

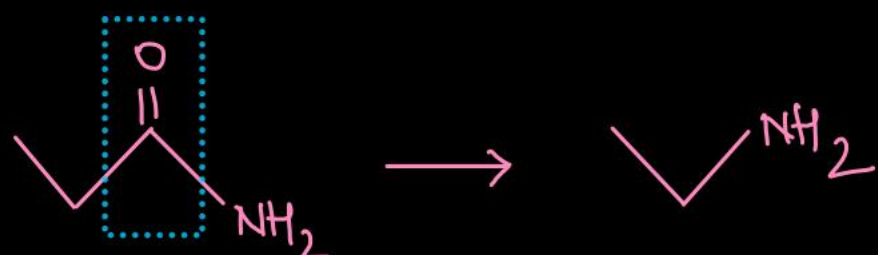
Amines

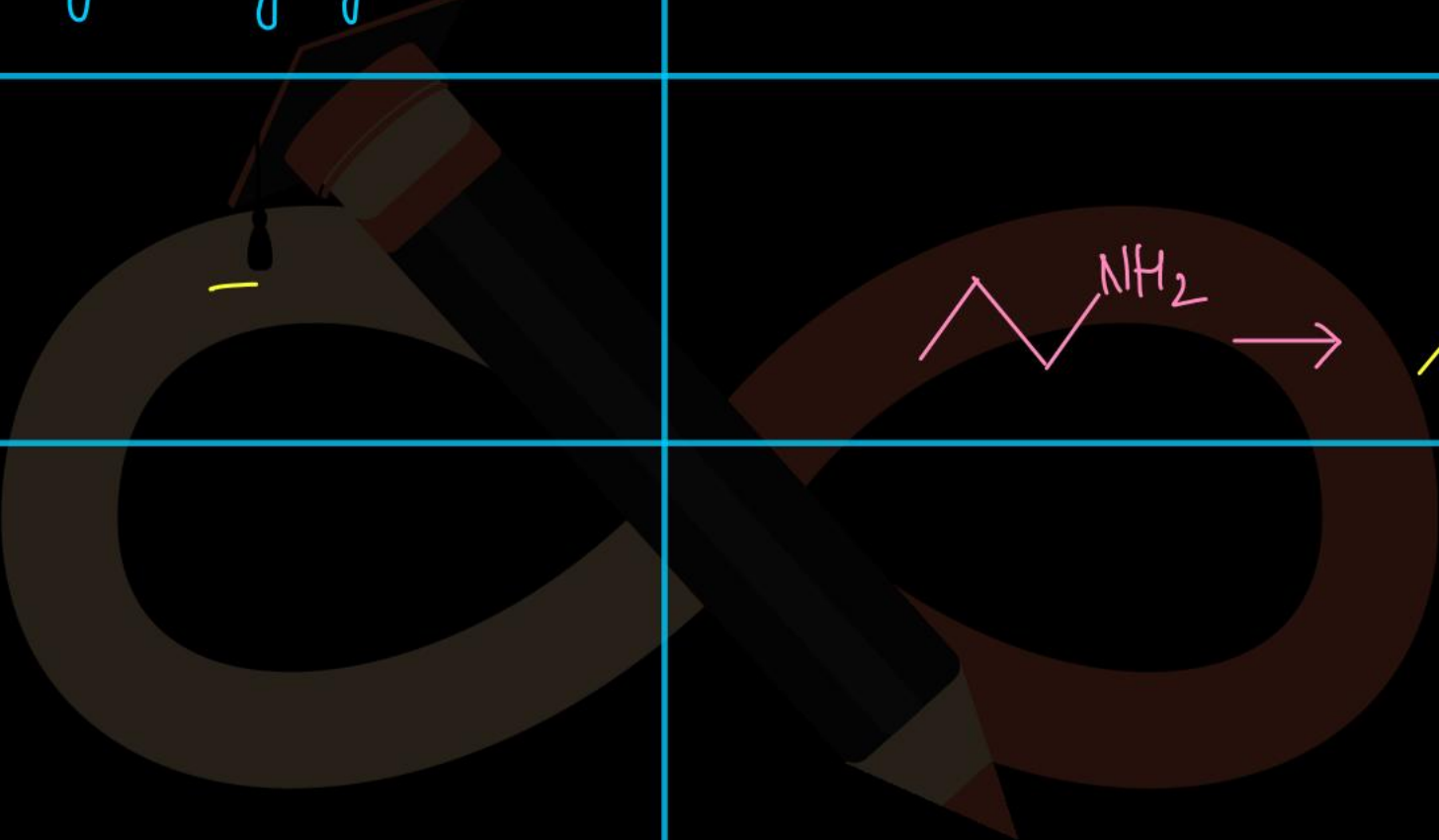
MOP:

1) Hoffman Bromamide Rxn	5
2) Gabriel Phthalamide Rxn	8
3) Ammonolysis	10
4) Reduction Rxn's	10
i) Nitro comp	
ii) Cyanide	
iii) Amides	
*) Diazonium Salt	21
→ Sandmeyer's rxn	
→ Gatterman's rxn	
→ che rxn's	22
*) Coupling rxn	23
Orange, Yellow, Red	

Properties:

1) Diazotisation of Aromatic amine	12
2) Rxn of 1° amine with HNO_2	13
3) Pinacol diazotisation rxn	13
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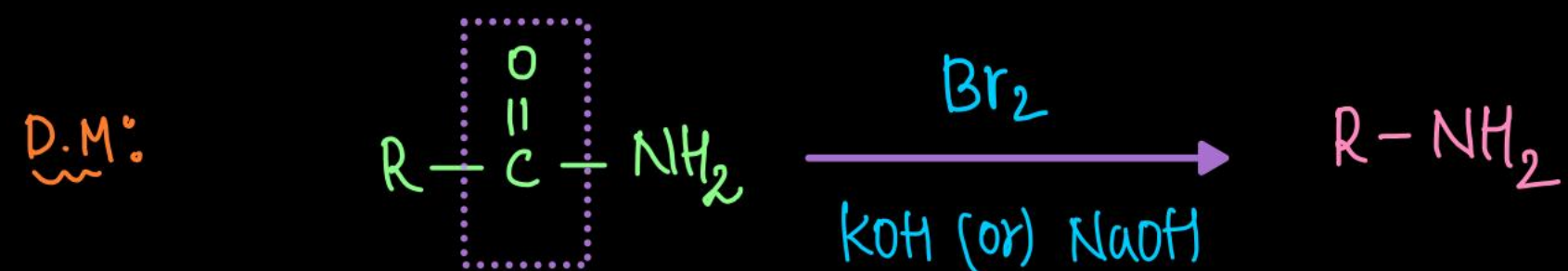
No.	Reagent	Process/rxn name	Rxn	points
1)	$\frac{\text{Br}_2}{\text{KOH (or) NaOH}}$	Hoffman bromide degradation		*) only 1°-amine *) succinamide
2)	KOH R-X aq, NaOH	Gabriel phthalimide synthesis		*) only 1°-amine
3)	$\frac{\text{CHCl}_3}{\text{KOH} / \Delta}$	Carbylamine/isocyanide test	$\text{R-NH}_2 \longrightarrow \text{R-CN}$	*) only 1° amines
4)		Hinsberg reagent (Benzene Sulphonyl chloride)	$\text{R-NH}_2 \longrightarrow \text{BSC} - \underset{\text{H}}{\underset{ }{\text{N}}} - \text{R}$	*) 1° → Soluble 2° → Insoluble 3° → No rxn
5)	LiAlH_4 (or) H_2 / Ni	Reduction of cyanide	$\text{R-CN} \longrightarrow \text{R-CH}_2\text{-NH}_2$	

6)	$\frac{\text{H}_2}{\text{N}_2/\text{Pt}/\text{Pd}}$ $\text{Fe/Sn} + \text{HCl}$	Reduction of Nitro	$\text{R}-\text{NO}_2 \longrightarrow \text{R}-\text{NH}_2$	*) Fe + HCl is best
7)	P_2O_5	*) dehydrating agent	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}_2 \longrightarrow \text{R}-\text{CN}$	
8)	HNO_2			*) only for 1°

9)	$\xrightarrow[0-5^{\circ}\text{C}]{\text{NaNO}_2 + \text{HCl}}$	diazotisation	$\text{Ph-NH}_2 \rightarrow \text{Ph-N}_2^+\text{Cl}^-$	* 2° $\rightarrow$ Yellow
10)	CuX_2 / HX	Sandmeyer's rxn	$\text{BDC} \rightarrow \text{Ph-X} + \text{N}_2$	-
11)	Cu / HX	Gattermann rxn	$\text{BDC} \rightarrow \text{Ph-X} + \text{CuX} + \text{N}_2$	-
12)	$\xrightarrow[\Delta]{\text{HBF}_4}$	Balz schiemann rxn	$\text{BDC} \rightarrow \text{Ph-F}$	-
13)	$\text{H}_3\text{PO}_2 / \text{H}_2\text{O}$	Replacement by H	$\text{BDC} \rightarrow \text{Ph-H}$	-
14)	H_2O	prep of phenol	$\text{BDC} \rightarrow \text{Ph-OH}$	-

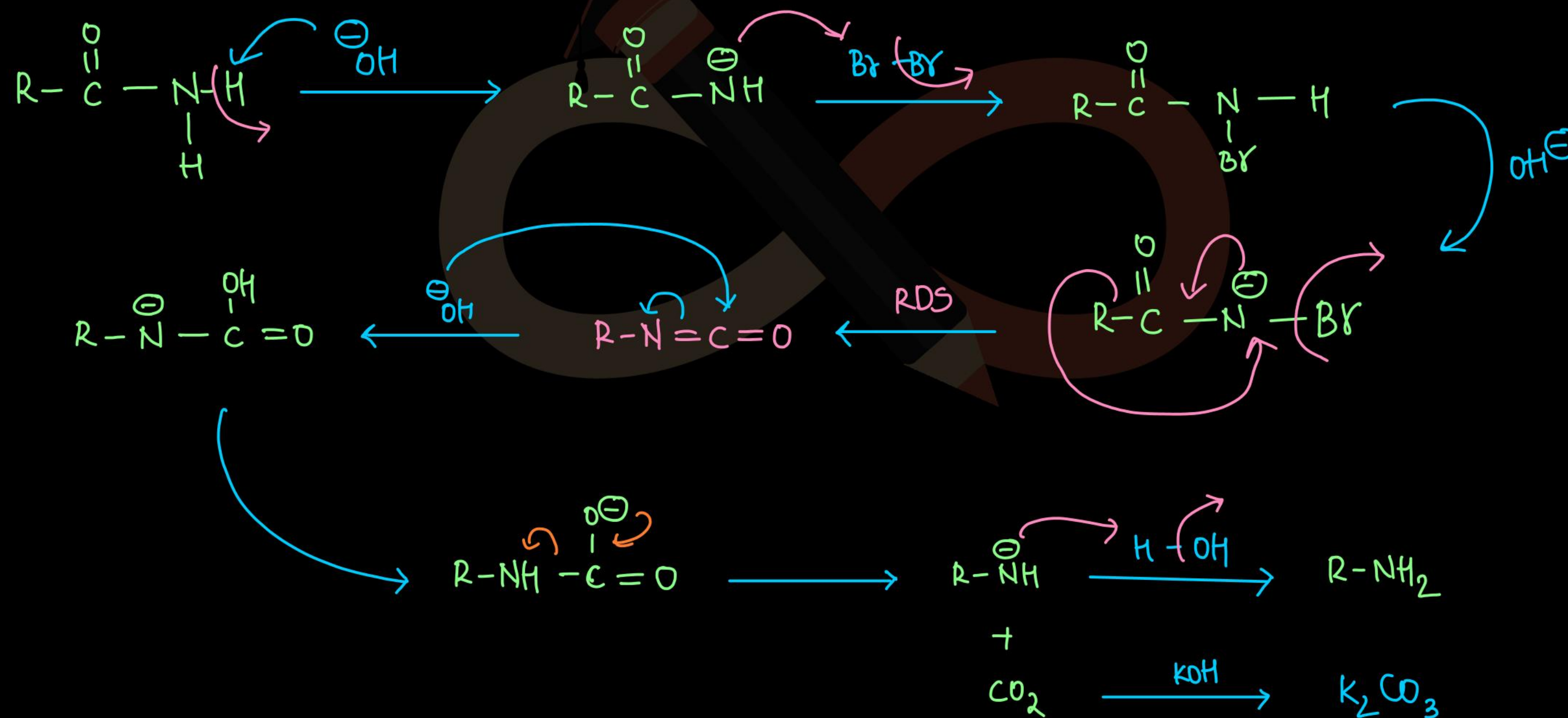
MOP:

1) Hoffman Bromamide degradation :-



*) Only 1^o amine

Mech:-

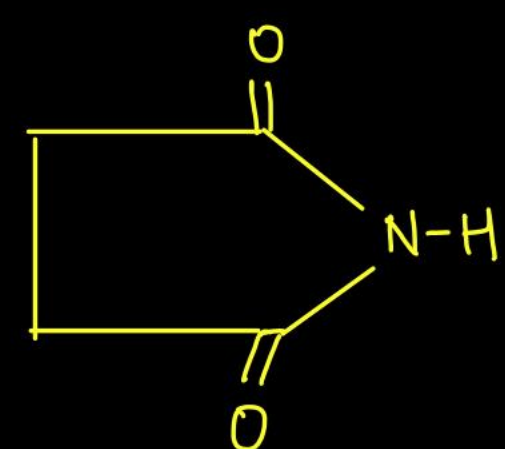


Imp points :

- 1) Migration of Group is the RDS
- 2) Purely Intra molecular migration
- 3) Retention of Configuration
- 4) Step down (degradation rxn)
- 5) 2° & 3° do not give this rxn

Note:-

*)

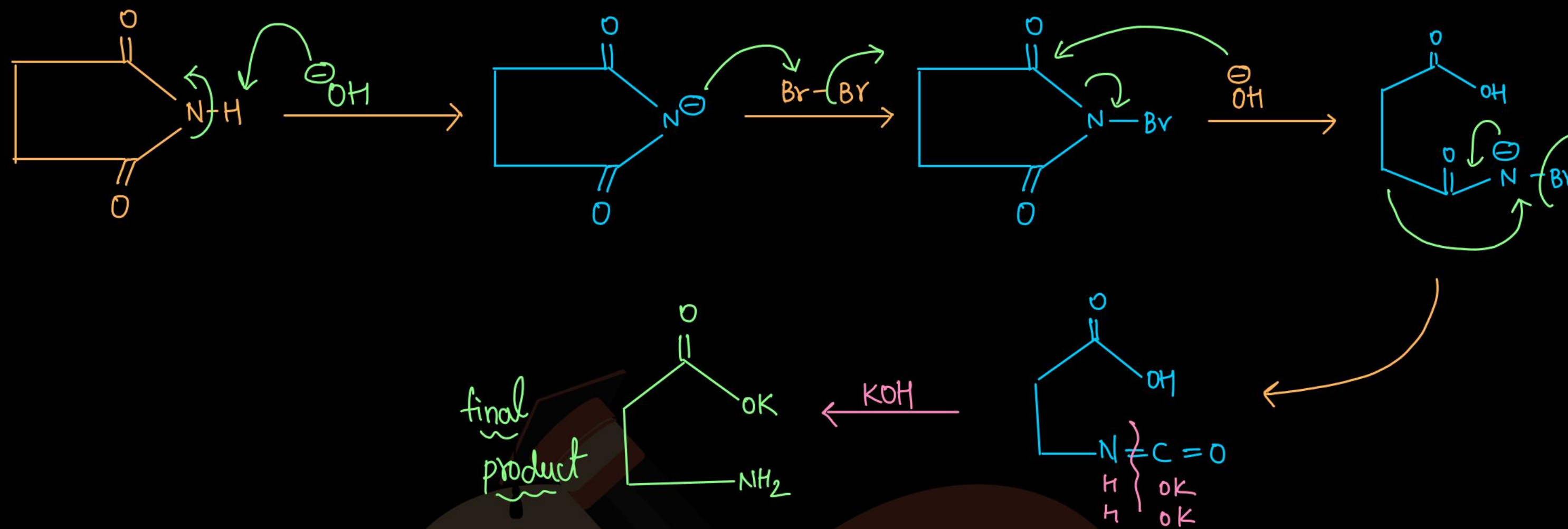


(succinamide)



Gives Hoff Brom Rxn ✓

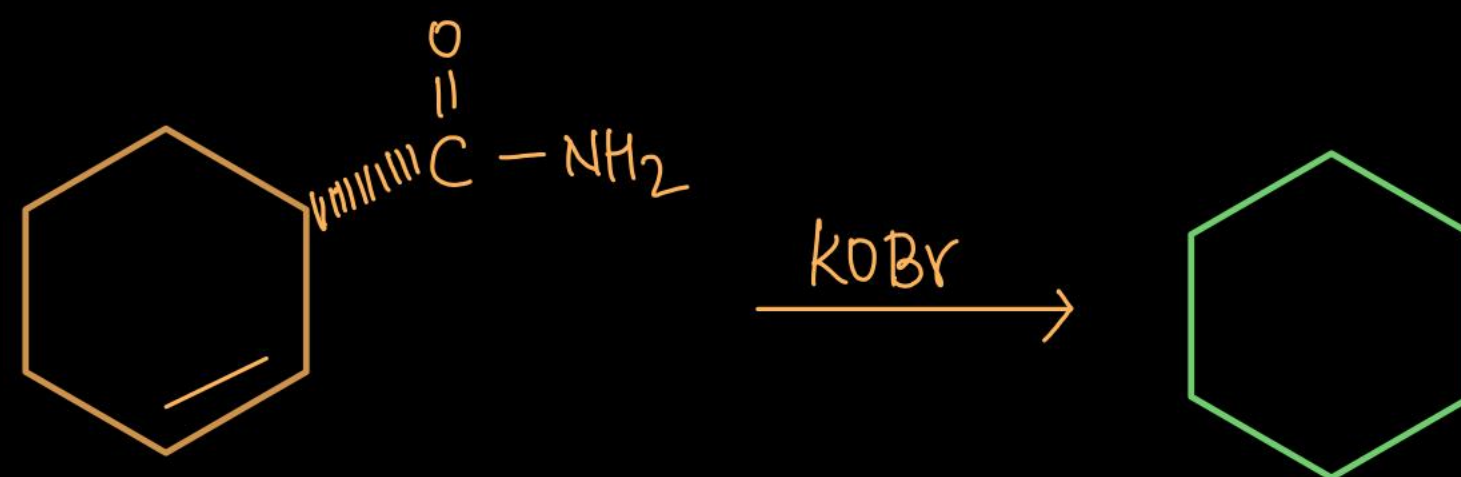
Mech:-

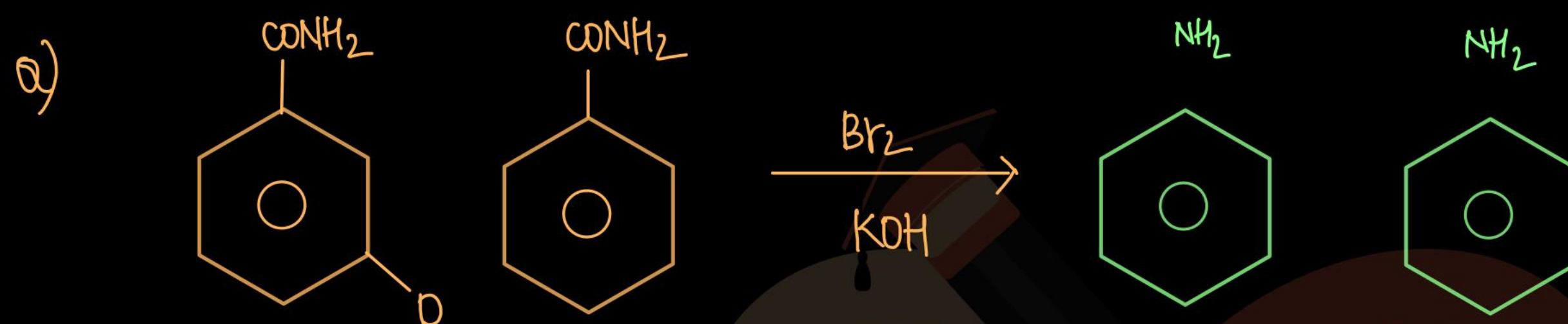
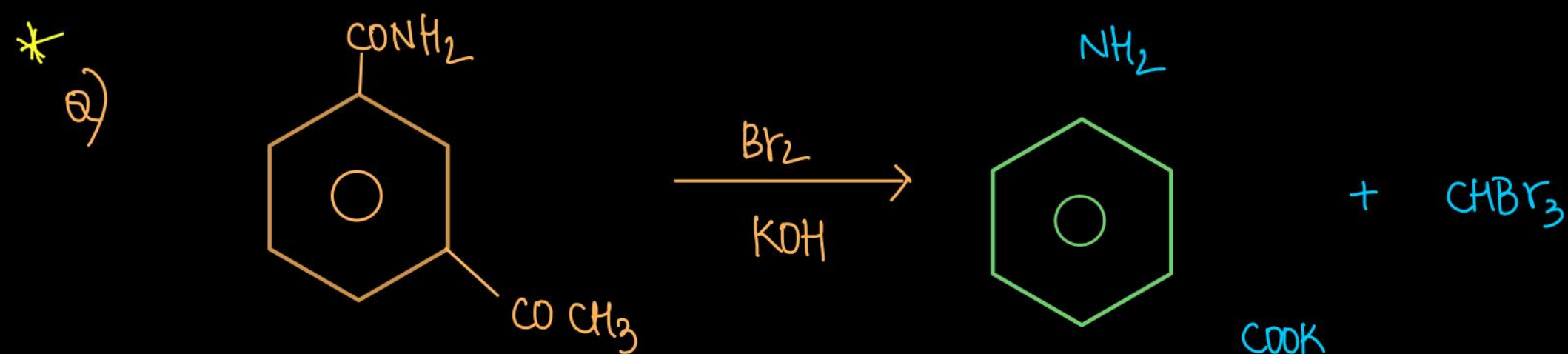


Q)

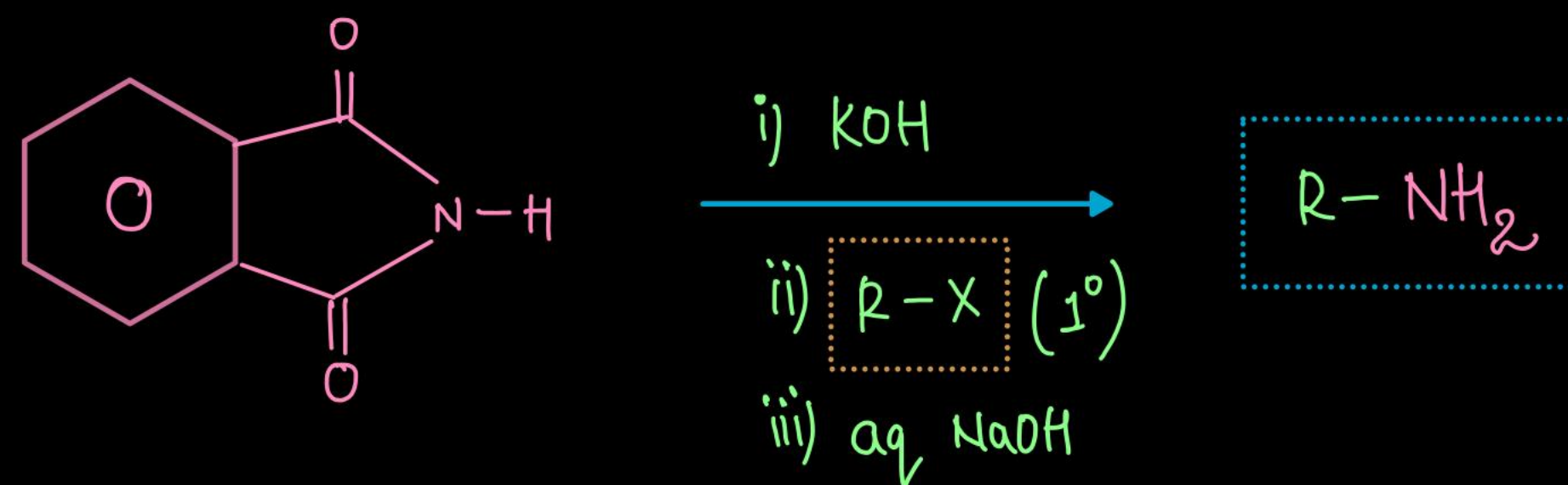


Q)

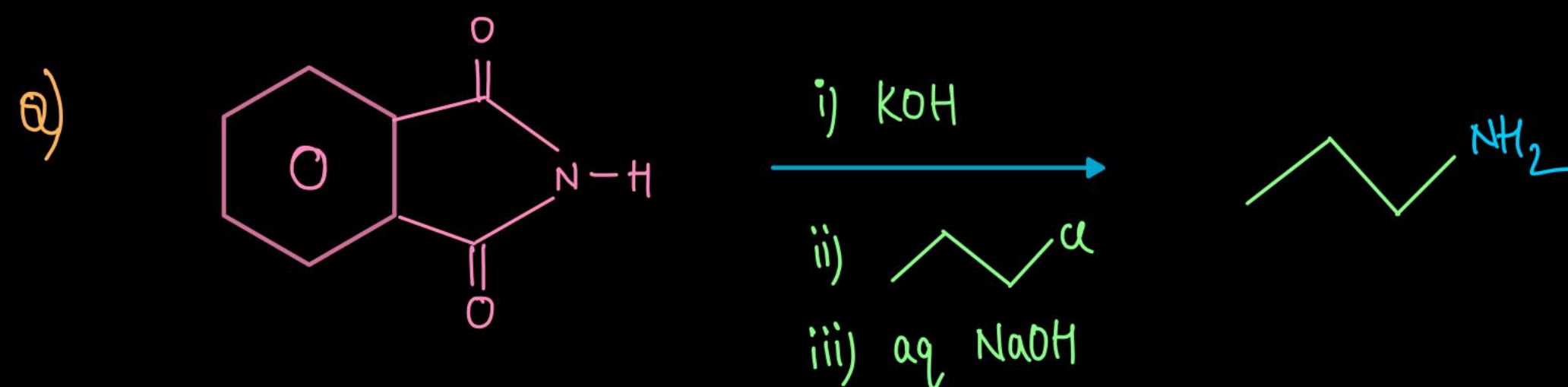
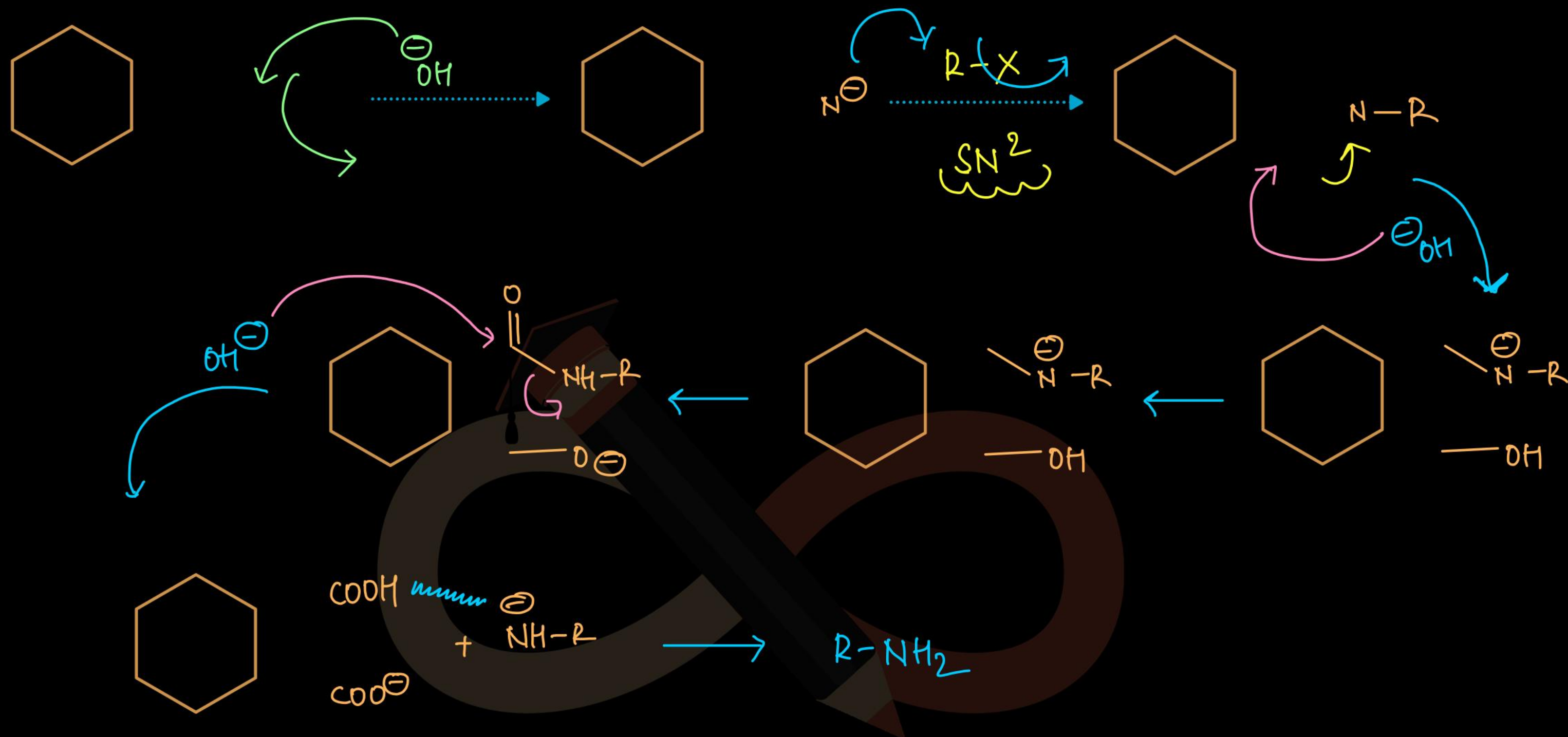




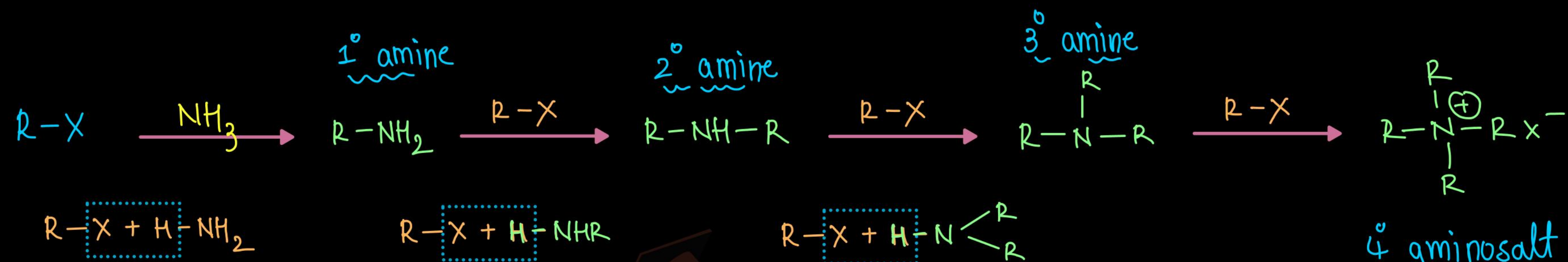
② Gabriel phthalimide synthesis :- (for preparation of 1° aliphatic amine)



Mech :-



③ Ammonolysis :



④ Reduction Rxn

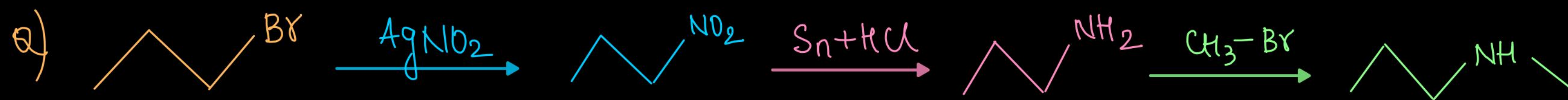
i) Nitro Compounds :

Reagents : H_2/Ni (or) Pt (or) Pd (or)

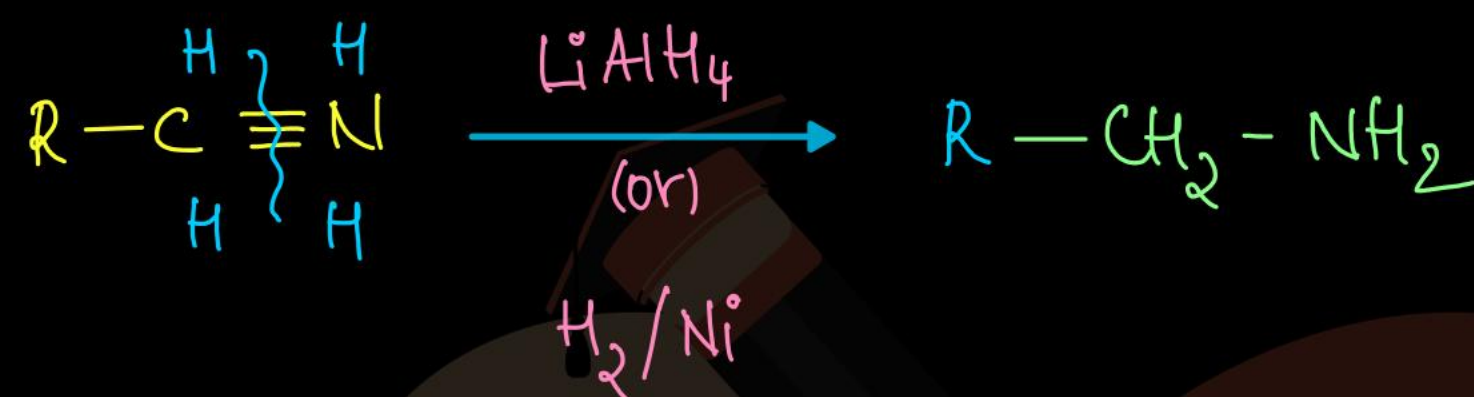
Fe (or) $Sn + HCl$



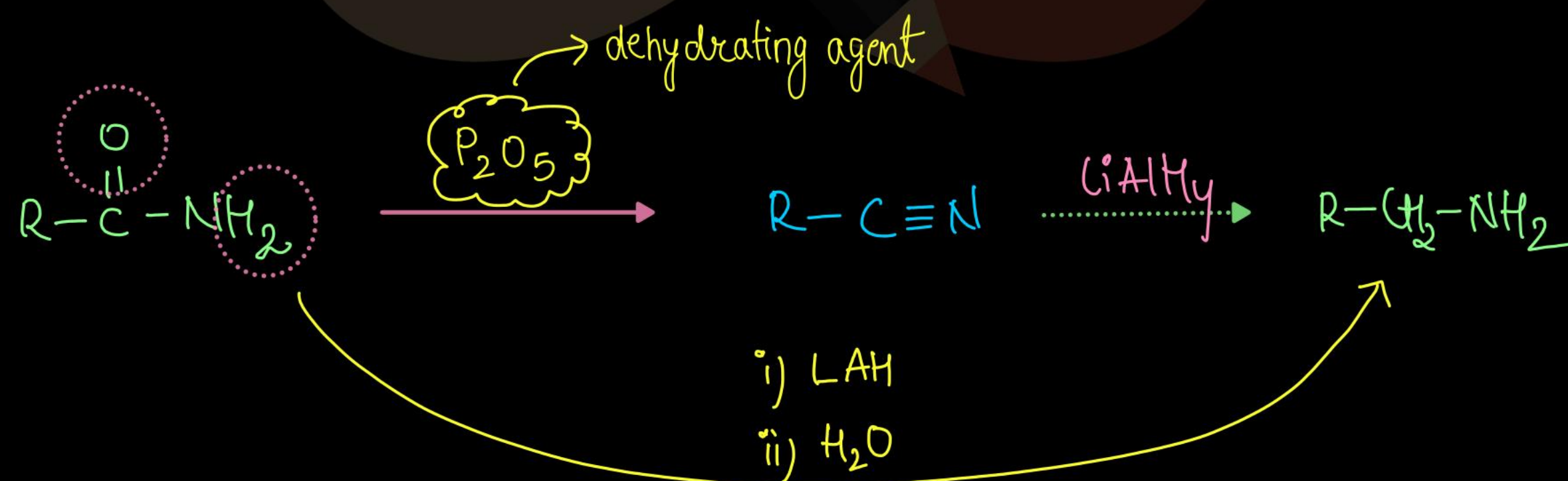
* $Fe + HCl$ is preferred
because HCl is produced.



ii) Cyanide:

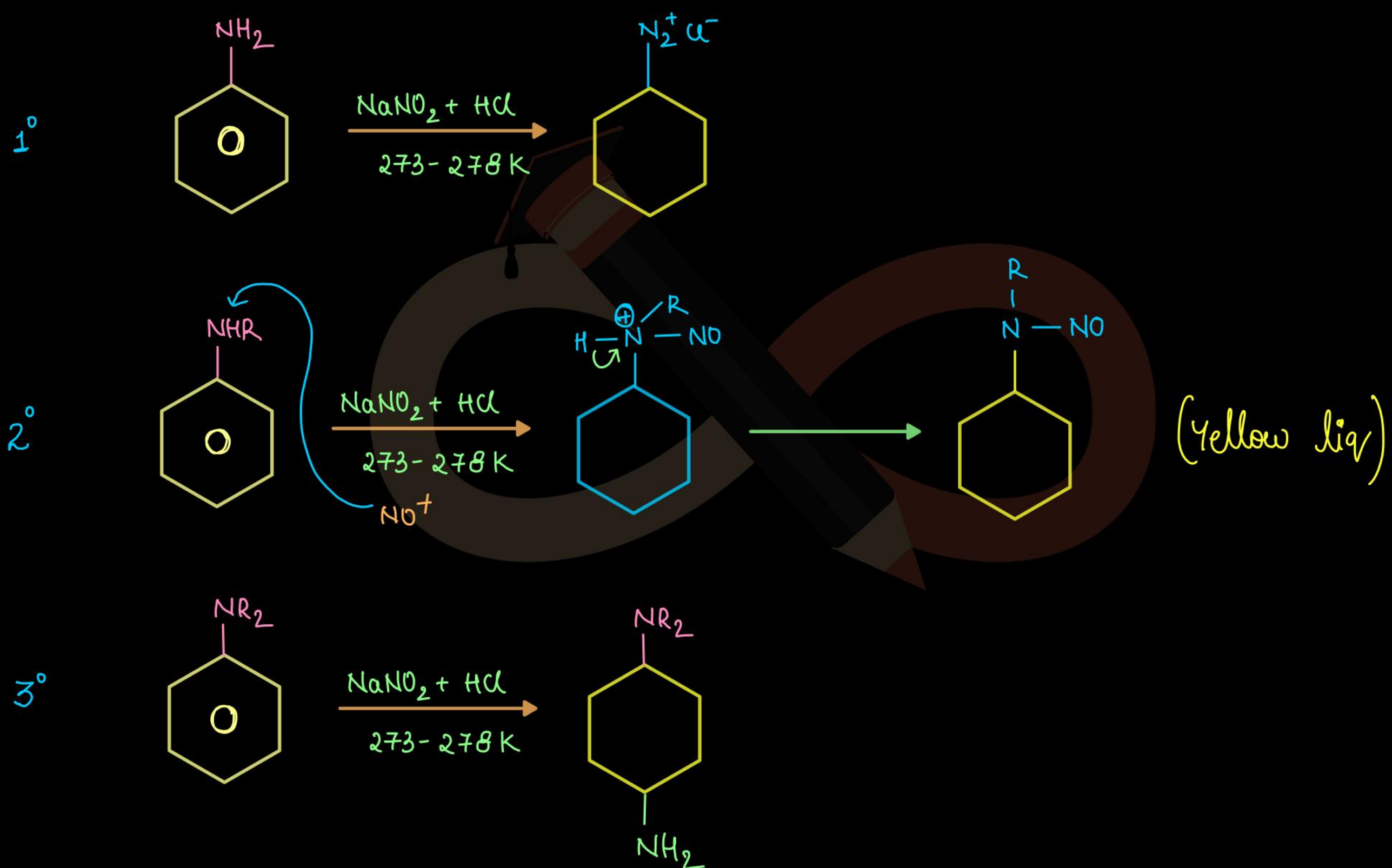


iii) Amides :-

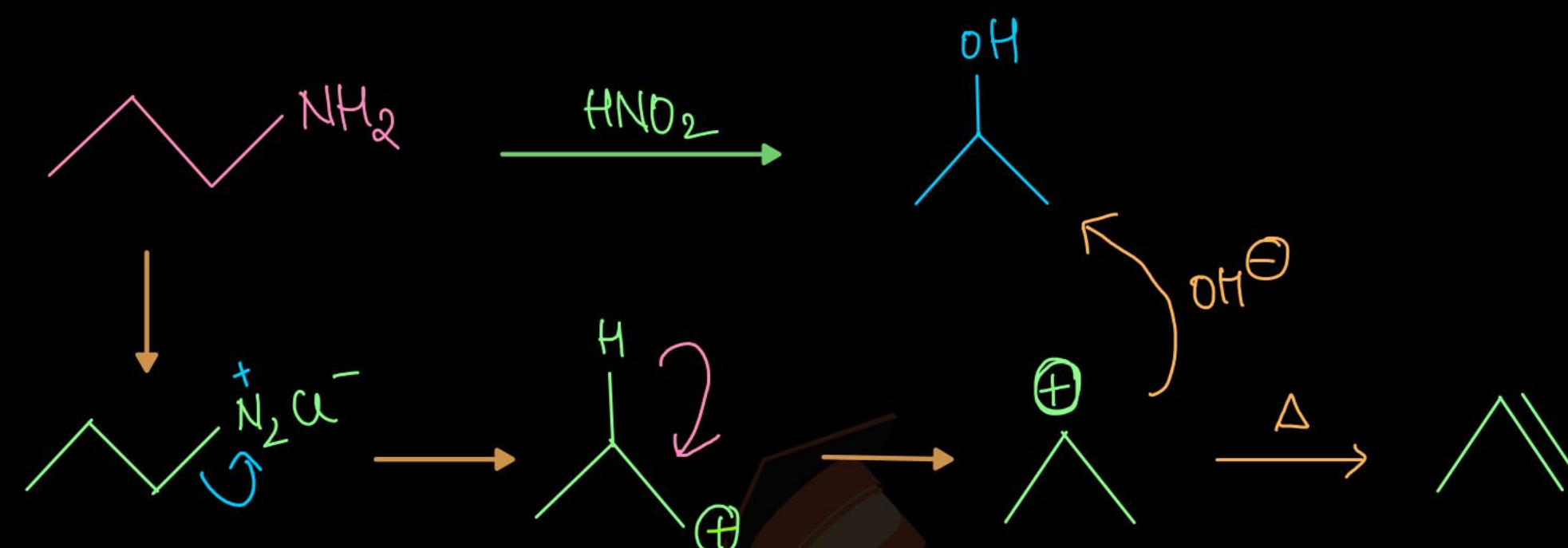


Properties :-

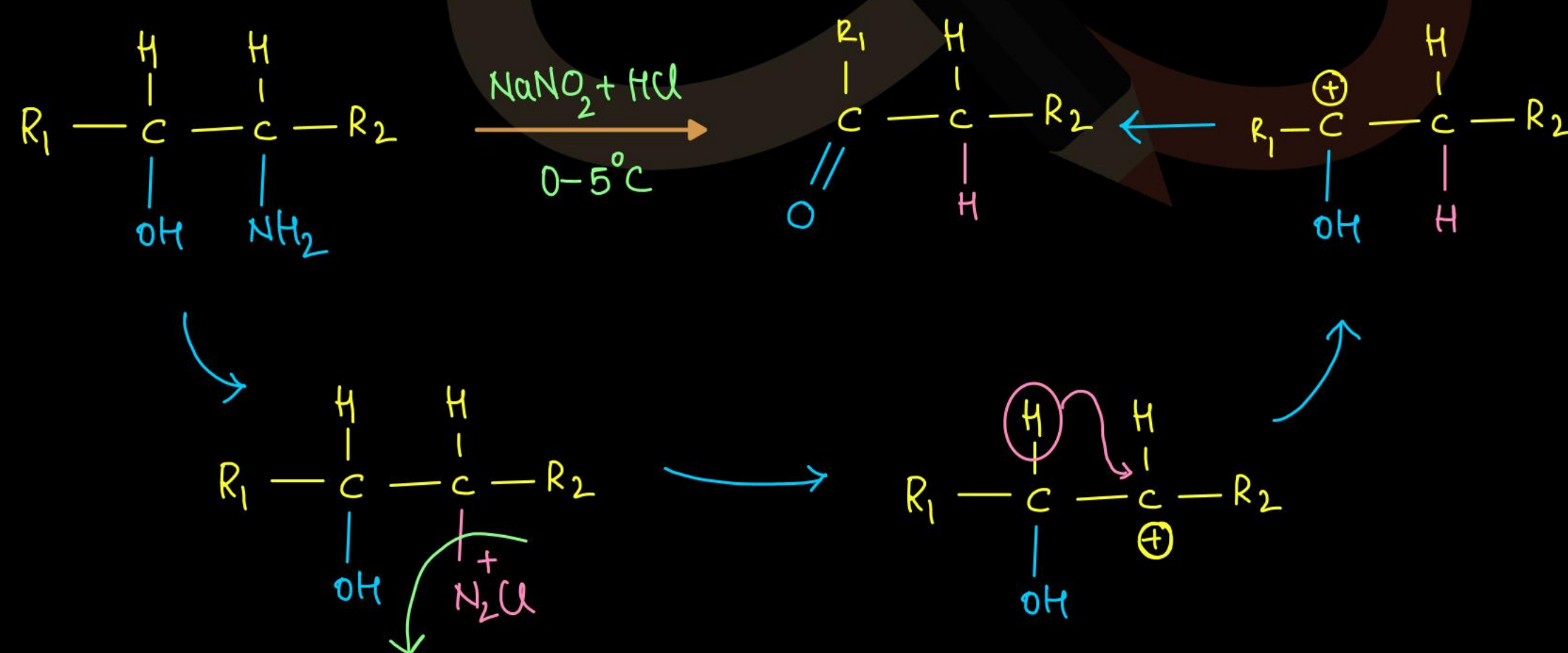
1) Diazotisation of Aromatic amine :



2) Rxn of aliphatic 1° amine with HNO_2 .

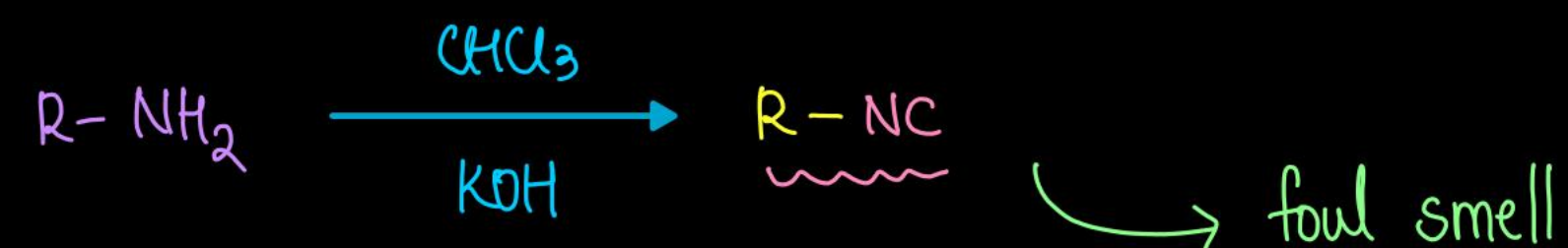


3) Pinacol diazotisation rxn:

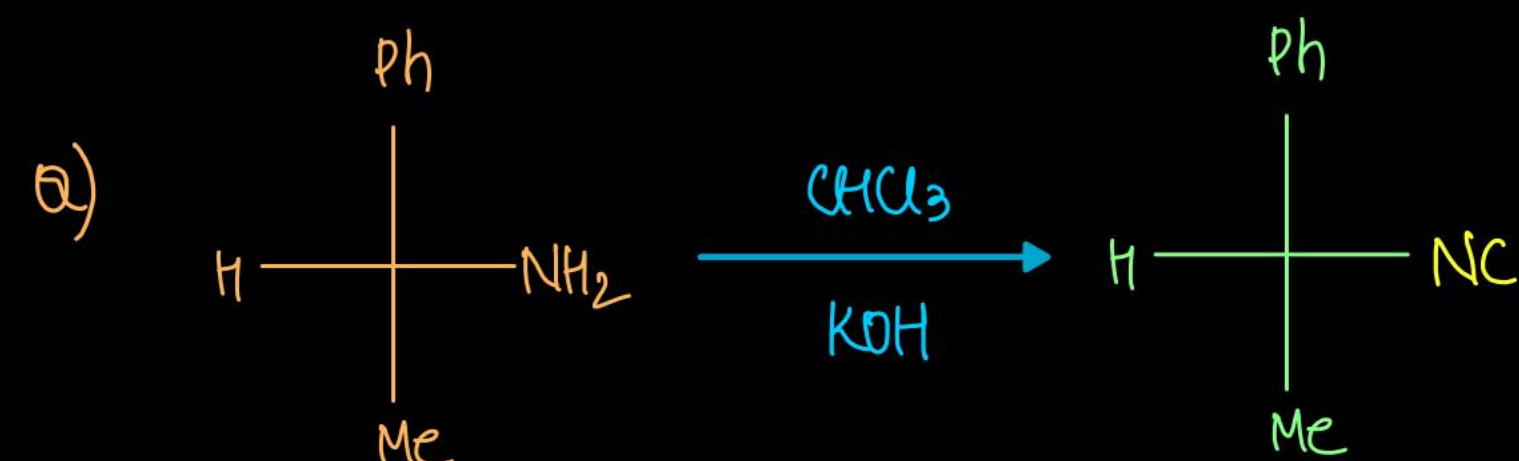
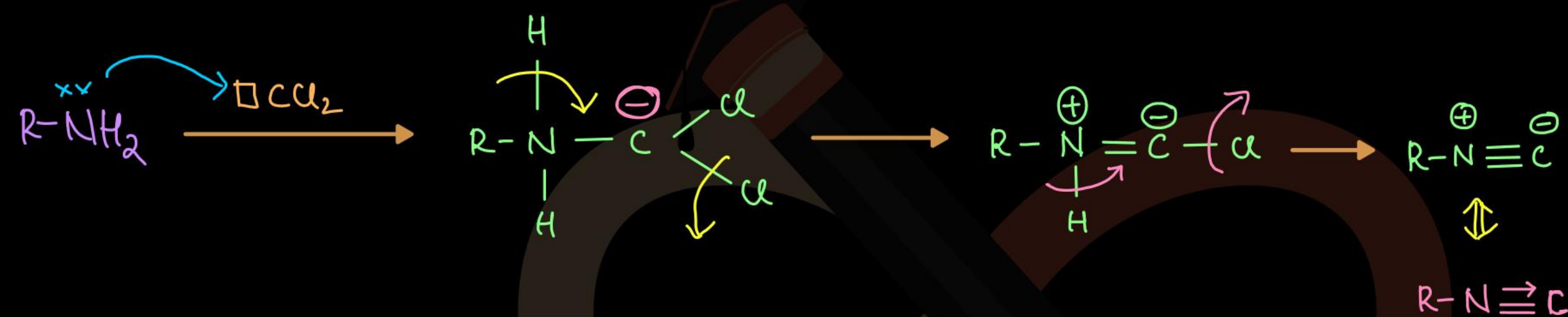


4) Carbylamine Test (Isoyanide test) :-

* only 1° amine

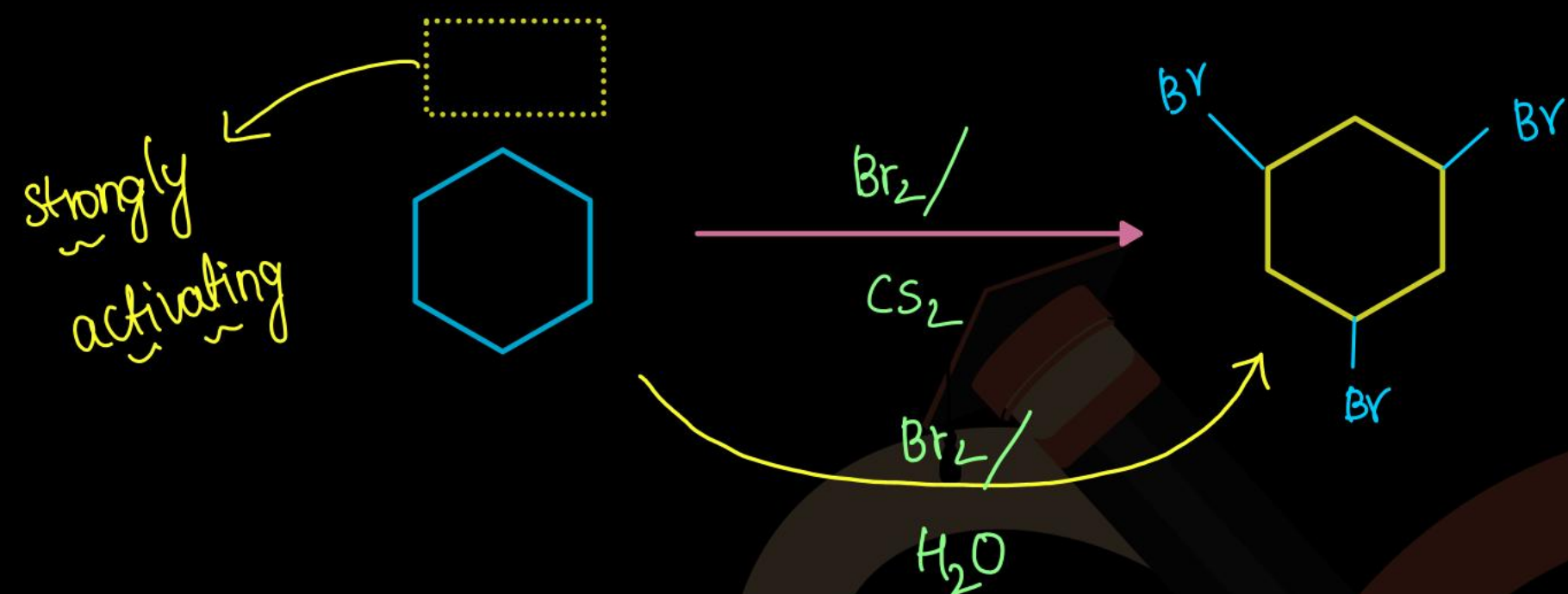


Mech:-

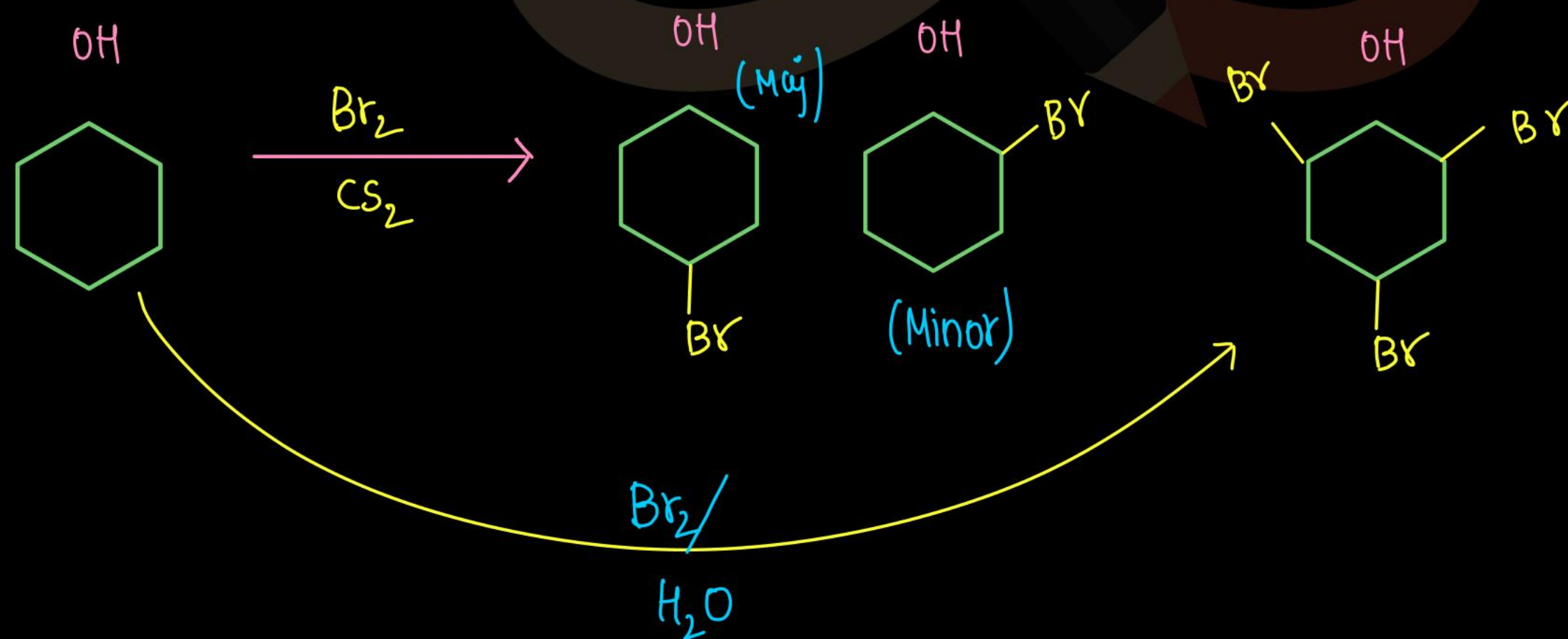


⑤ EAS of Aniline

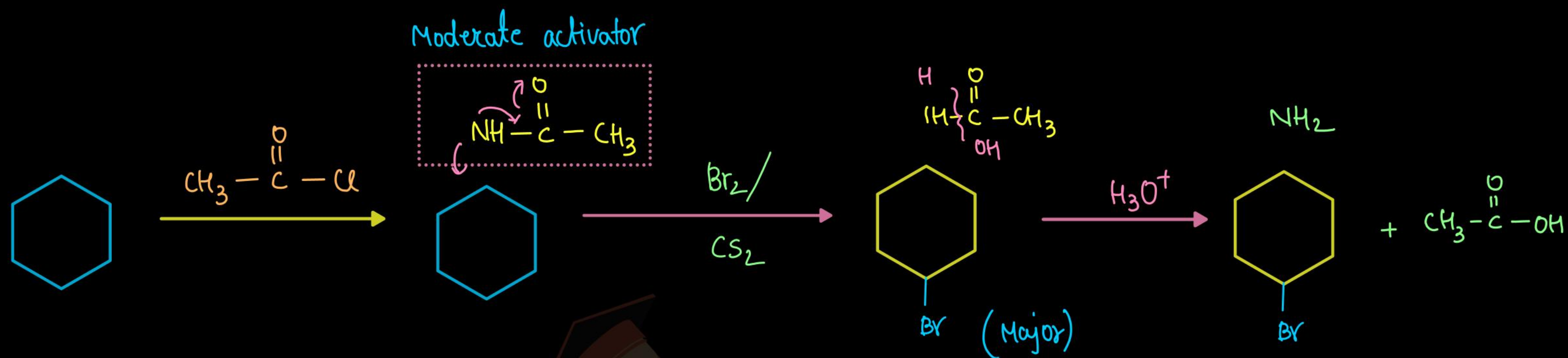
i) Bromination



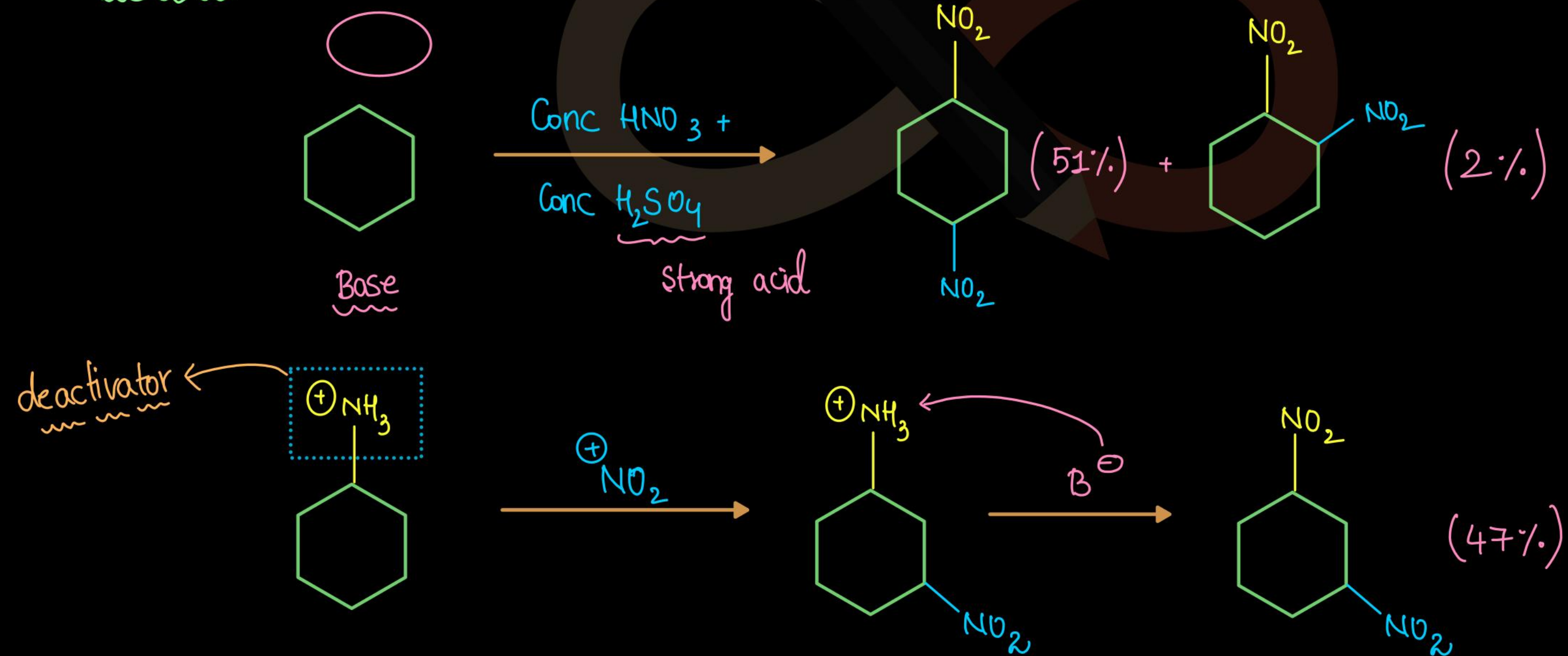
Note:-



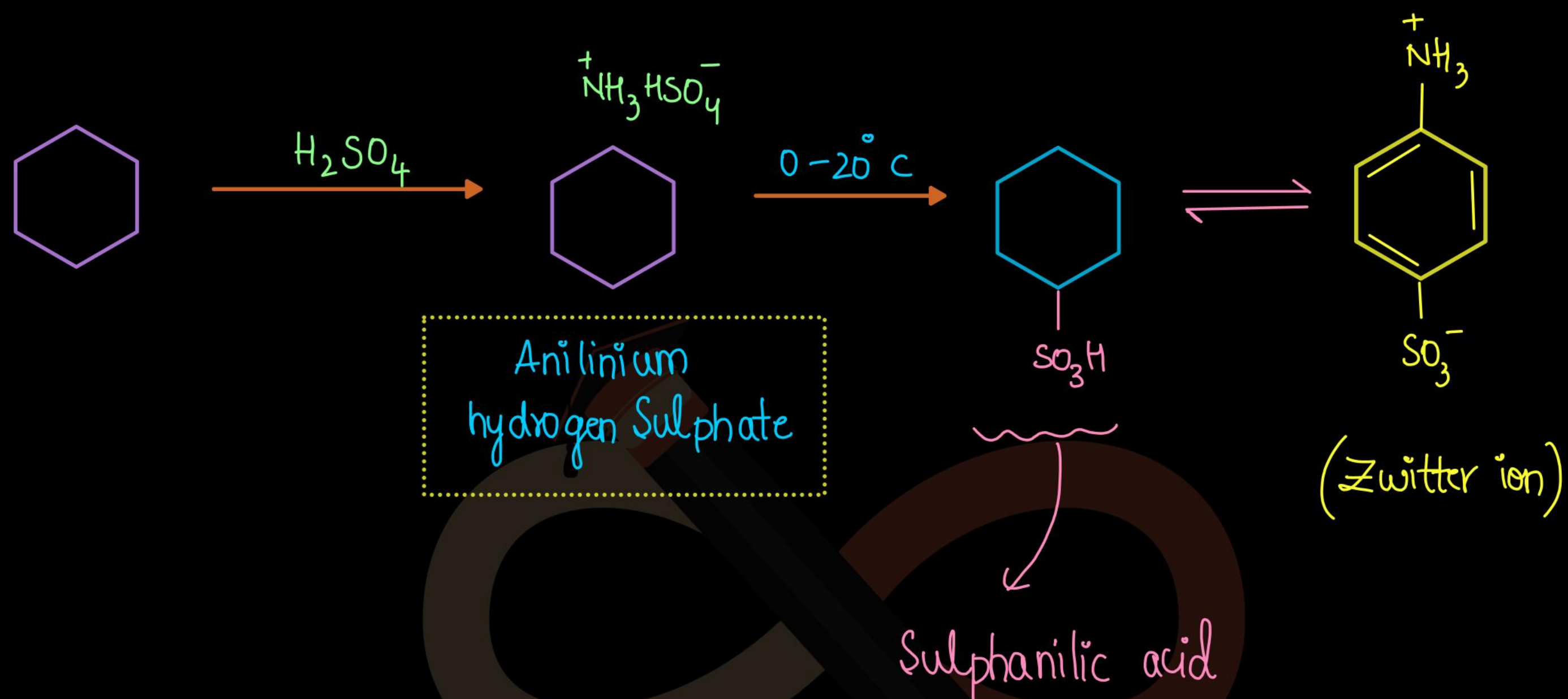
* for Mono bromination ;



** ii) Nitration



iii) Sulphonation :



* Aniline does not undergo Friedal Crafts rxn due to
Salt formation with AlCl_3 .

⑥ Basic Nature

- i) Amines > Amides > Cyanides
- ii) Aliphatic > Aromatic
- iii) localised LP > delocalised LP

*)

R = Me $2^\circ > 1^\circ > 3^\circ$ (aq med)

R = Et $2^\circ > 3^\circ > 1^\circ$ (aq med)

$3^\circ > 2^\circ > 1^\circ$ (gaseous phase)

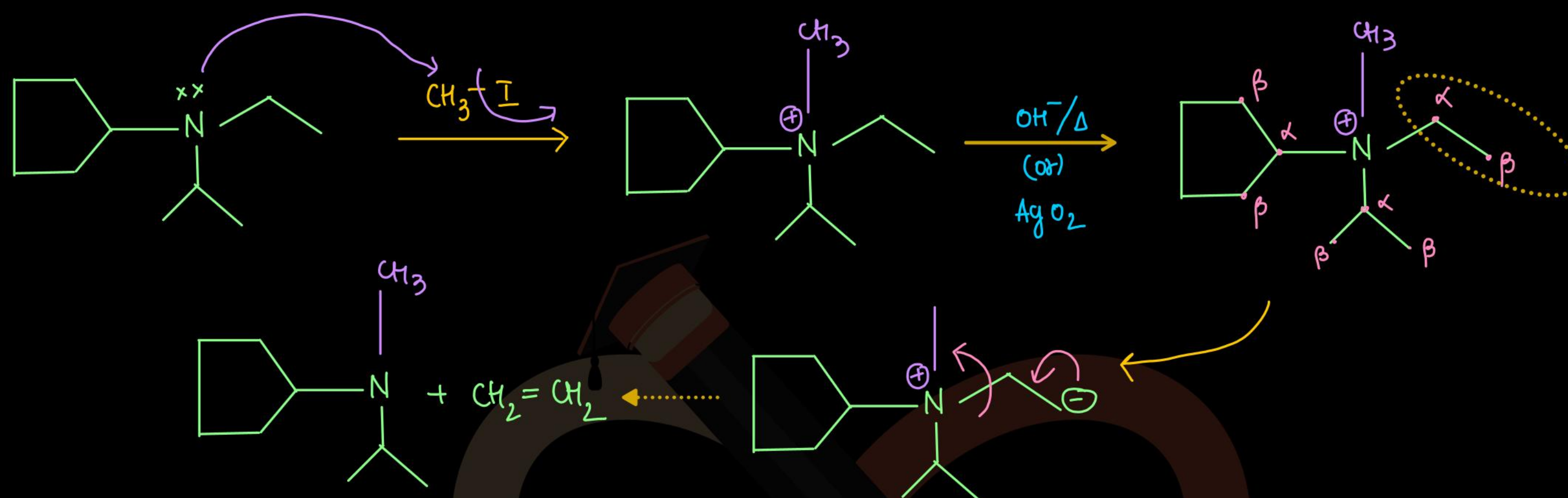
$3^\circ > 2^\circ > 1^\circ$ (gaseous phase)

*)

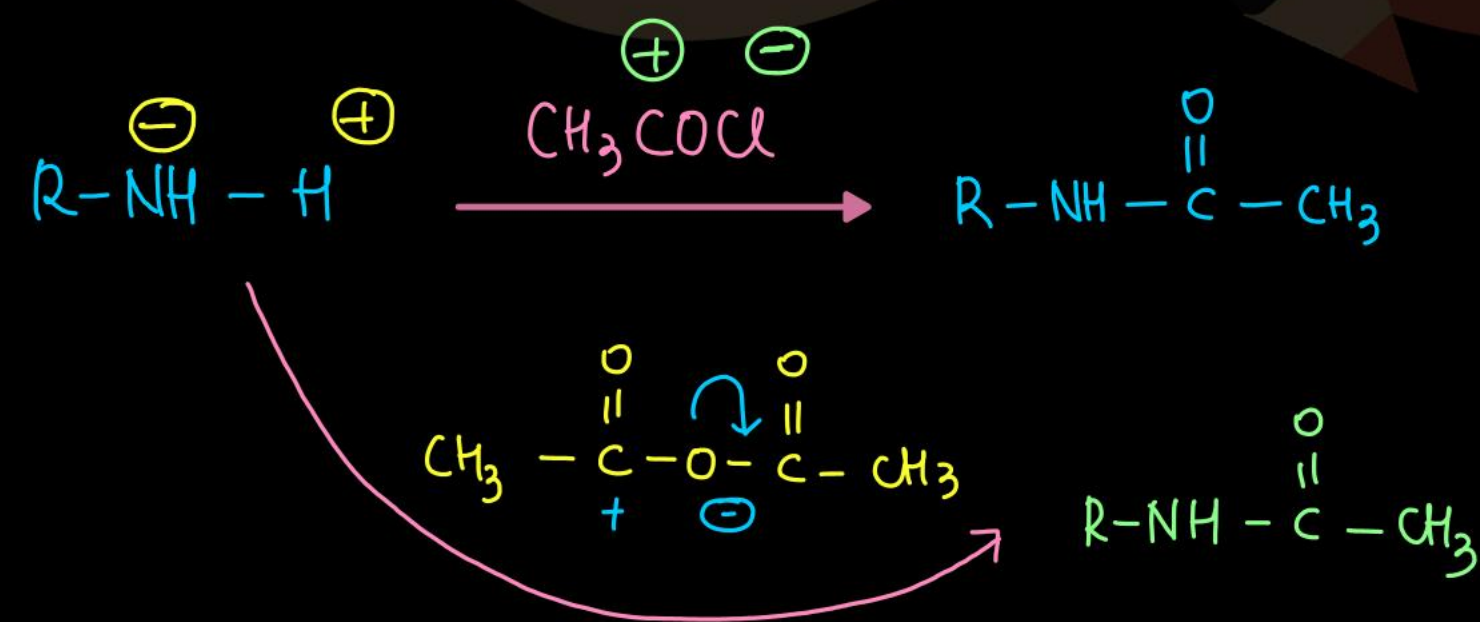
p_{kb} of Ammonia is 4.75

p_{kb} of Aliphatic amines 3 - 4.22

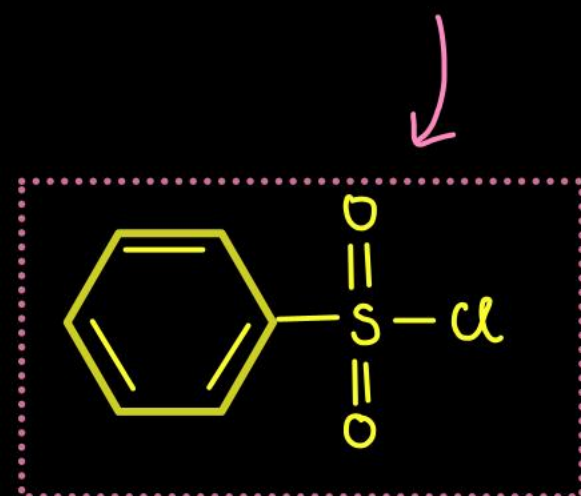
⑦ Heating of Quaternary amines : (E_{1cb})



⑧ Acetylation :



⑨ Rxn with Benzene Sulphonyl chloride



Hinsberg's Reagent : alternative : p-toulene Sulphonyl chloride



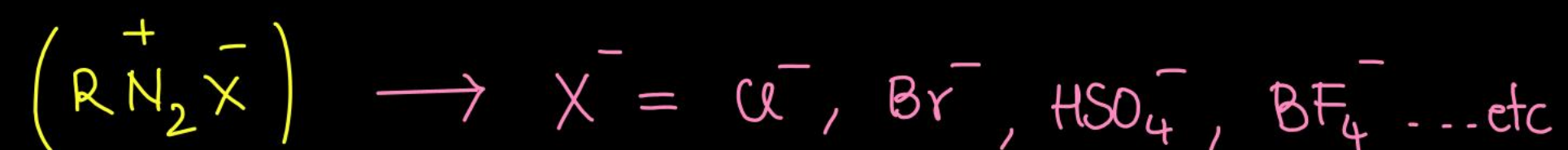
(soluble in alkali)



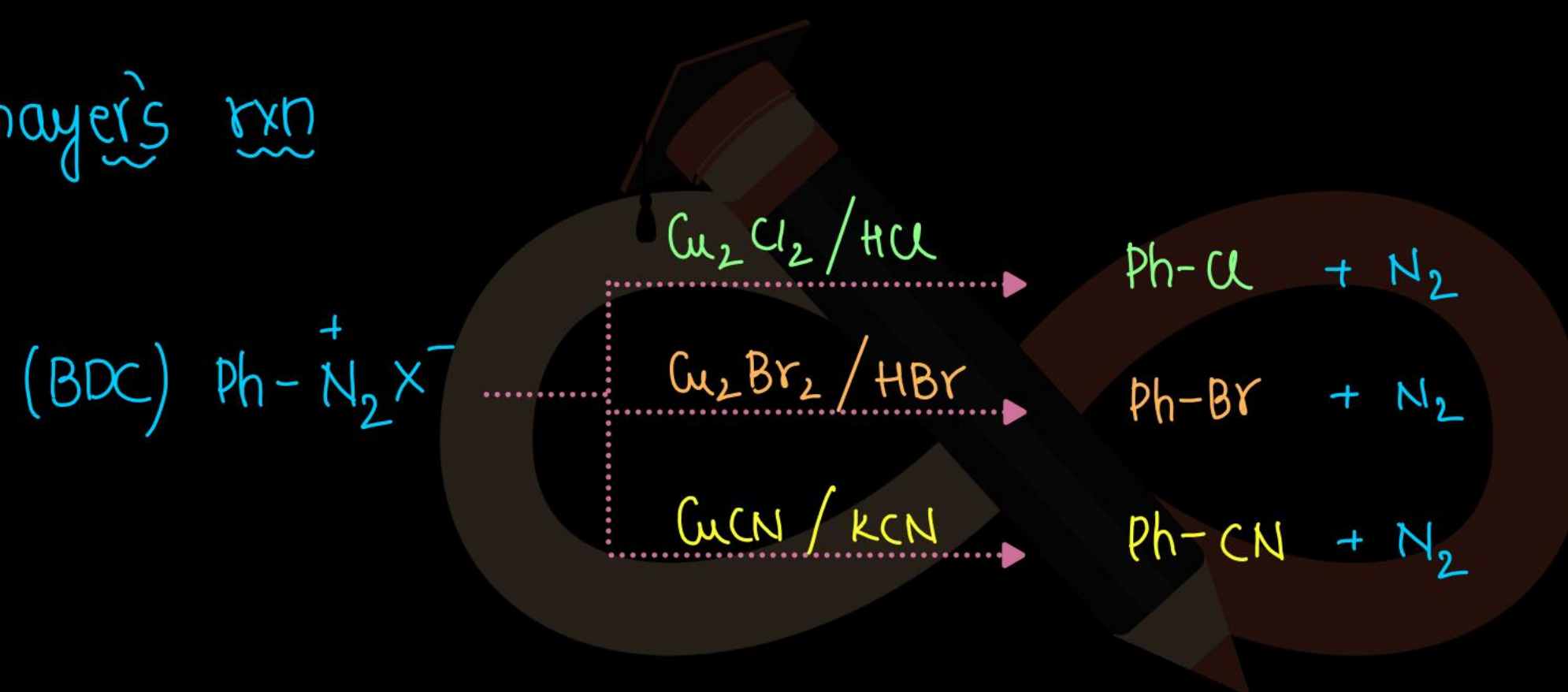
(insoluble in alkali)

3°) NH_3 $\times$ No reaction.

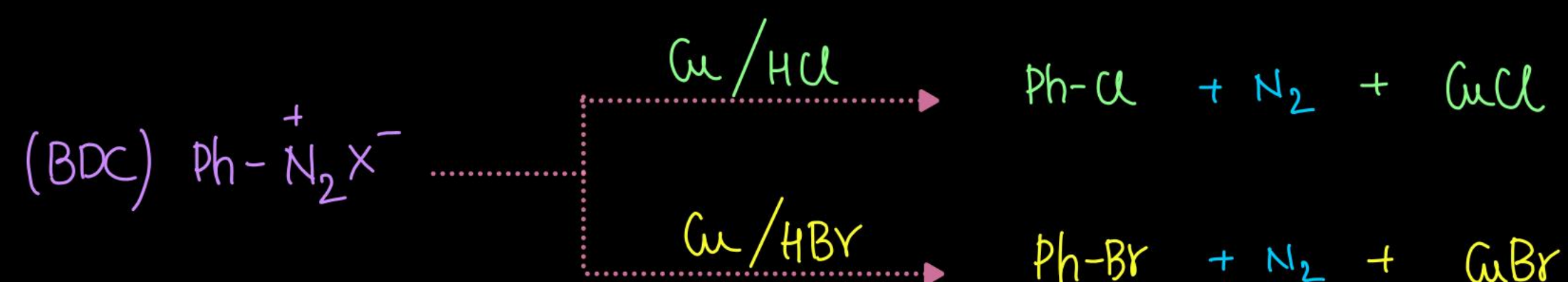
Diazonium Salt



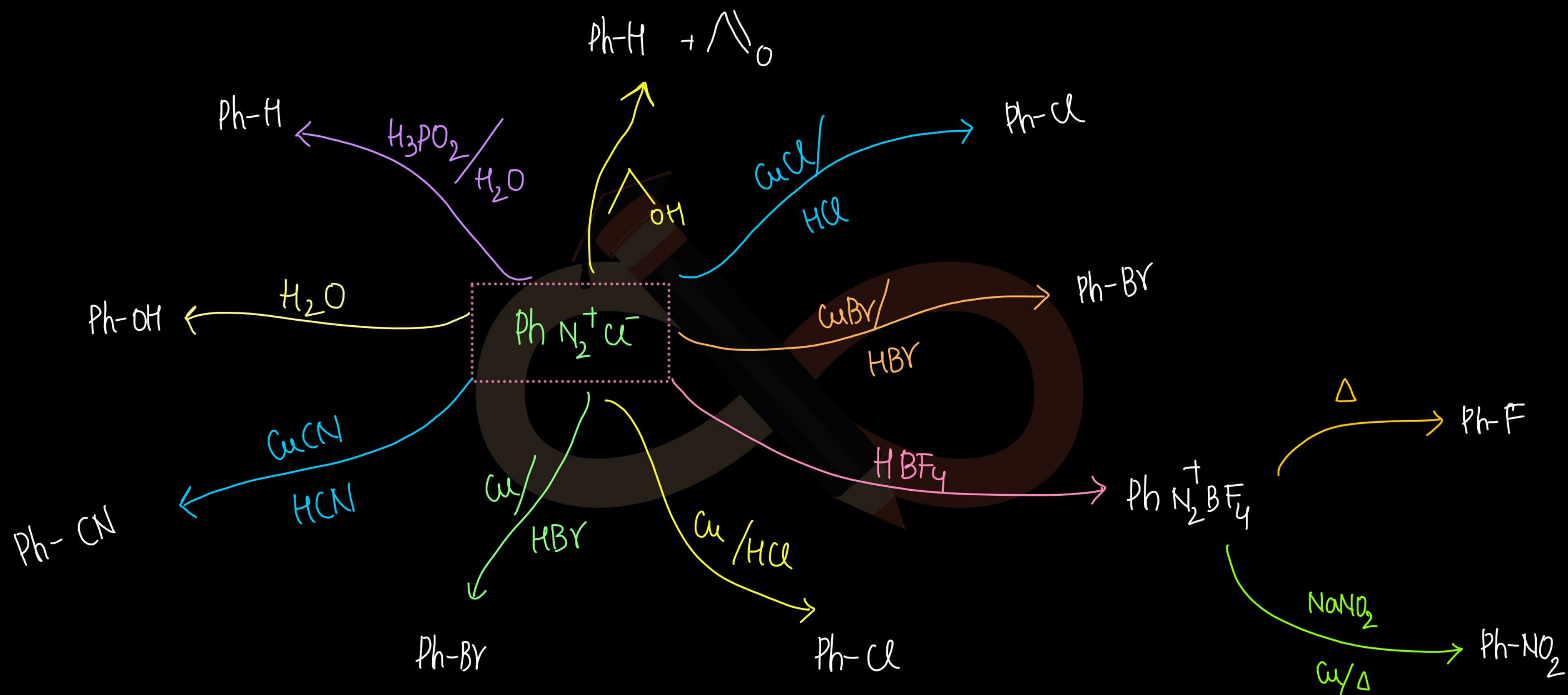
* Sandmeyer's rxn



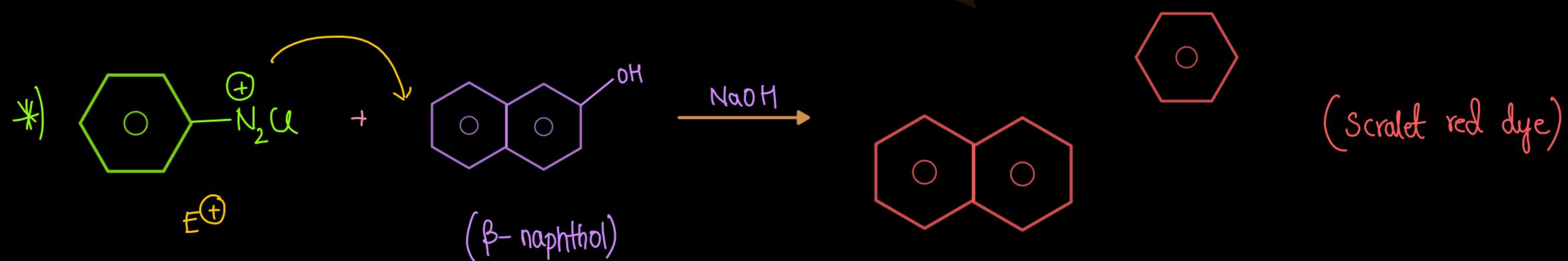
* Gatterman rxn



* chemical rxn's



Coupling rxn :- (EAS)



NCERT

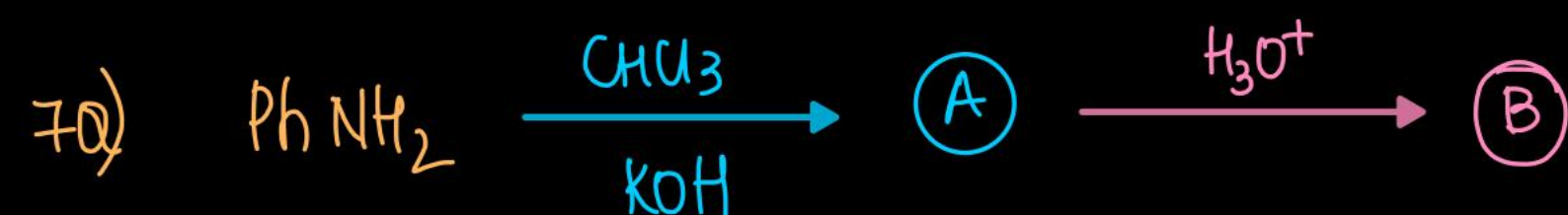
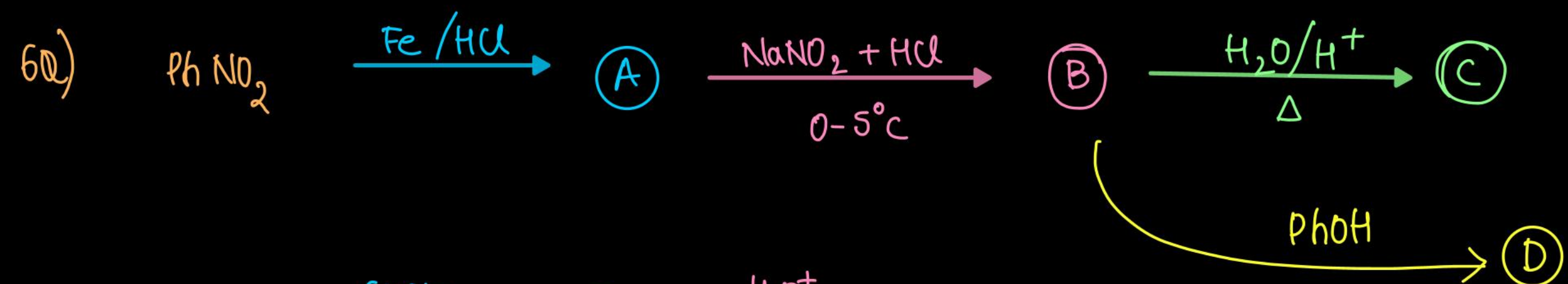
- * adrenaline & ephedrine : Secondary amine Grp.
- * Novacin $\longrightarrow$ used as an anaesthetic
- * Benadryl $\longrightarrow$ antihistaminic drug (3° amine Grp)
- * 4° (quaternary Ammonium salts) $\longrightarrow$ Surfactants

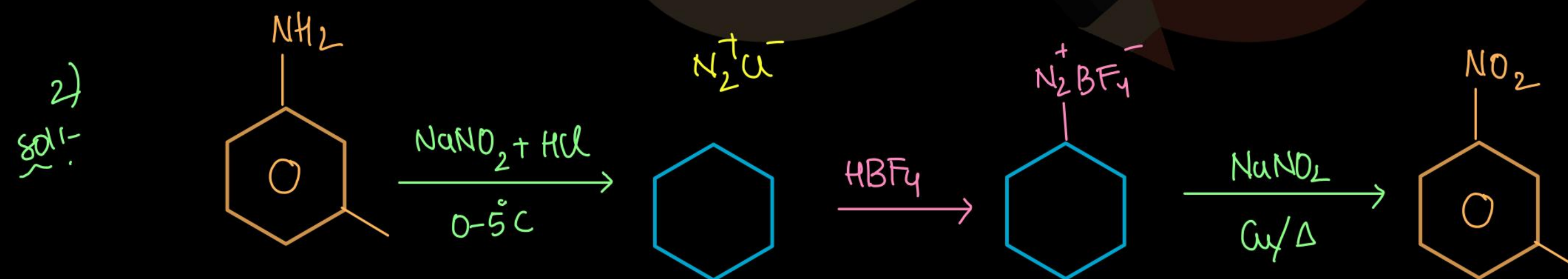
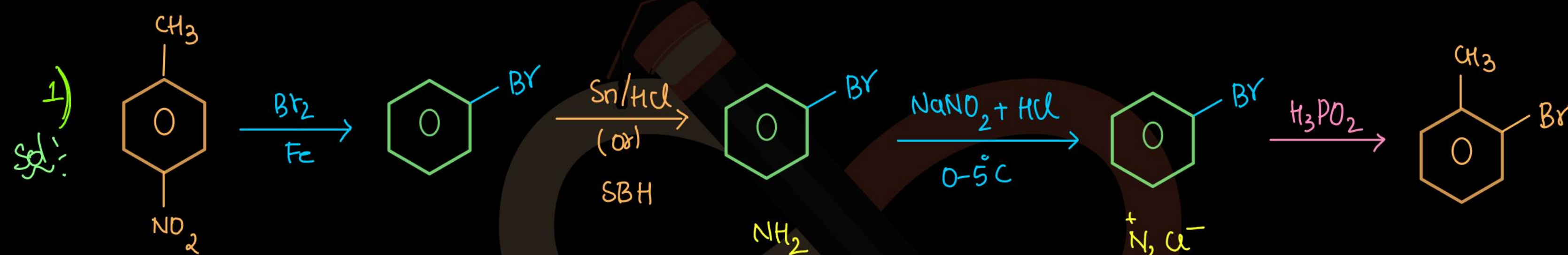
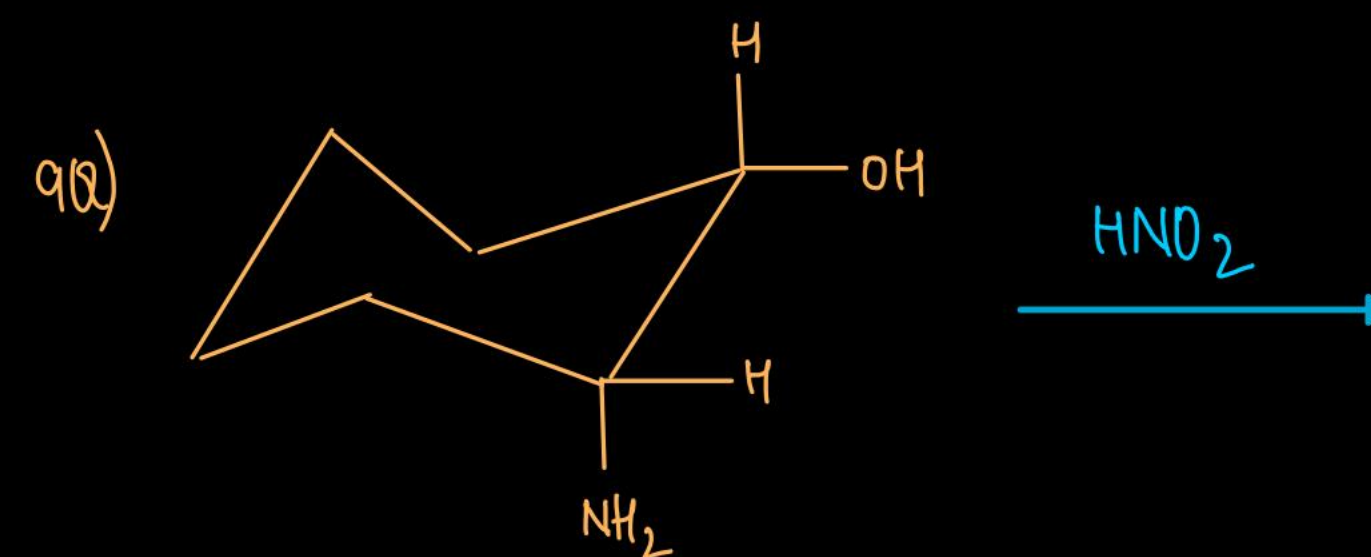
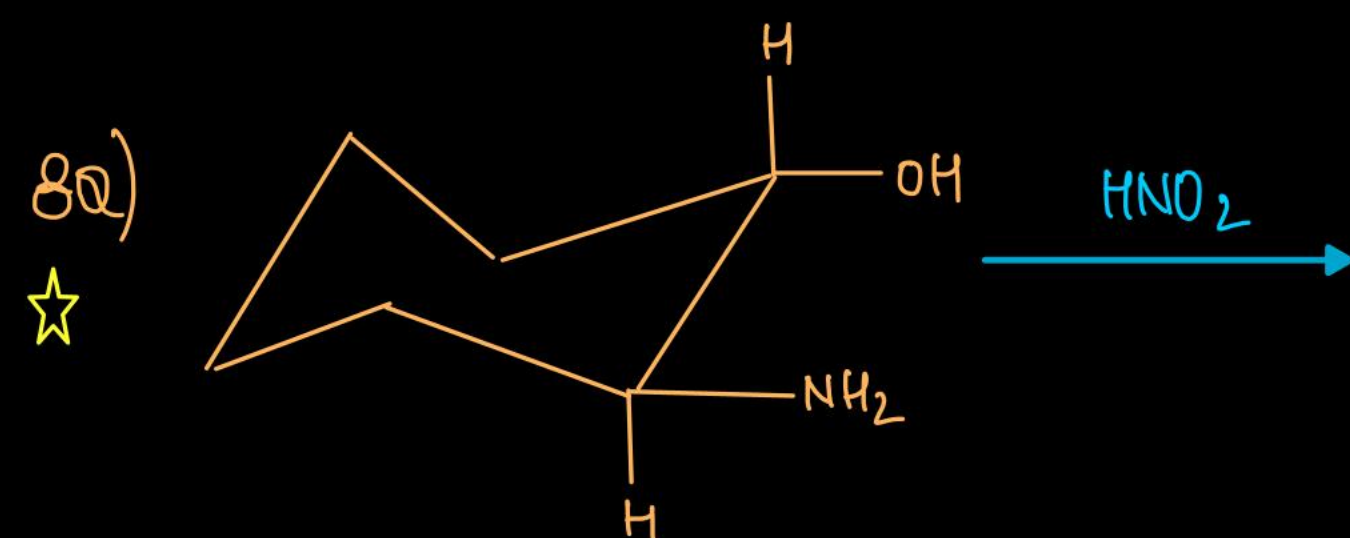
Practice :-

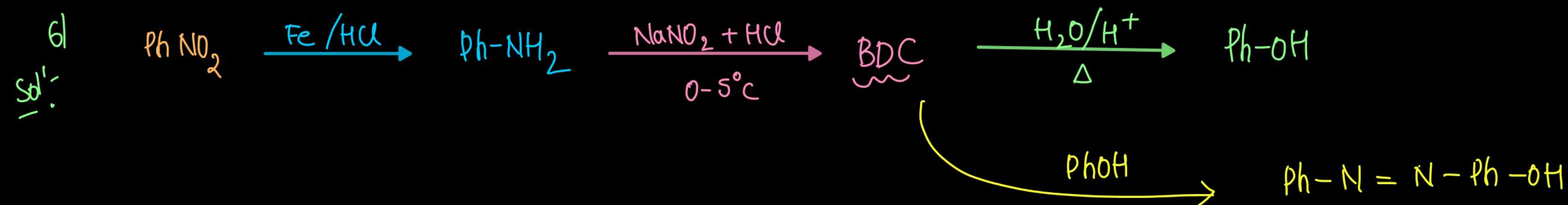
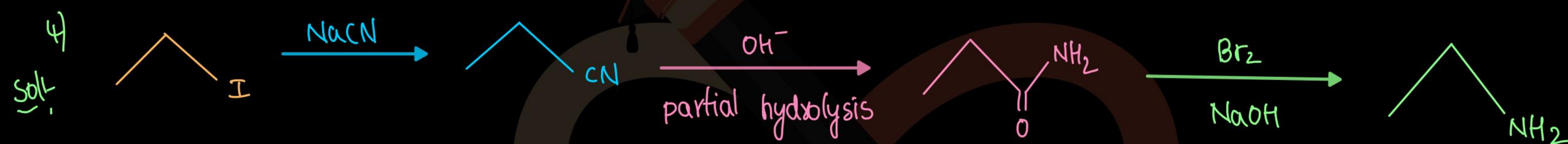
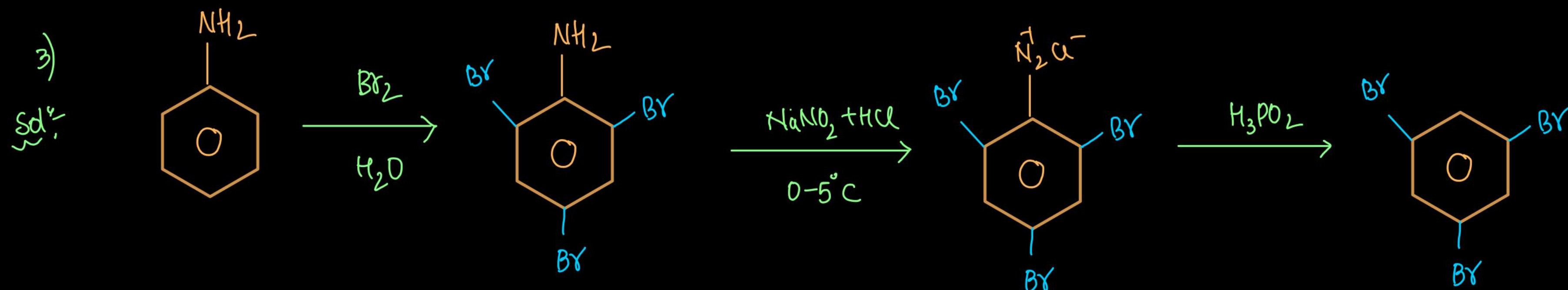
1Q) Convert 4-nitro toluene to 2-bromo toluene

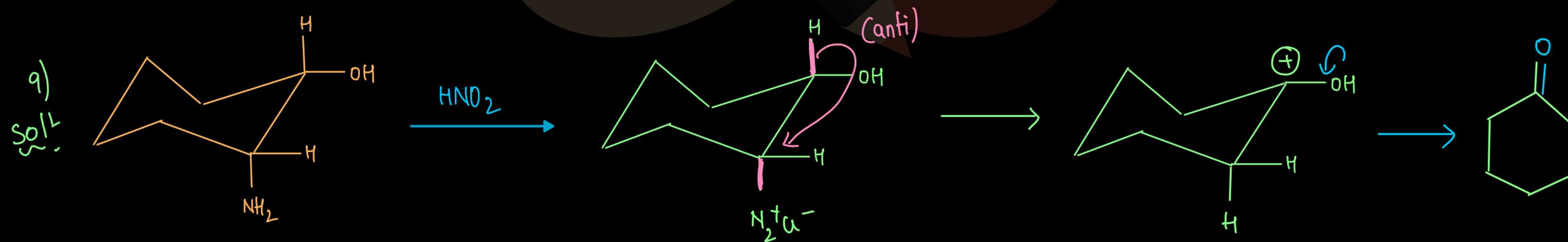
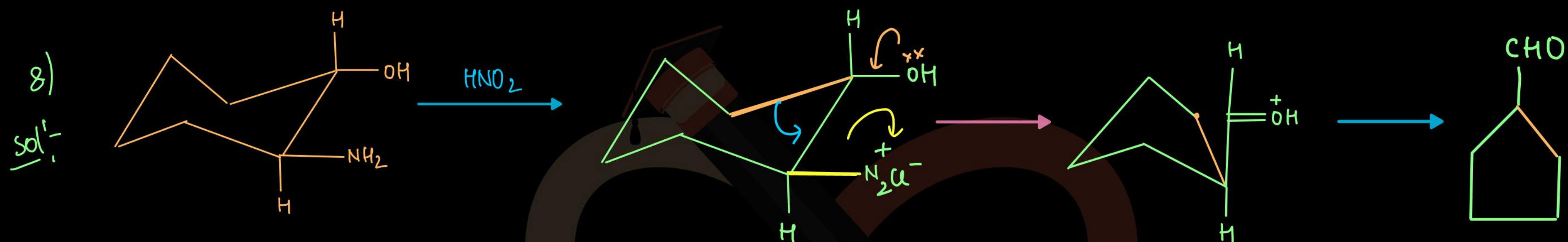
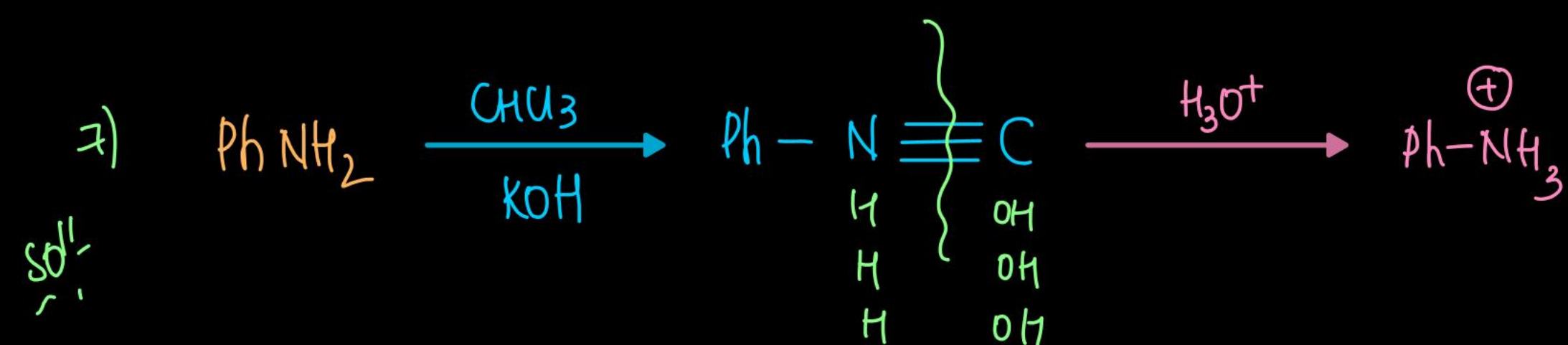
* 2Q) Convert 3-methyl aniline to 3-nitro toluene

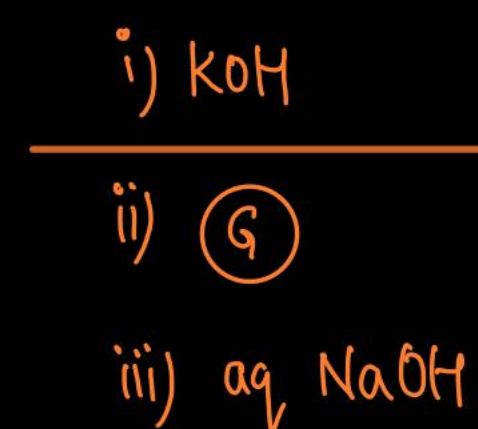
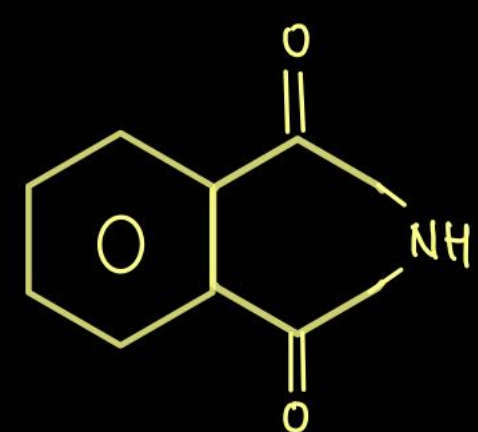
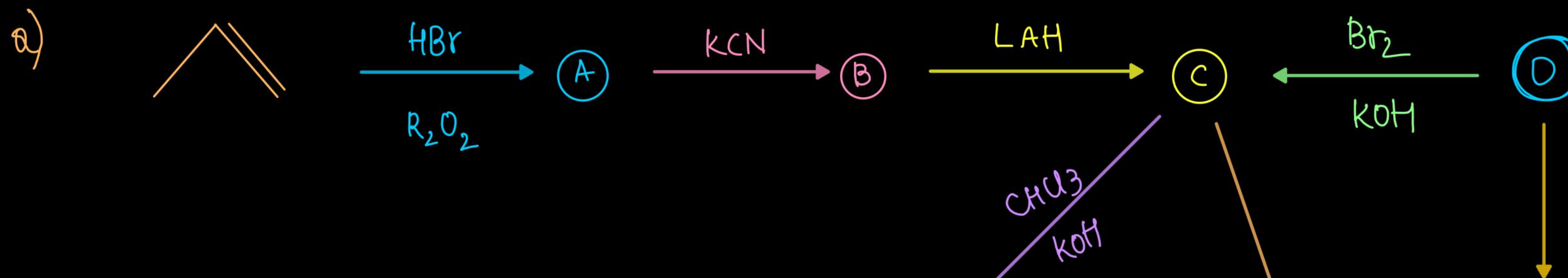
3Q) Convert aniline to 1,3,5-tribromo benzene









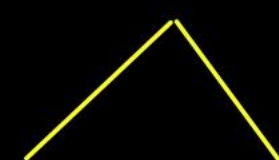


(C)

(F)

Alcohol

ThO₂

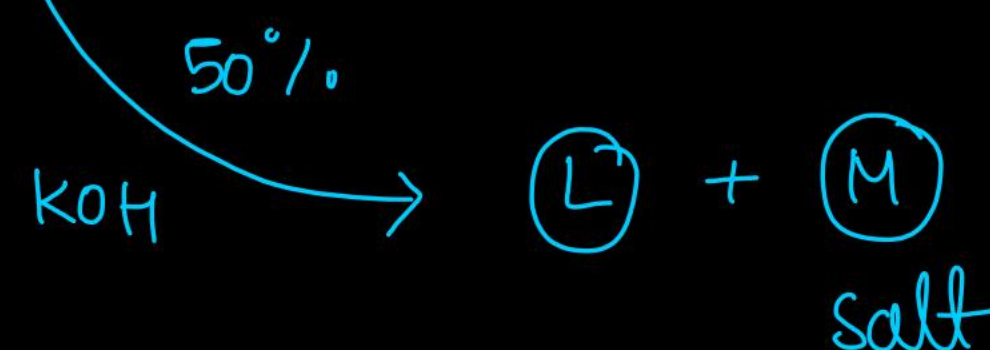


$\xleftarrow[\text{Red P}]{\text{HI}}$

(J) + (K)

$\xleftarrow[\text{Zn}]{\text{O}_3 + \text{cdy}}$

(I)



Solⁿ:

