

Carbonyl compounds :

Properties -2 :

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I) 1) Aldol Condensation

→ Carbonyls having α -H ; $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$
 α -C

→ Reagent :- dil Base like $\left\{ \text{NaOH}, \text{KOH}, \text{Ba(OH)}_2 \right\}$
or
acidic med H^+ $\left\{ \text{Na}_2\text{CO}_3, \text{K}_2\text{CO}_3 \right\}$

* Base
catalysed

:- Aldehyde

enolate

$\xrightarrow{\Delta}$
(E, Cb)

α - β unsaturated

* Acid
Catalysed

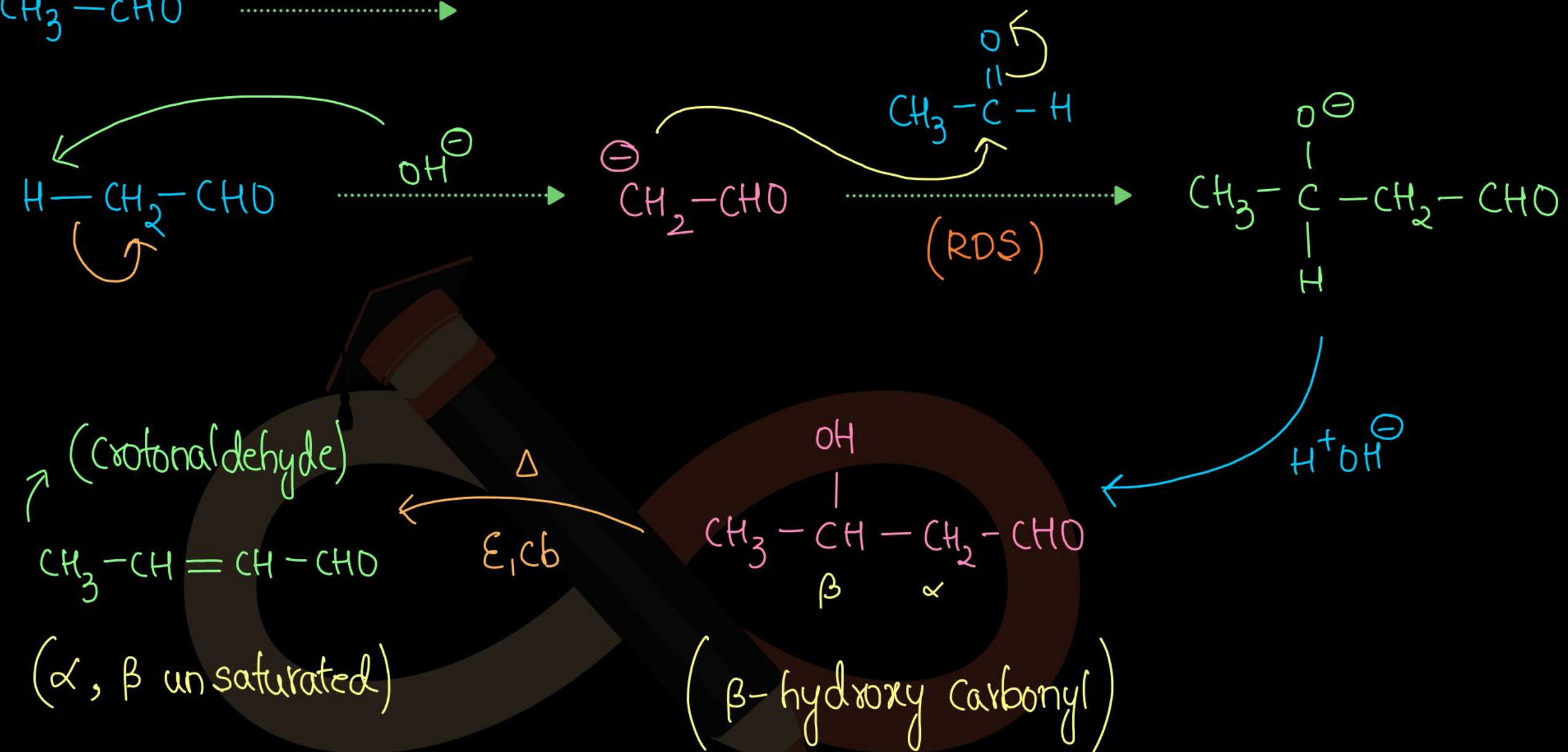
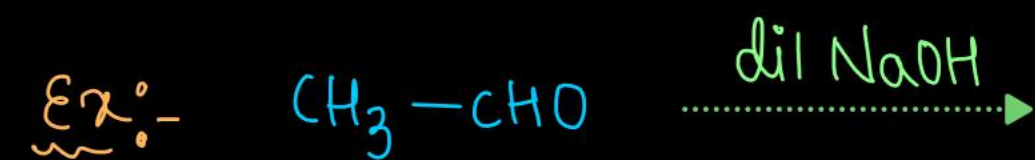
:- Aldehyde

enol

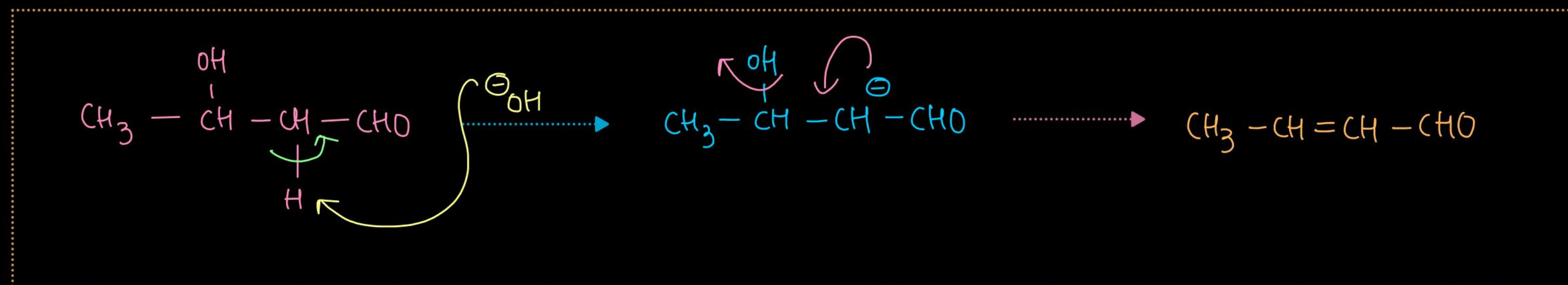
$\xrightarrow{\Delta}$
(E₁)

α - β unsaturated

i) Base catalysed mech:-



E,cb:-

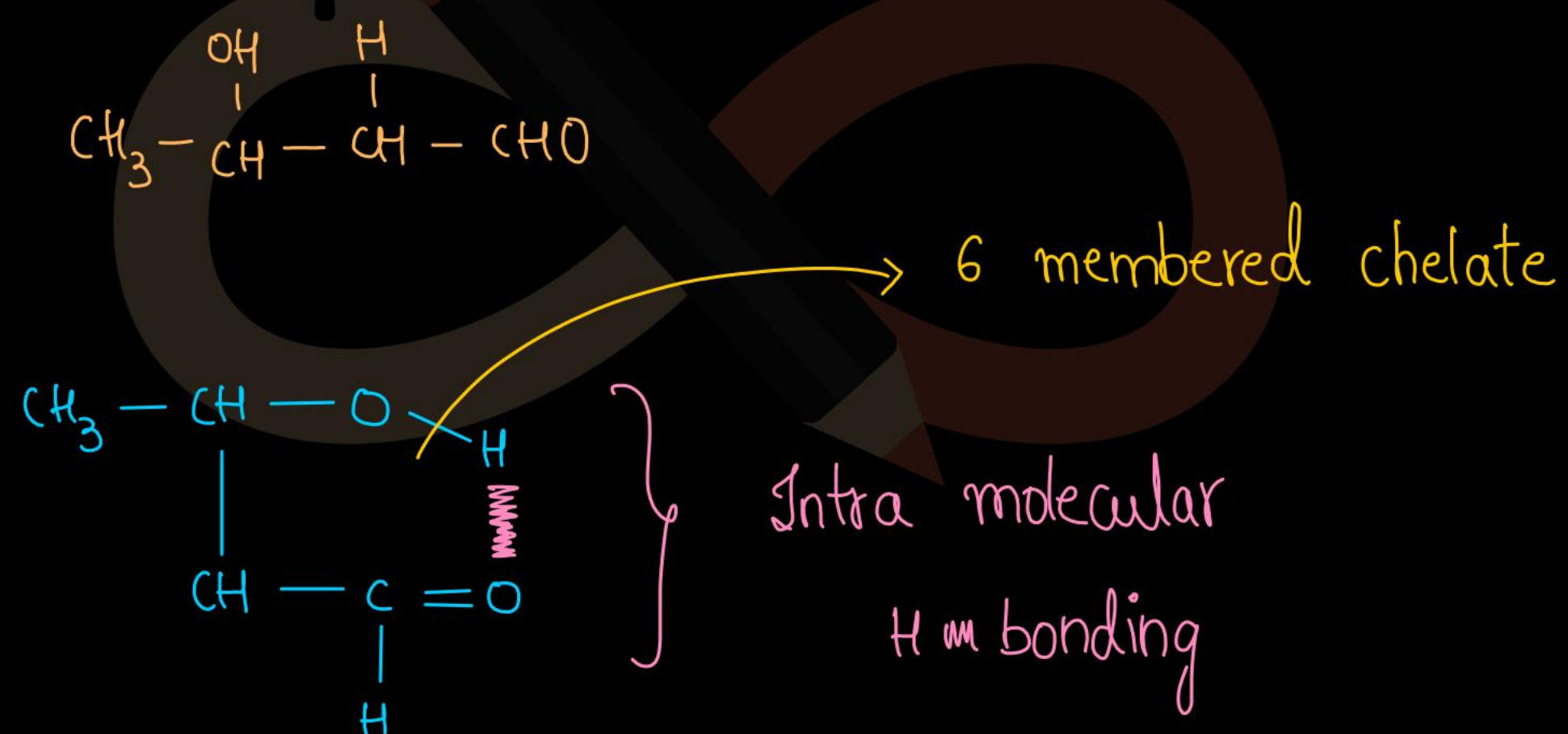


* Imp points :-

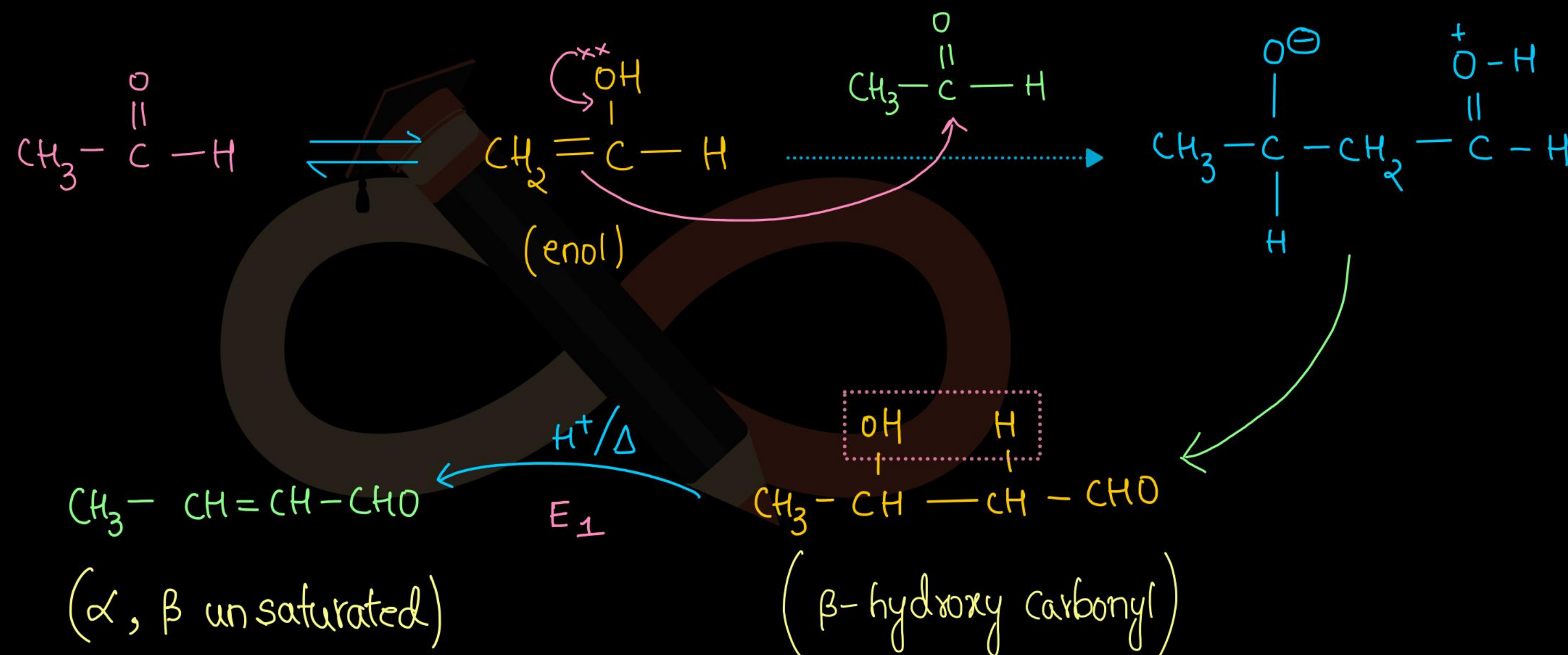
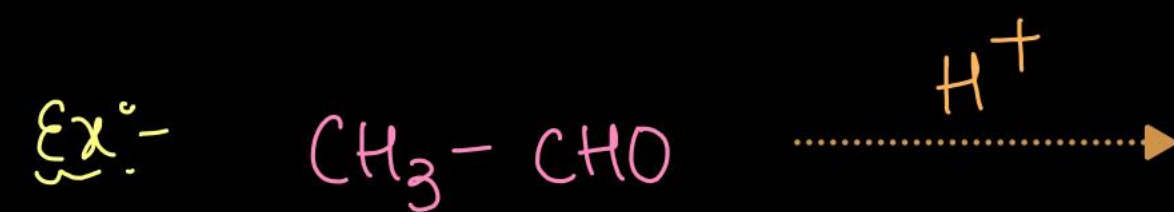
1) Carbanion is formed

* 2) Attack of Nucleophile ($C^\ominus$) is RDS $\propto \frac{1}{SH}$

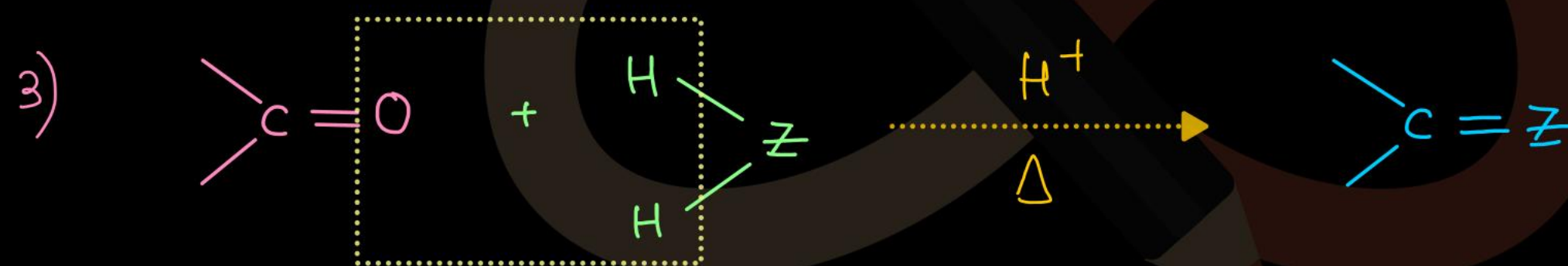
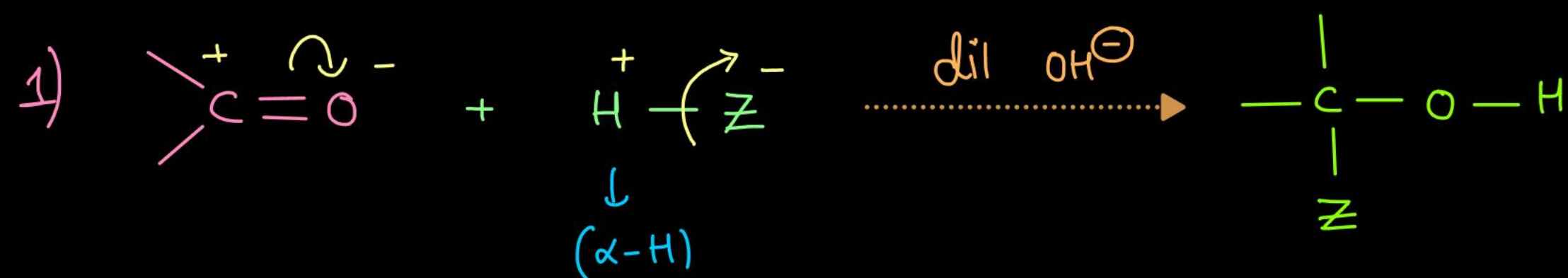
3) β -hydroxy aldehyde (aldol) is more stable due to Intra molecular H mm Bonding



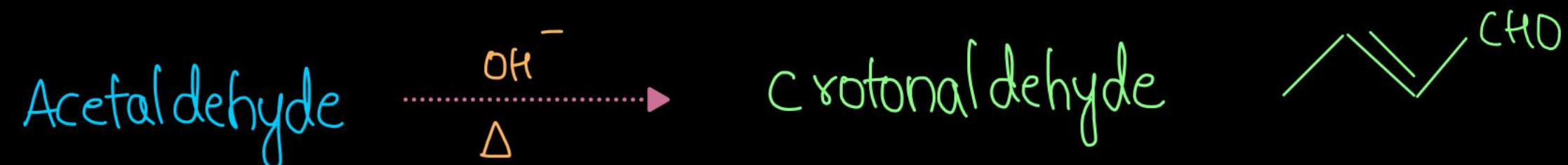
ii) Acid catalysed mech :-



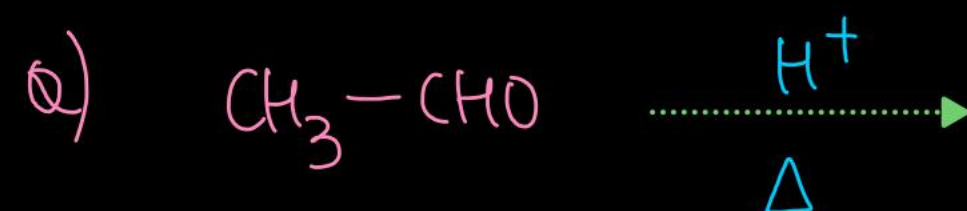
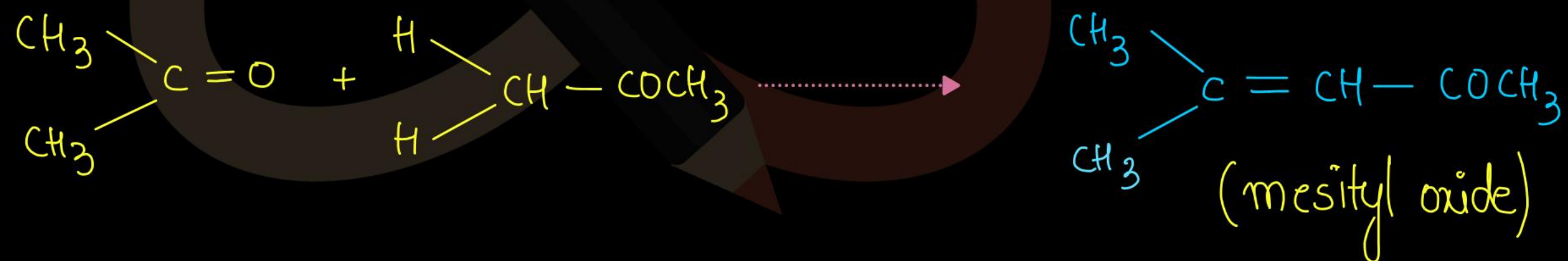
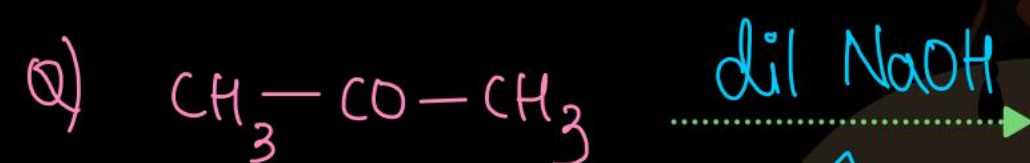
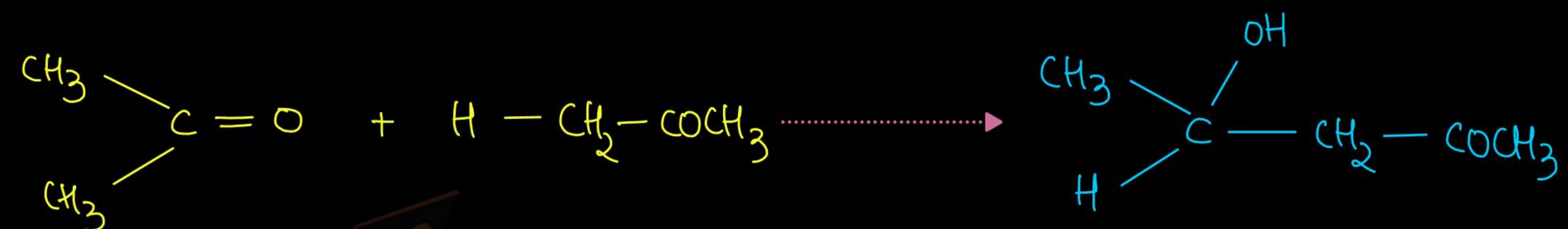
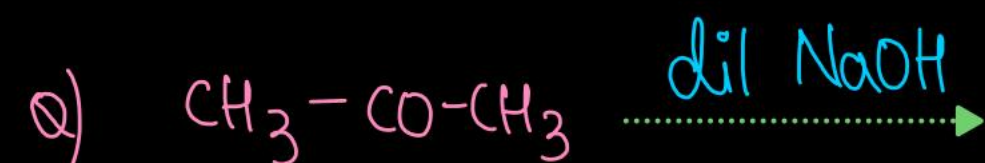
★ D.M :-



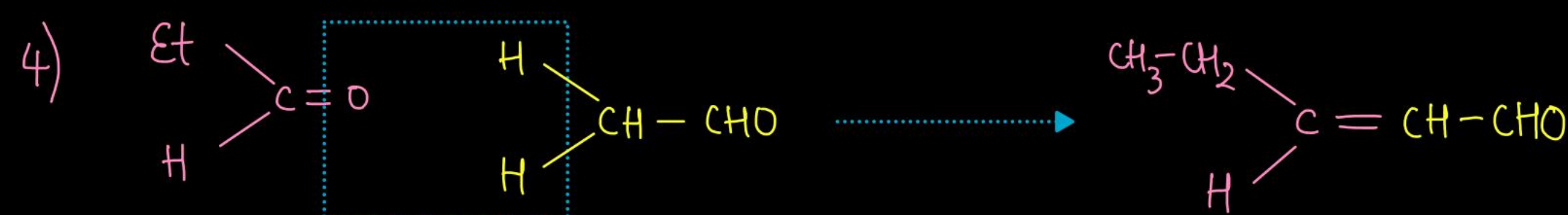
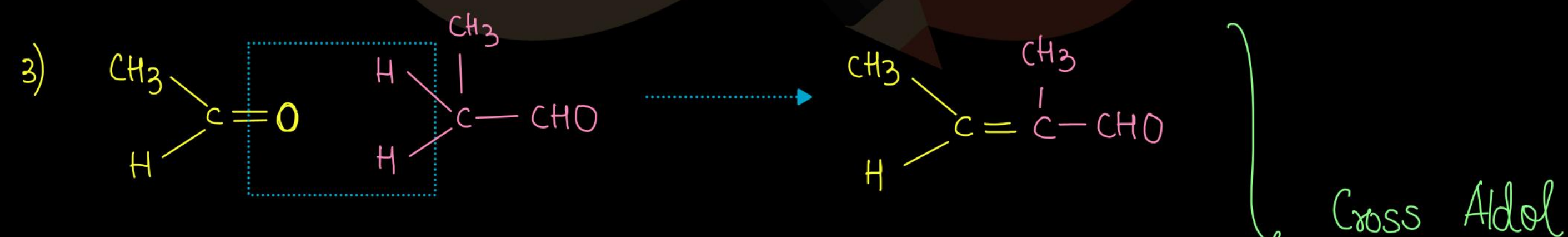
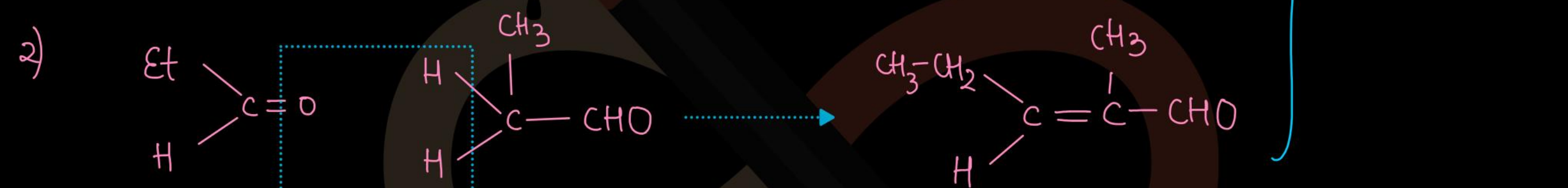
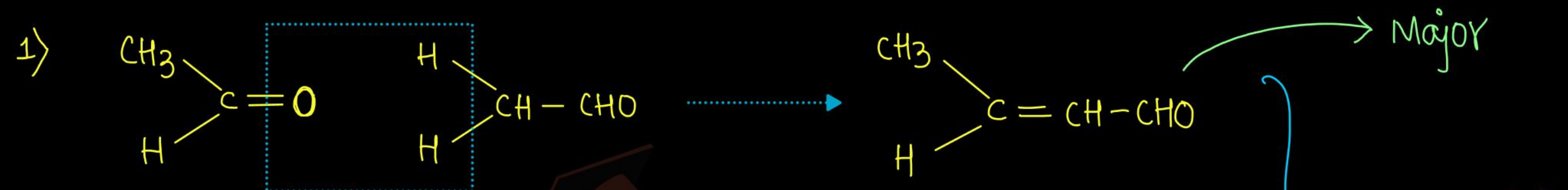
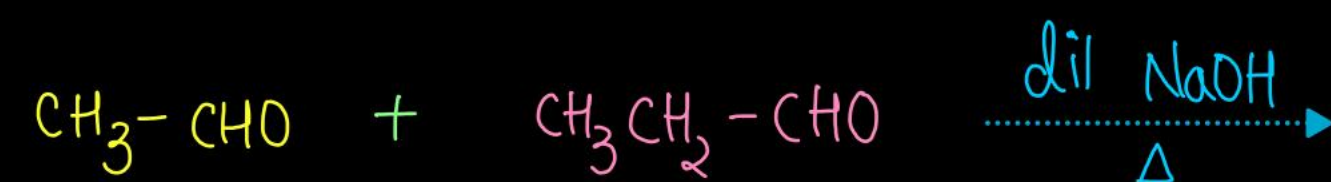
Note :-

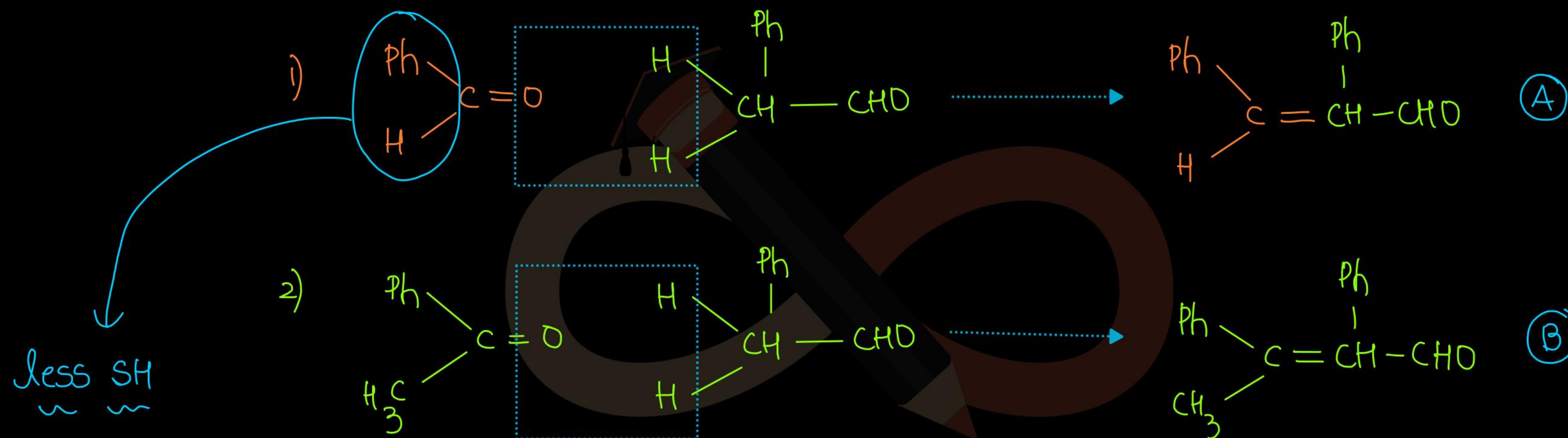
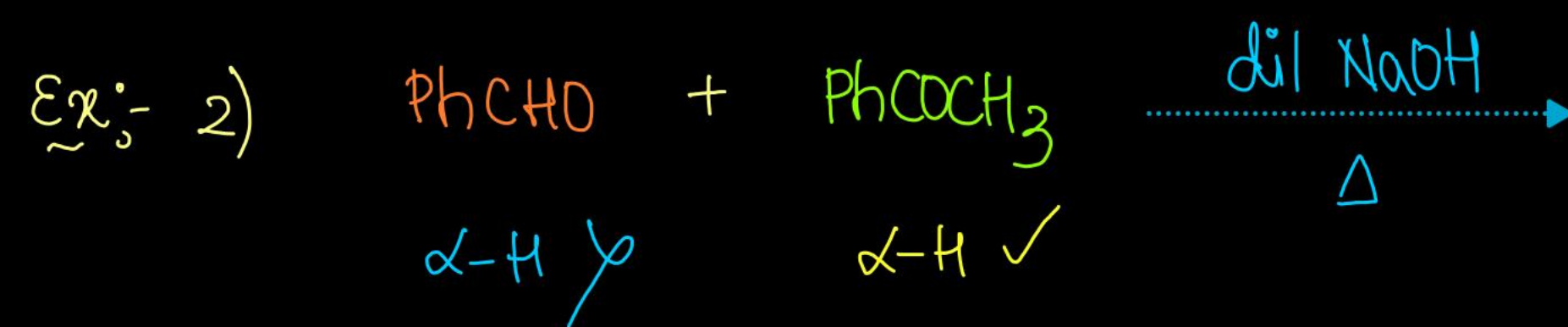


Ex:-



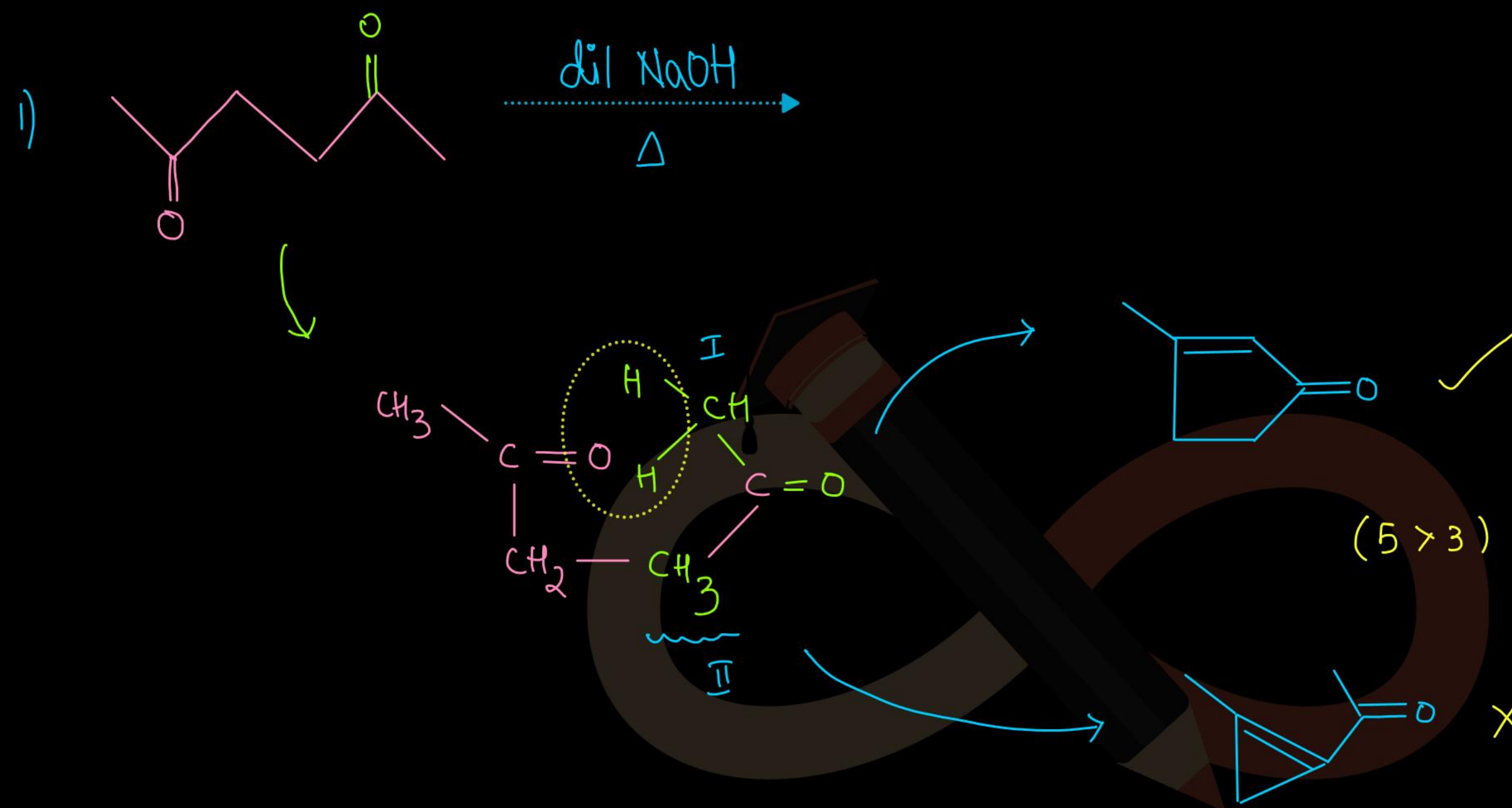
2) Cross Aldol

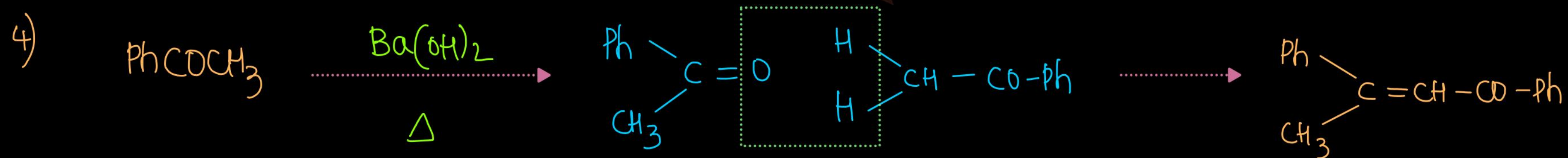
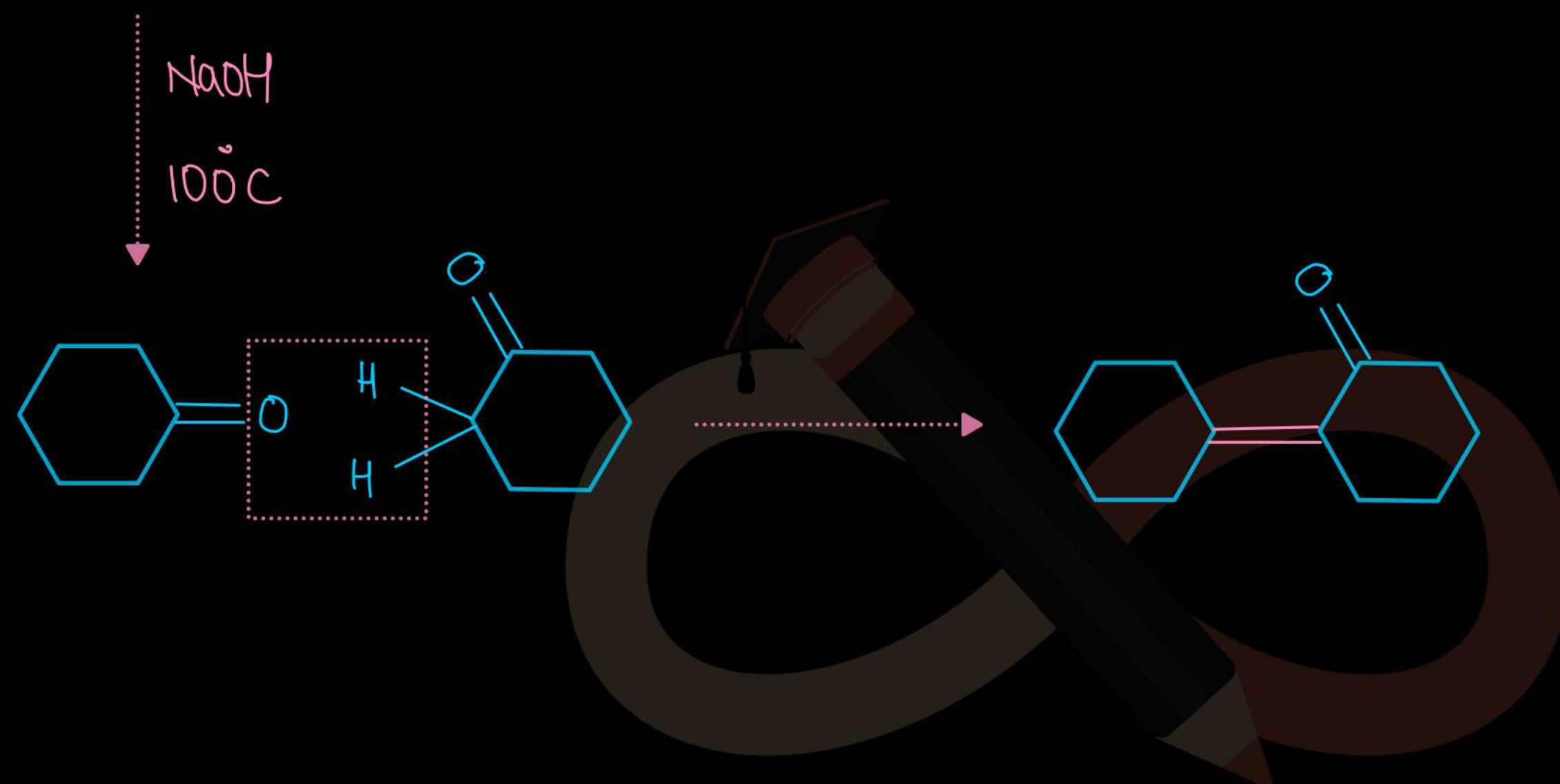
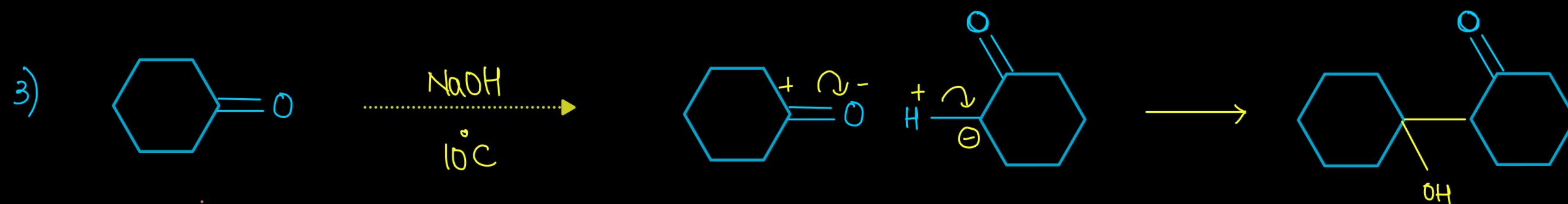




$\Rightarrow$ Hence product A is more stable

3) Intra Aldol :- (ring formation $6 > 5 > 7 > 4 > 3$)

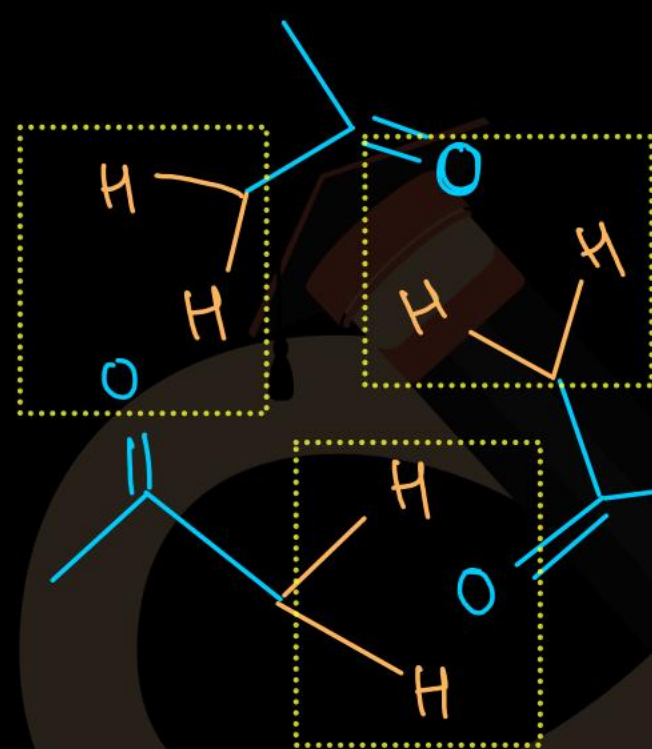




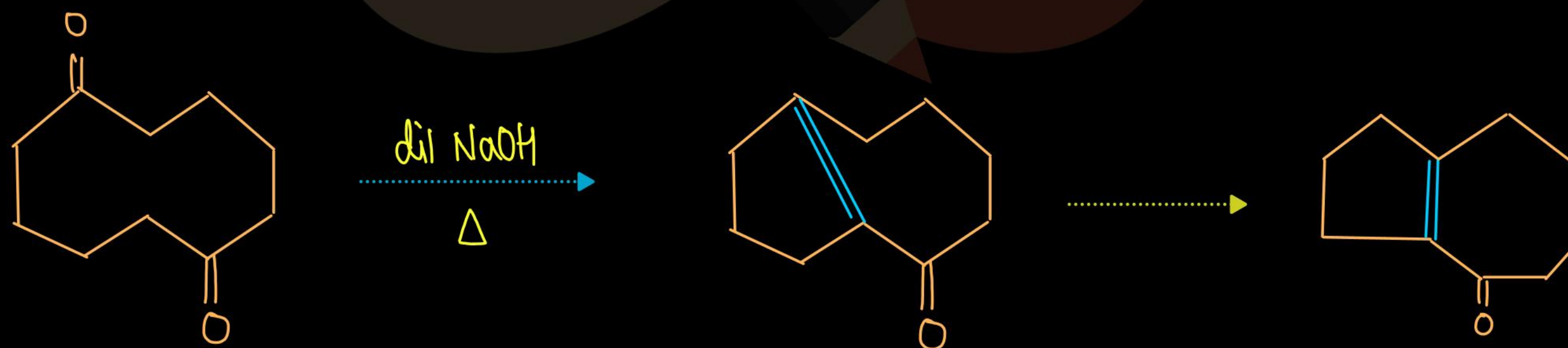
Imp:



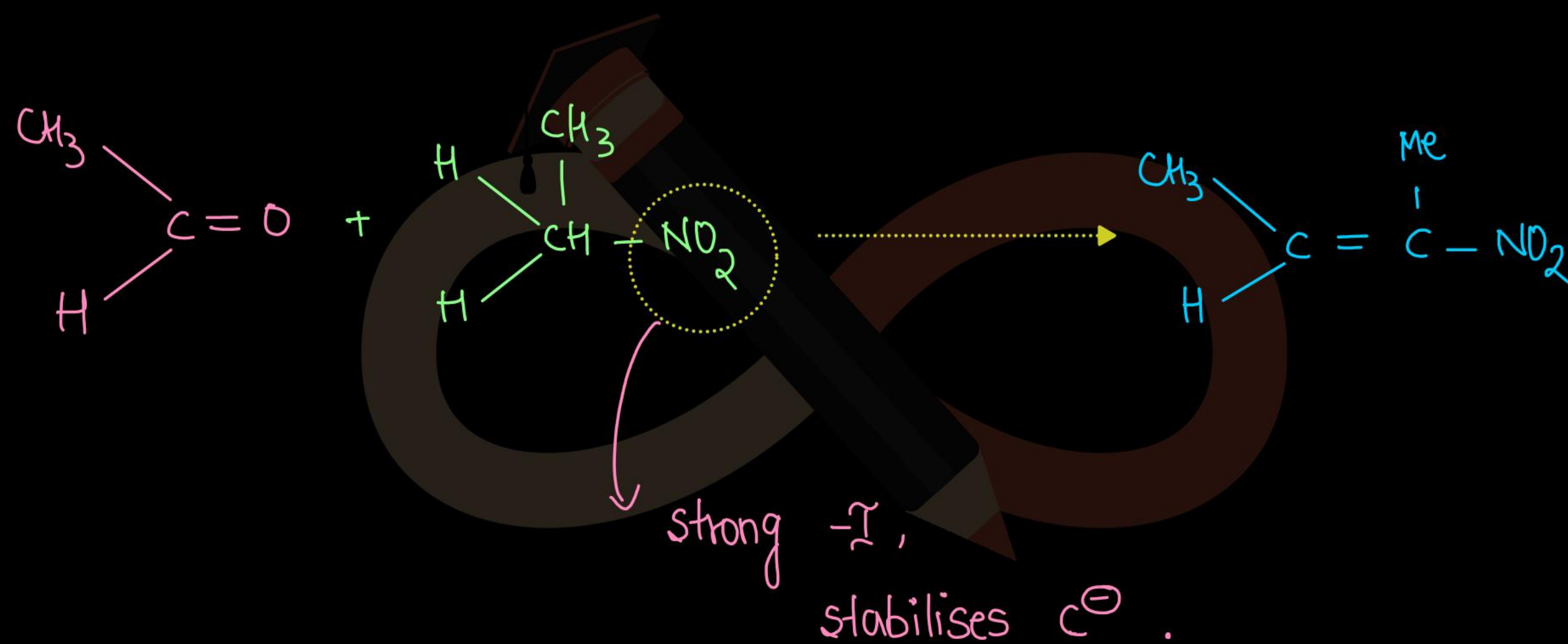
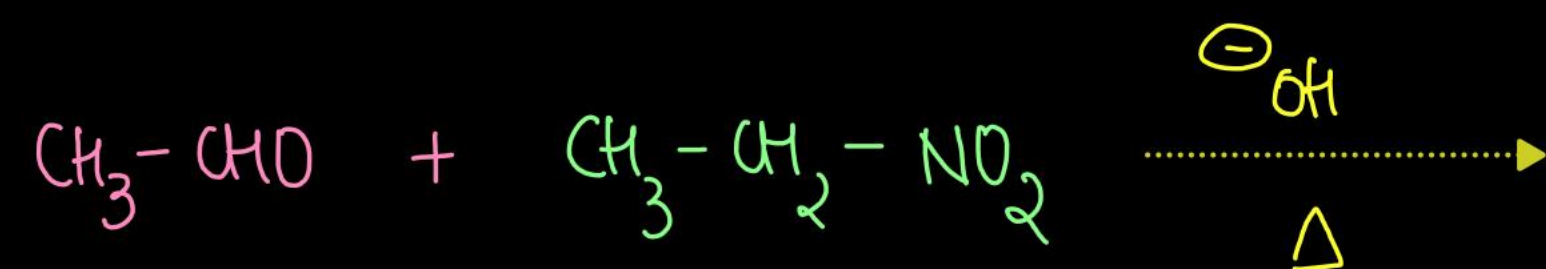
3
moles



*)

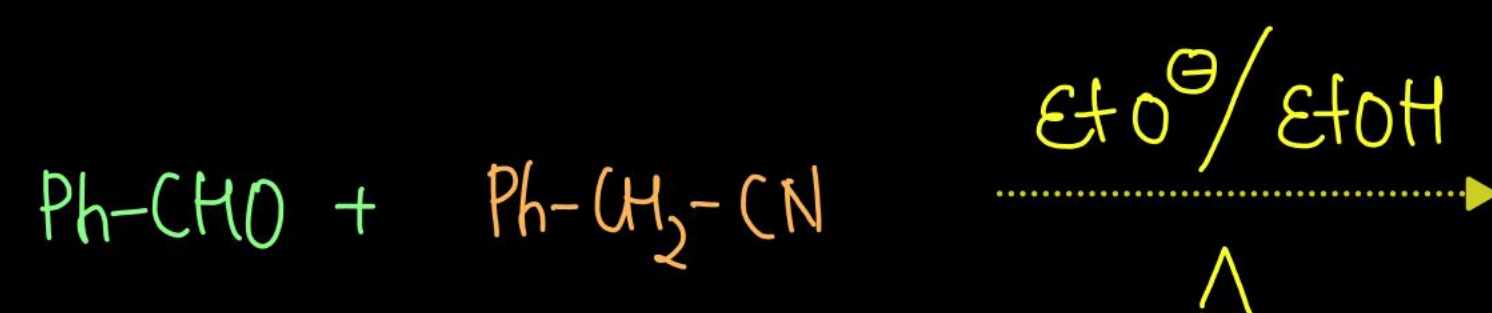


4) Nitro Aldol :



$\Rightarrow [H_2 - Z]$ from Nitro alkane.

5) Cyano aldol :-

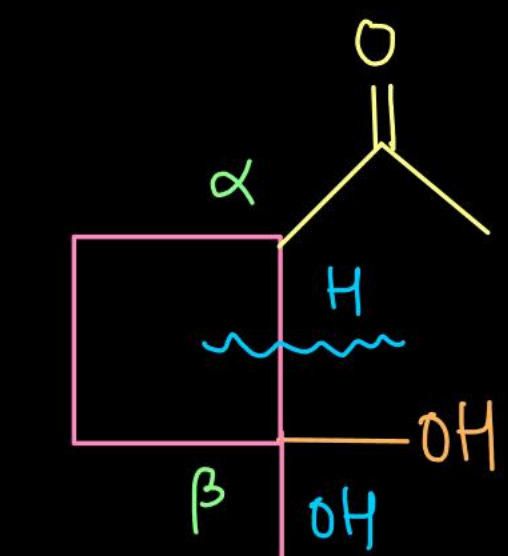


* $\text{OH}^\ominus/\text{H}_2\text{O}$ cannot be used because cyanide will be hydrolysed.

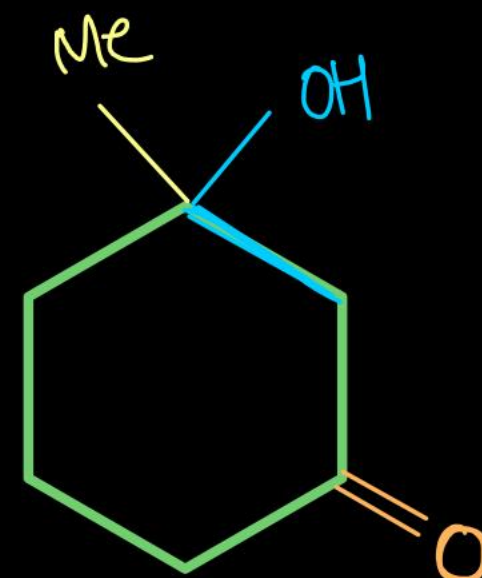
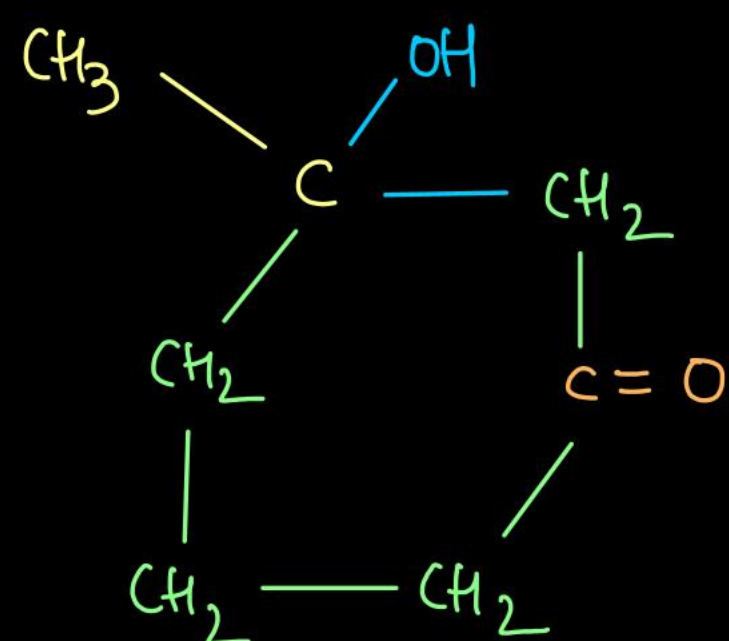
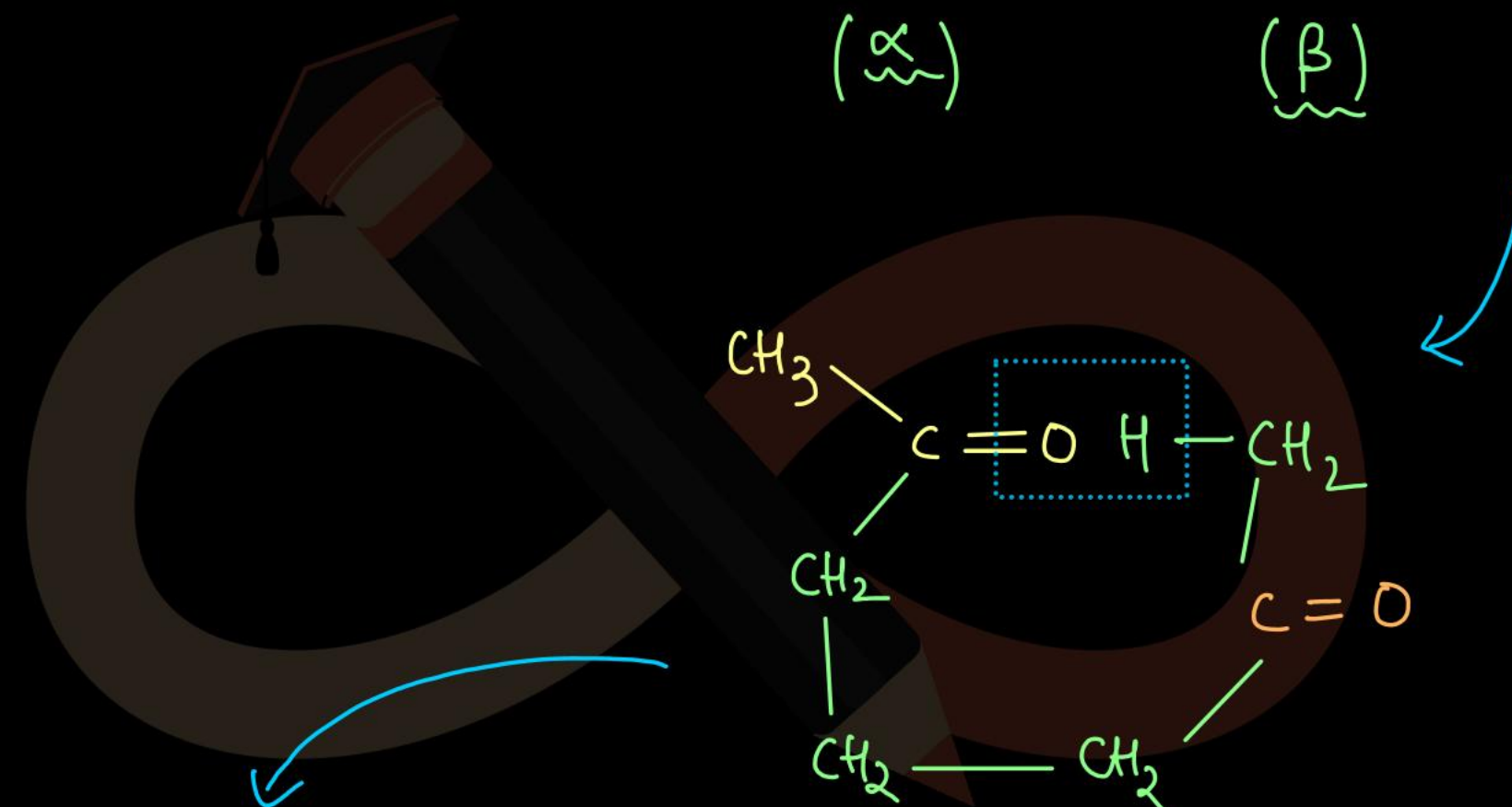
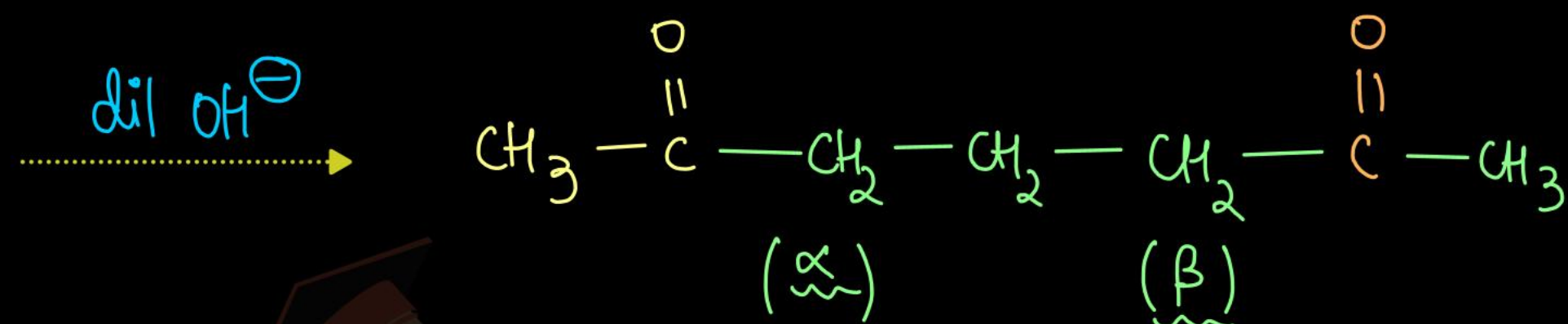


always use :- $\text{H}_2\text{-Z}$ { cyanide part }

6) Retro Aldol :



β -hydroxy
carbonyl



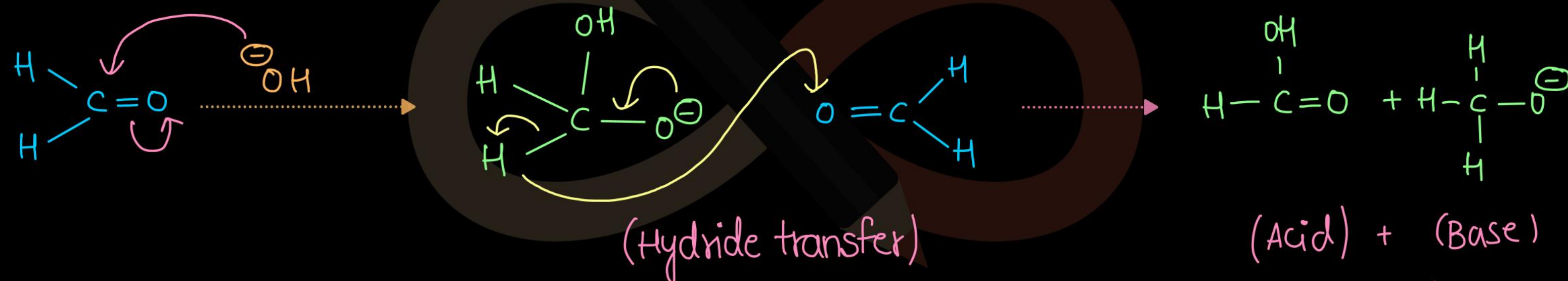
(β -hydroxy
carbonyl)

II) Cannizzaro Rxn :-

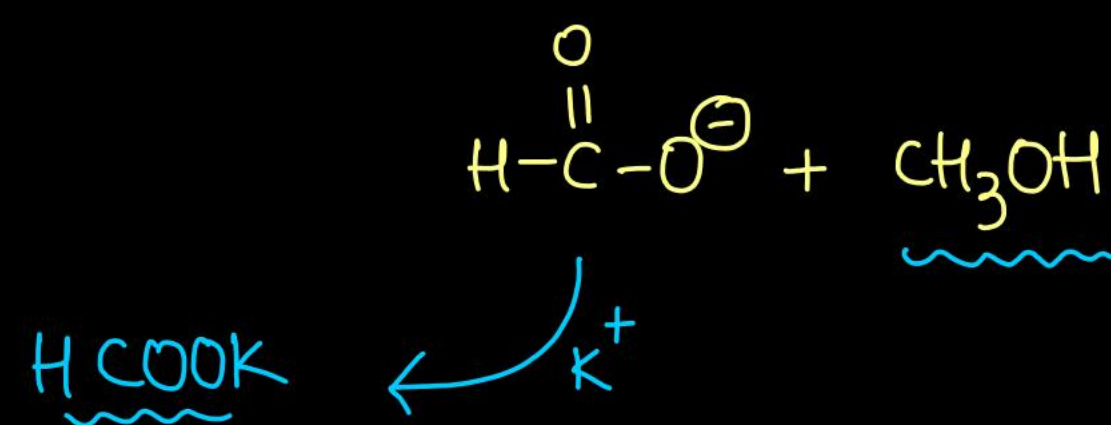
→ Carbonyls comp. not having α -H

→ Reagents : Conc KOH (or) 50% KOH (or) 50% NaOH

Mechanism :-



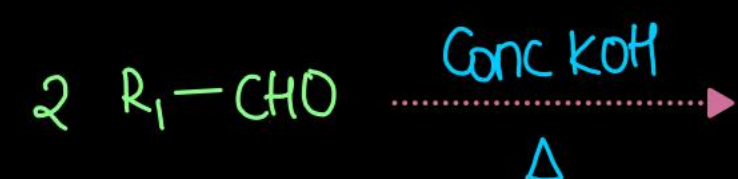
RDS



Imp points :-

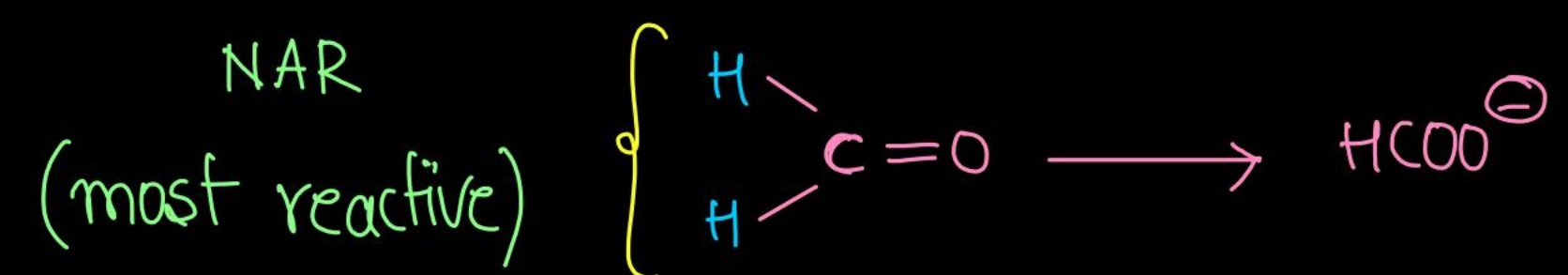
- 1) Redox rxn
- 2) Disproportionation rxn
- 3) $r = k [R]^2 [OH^-]$ {at 50% KOH}
molecularity = 2 order = 3
- 4) $r = k [R]^2 [OH^-]^2$ {at 90% KOH}
 $\Rightarrow$ order = 4
- 5) Migration of H^- is the RDS
Hydride donor tendency $\propto$ formation of C^+
- 6) Isotopic effect is observed
- 7) More electrophilic carbons gets oxidised (NAR reactivity)

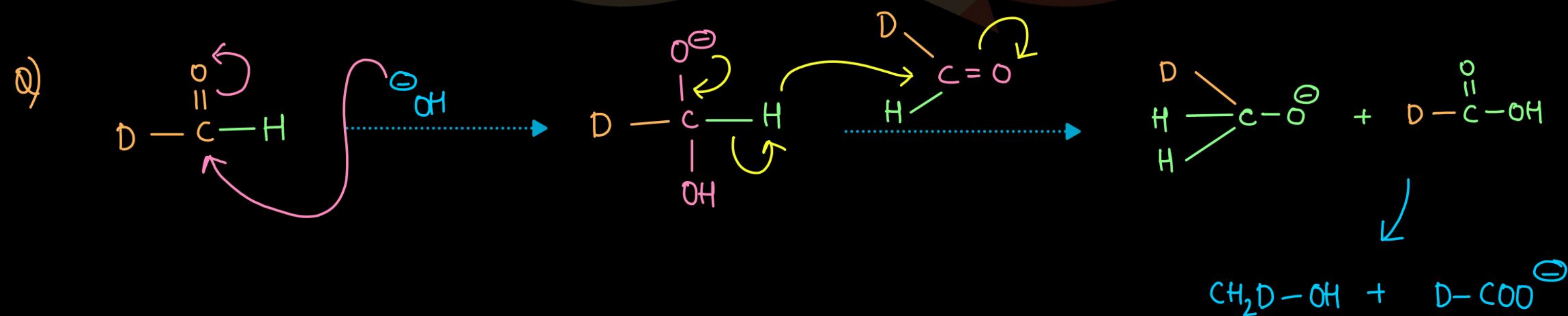
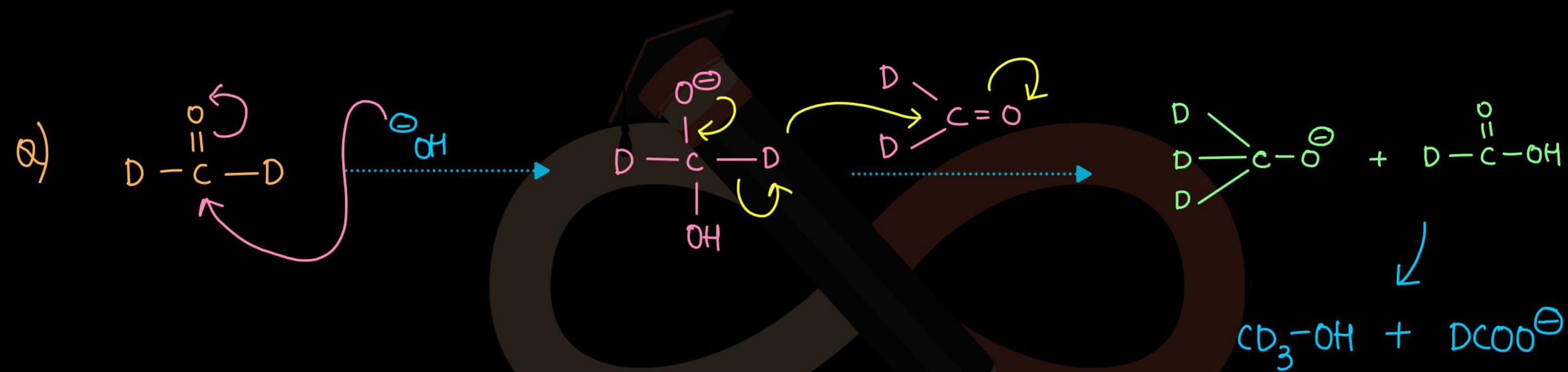
DM:-



* Imp note :

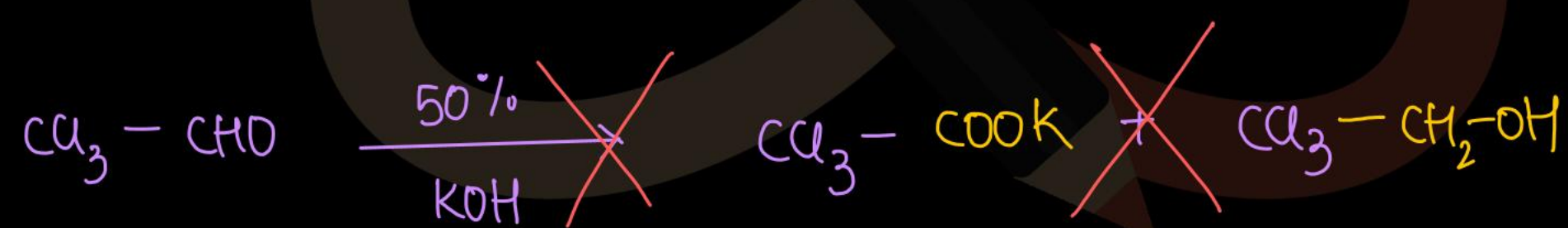
⇒ In cross Cannizzaro, if one of the Ald is 'HCHO' then it will always be oxidised.



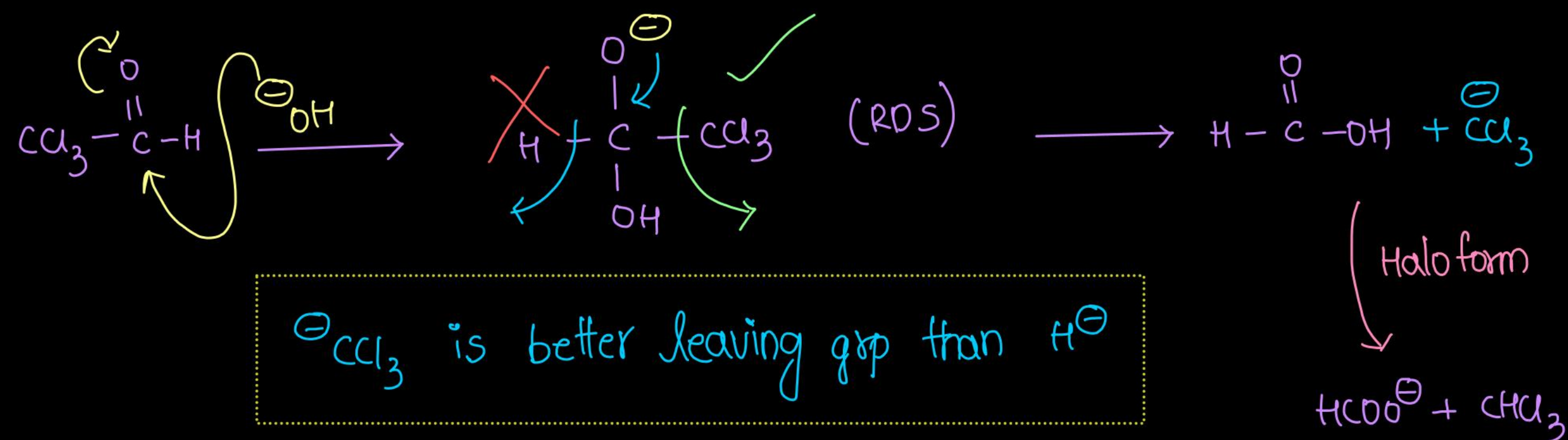




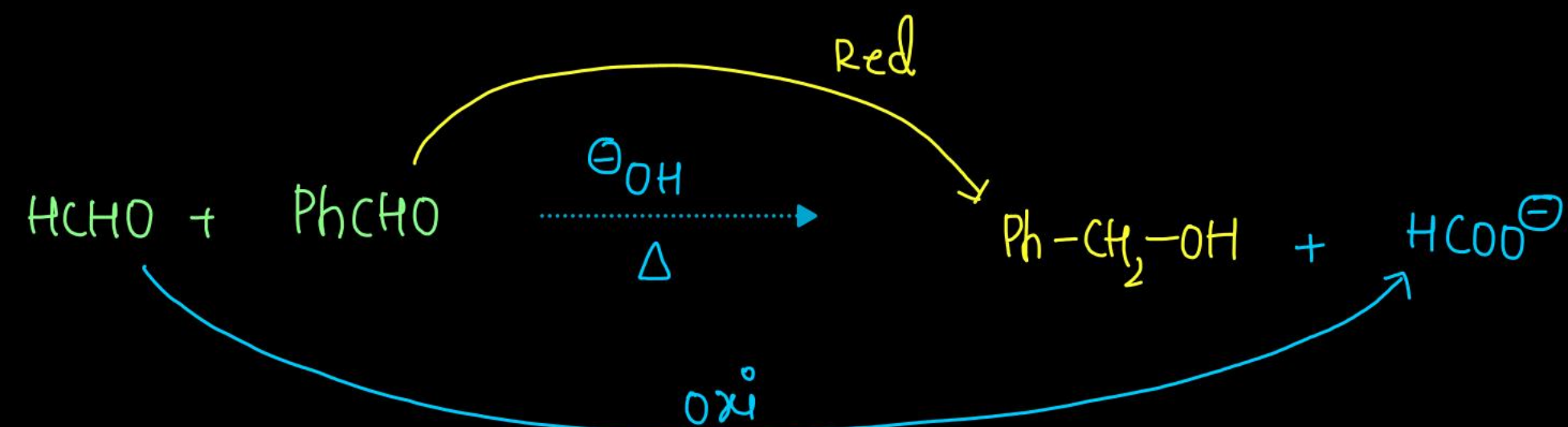
★ CHO-CCl_3 (chloral) doesn't undergo cannizzaro



because ;

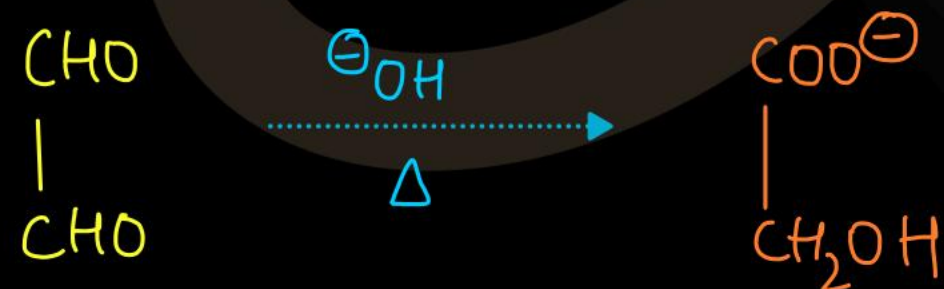


2) Cross Cannizzaro

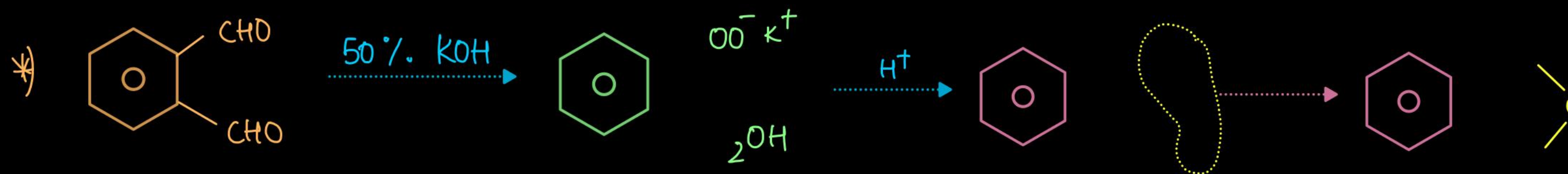


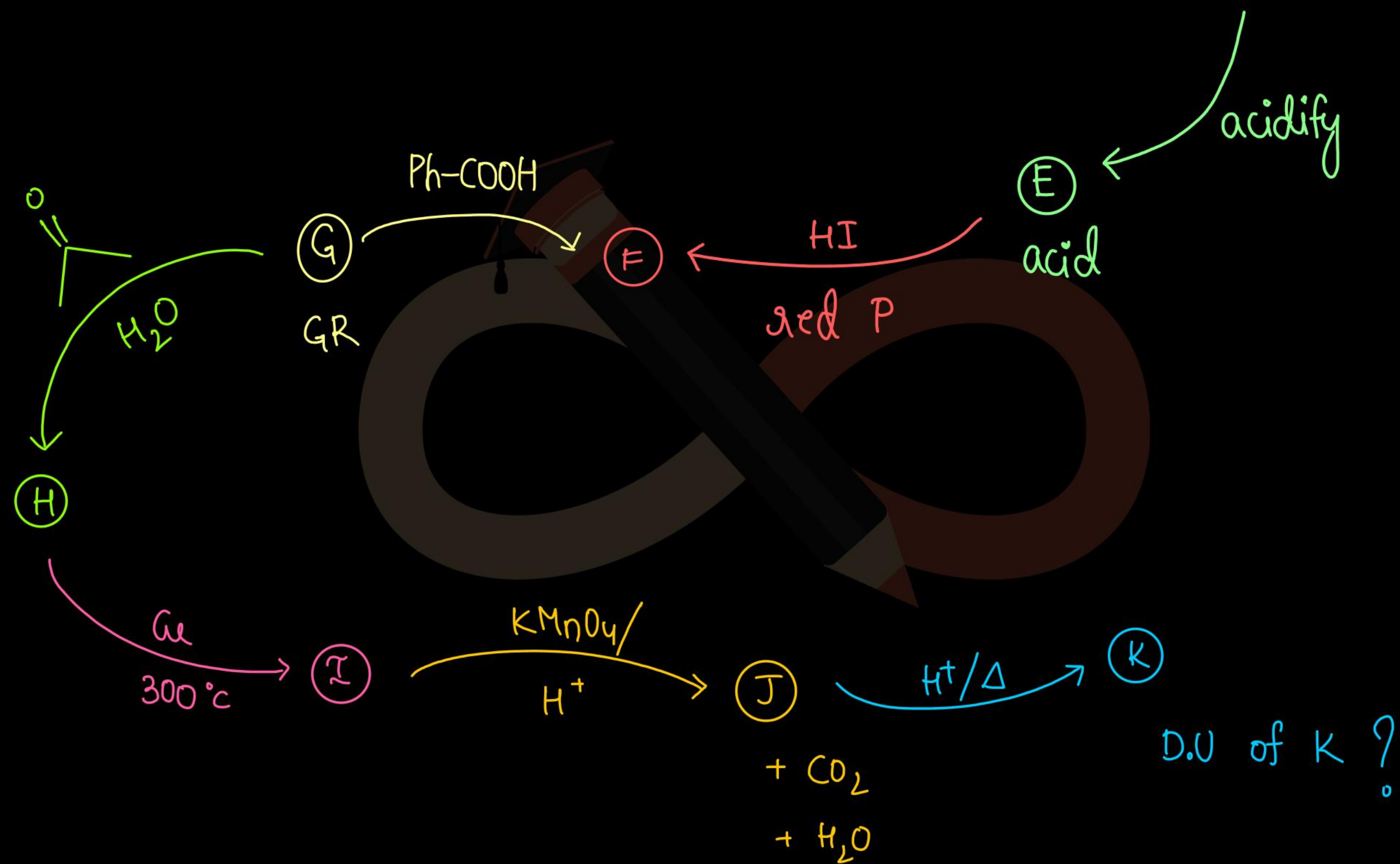
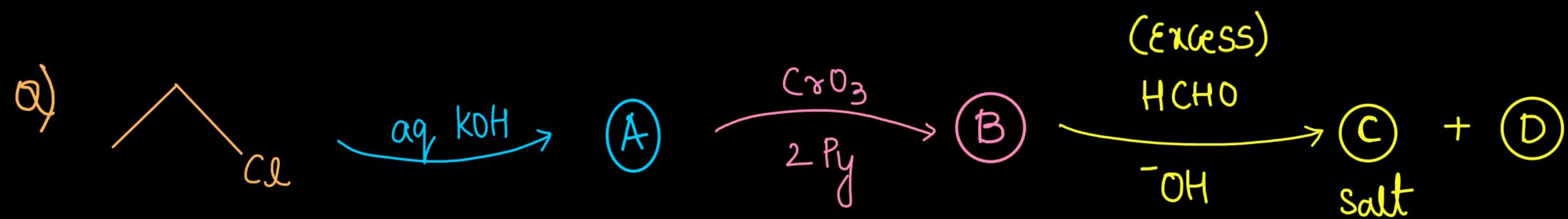
* Cross cannizzaro is only a redox rxn but not a disproportionation rxn.

3) Intra molecular Cannizzaro :



Ex:-



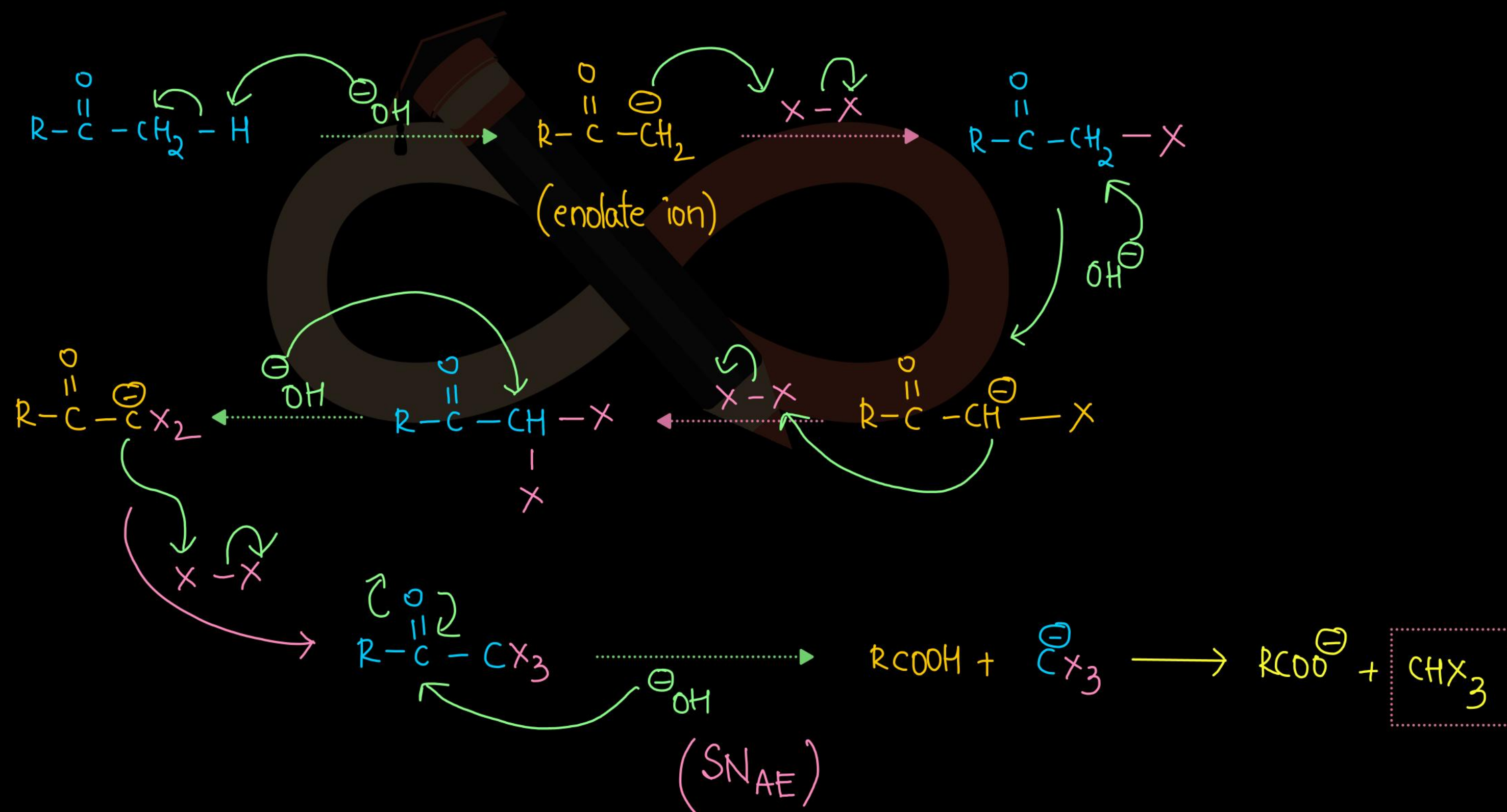


III) i) Haloform rxn :

→ Methyl ketones $R-\overset{\overset{O}{\parallel}}{C}-CH_3$

→ Reagents : $X_2/\underset{K}{NaOH}$ (or) $\underset{K}{NaOX}$ (or) $CaOCl_2$

Mech :-



Imp points :-

1> Carbanion Intermediate is formed

2> Oxidation rxn

3> Degradation rxn

4> Formation of enolate ion is RDS

5> Rate of formation : $\text{CHF}_3 \approx \text{CHCl}_3 \approx \text{CHBr}_3 \approx \text{CHI}_3$

no. of moles $\text{X}_2 = 3$

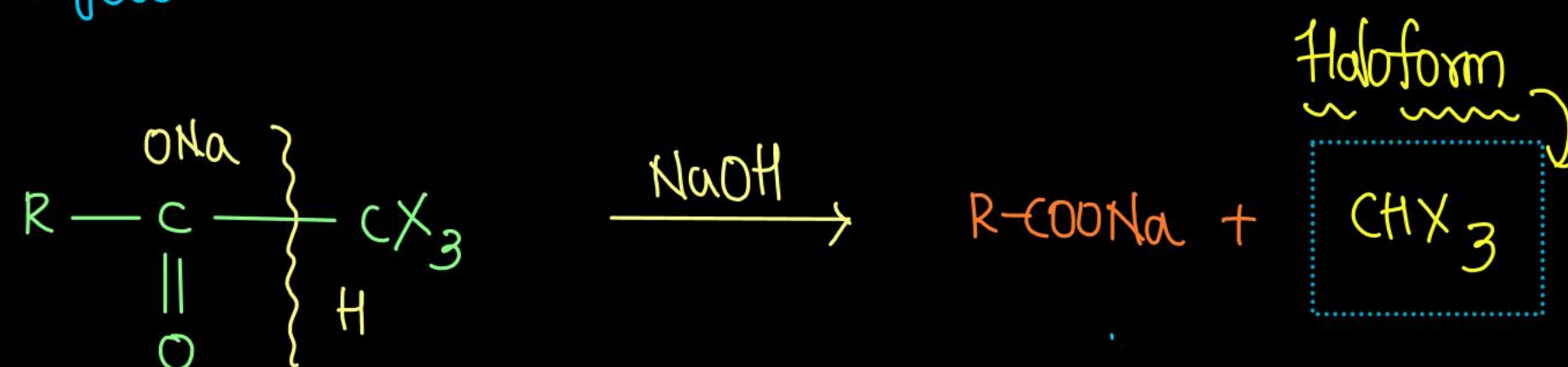
no. of moles $\text{OH}^\ominus = 3 + 1 = \underline{4}$

D.M :-

1) Halogenation



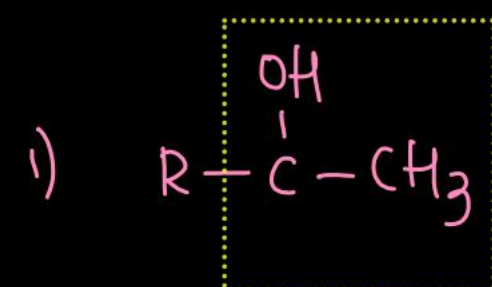
2) Alkaline hydrolysis :



Note:-

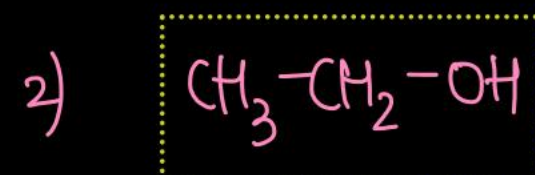
Compounds:

Haloform test:



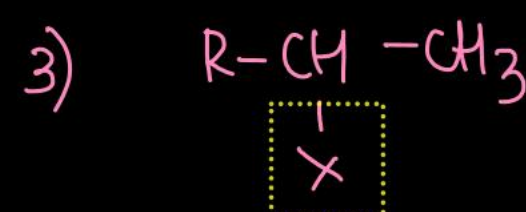
✓

2° alc can be oxidised by Halogen to ketone



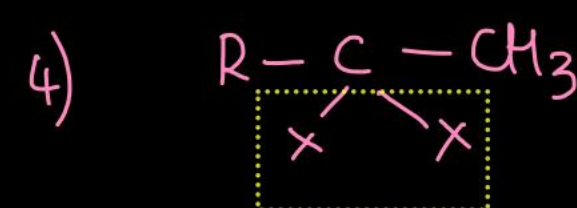
✓

1° alc $\rightarrow$ ald $\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$ ✓



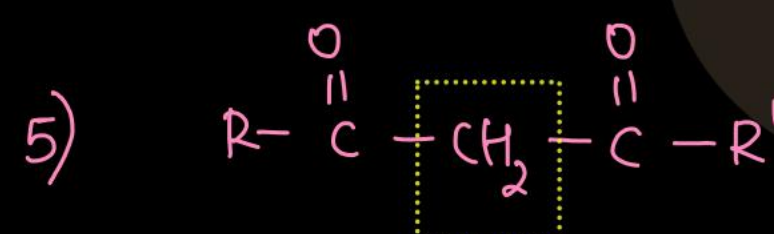
✓

$\text{S}_\text{N}^2 \Rightarrow \text{X}$ will be replaced by OH



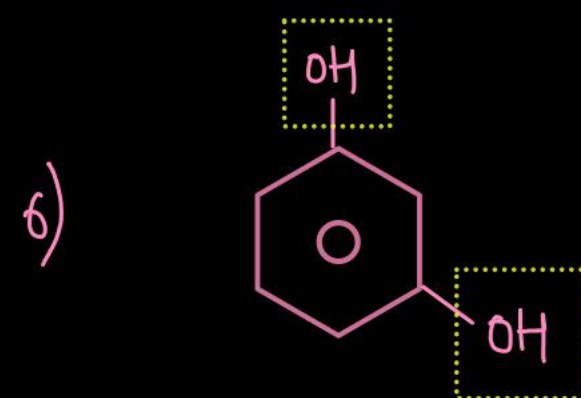
✓

$\text{S}_\text{N}^2 \Rightarrow \text{OH}-\text{C}-\text{OH} \Rightarrow \text{O}=\text{C}$



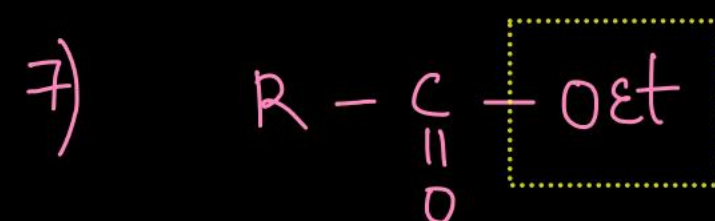
✓

Active methylene grp $\rightarrow \text{CX}_2 \rightarrow$ alkaline hydro



✓

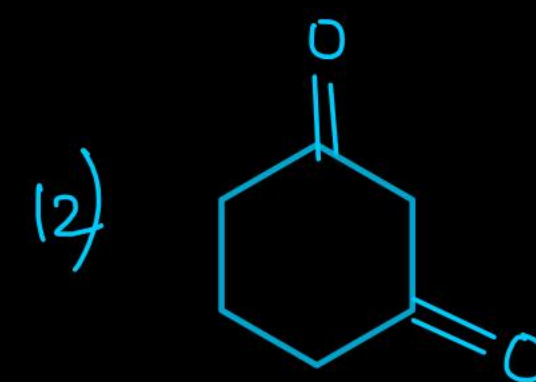
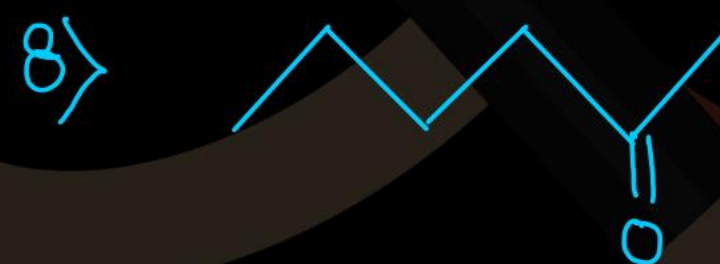
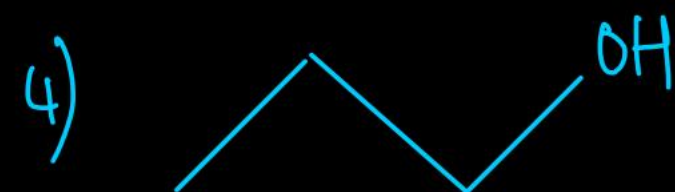
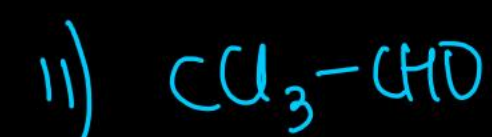
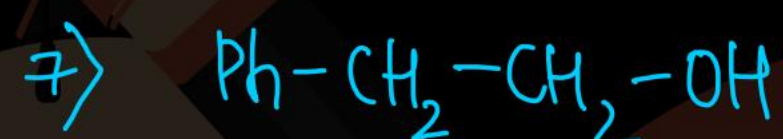
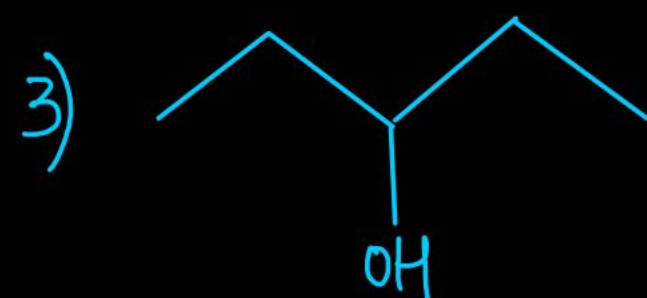
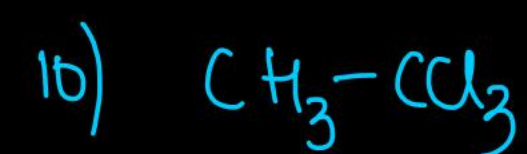
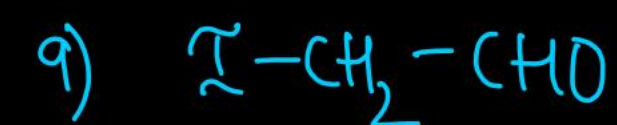
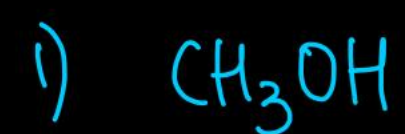
tautomerism $\rightarrow \beta$ di ketone

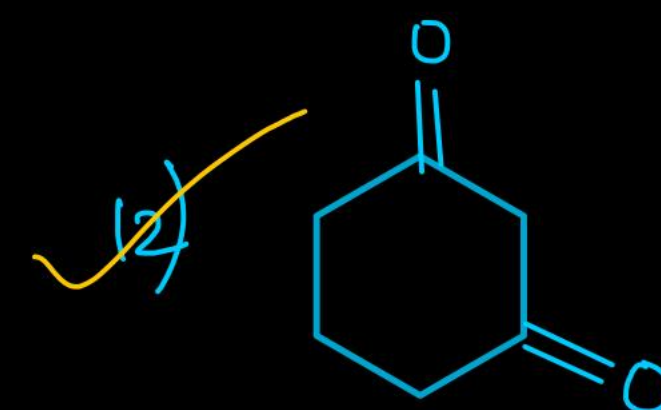
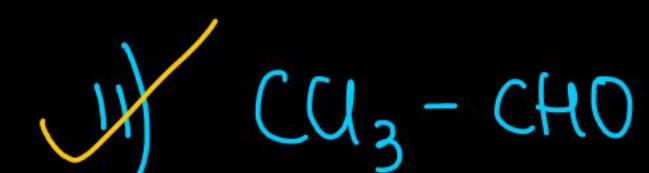
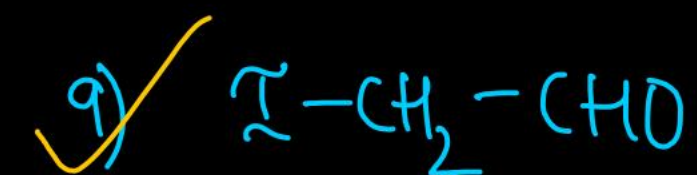
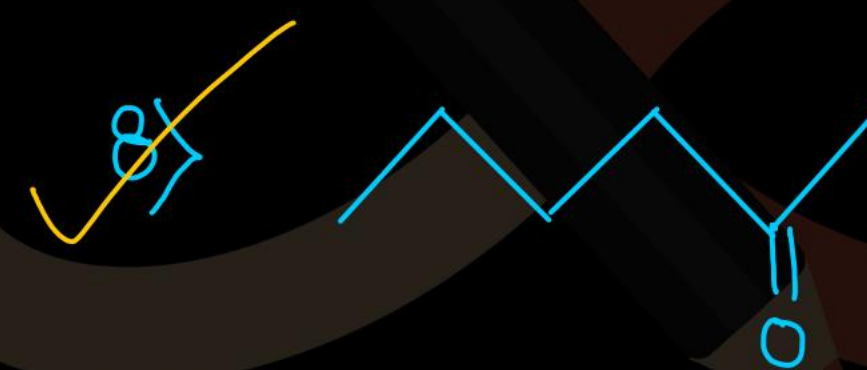
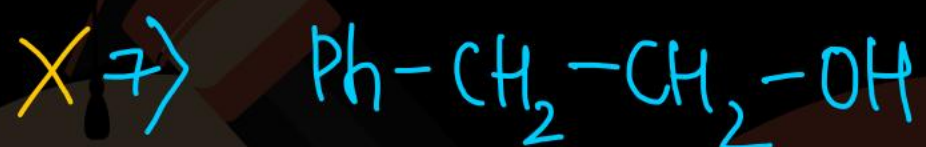
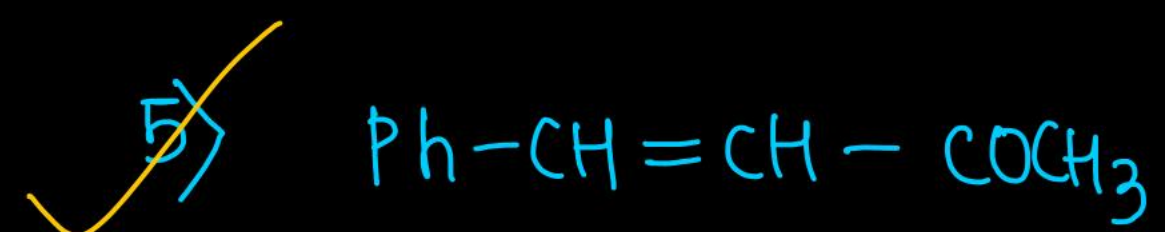
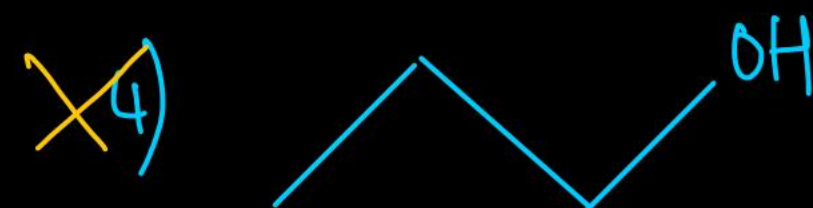
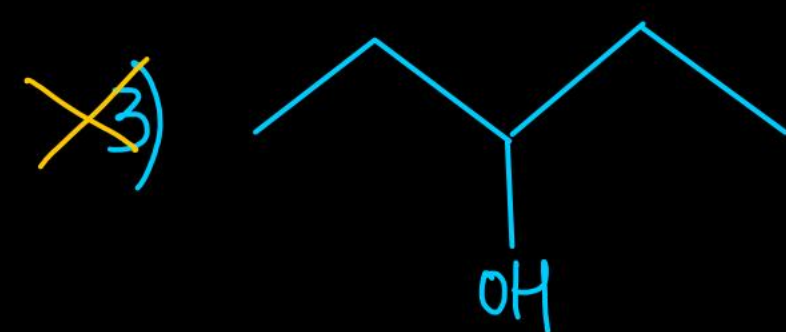
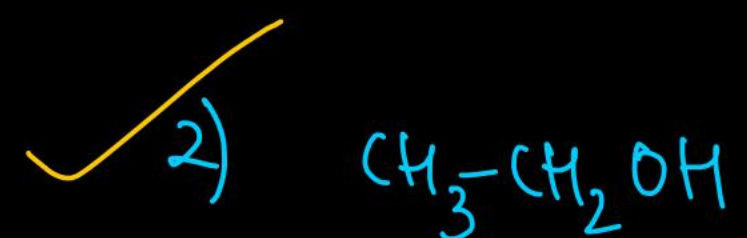


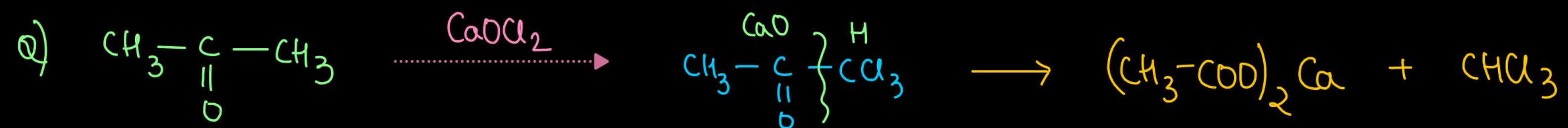
✓

on hydrolysis $\rightarrow \text{EtOH} \rightarrow$ only 1° alc to give Haloform

Q) Find the comp which give +ve Haloform Test ?

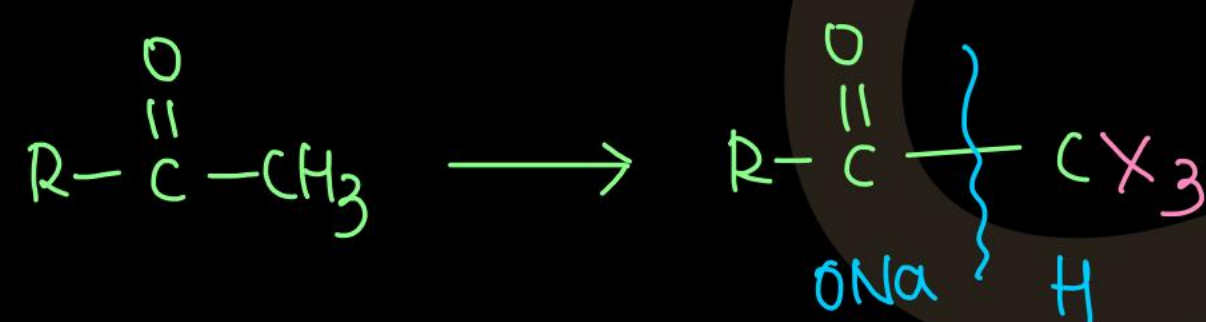






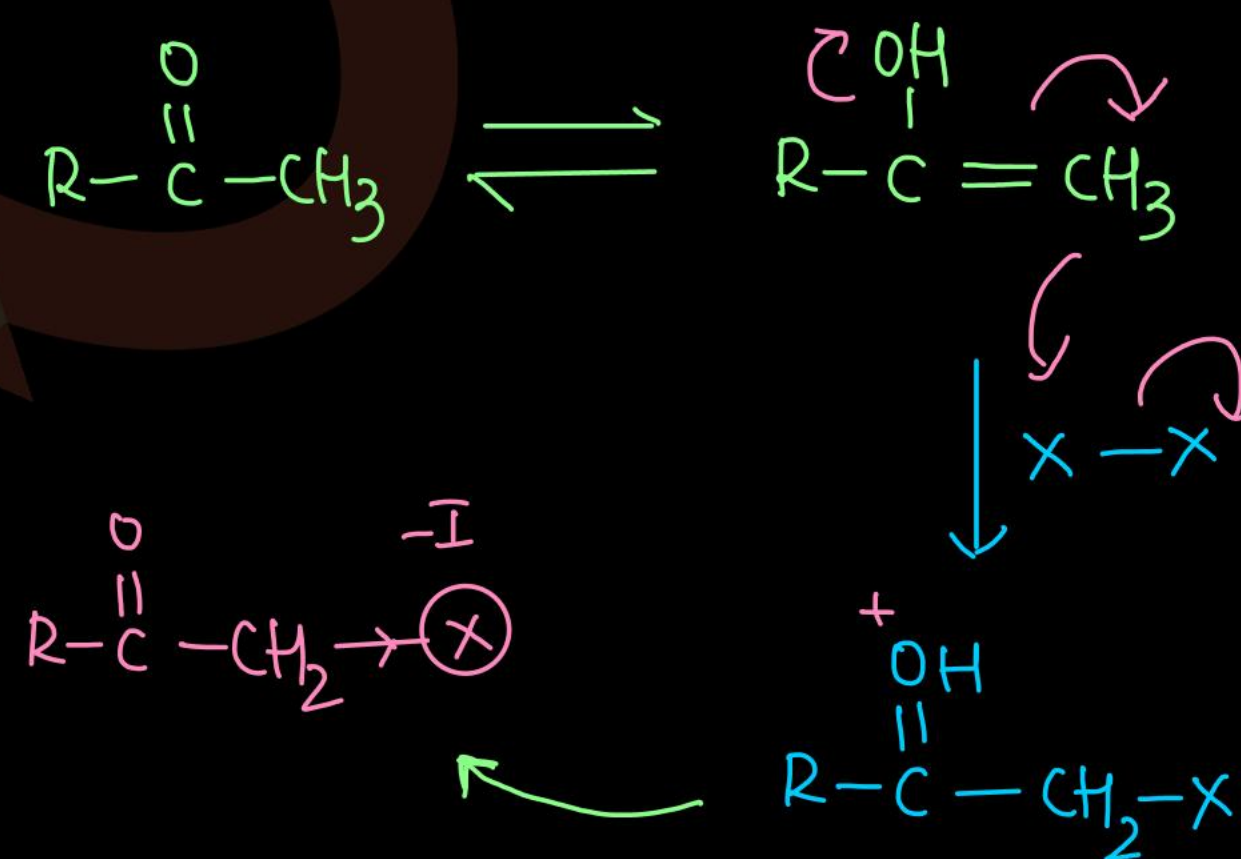
* Haloform in acidic v/s Basic med

1) Basic med : Trihalogenation



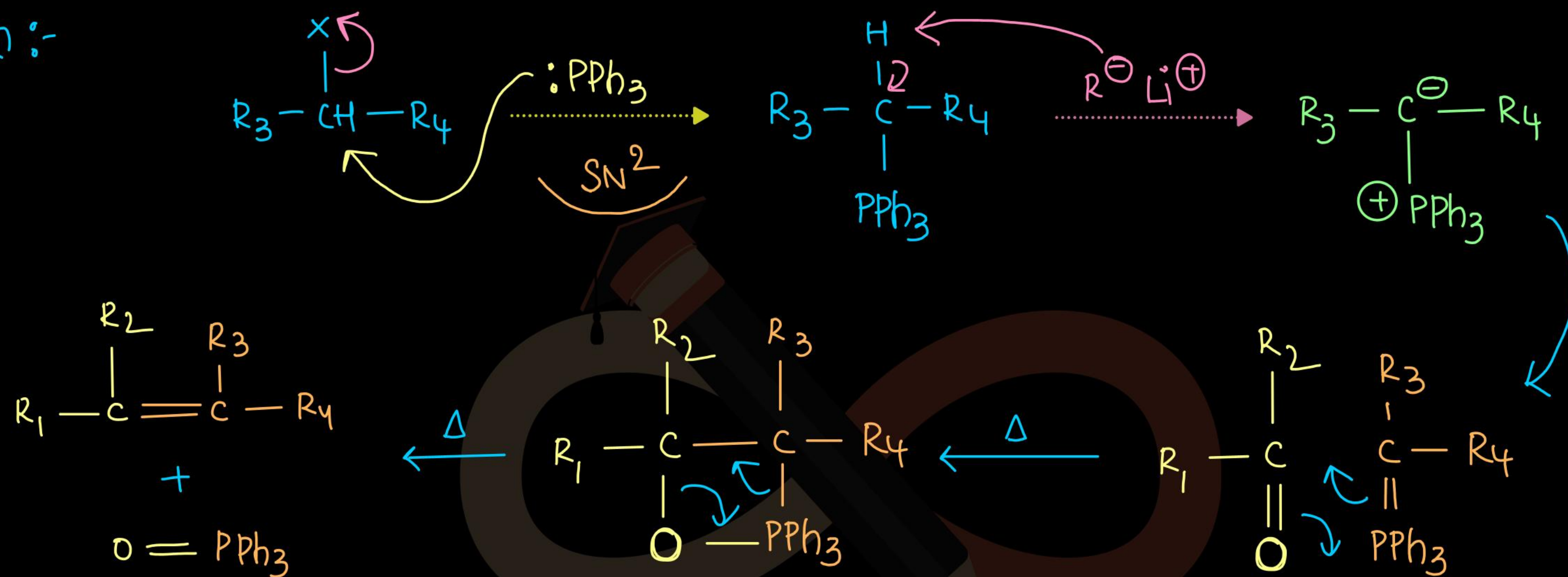
⇒ As rxn proceeds,
rate ↑.

2) Acidic med : Monohalogenation

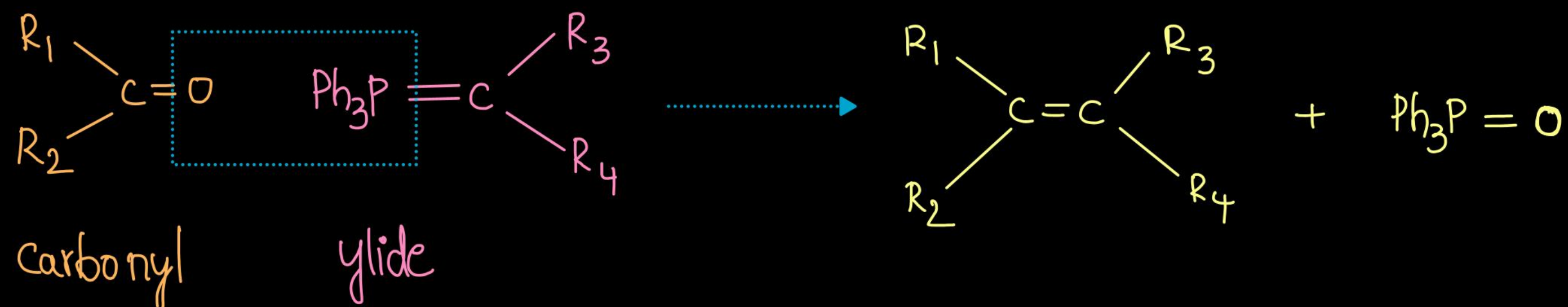


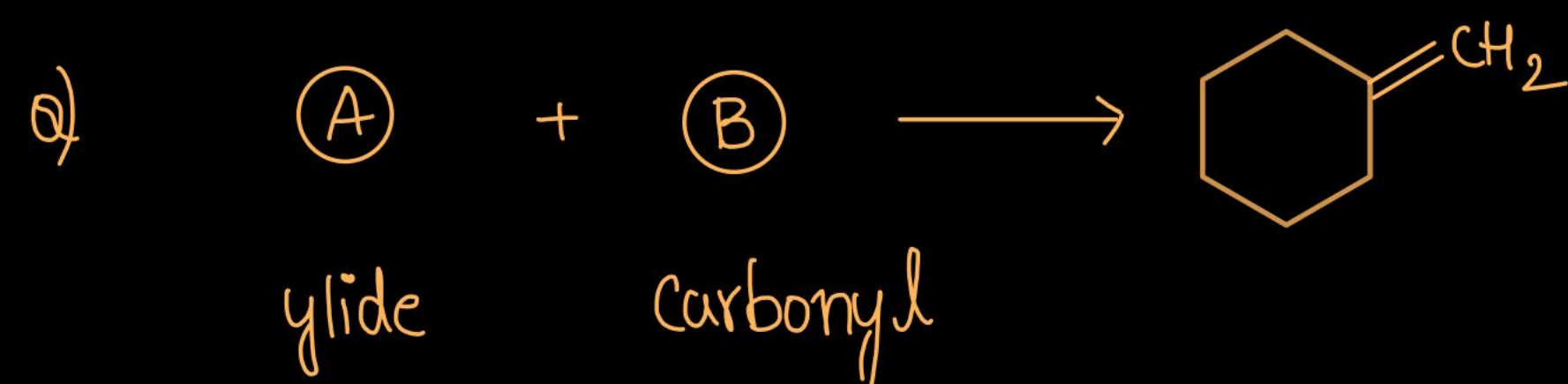
2) Wittig rxn :

Mech :-

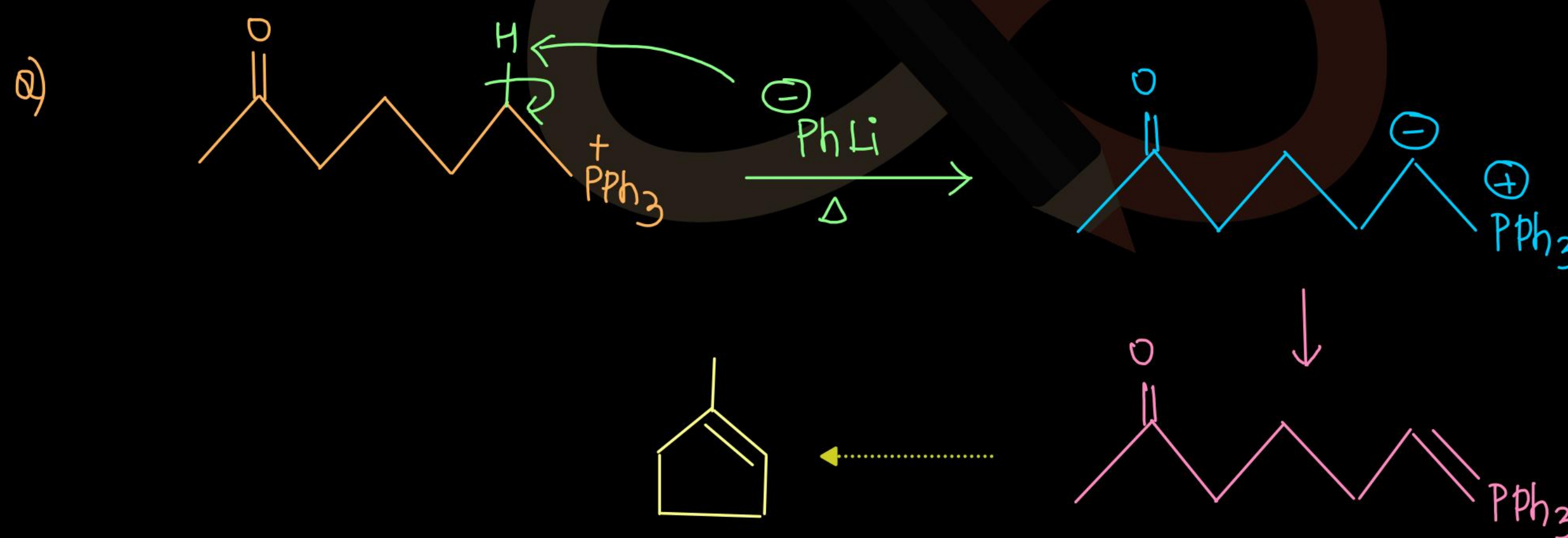
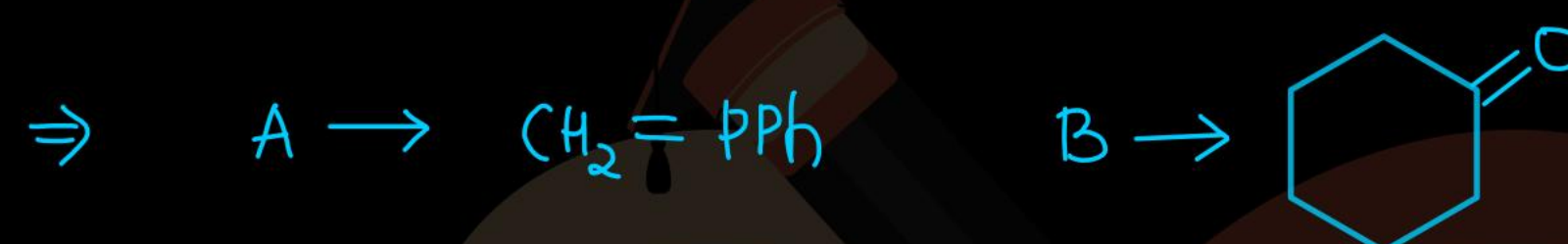


DM :-

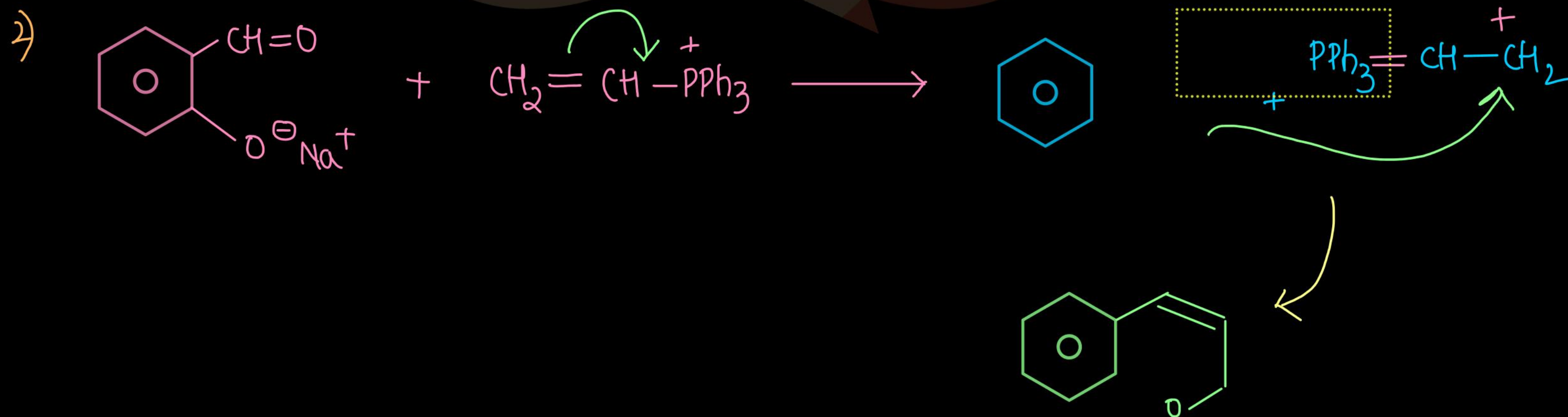
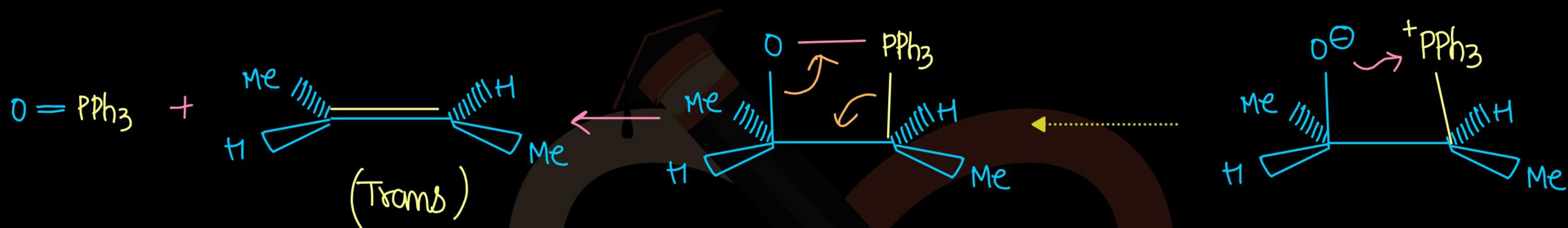
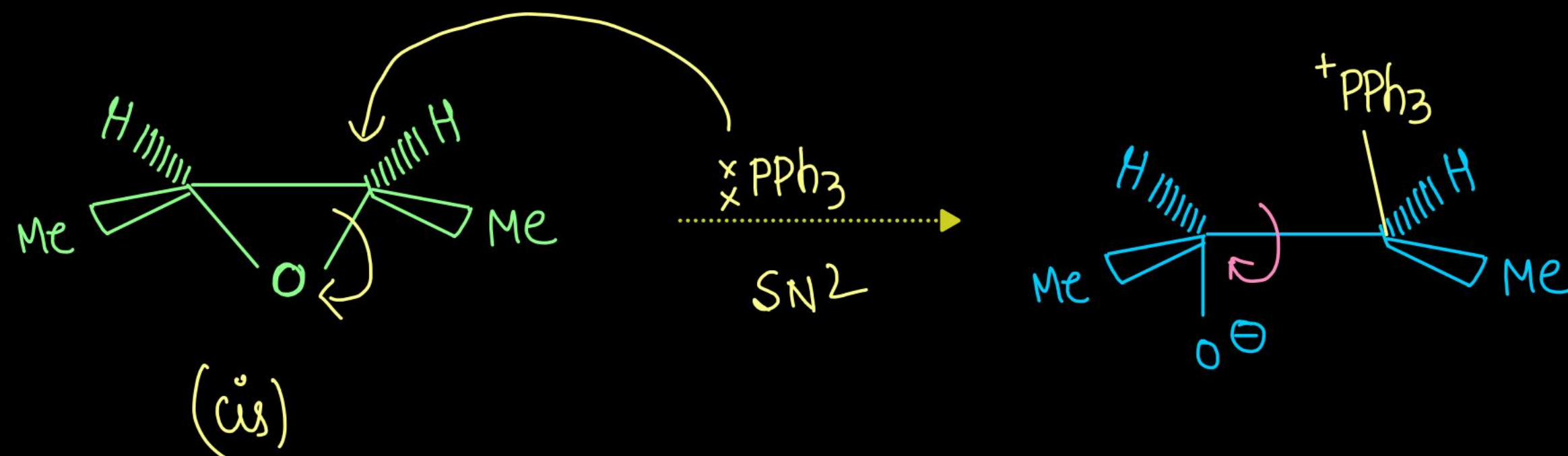




Sol:- Always less hindered (SH $\downarrow$) must be ylide



Ex^o- 1)

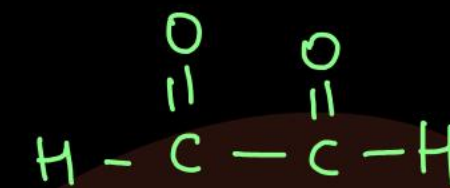
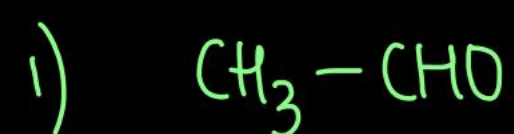


3) Oxidation by SeO_2 (Riley reaction) :-

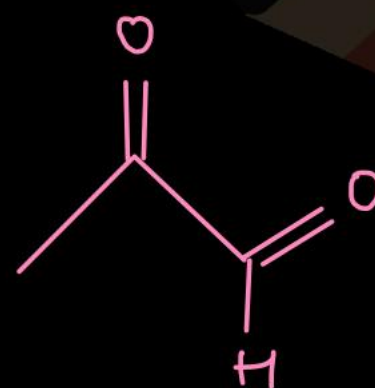
1) It oxidises active position of Carbonyl group $\left[\boxed{\text{CH}_2} \overset{\text{O}}{\parallel} \text{C} - \right]$

2) SeO_2 preferentially oxidise methyl grp rather than methylene grp

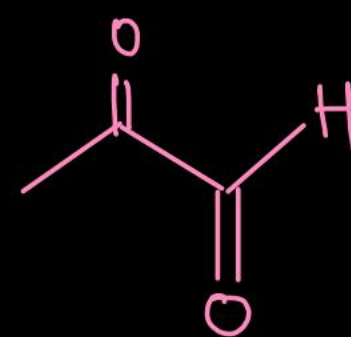
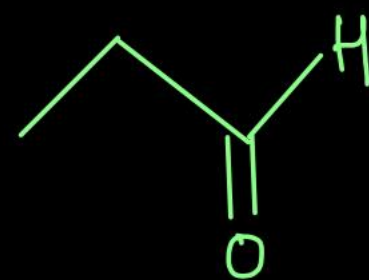
Ex:-

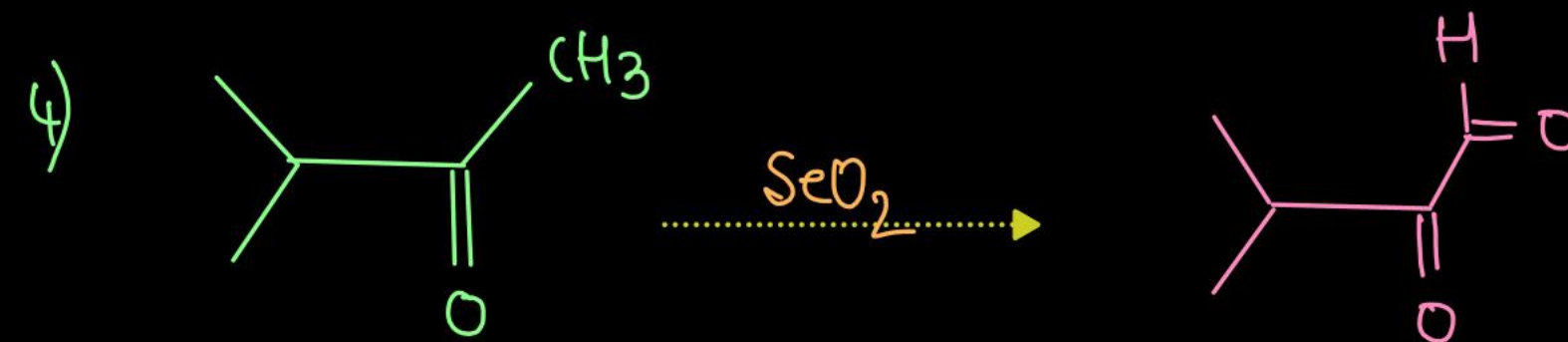


2)

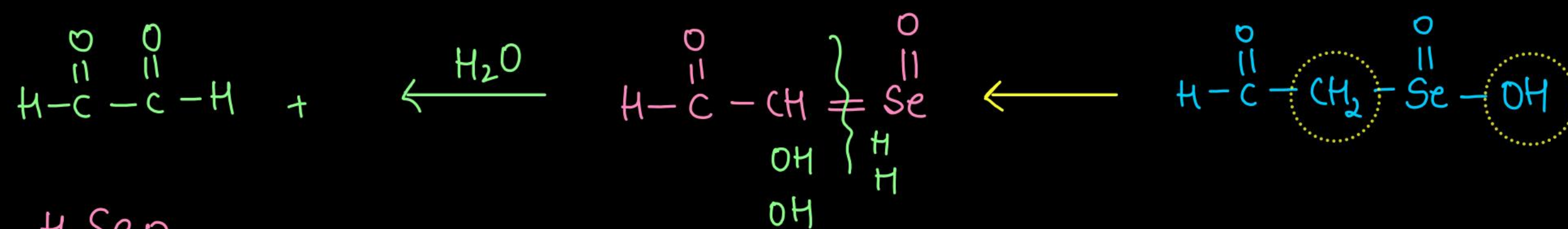
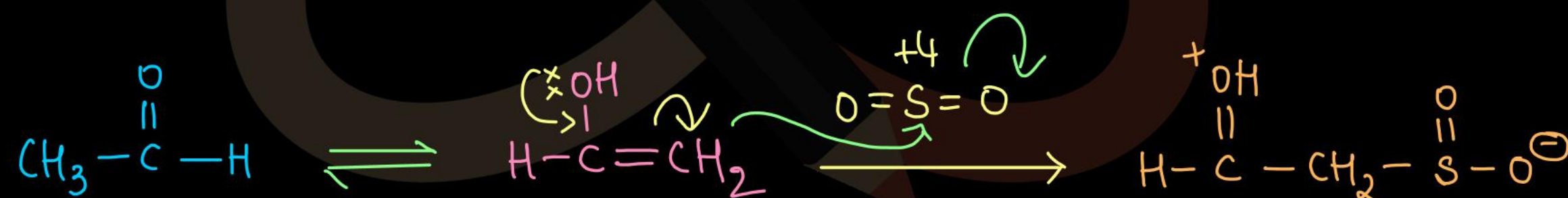


3)

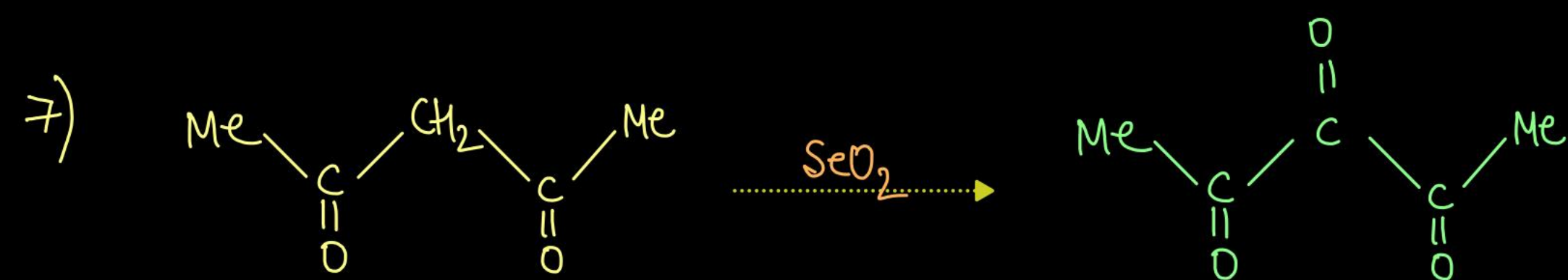
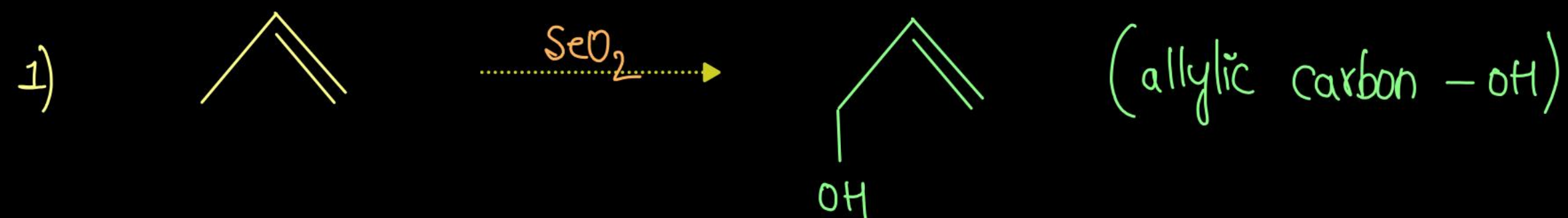




Mech :-



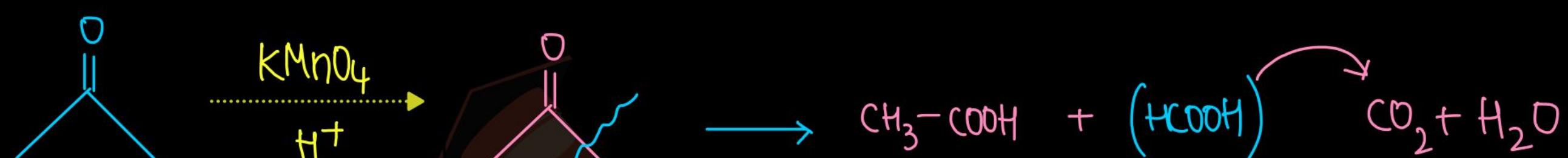
Note:-



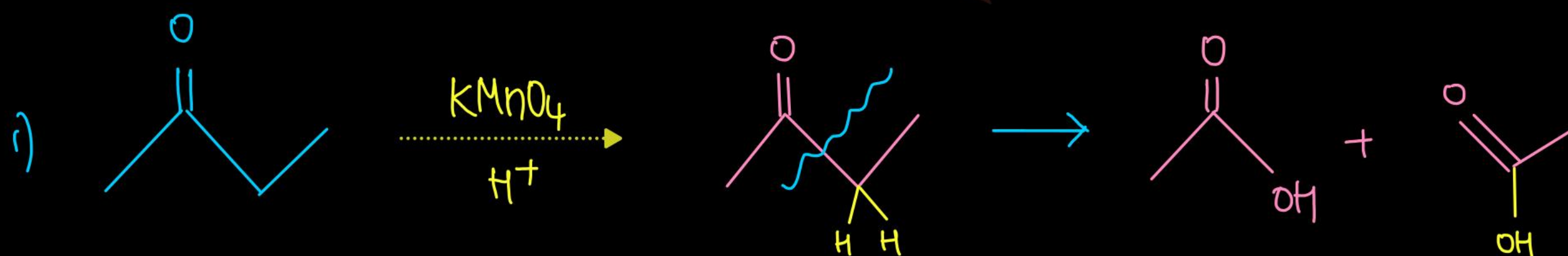
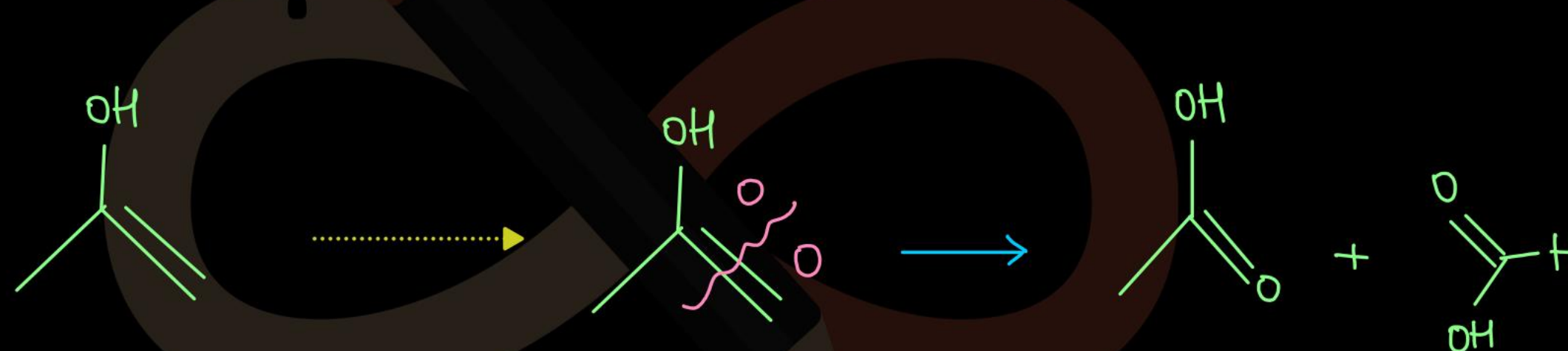
4) Popoff's rule :

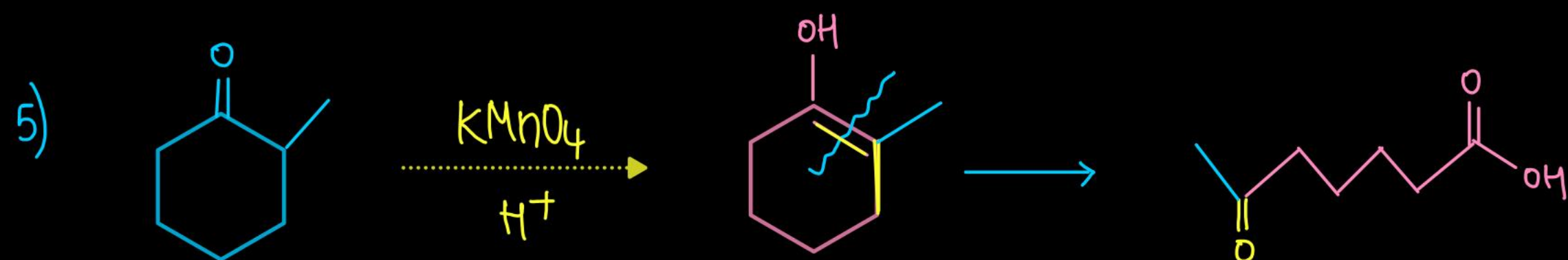
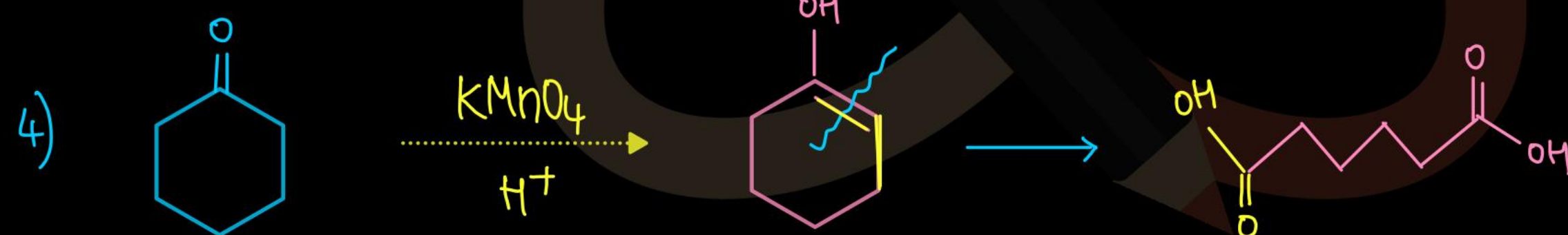
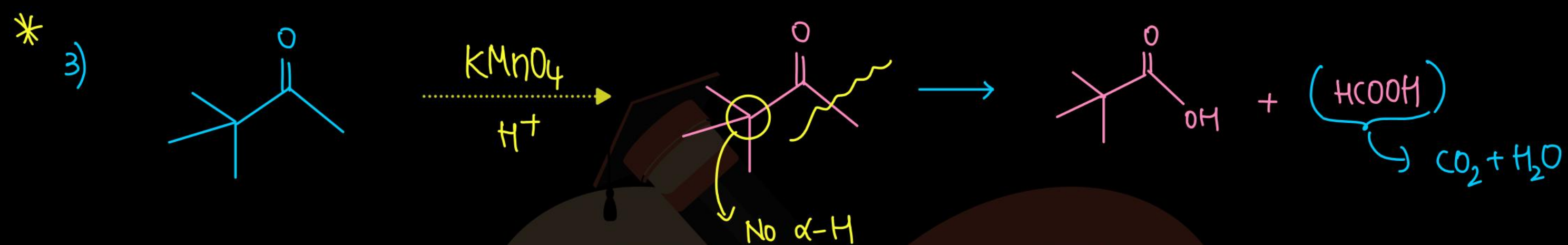
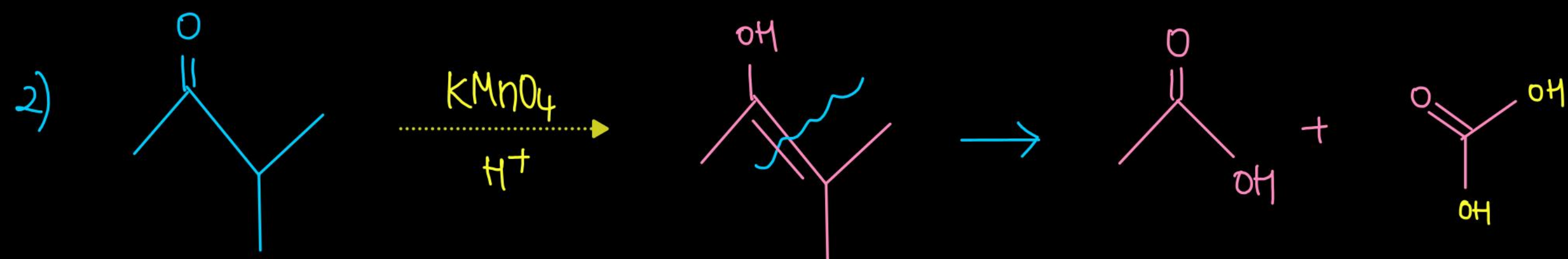
→ keto grp always stays with smaller alkyl group

Ex:-

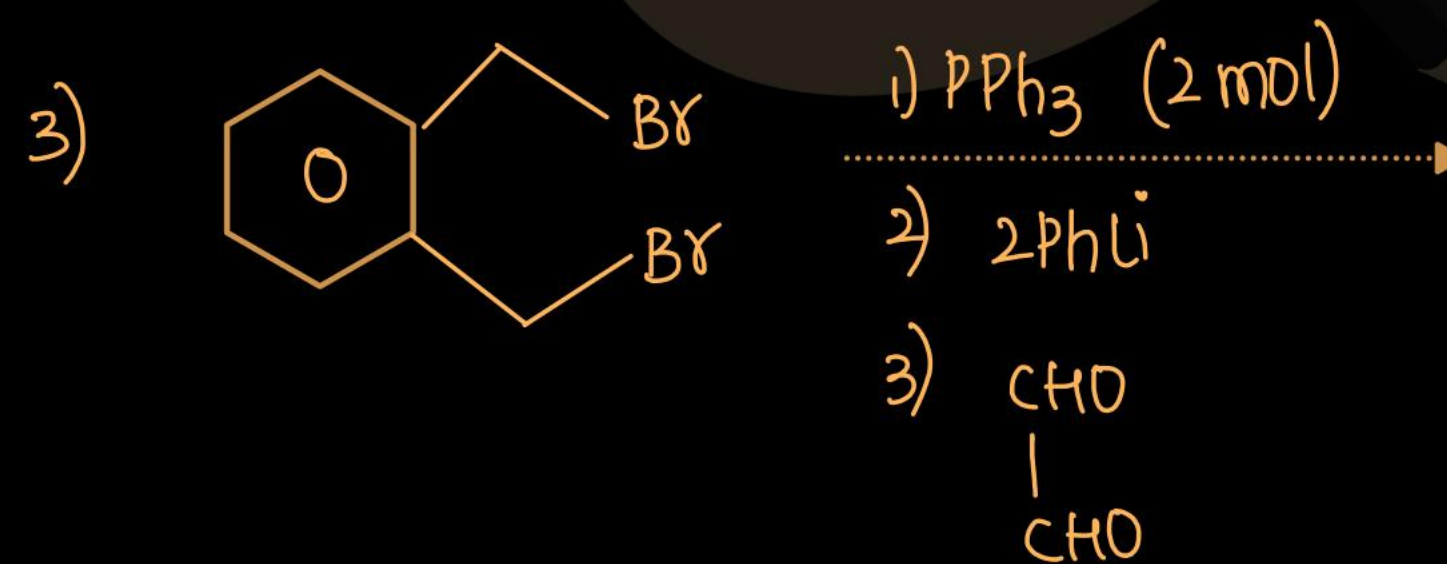
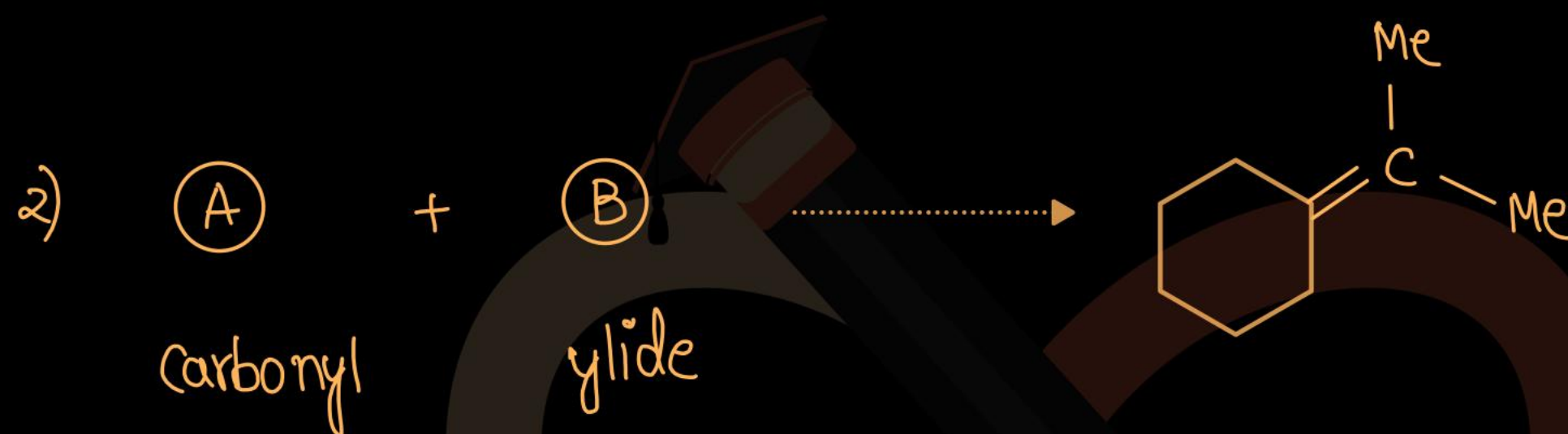
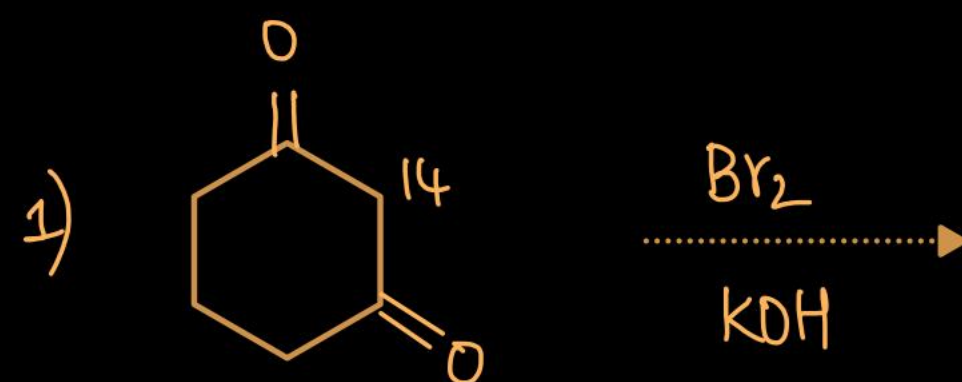


DM:-





Practice :



Sol:-

