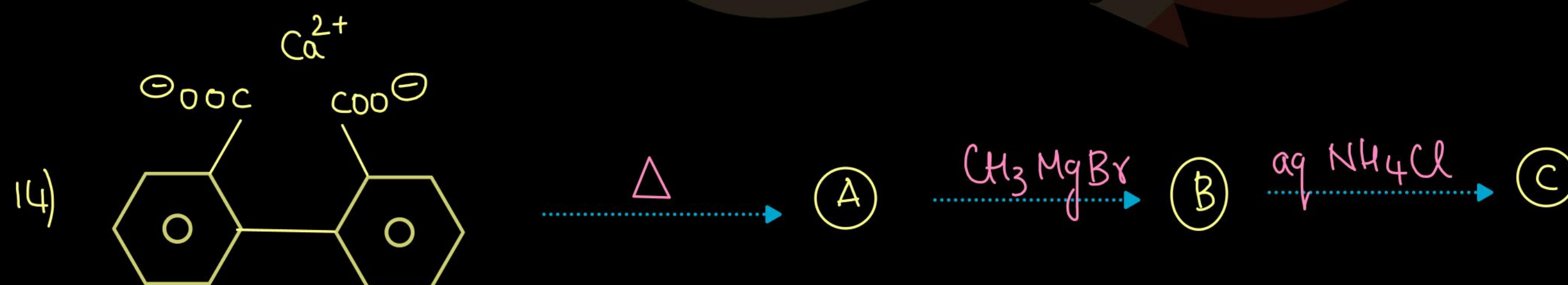
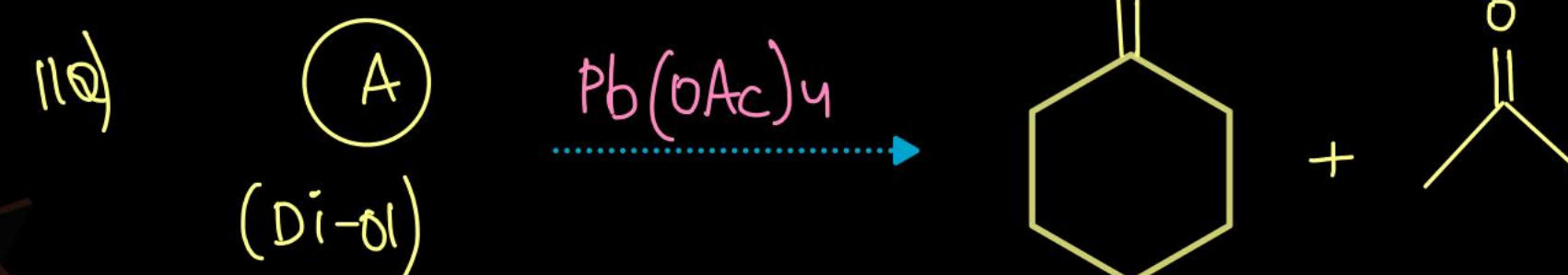
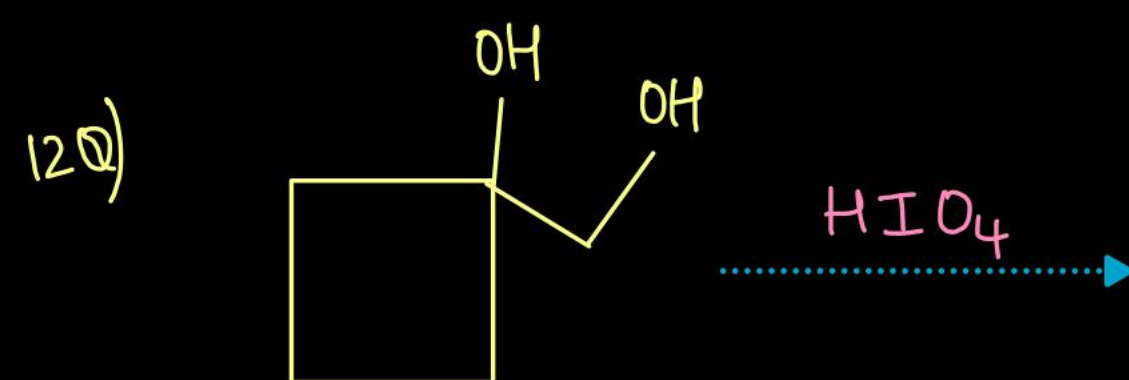


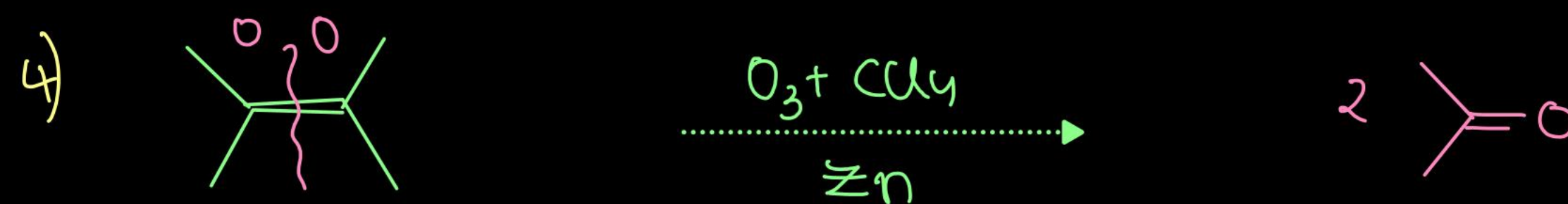
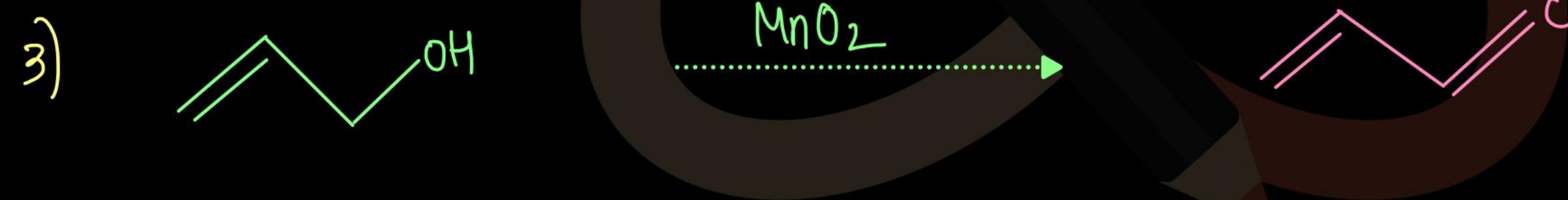
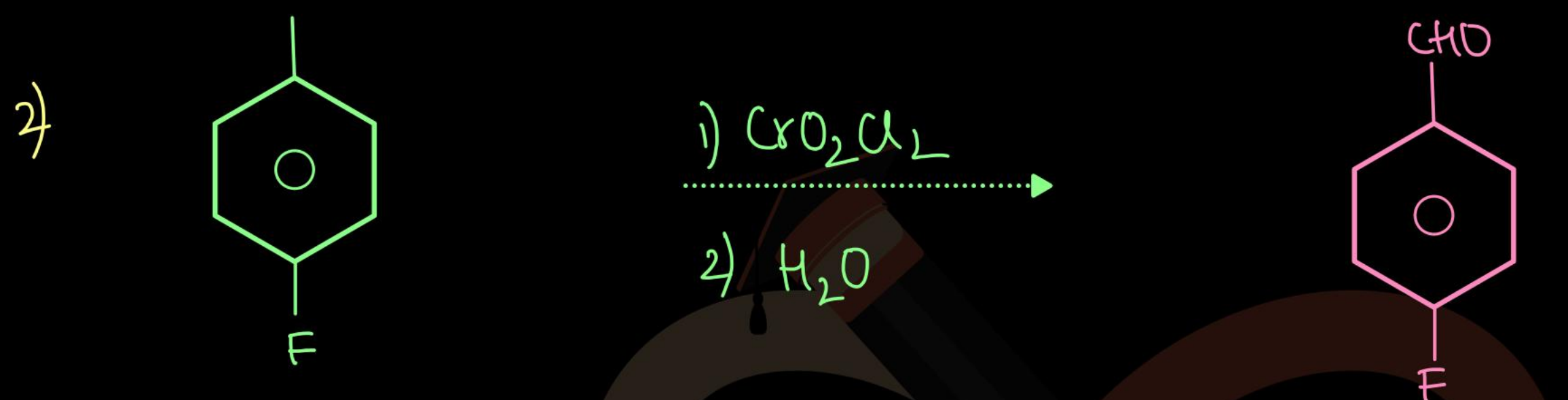
4) OMDM of alkyne :

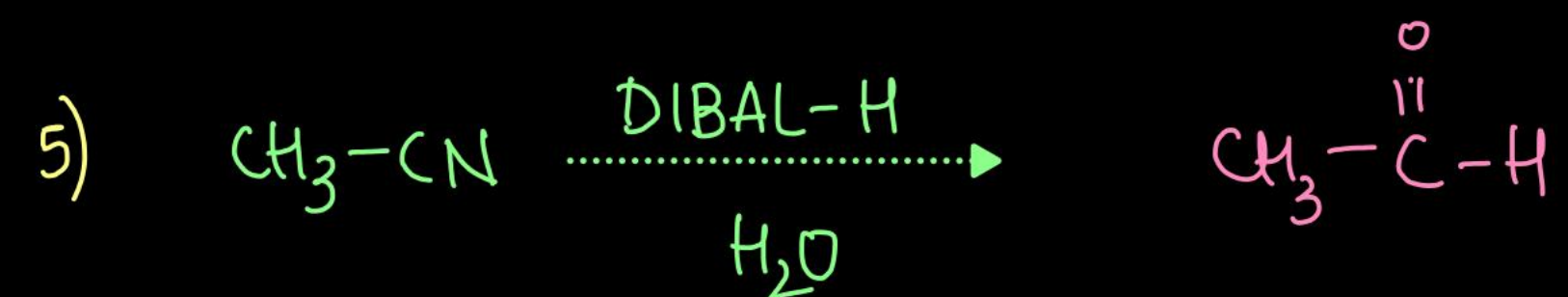


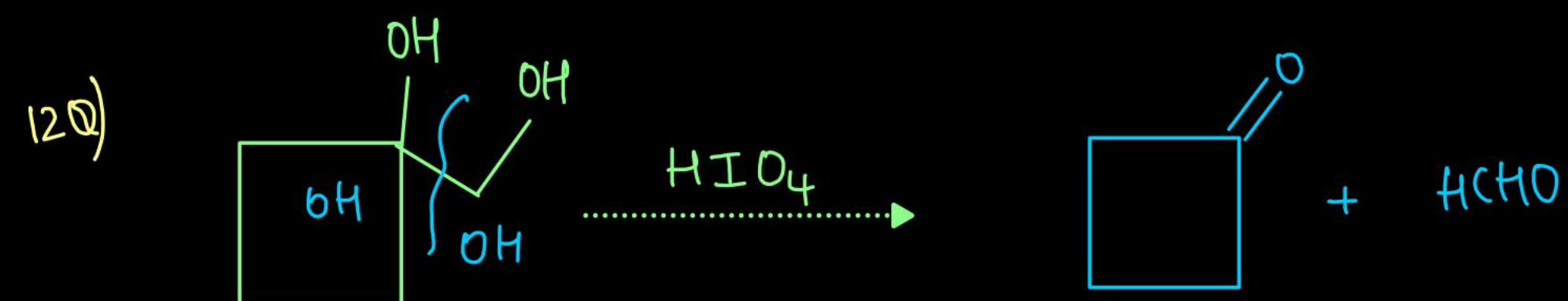
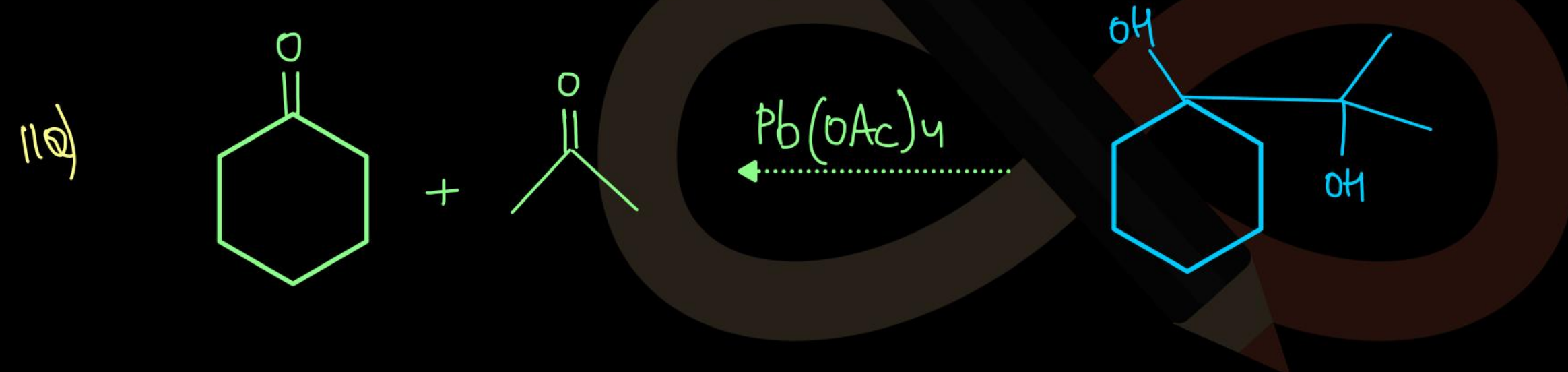
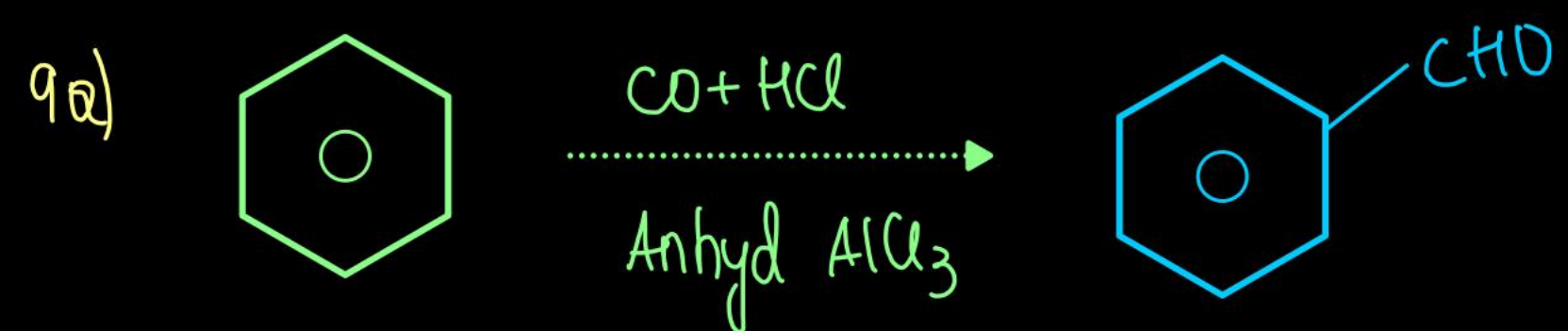
Practice :-

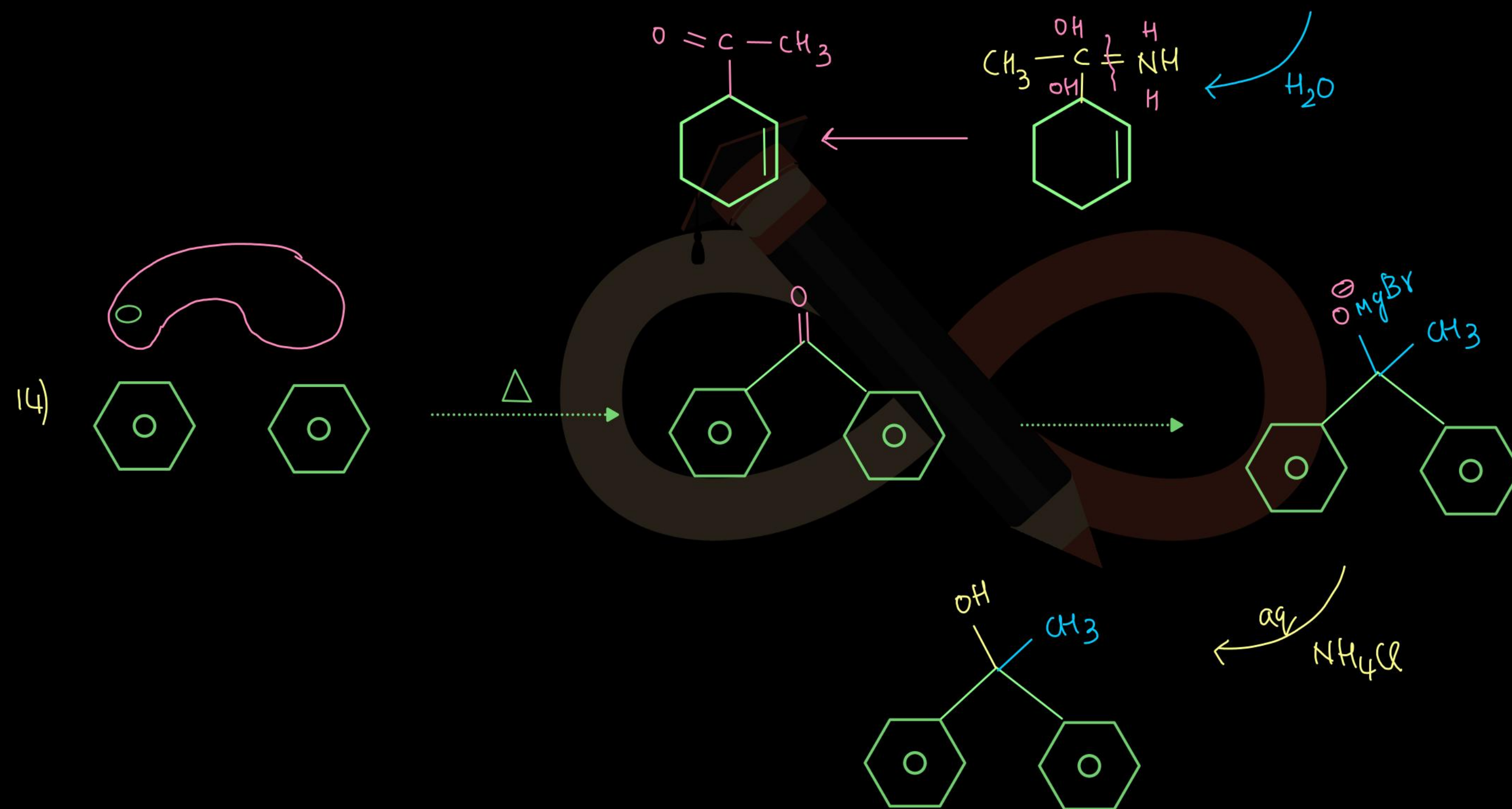
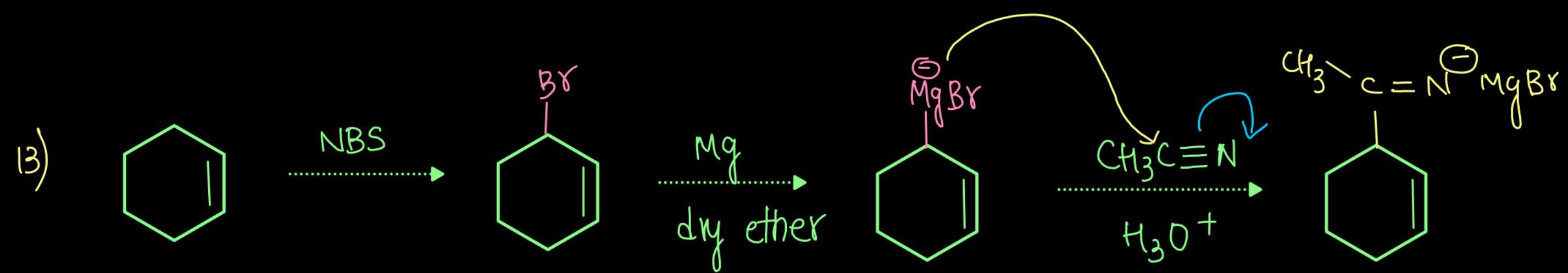




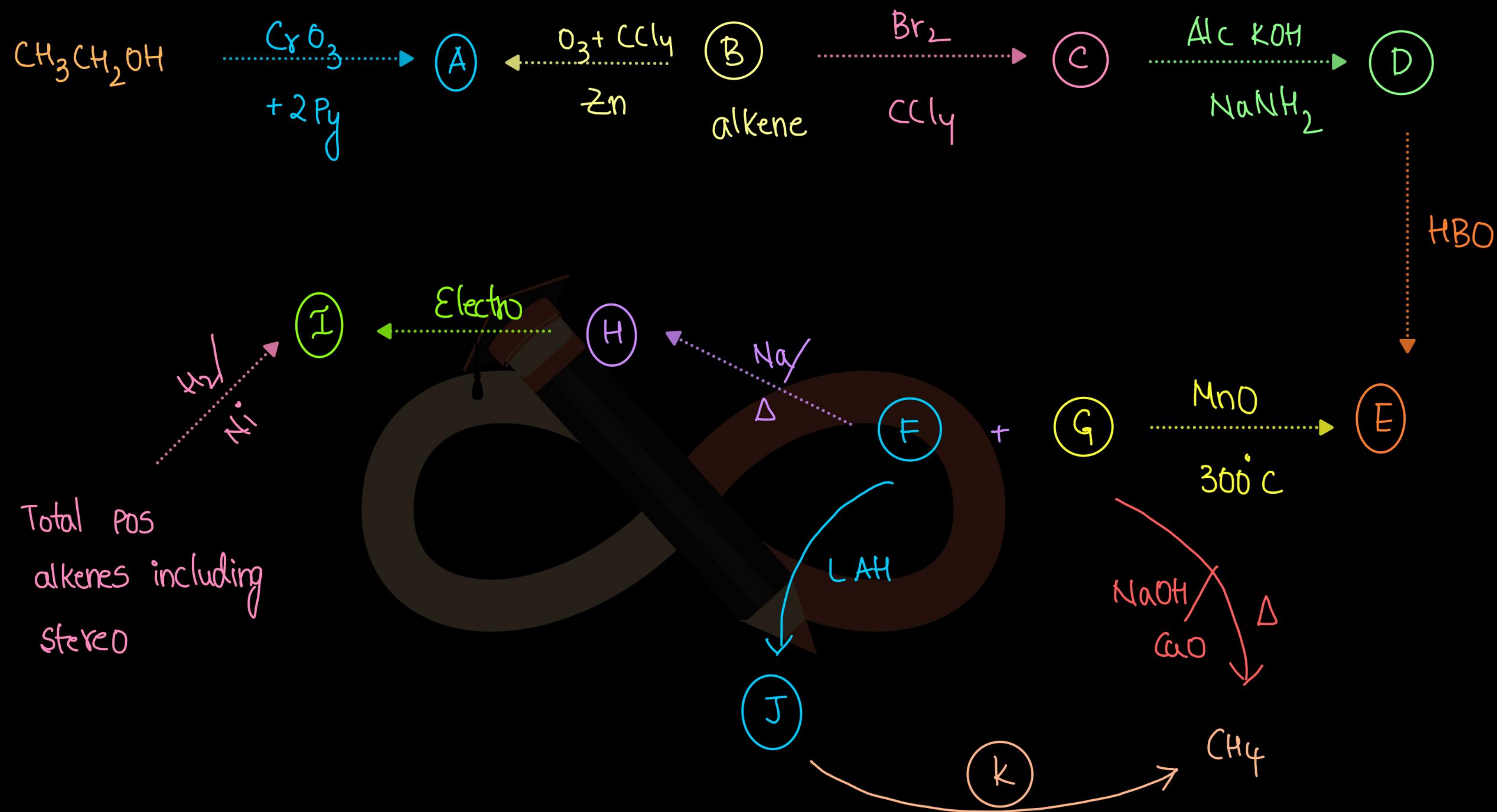




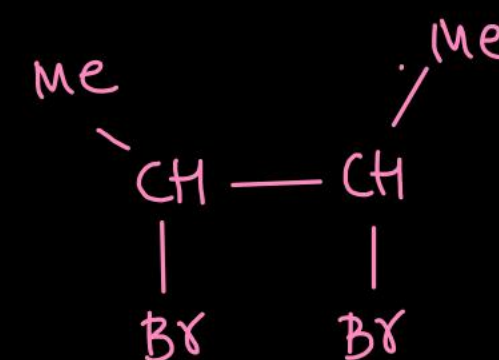
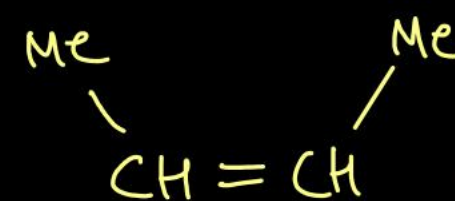
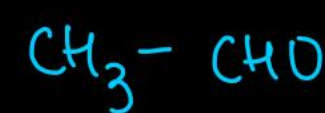
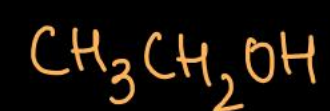




Q)

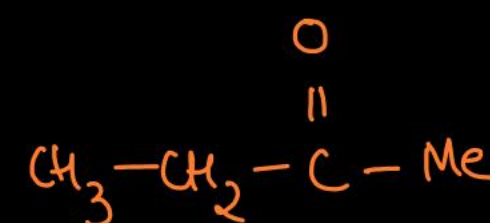


Q)



Alc KOH

NaNH_2



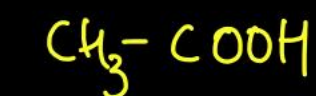
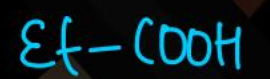
HBO



Electro



Δ



MnO

300°C



(c/t)

Total pos
alkenes including
stereo

(3)

LAH



$\text{NaOH} \xrightarrow{\text{CaO}} \Delta$

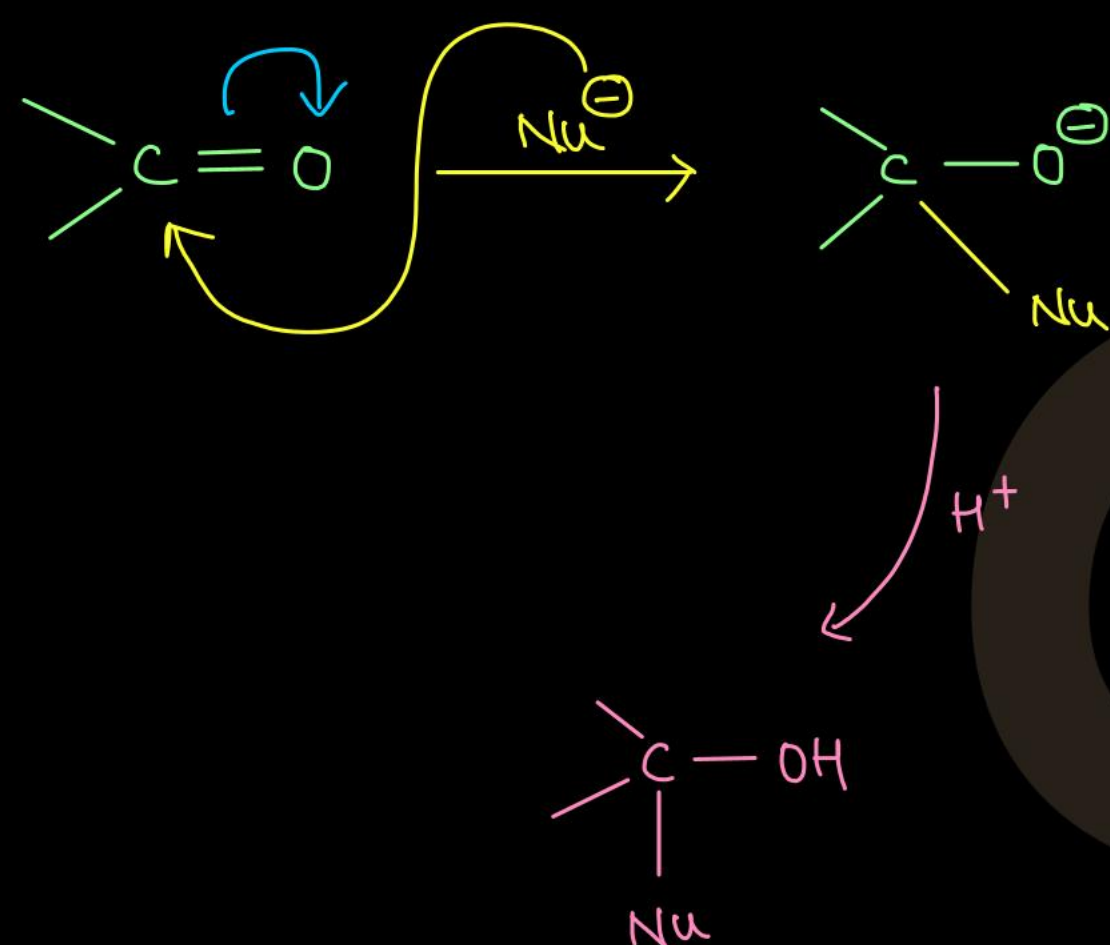
MeMgBr



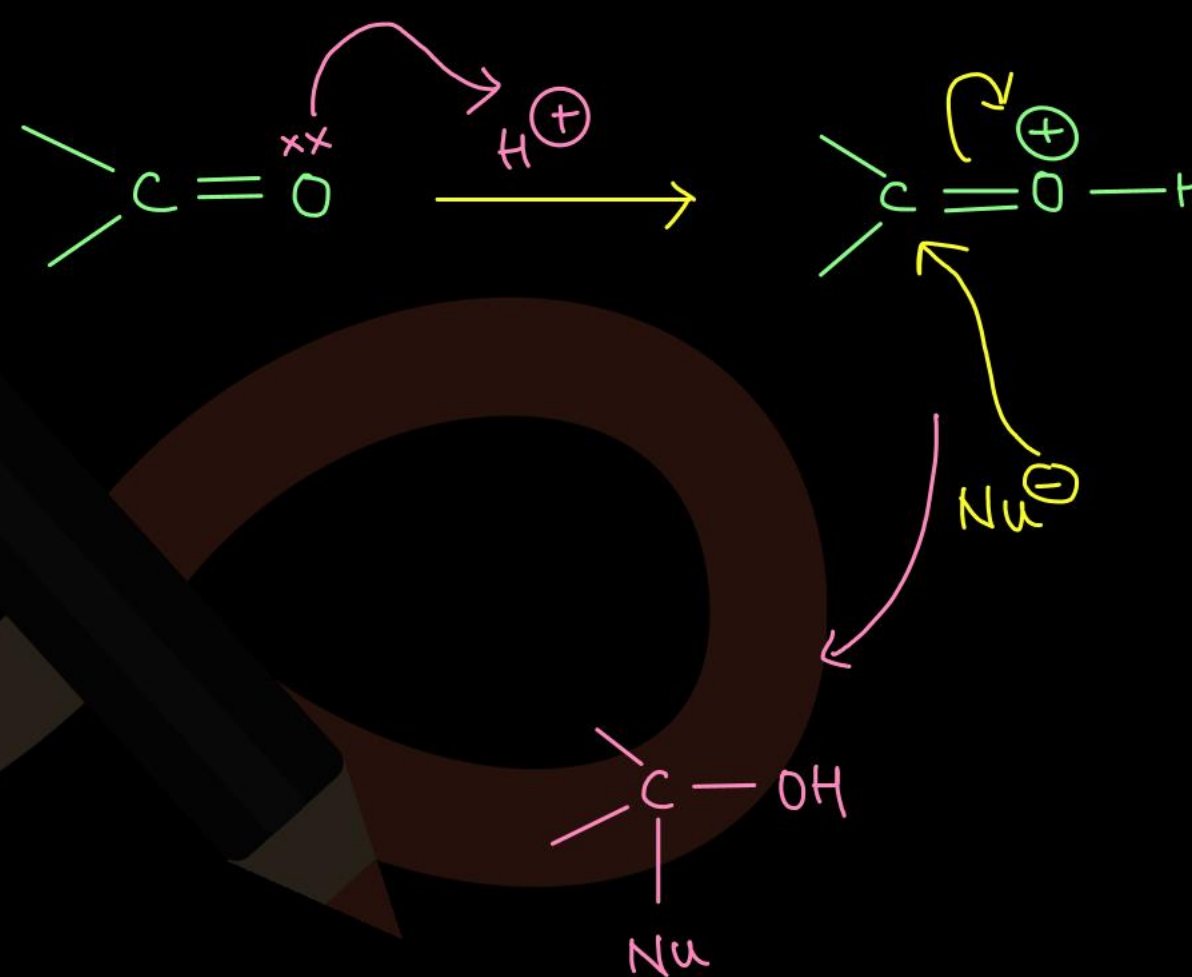
Properties :-

I) Nucleophilic Addition rxn (NAR)

a) In Basic Med



b) In acidic med

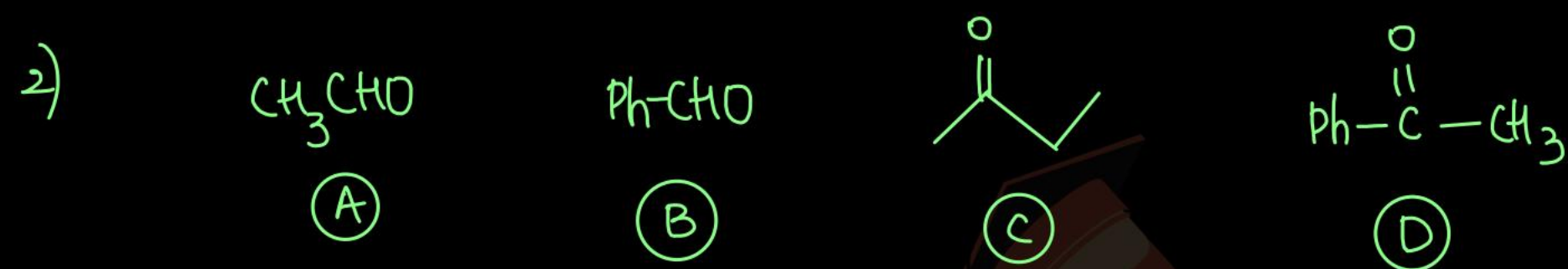


★ ME :-

$$\Rightarrow \text{Reactivity} \propto \frac{1}{SH}$$

$$\propto \text{Electrophilicity of C (ald} > \text{ketone)}$$

Q) Compare reactivity towards NAR :



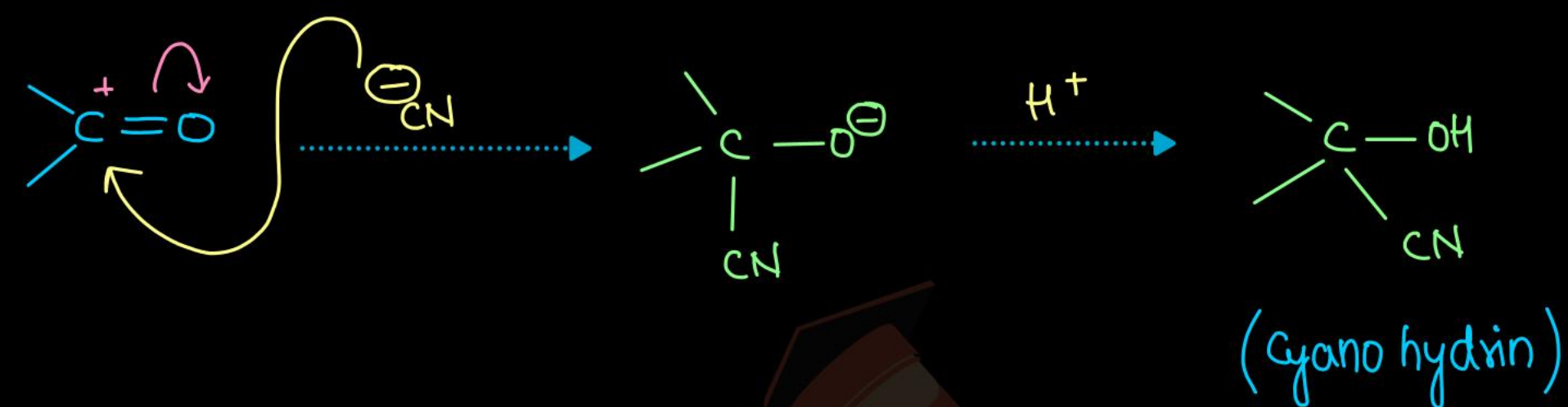
Sol:-



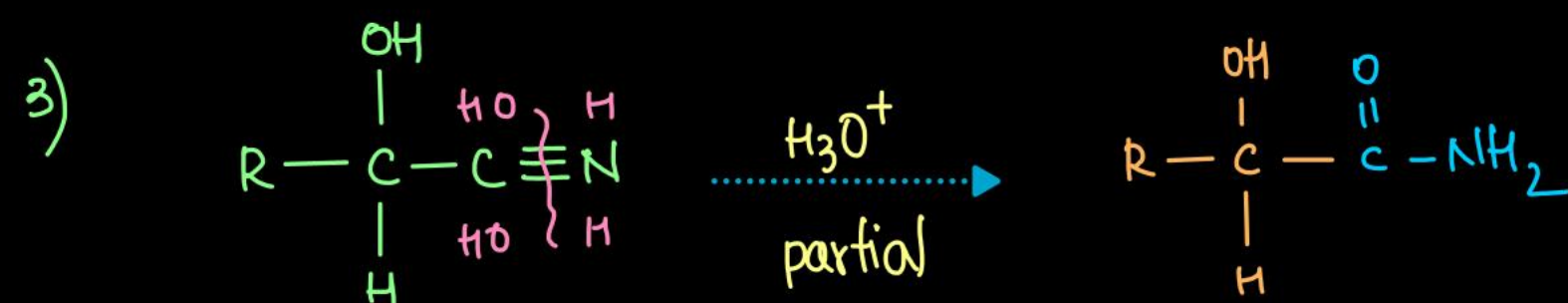
(ald > ketone)

NAR

i) Rxn with HCN (At pH 9-10)



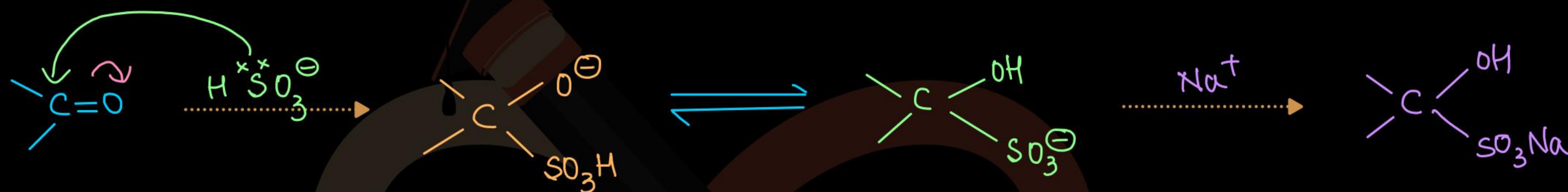
★ MT: Rxn's of α -hydroxy cyanamide:



2) Rxn with NaHSO₃ :-



Mech :-



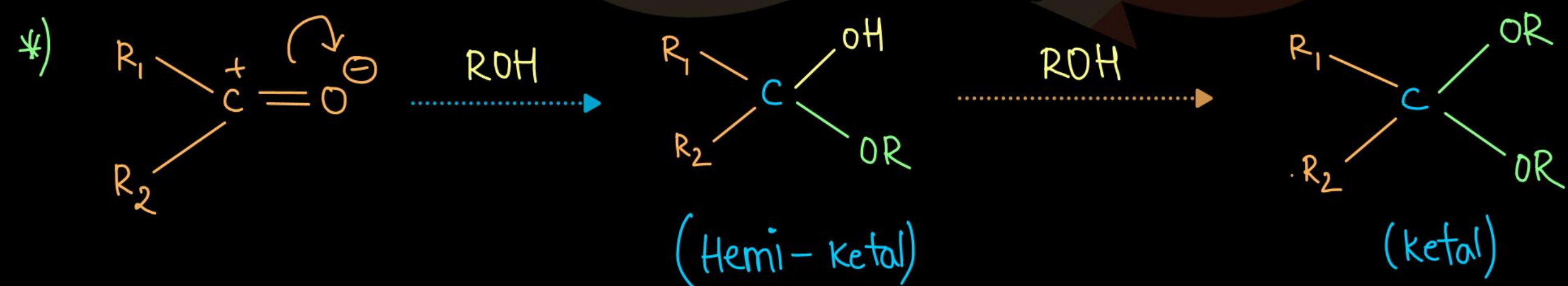
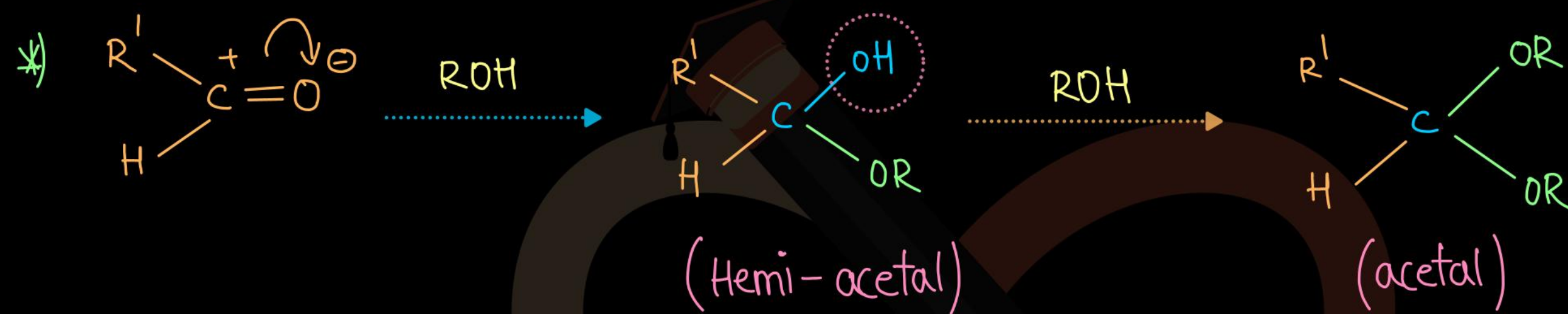
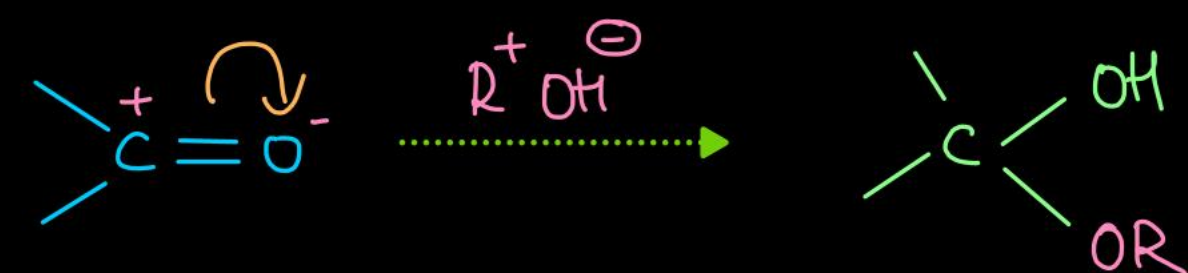
★ Note :-

⇒ Rxn is crowd sensitive. Only Ald and Methyl ketone react with NaHSO₃

Ex:-



3) Rxn with ROH :

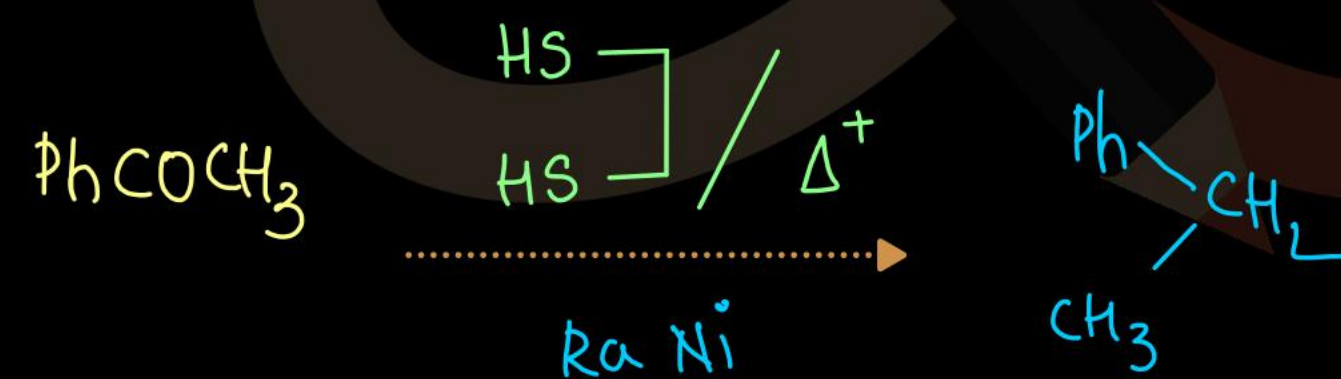


* Mozingo's reduction :-

Carbonyl $\longrightarrow$ alkane

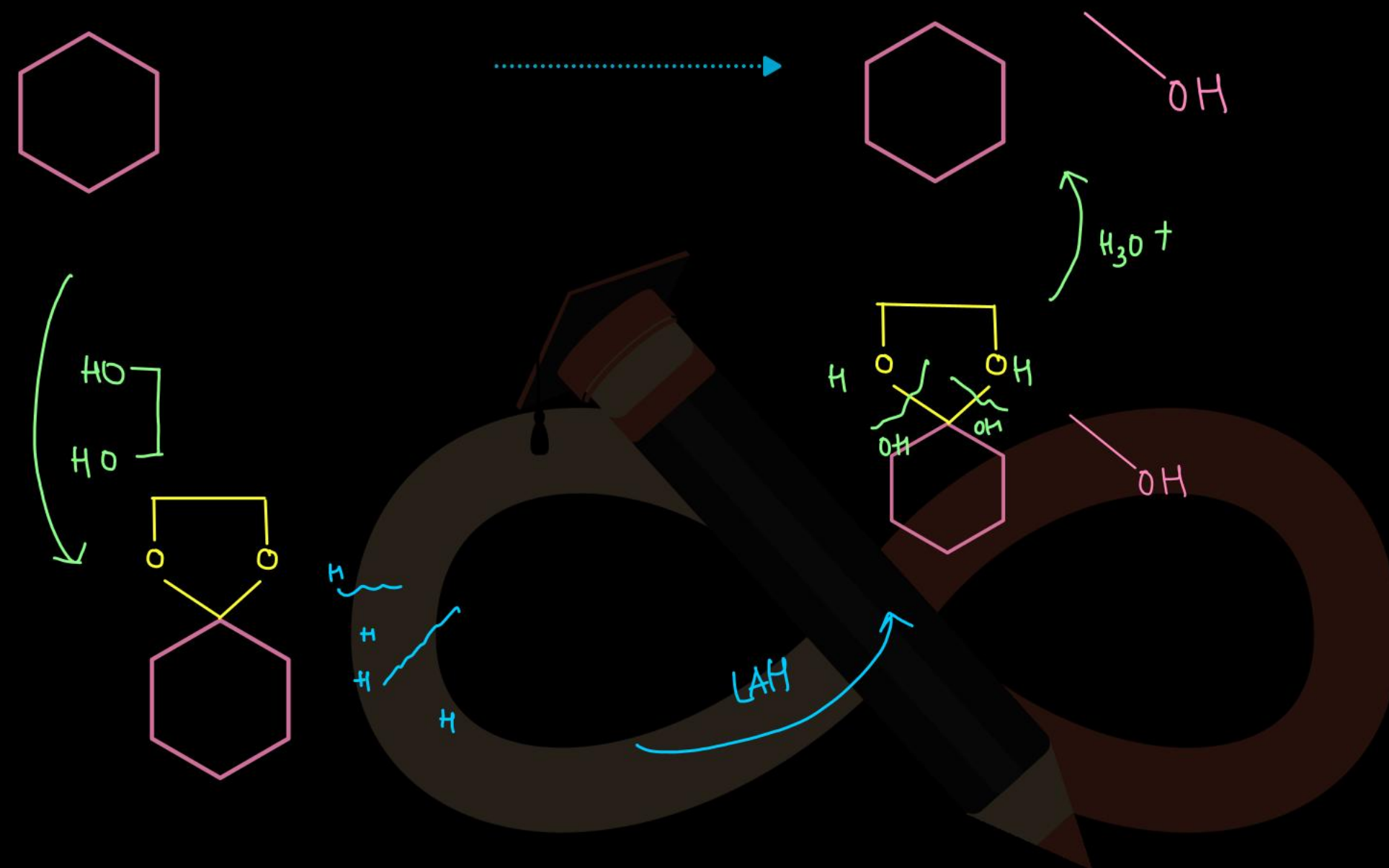


Ex^o:-

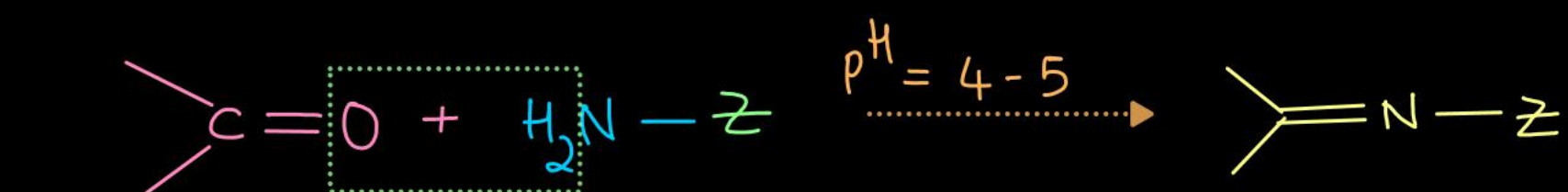


* Protection of Group :-

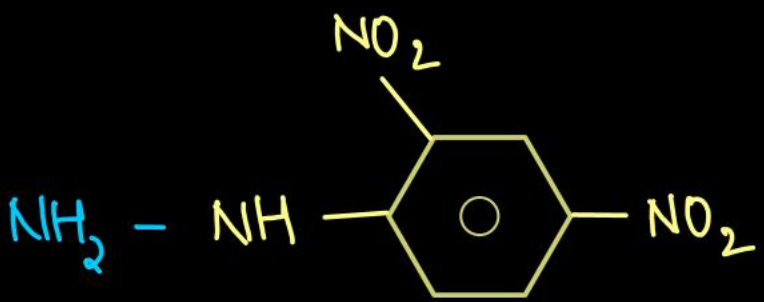
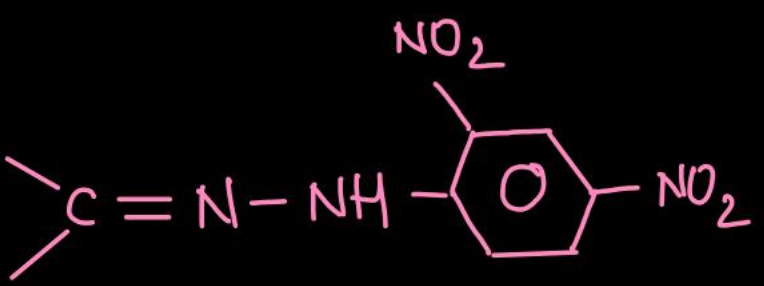
Convert :



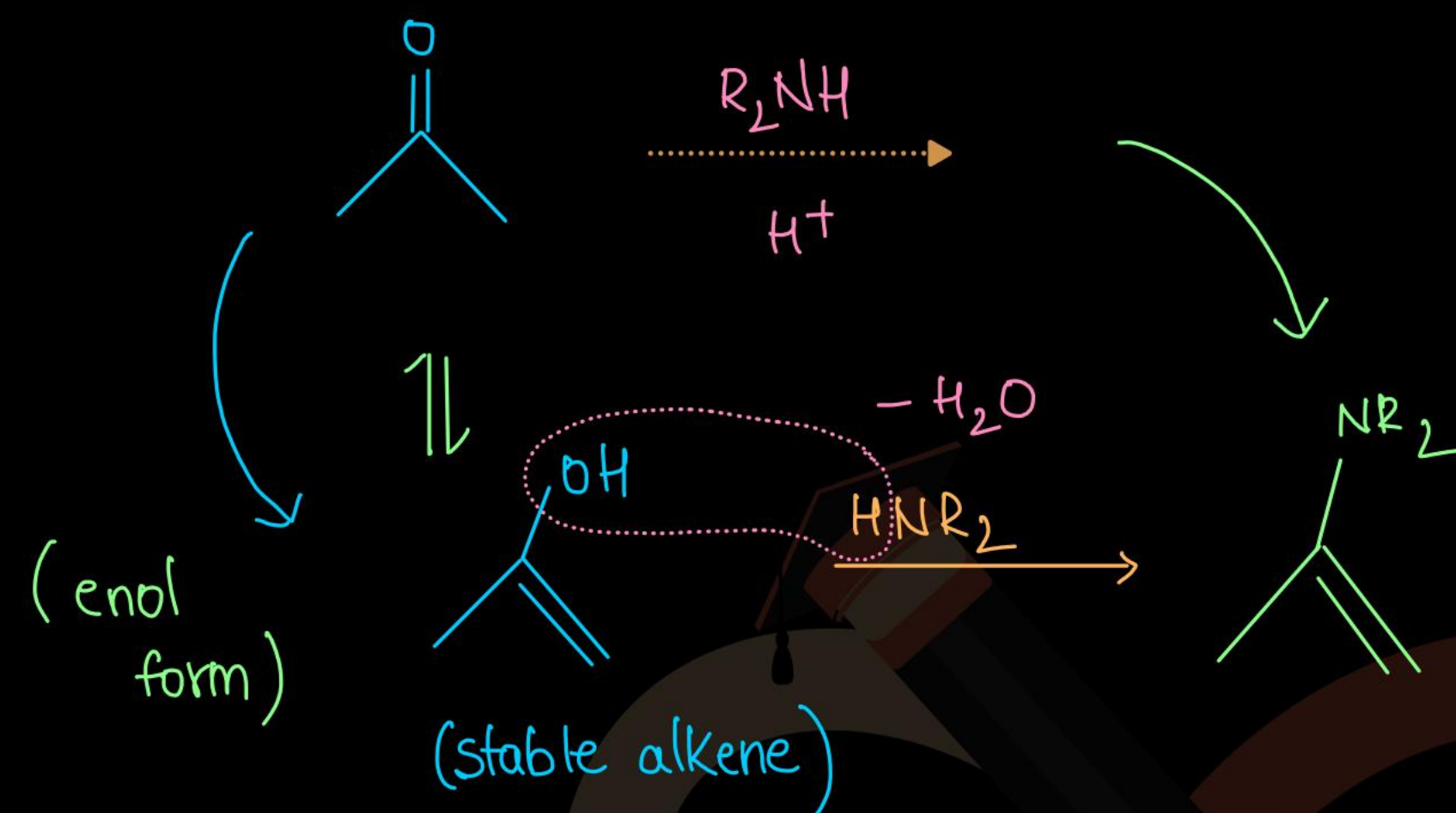
4) Rxn with NH₂-Z (Z = H, OH, ...)



* Slight acidic medium is required

<u>Z</u>	<u>Reagent</u>	<u>Reagent name</u>	<u>Product</u>	<u>Product Name</u>
H	NH ₃	ammonia	>C=N-H	imine
R	NH ₂ -R	1°-amine	>C=N-R	schiff's base
OH	NH ₂ -OH	hydroxyl amine	>C=N-OH	oxime
NH ₂	NH ₂ -NH ₂	hydrazine	>C=N-NH_2	Hydrazone
NHPh	NH ₂ -NHPh	phenyl hydrazine	>C=N-NHPh	Phenyl hydrazone
NHCONH ₂	NH ₂ -NHCONH ₂	Semi Carbazide	>C=N-NHCONH_2	Semi Carbazone
$\text{NH}_2 - \text{NH} - $ 		2,4- DNPH (Brady's reagent)		2,4 dinitro phenyl dyrozone (ROY) ppt

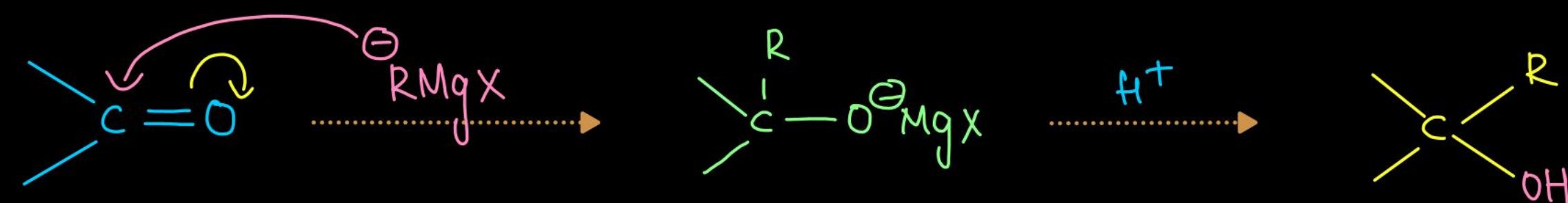
* Stork enamine rxn :



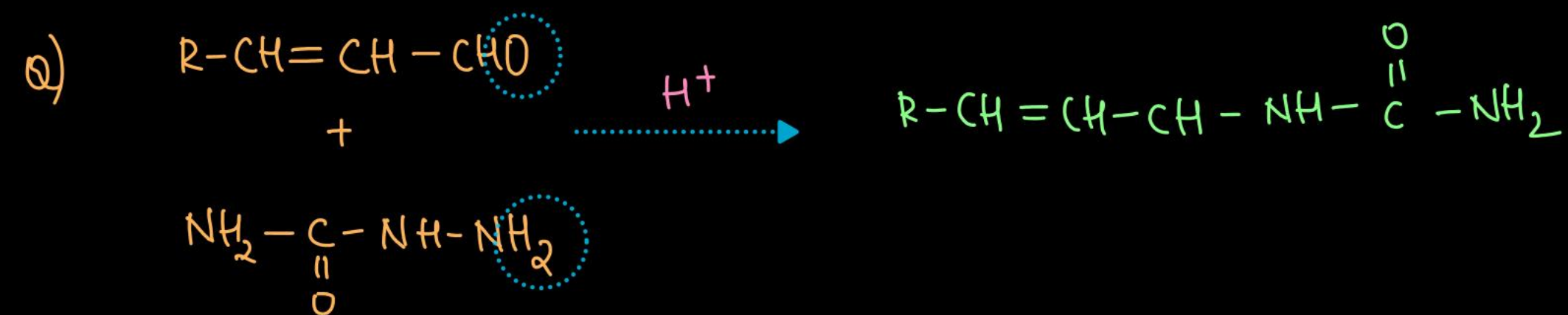
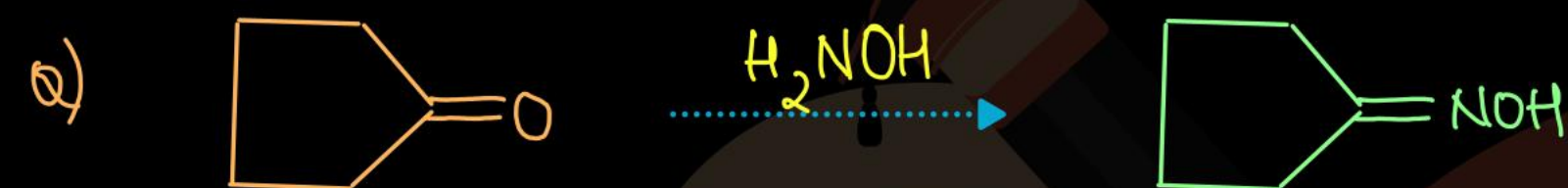
Ex^o

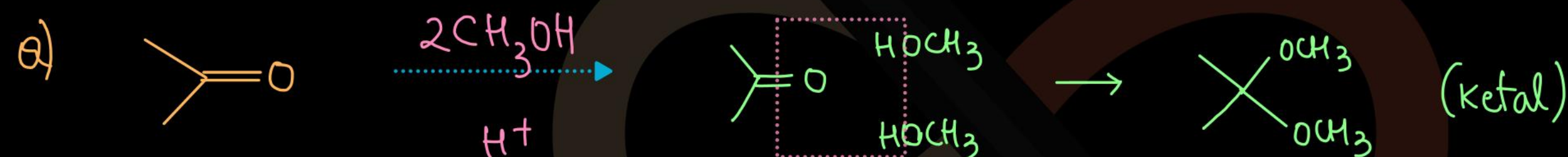
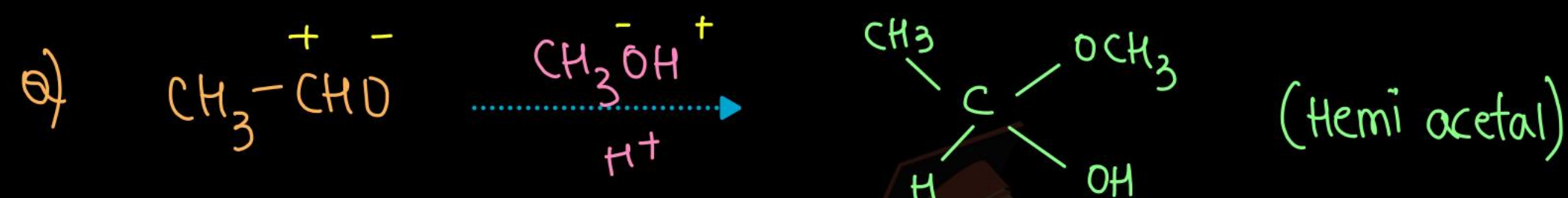


5) Rxn with GR :



Practice :





Properties :-

II) Reduction Reaction :

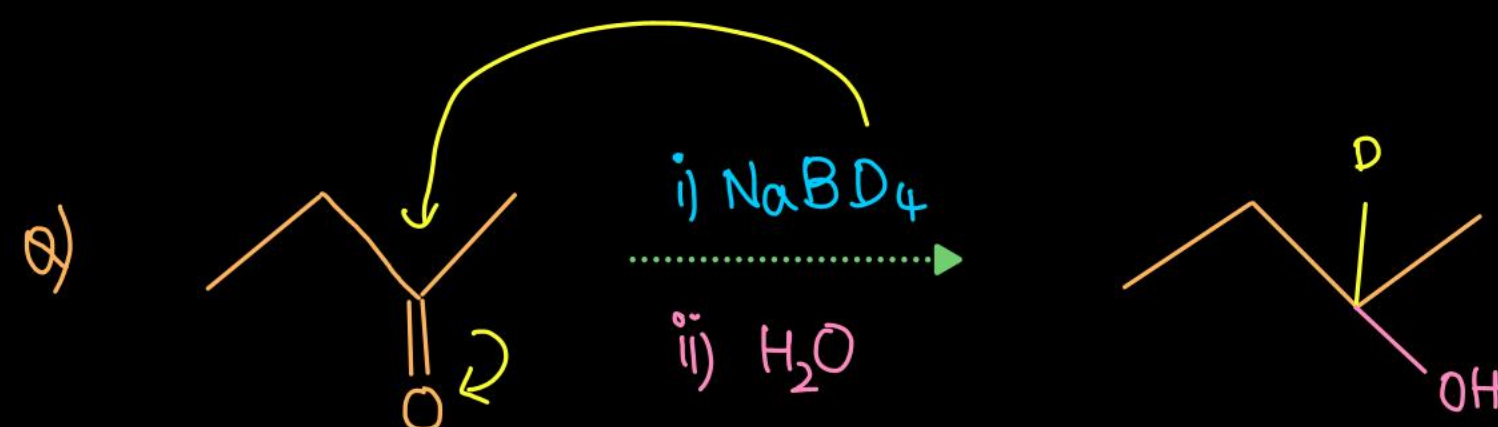
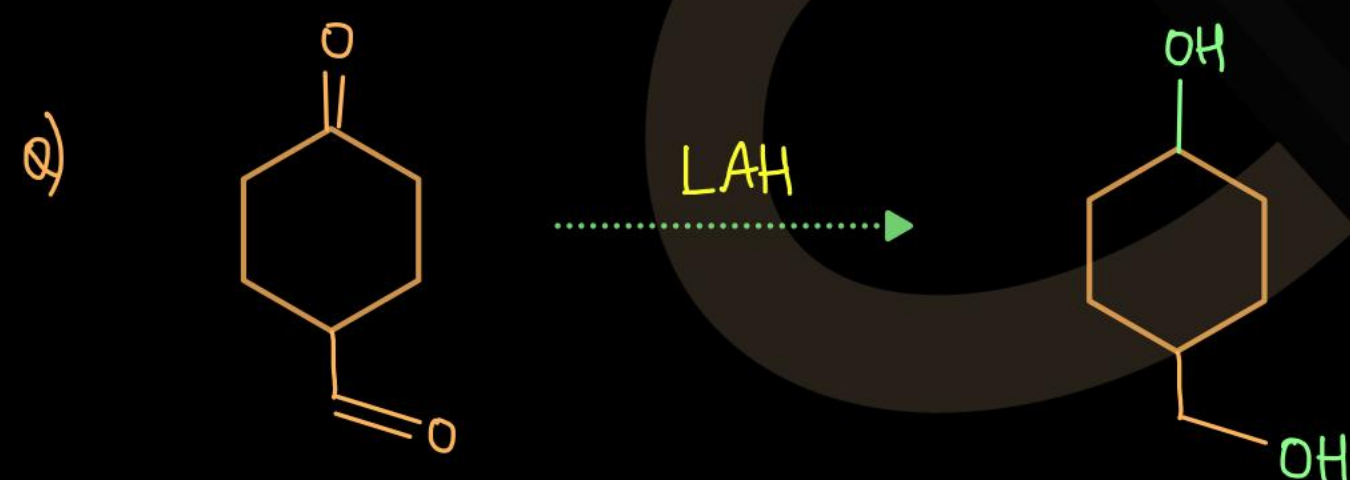
1) Carbonyl Comp $\longrightarrow$ Alcohol



1) LAH

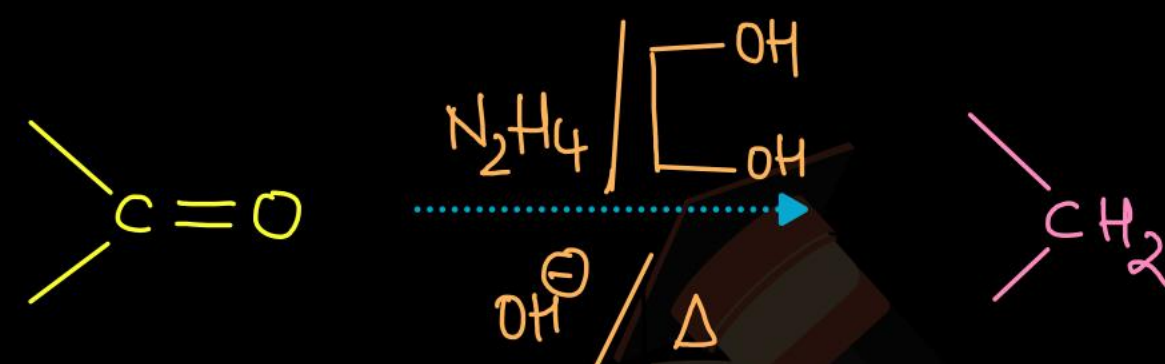
2) SBH

3) $\text{H}_2 / \text{Ni}, \text{Pt}, \text{Pd}$

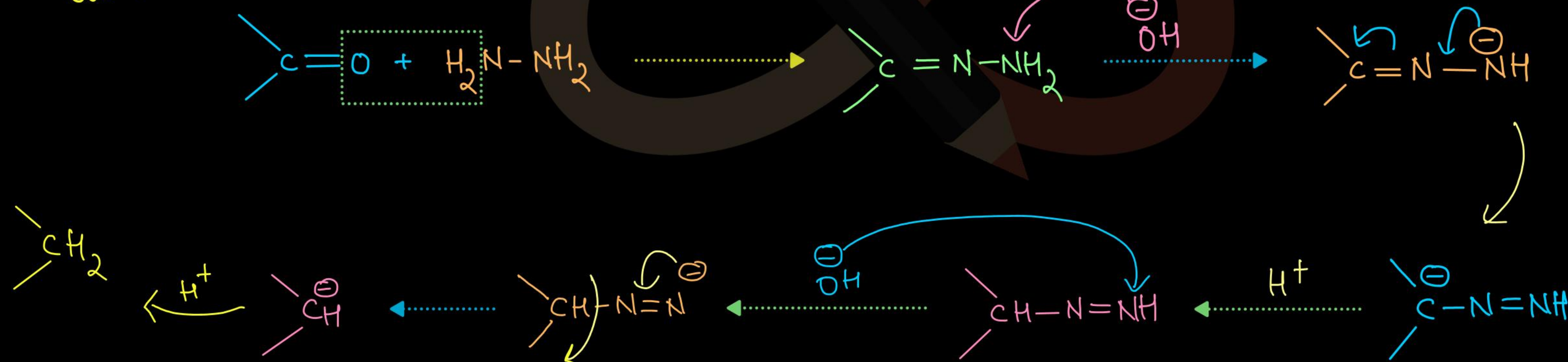


2) Carbonyl $\longrightarrow$ Alkane

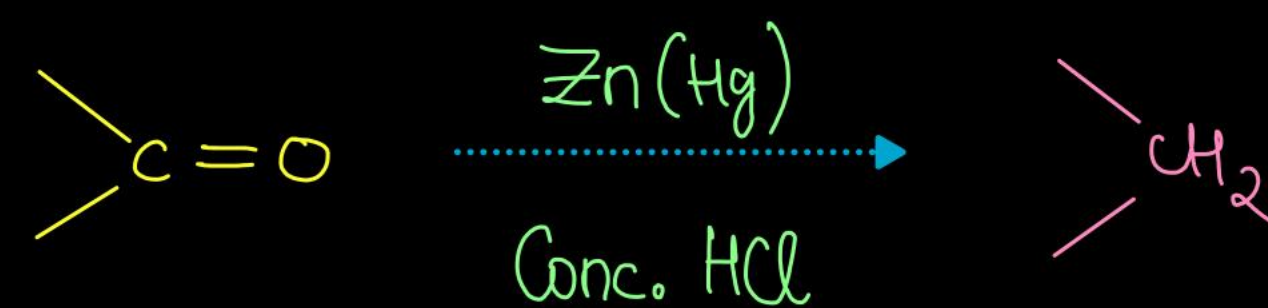
i) Wolf Kishner reduction :



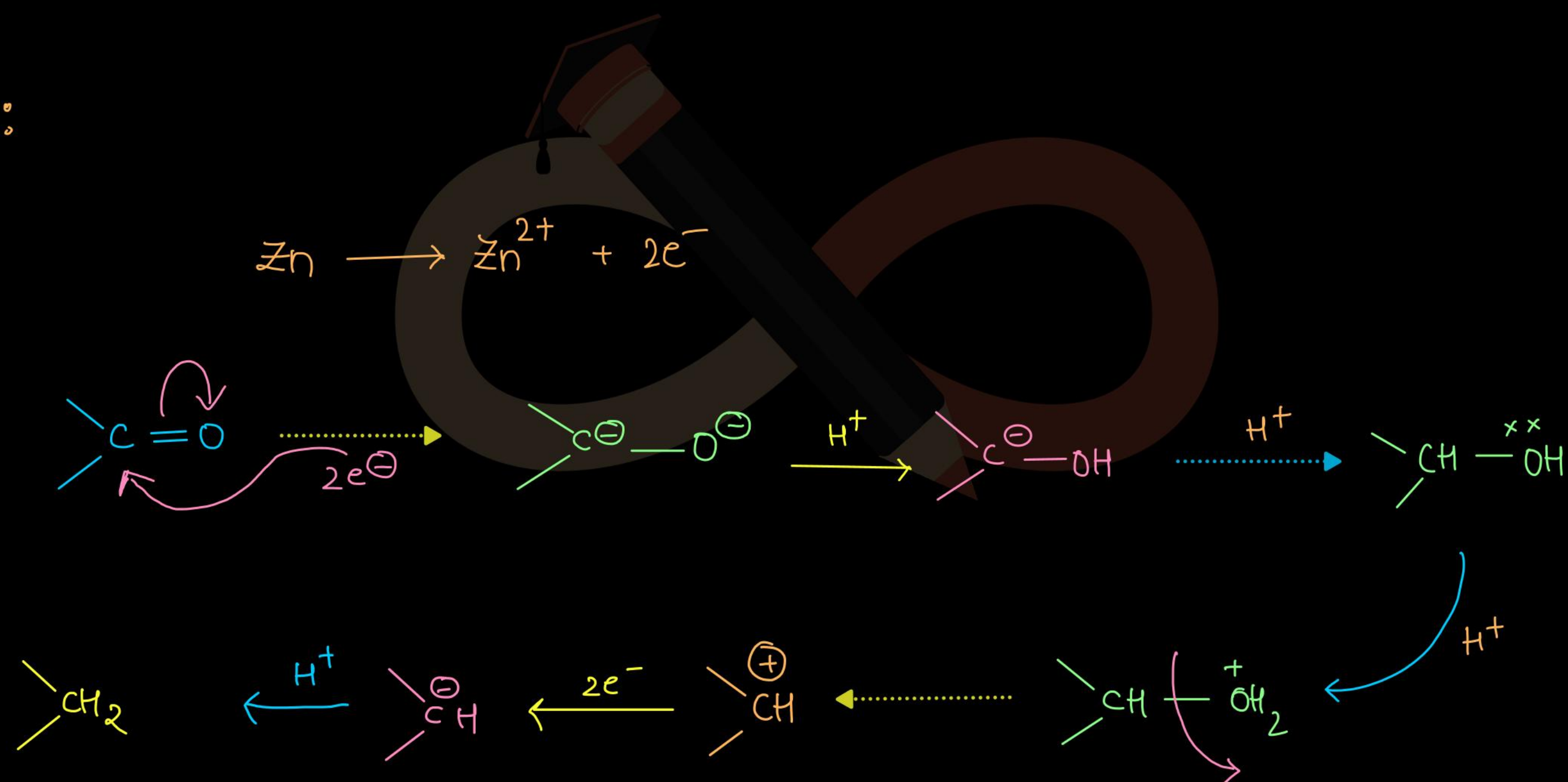
Mech:-



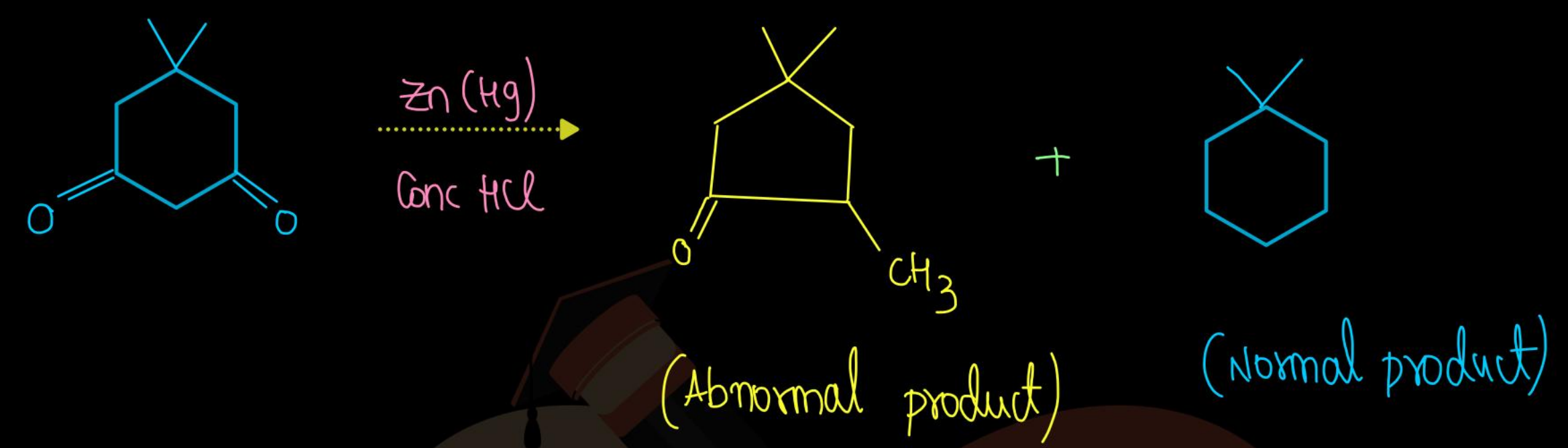
ii) Clemmensen's reduction :



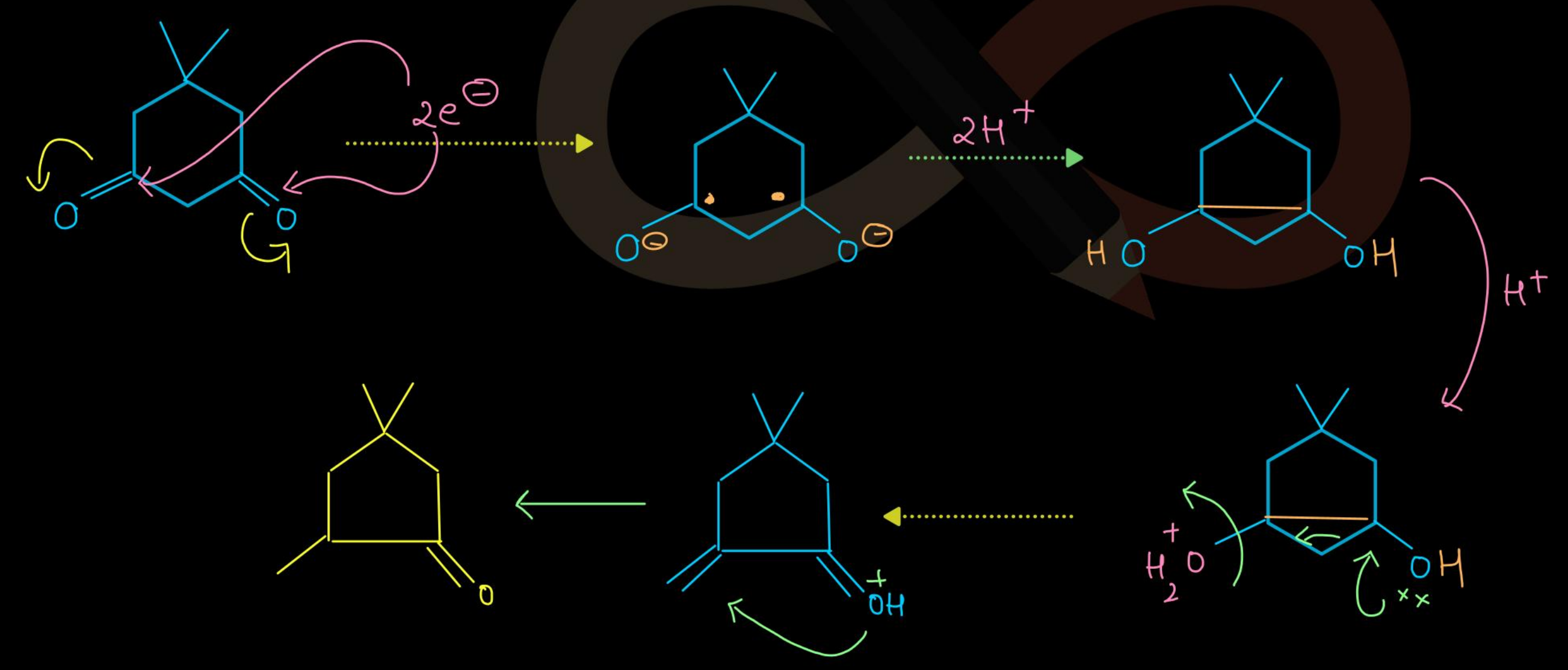
Mech :



★. Reduction of dicarboxyl compound.



Mech



iii) HI/red P :-

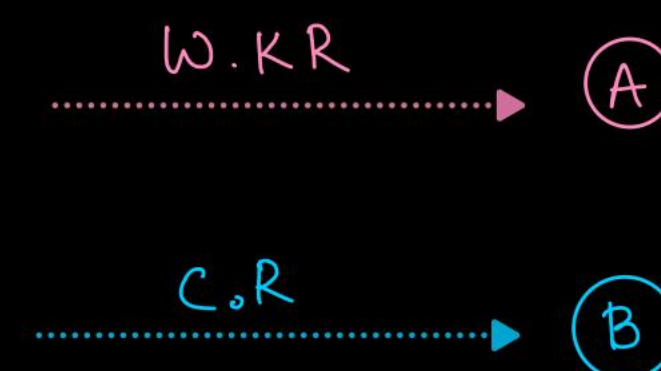
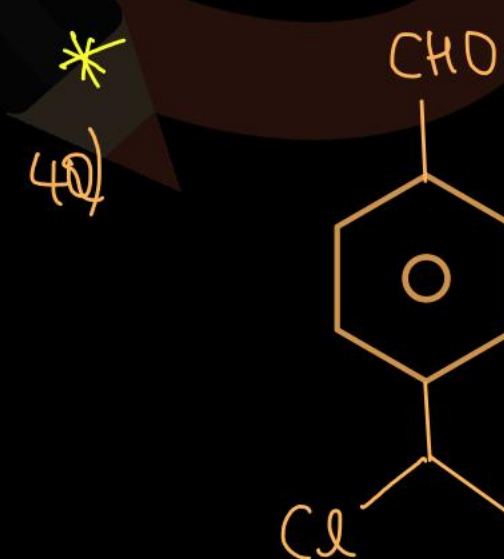
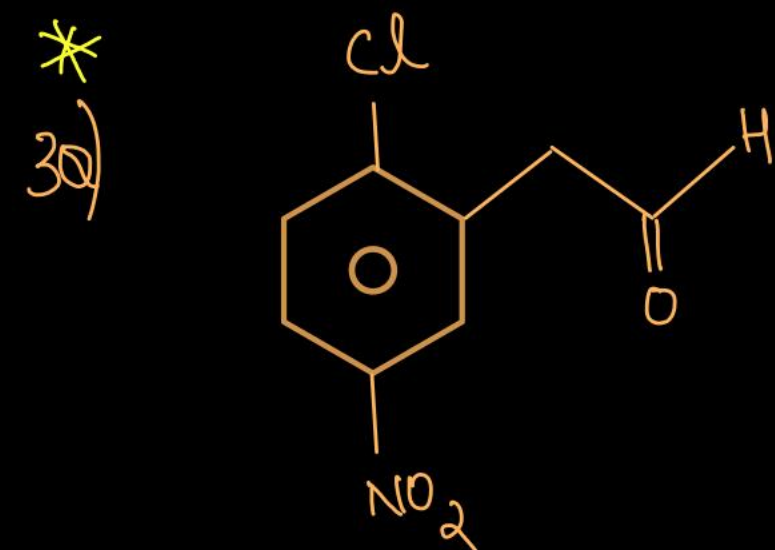
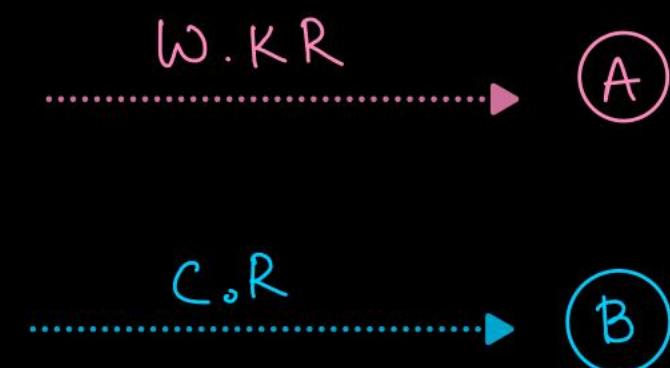
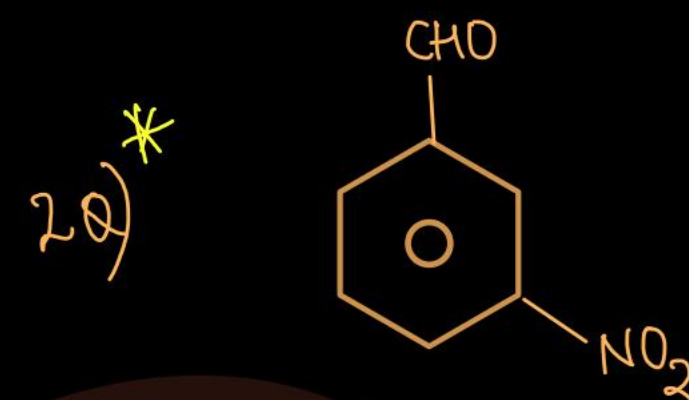
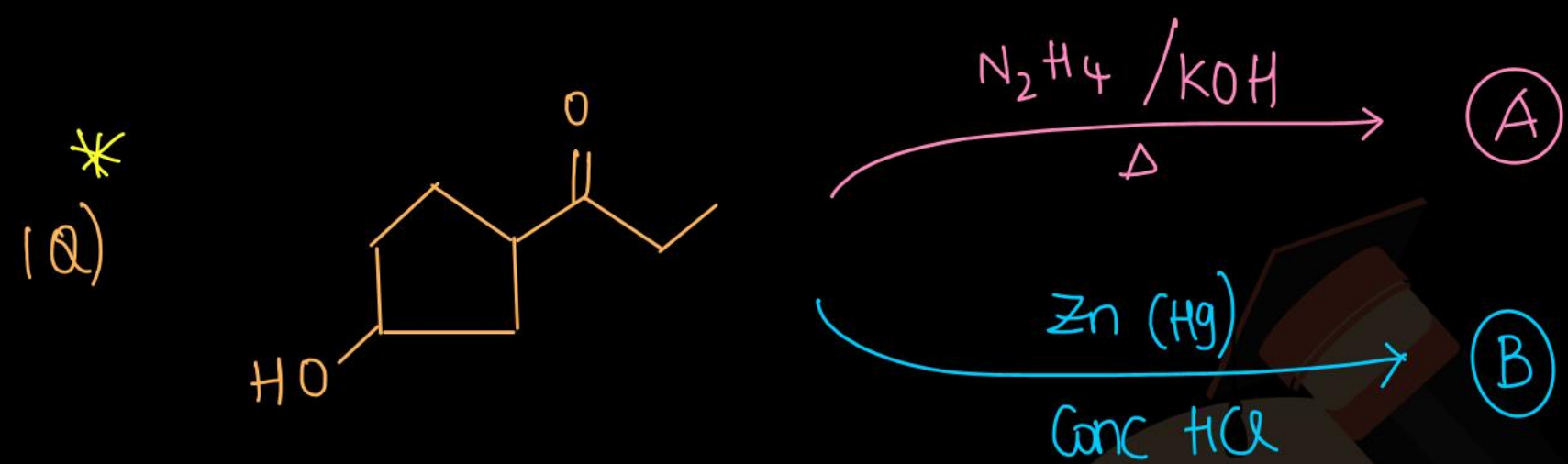


Reduces :

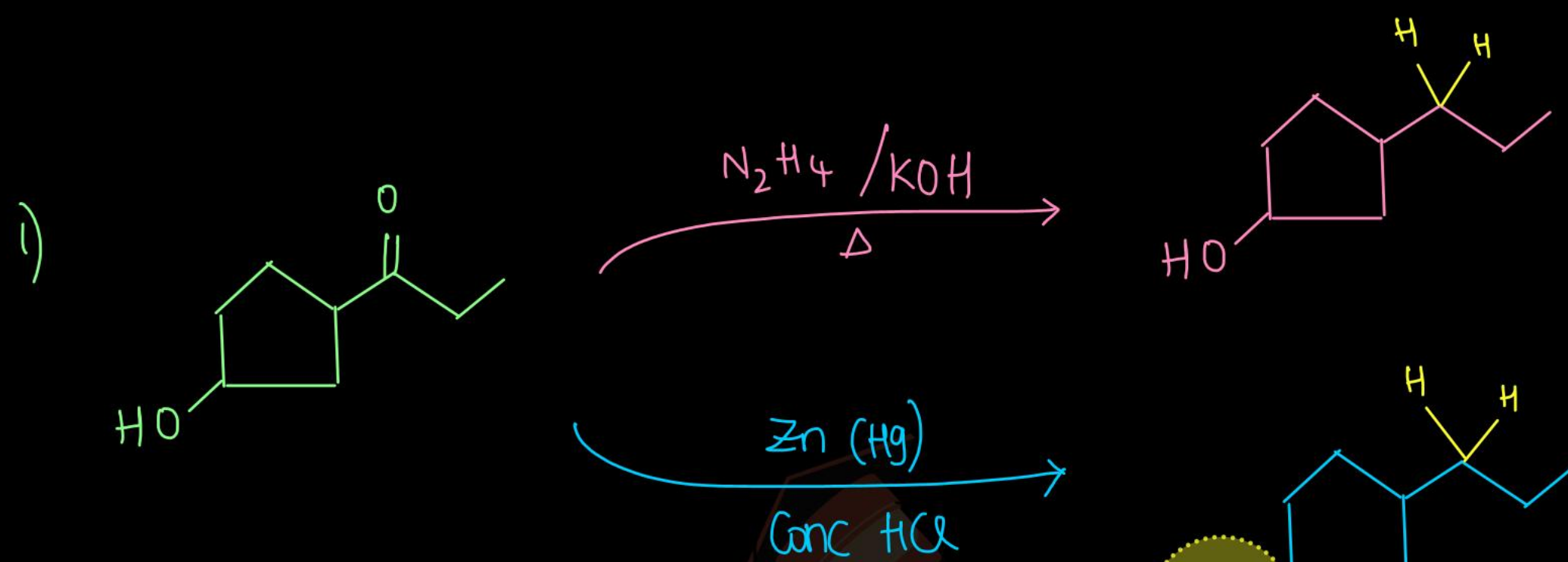
- 1) Carbonyls ✓
- 2) Alcohols ✓
- 3) Acids ✓
- 4) Acid derivatives ✓



Imp: CR v/s WKR :-

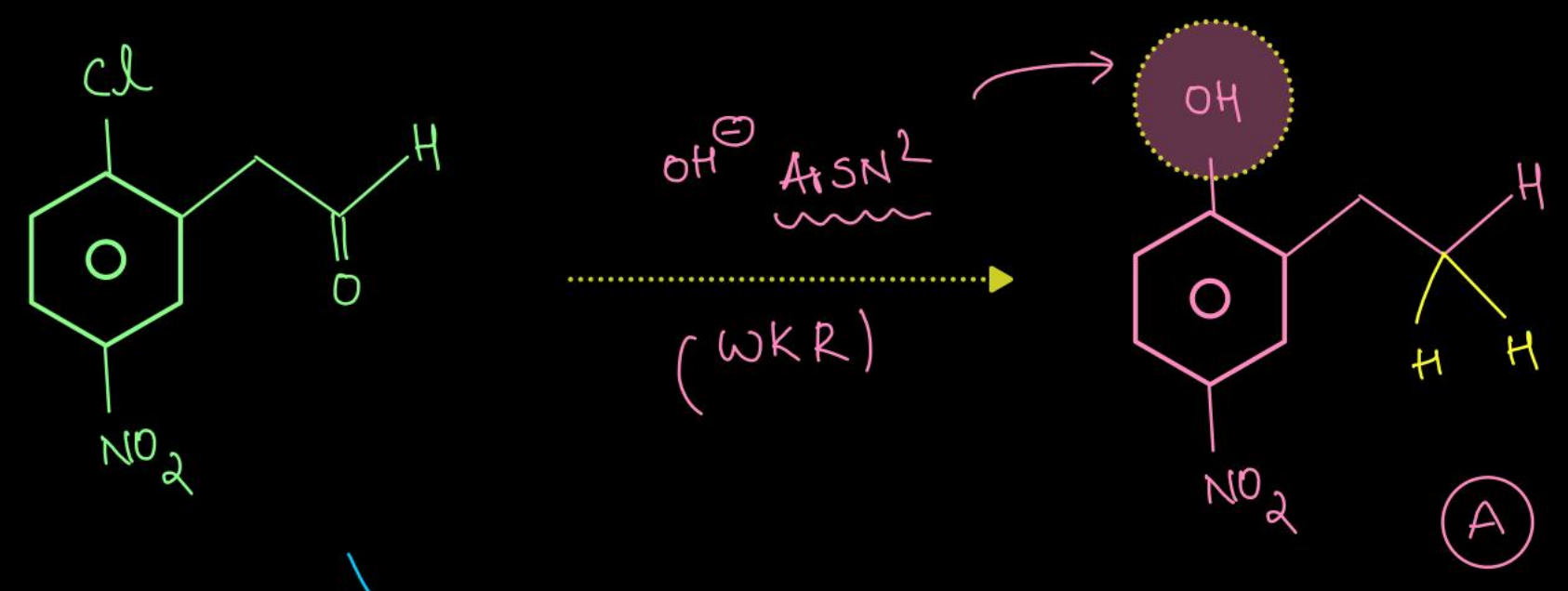


Sol:-

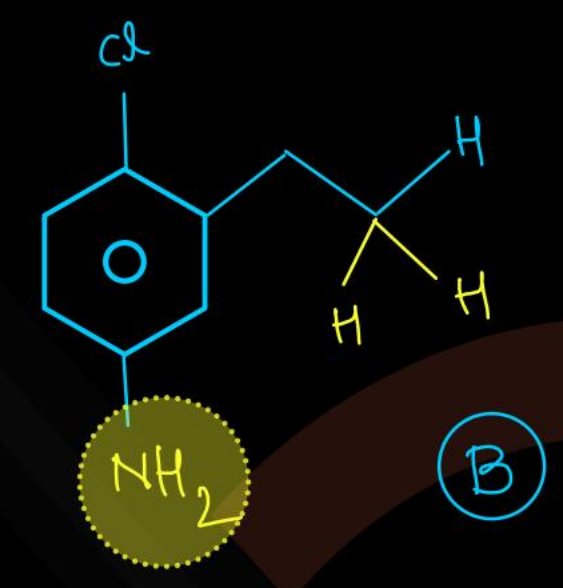


$\left\{ \begin{array}{l} \text{Zn(H}^+) : \text{Nitrobenzene} \\ \text{Aniline} \end{array} \right\}$

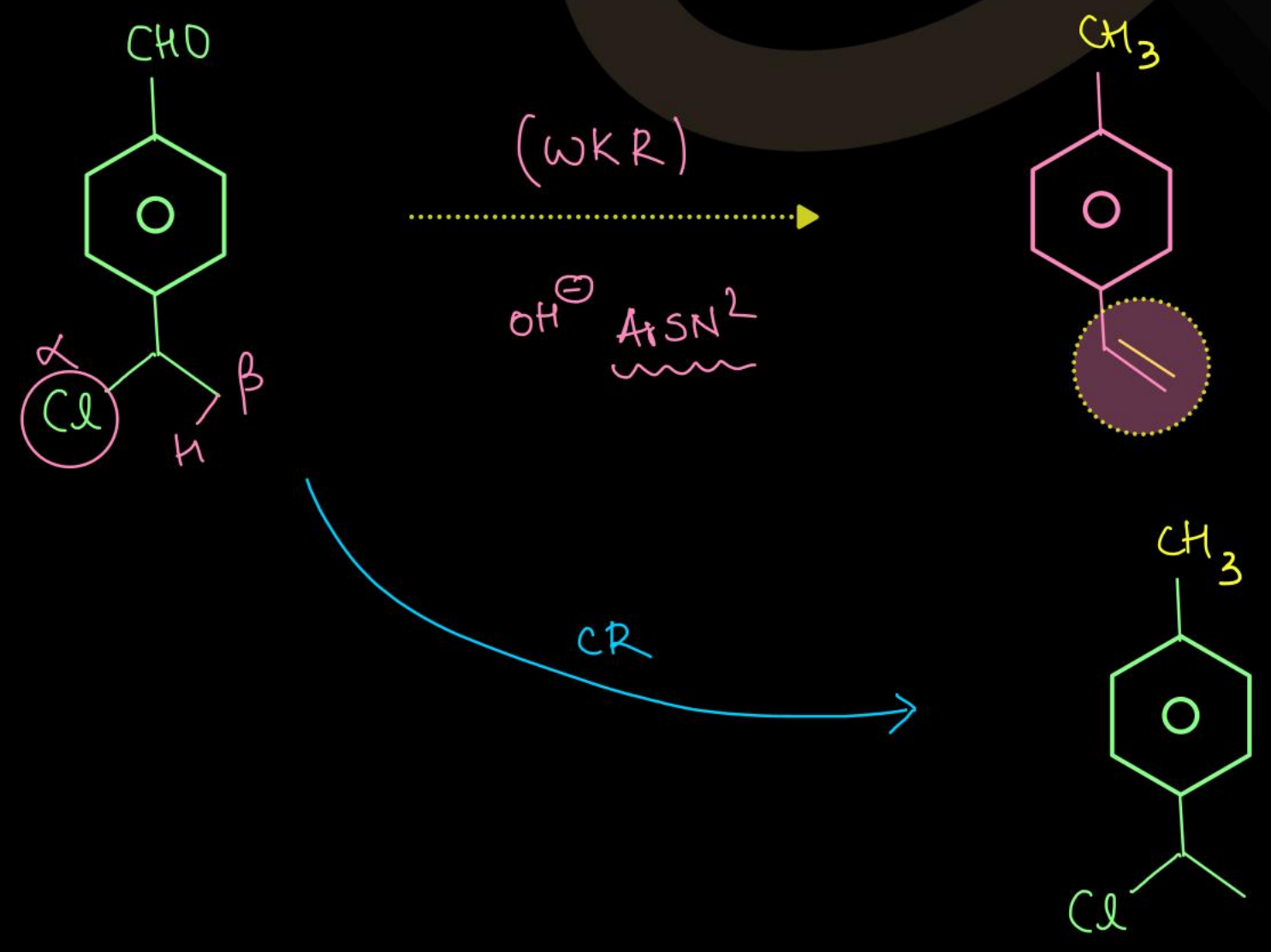
*
30)



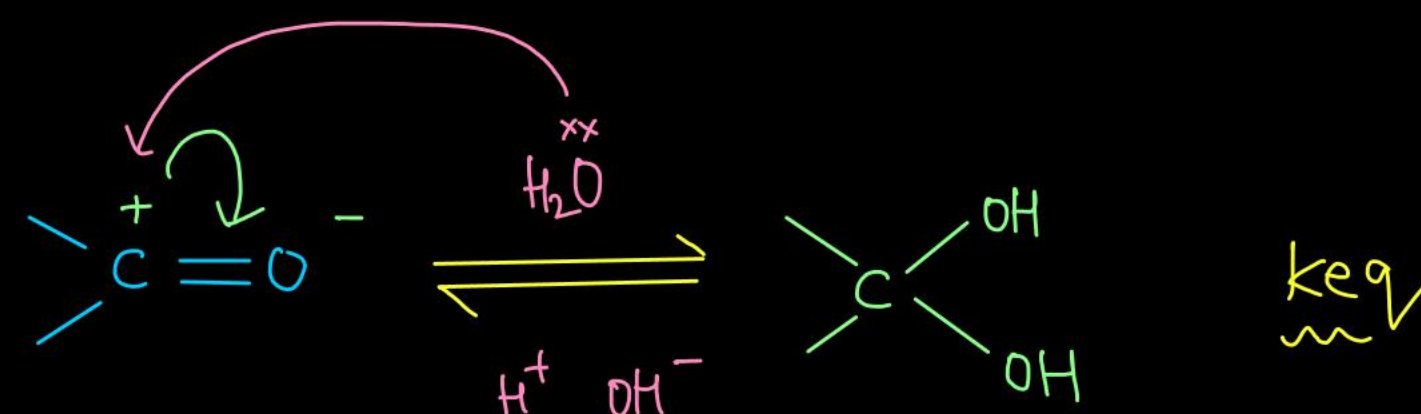
CR



*
40)



III) Stability of Gem diol :-



$\text{Keq} \uparrow$, fw Rxn $\Rightarrow$ Gem diol stable

$\text{Keq} \downarrow$, Bw Rxn $\Rightarrow$ Gem diol unstable

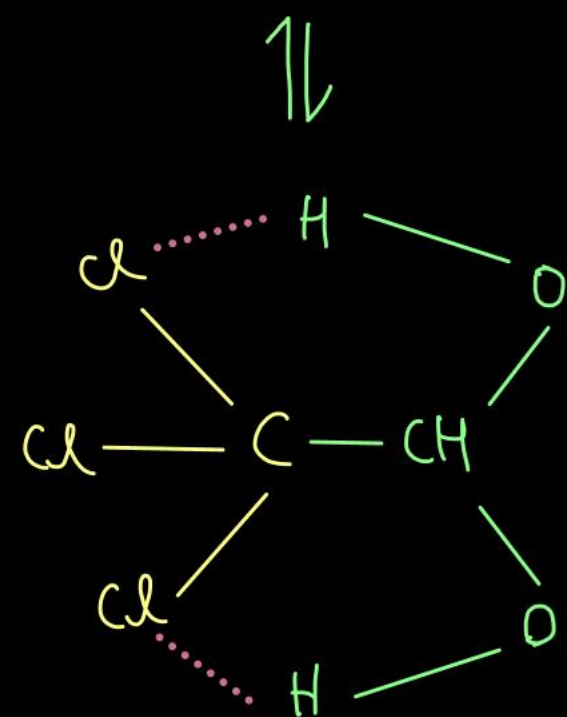
Imp points :-

$$1) \text{ Stability} \propto \frac{1}{\text{EDG}} \propto \text{EWG}$$

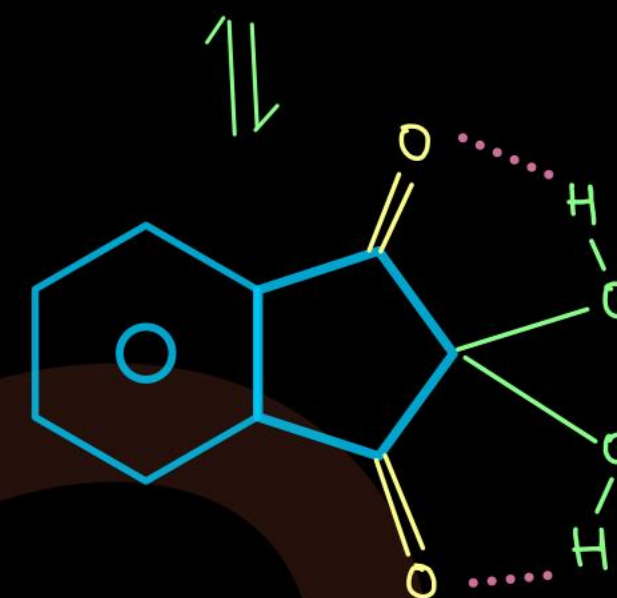
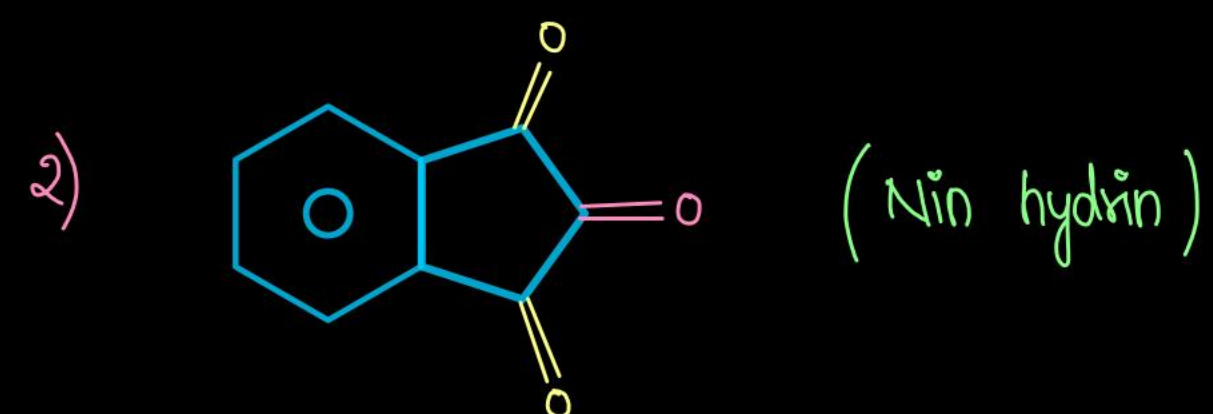
$$\propto \frac{1}{\text{Bulkyness}}$$

2) Reactivity towards H_2O (Al > ketone)

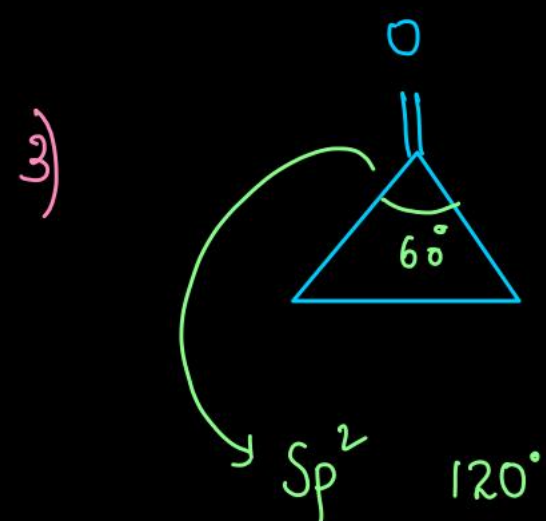
Examples :-



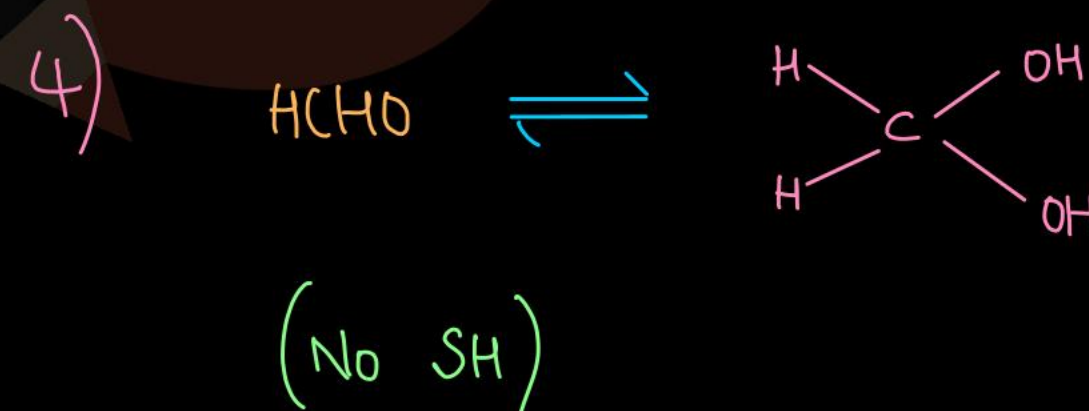
Intramolecular
H-bonding



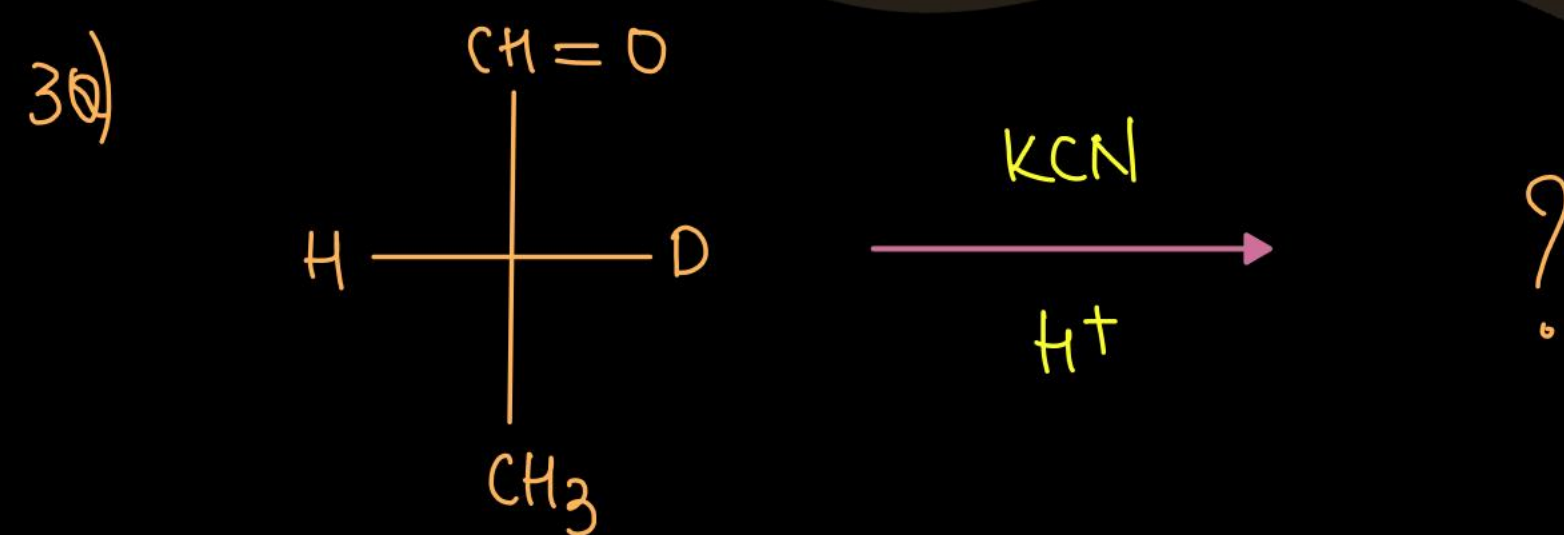
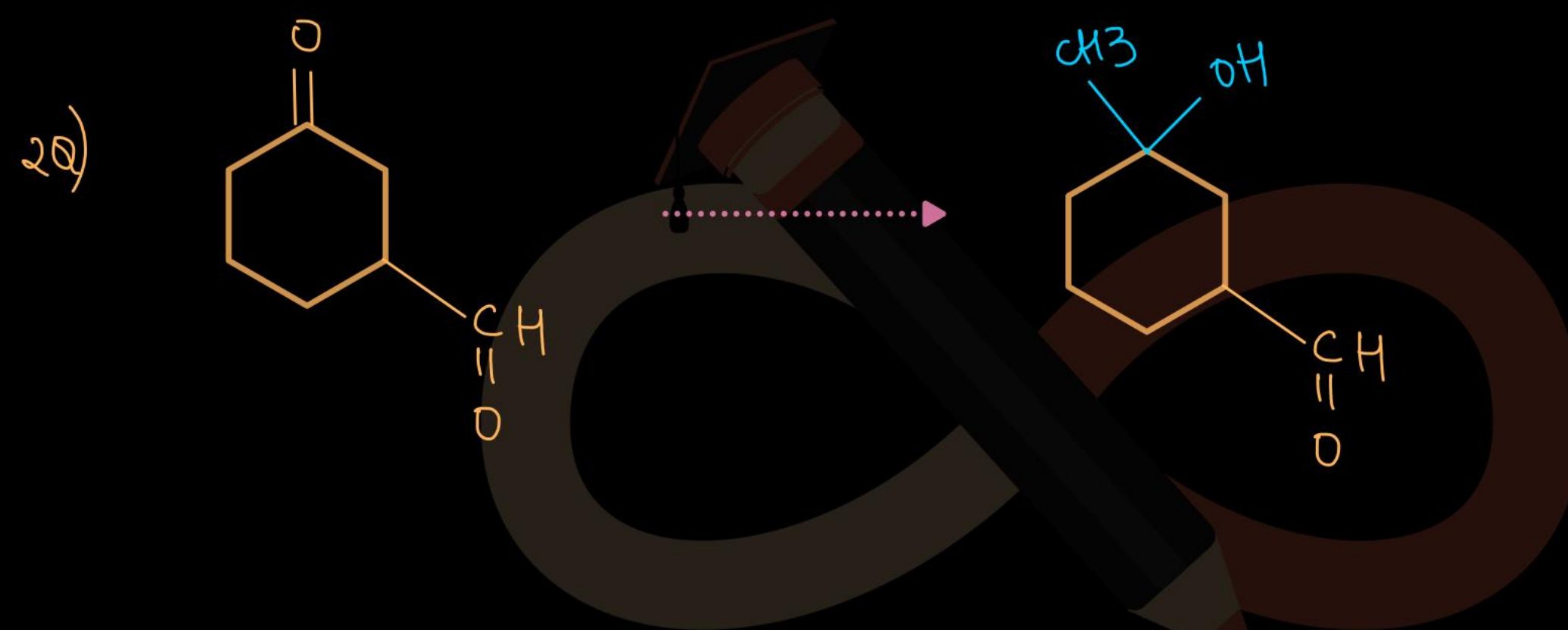
Intramolecular
H-bonding



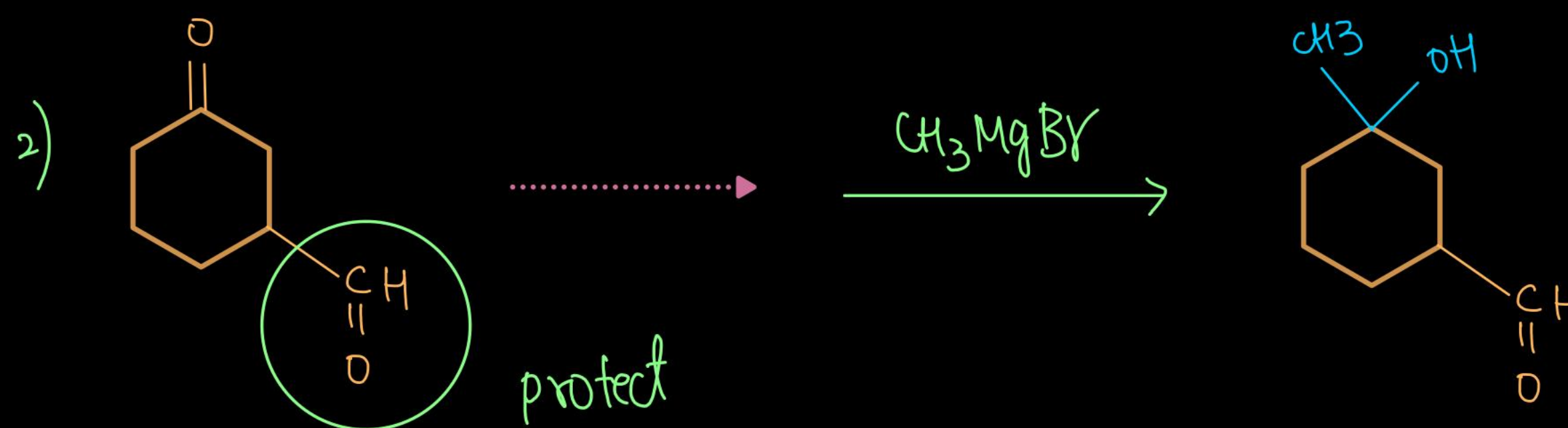
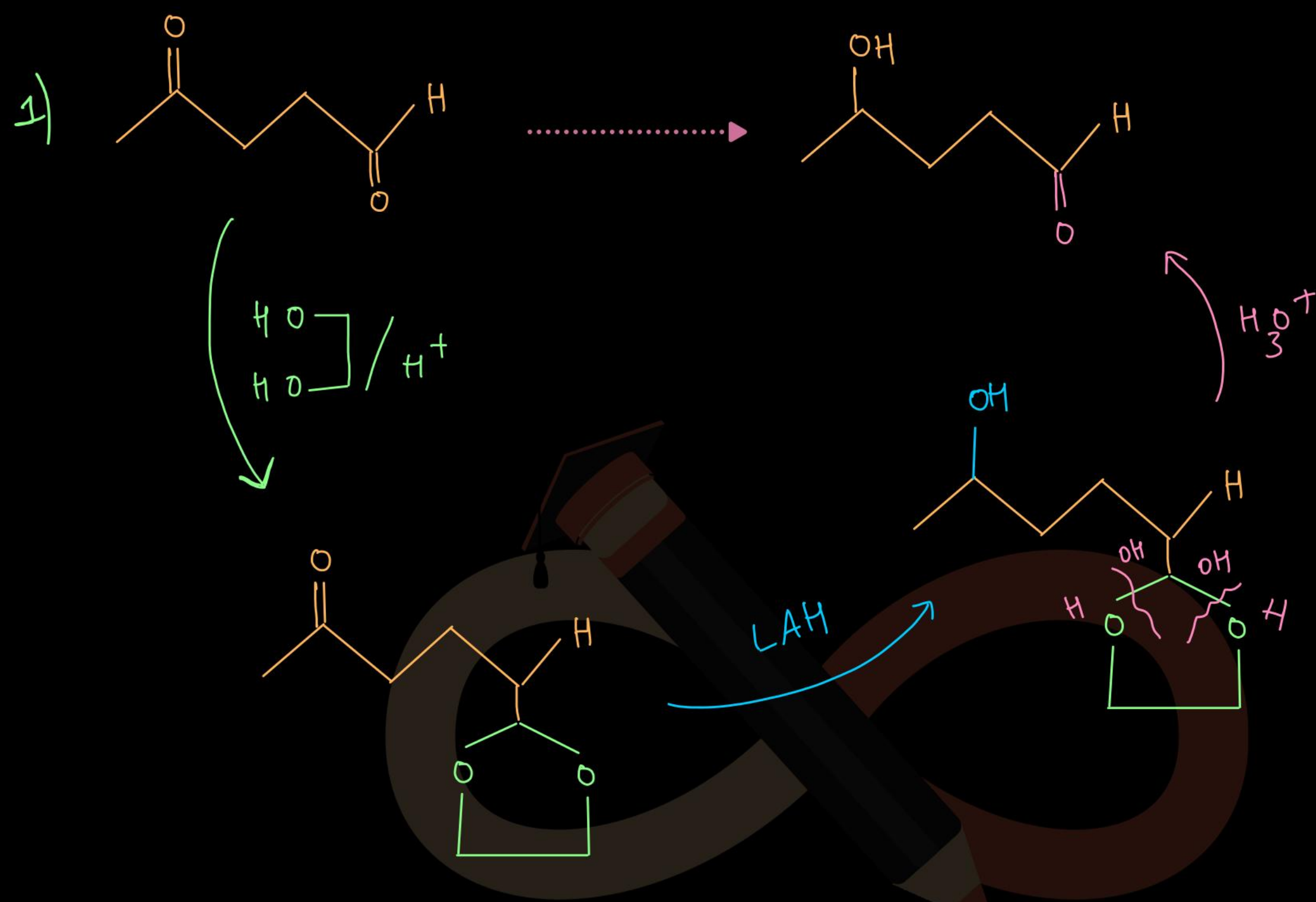
due to reduction in ring strain.

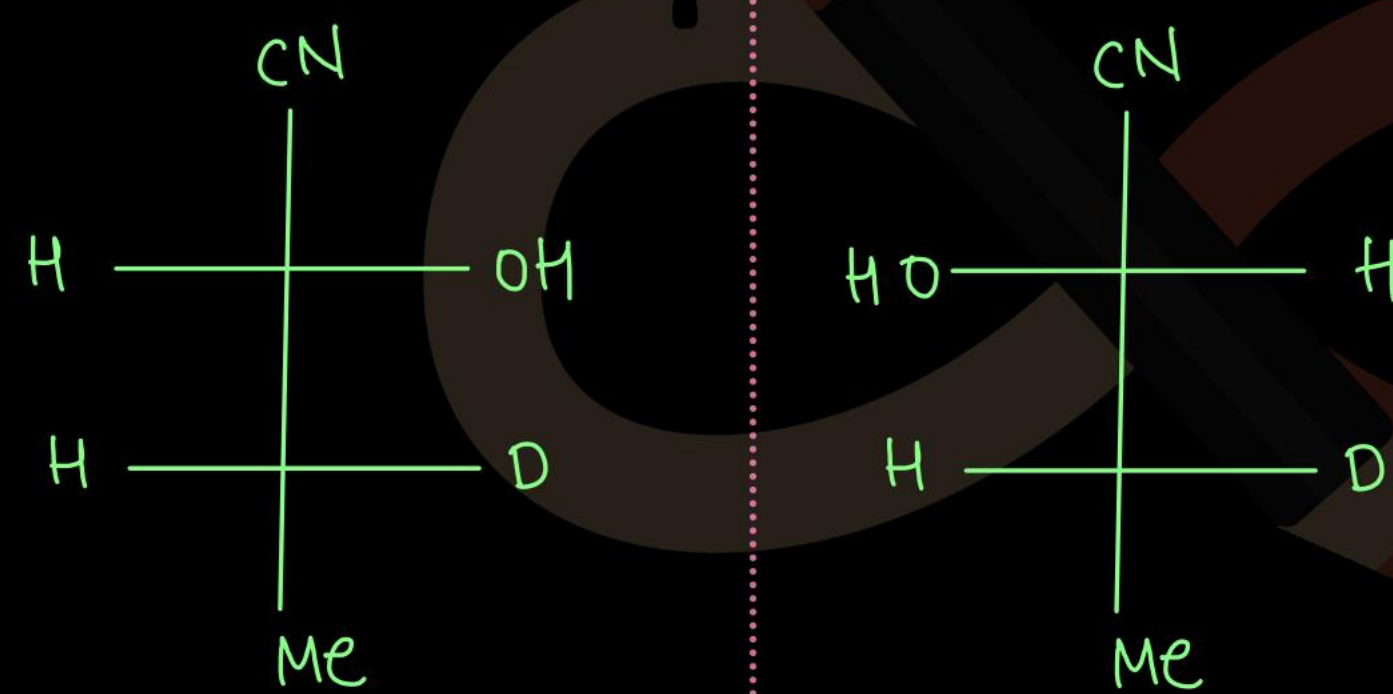
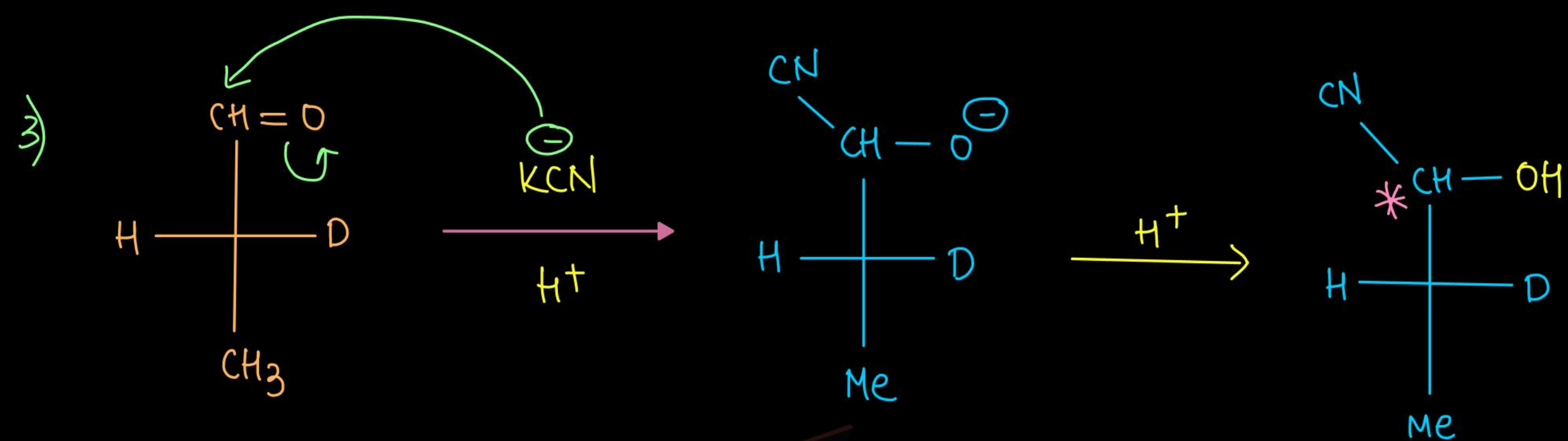


Practice :



Solⁿ:





Diastereomers

