

Aryl halides (Halo arenes)

MOP :-

- 1) From hydrocarbons (ESR) 2
- 2) From Amines (Sandmeyer's rxn) 3
- * Allylic / Benzylic substitution 6

Physical Properties :

* MP, BP 4

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ii) Nitration 21

iii) Sulphonation 21

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a) Alkylation 22

b) Acylation 22

③ Rxn with metal 23

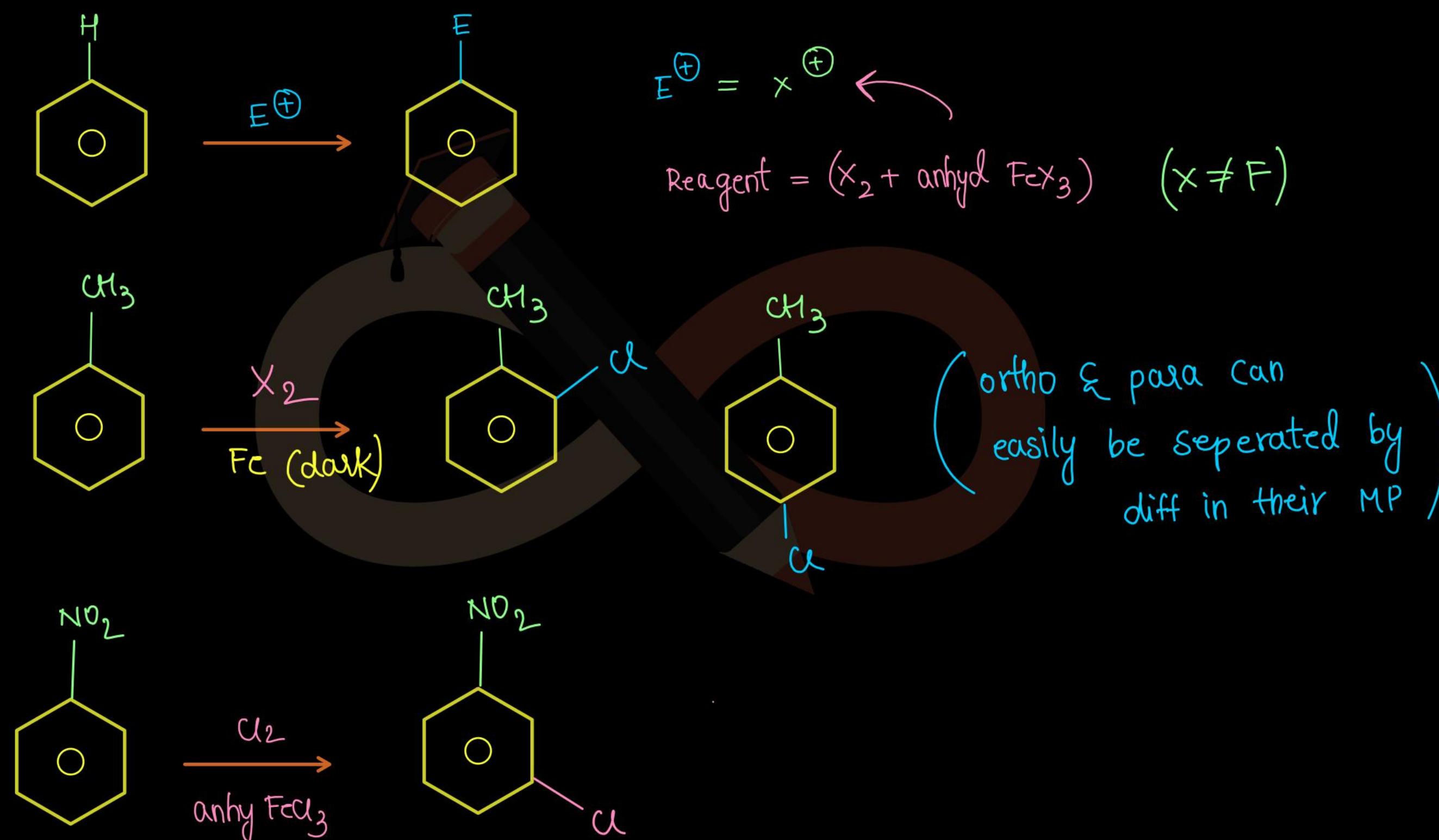
* Fittig rxn

* Wurtz Fittig

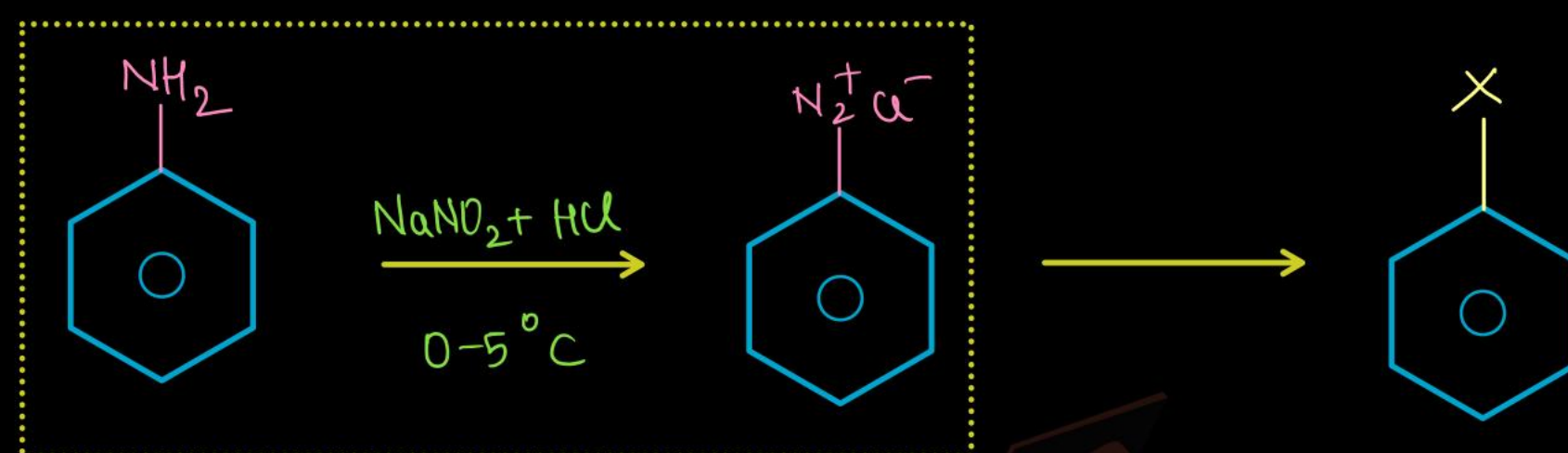
* Ullman rxn

1) From hydrocarbons

* Electrophilic Substitution rxn (ESR) :

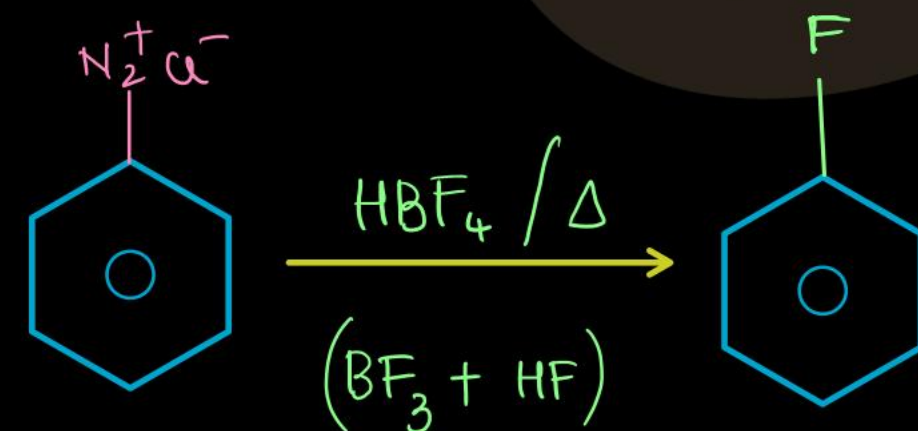


* 2) From Amines : Sandmayer's rxn



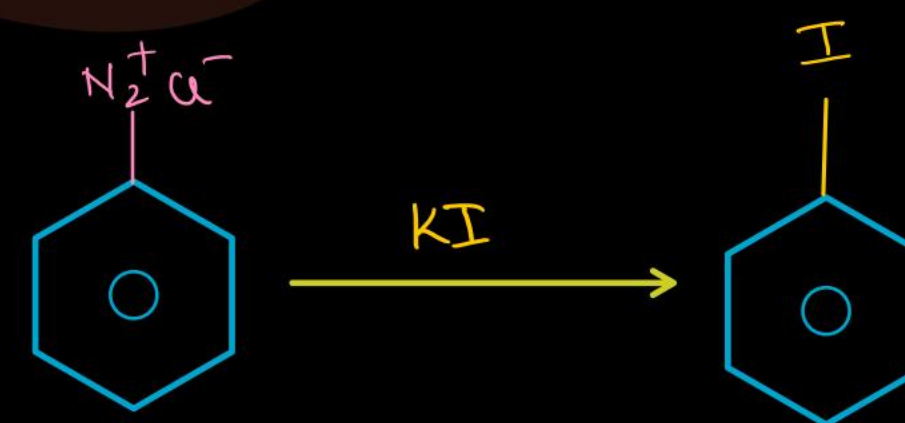
(Diazotisation)

for fluorobenzene

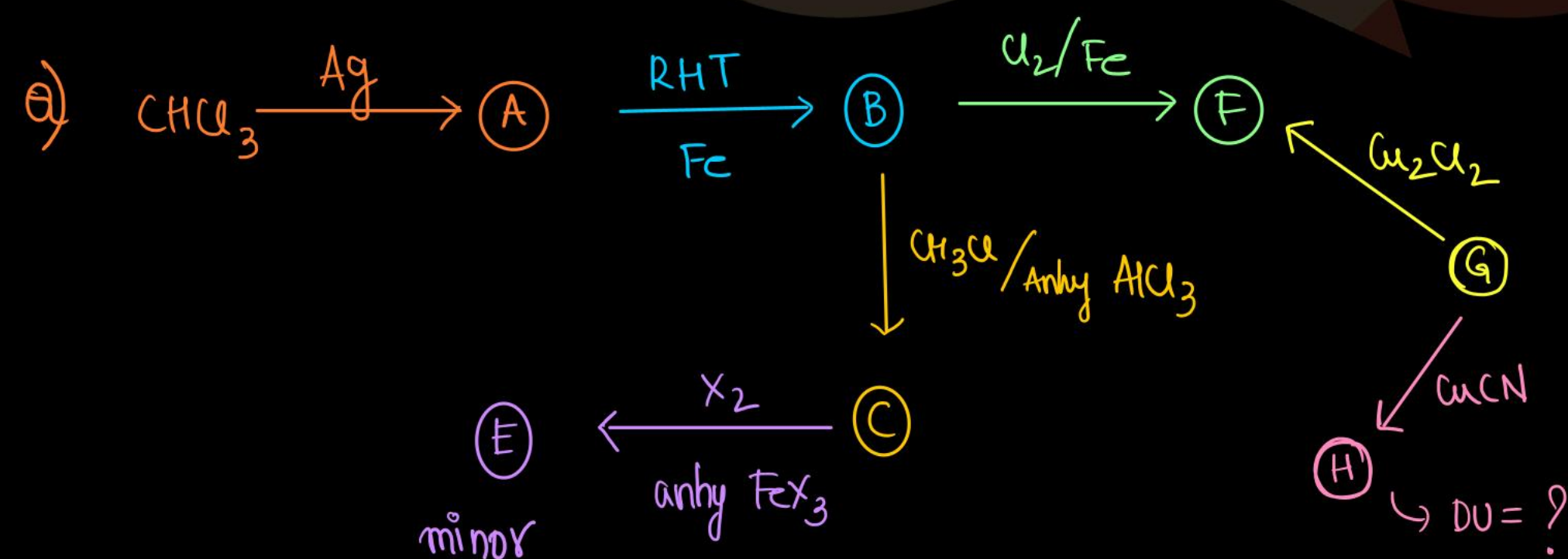
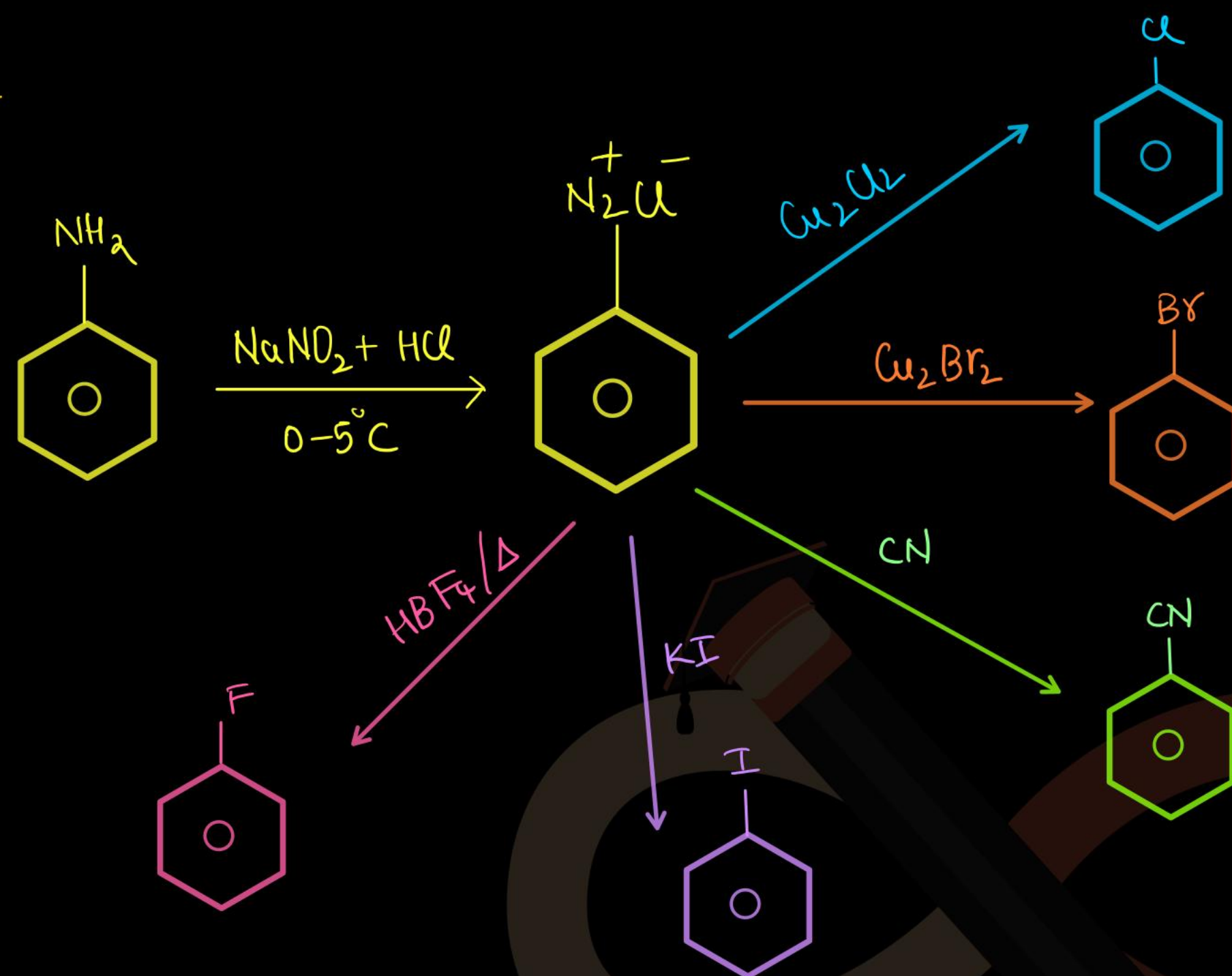


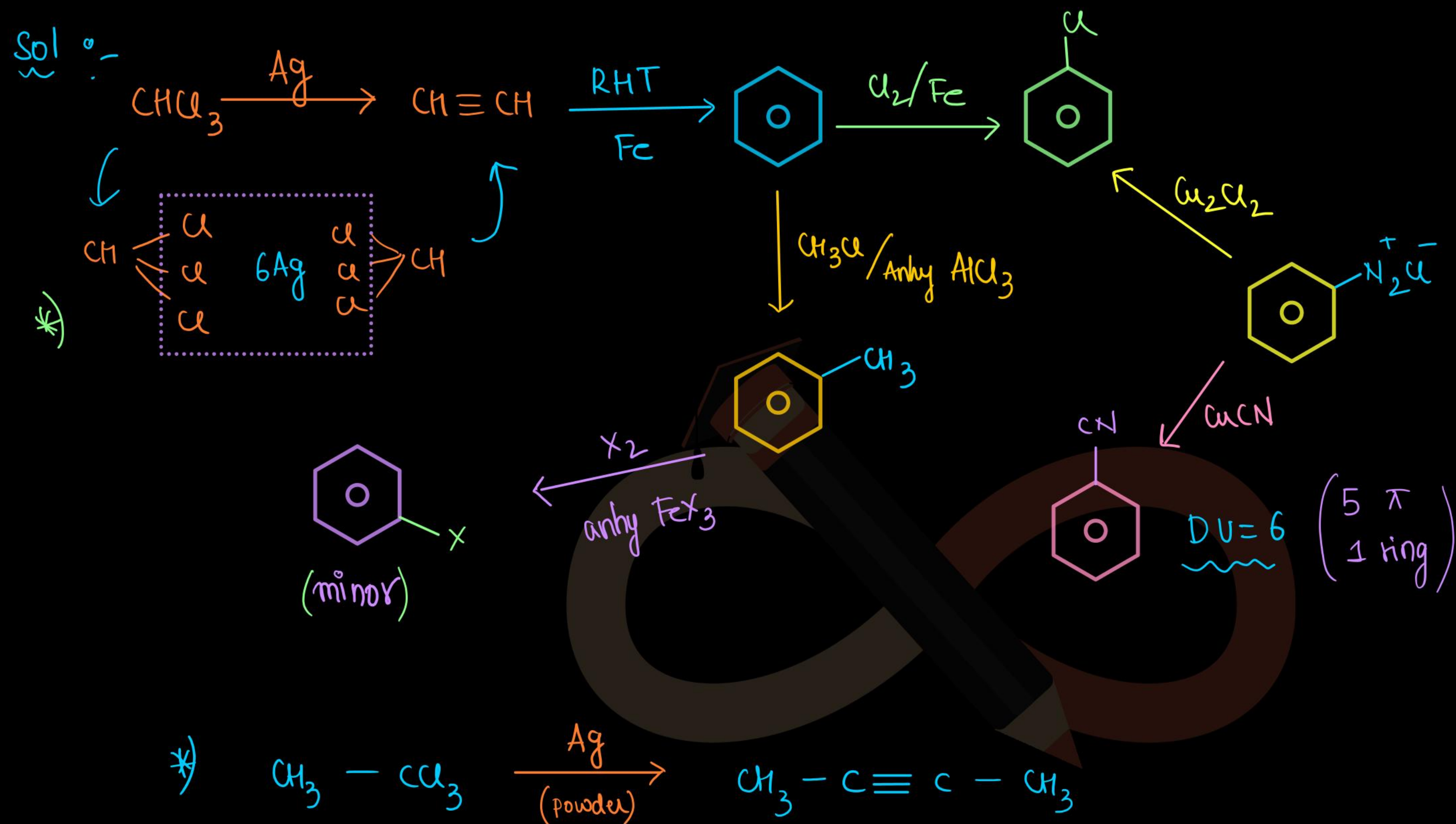
Balz Schiemen's Rxn

for Iodobenzene



Note:-

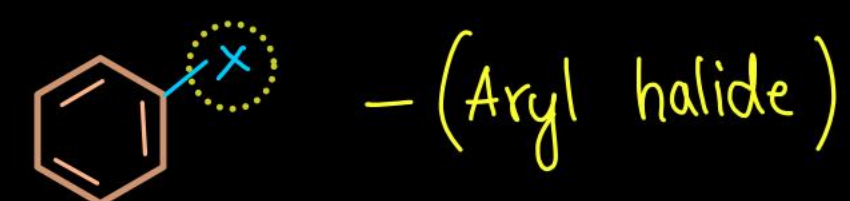




* Allylic/Benzylic Substitution:



Note :-



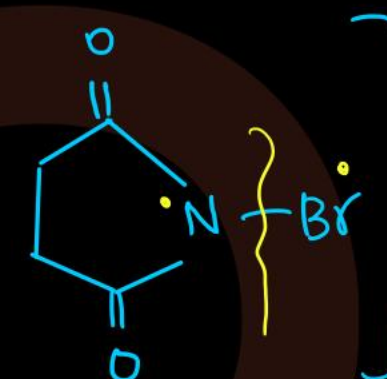
i) Bromination

Reagents :-

a) NBS

b) $\text{Br}_2/h\nu$

N-bromo Succinamide

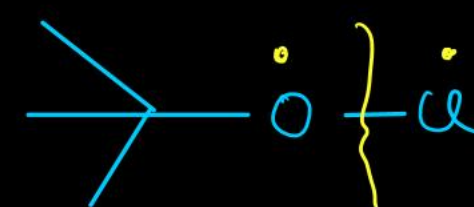


ii) Chlorination

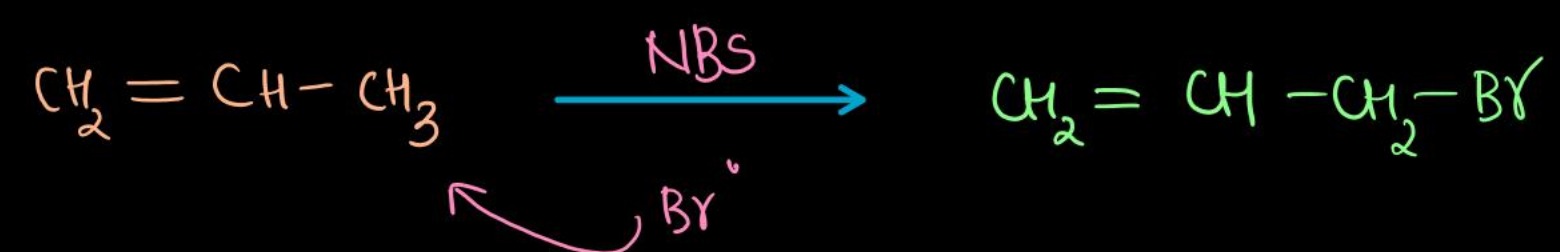
Reagents :-

a) $\text{Cl}_2/h\nu$

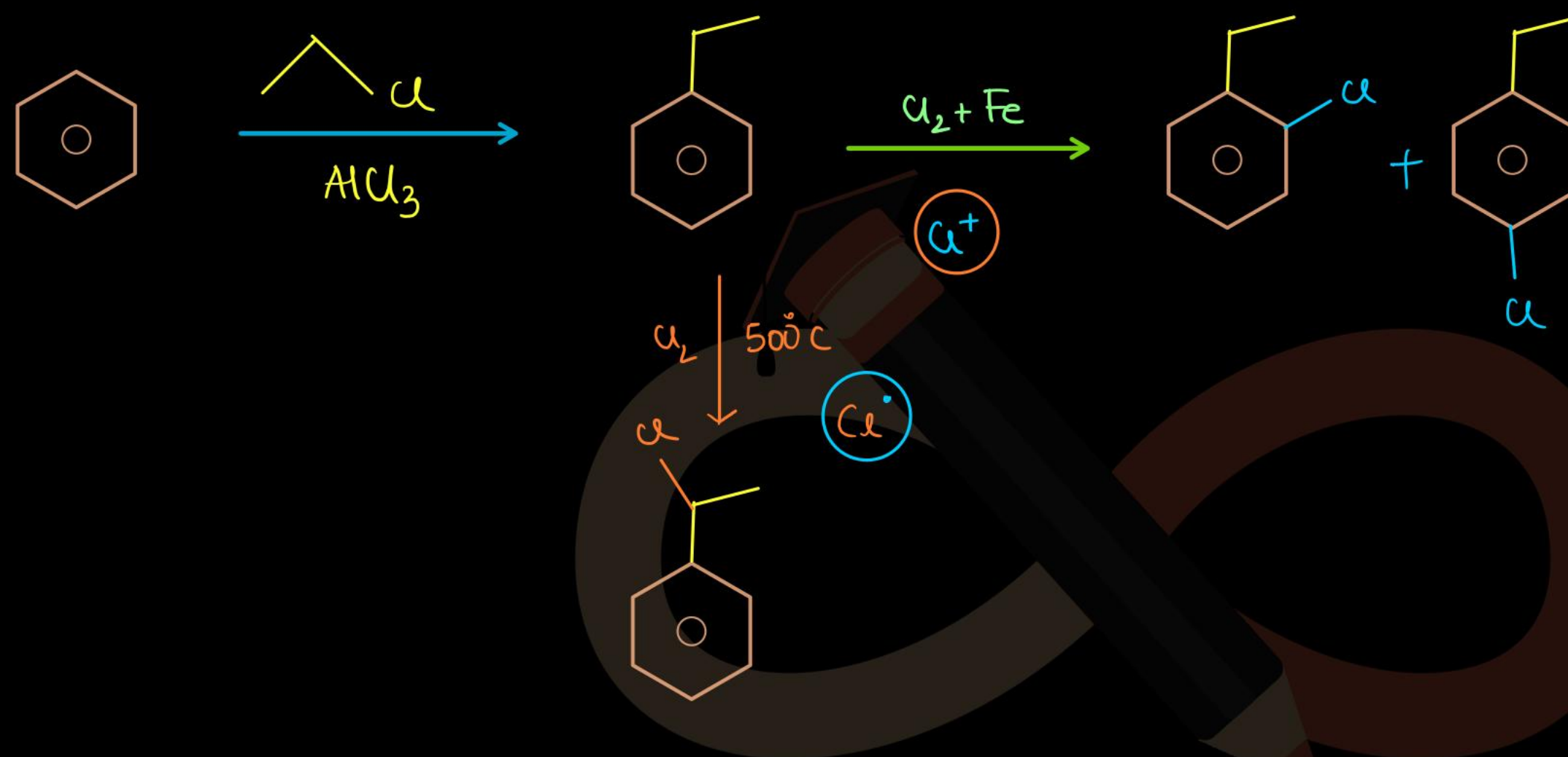
b) tBuOCl



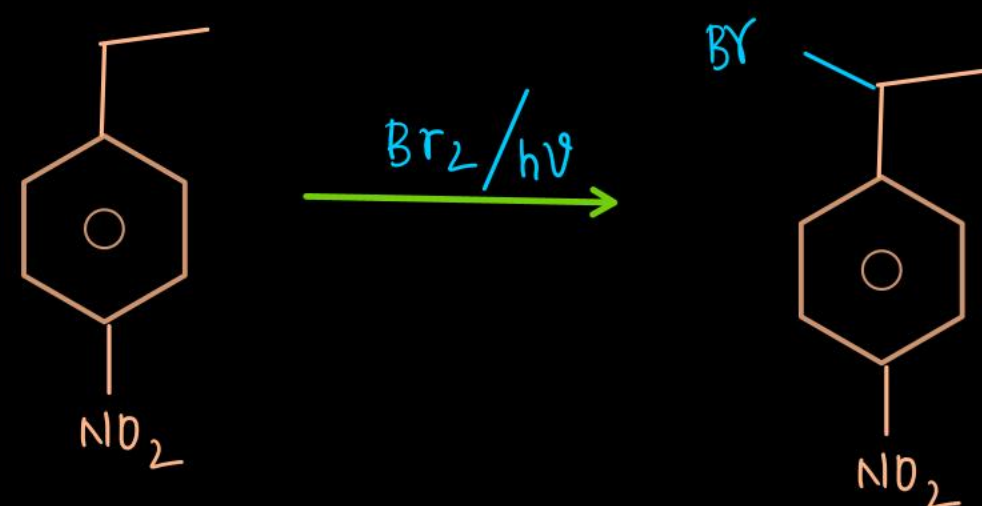
1)



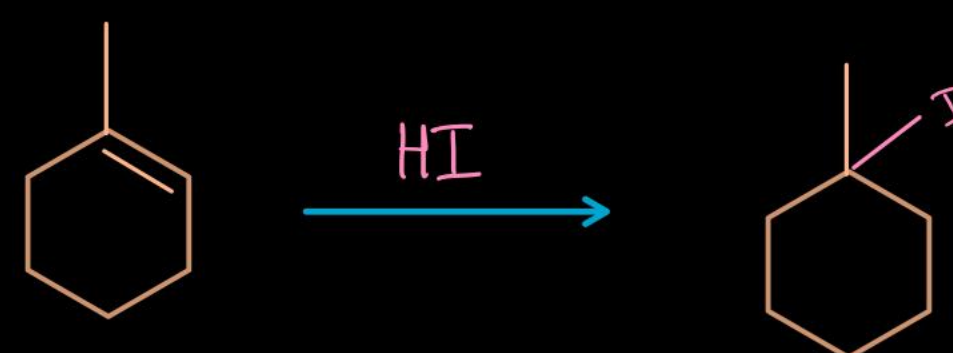
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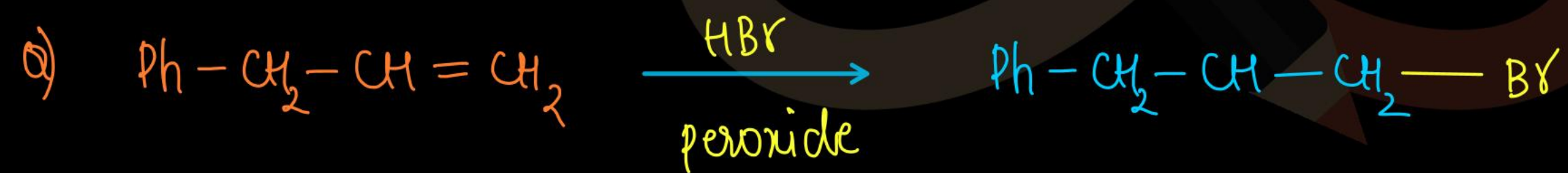
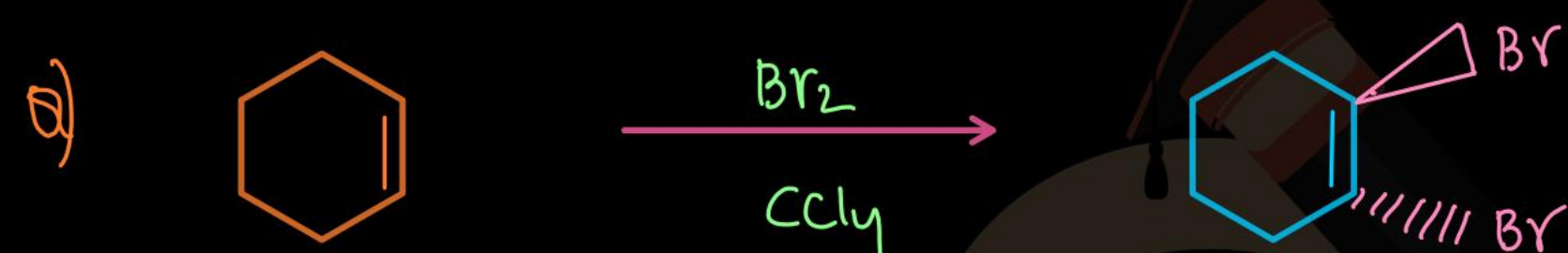
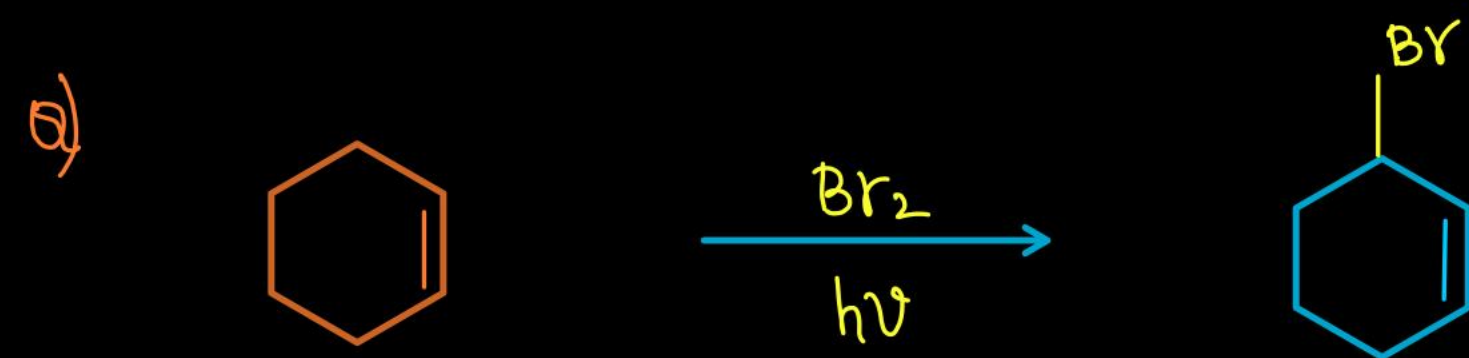
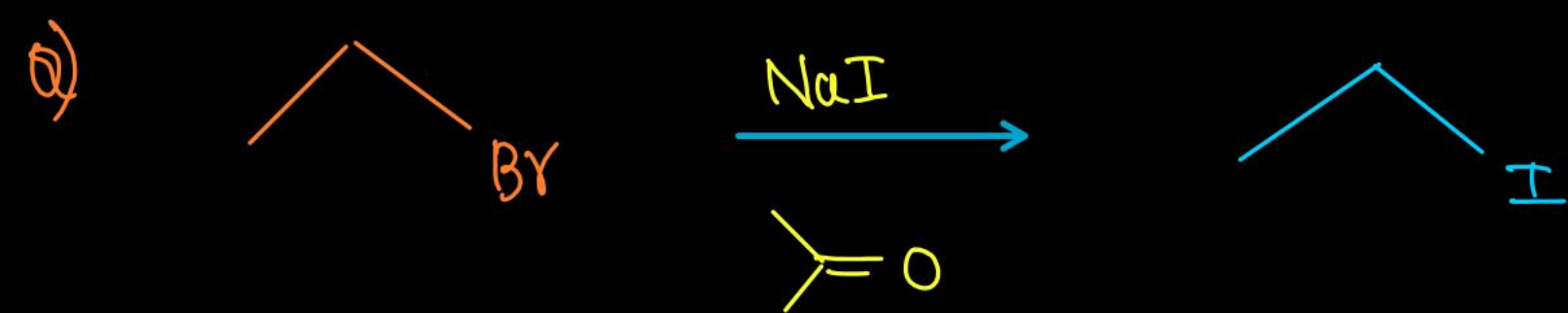


3)

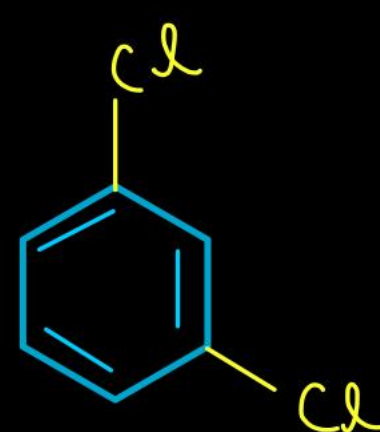
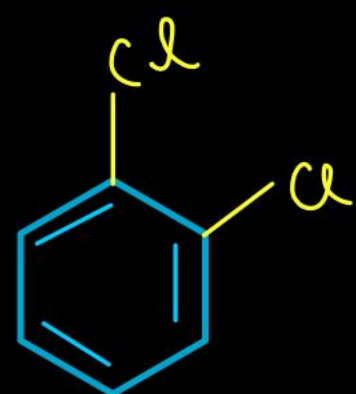


4)





Physical Properties :



B.P/K

453

446

448

($o > p > m$)

M.P/K

256

249

324

($m > o > p$)

*) due to symmetry of para-isomers that fits in
Crystal lattice better as compared to ortho & meta isomers

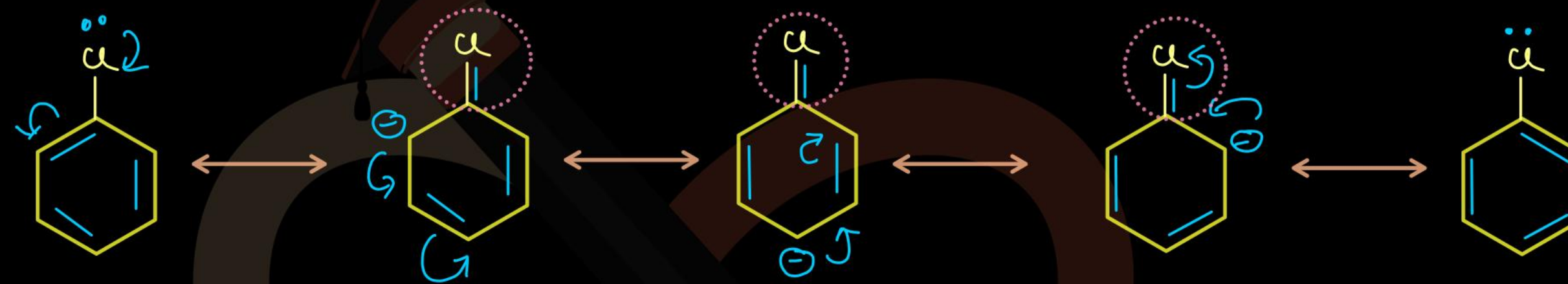
Aromatic SN^2 ($ArSN_2$ / SN_2Ar)

* Why does  not give $ArSN_2$?

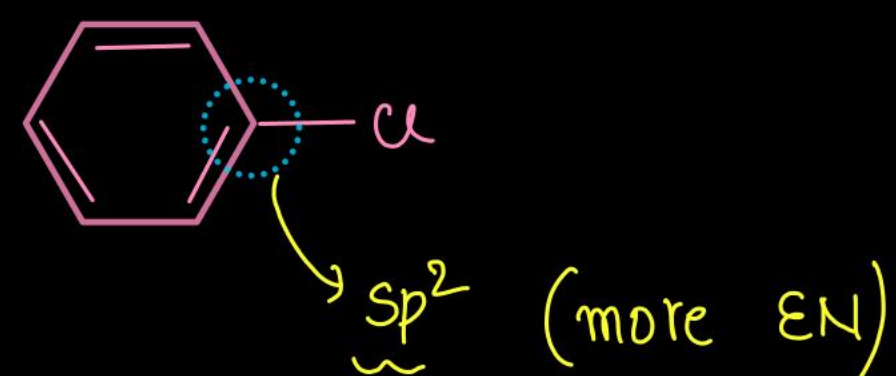
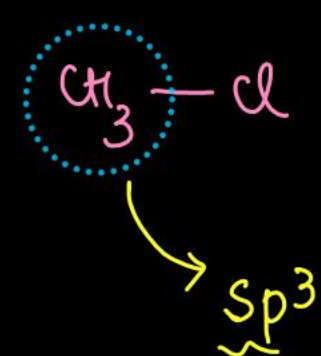
Reasons:-

1) Resonance

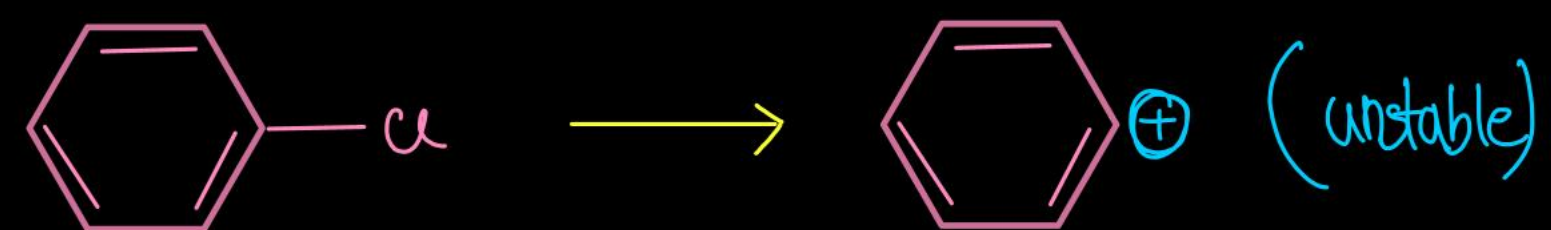
↓ partial double bond character



2) Difference in Hybridisation



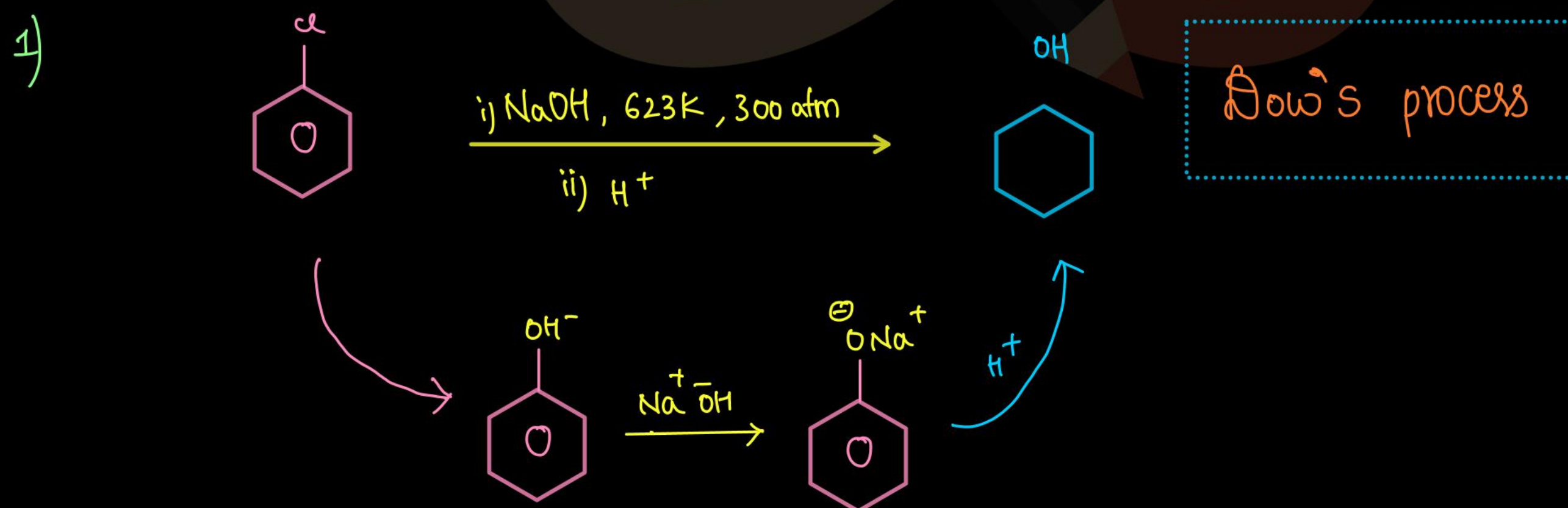
3) Instability of Phenyl cation :



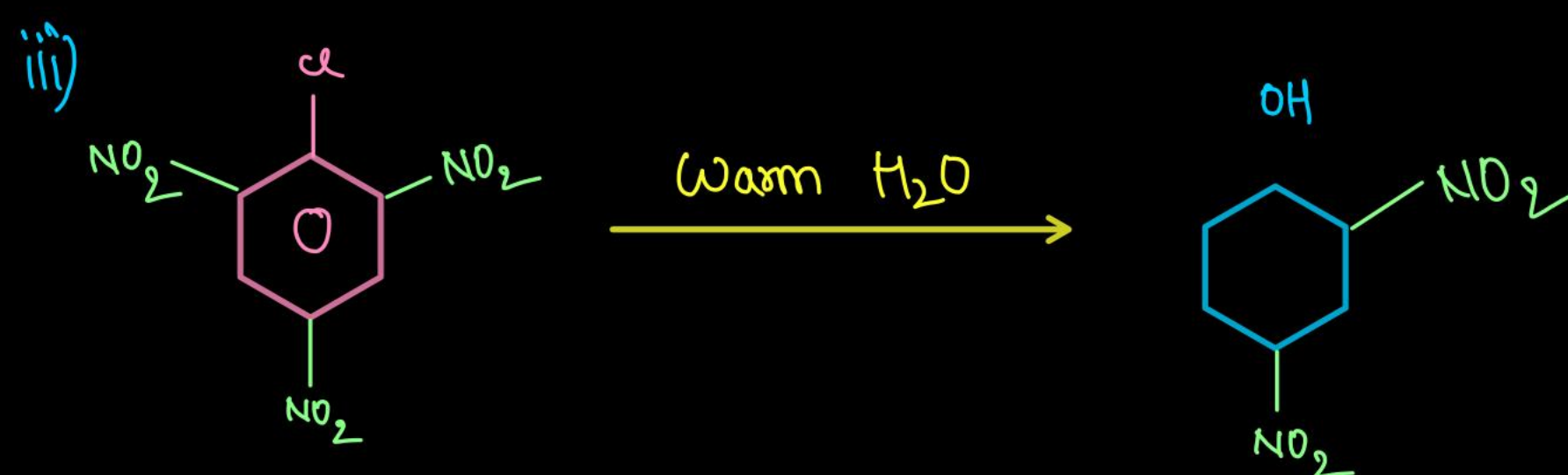
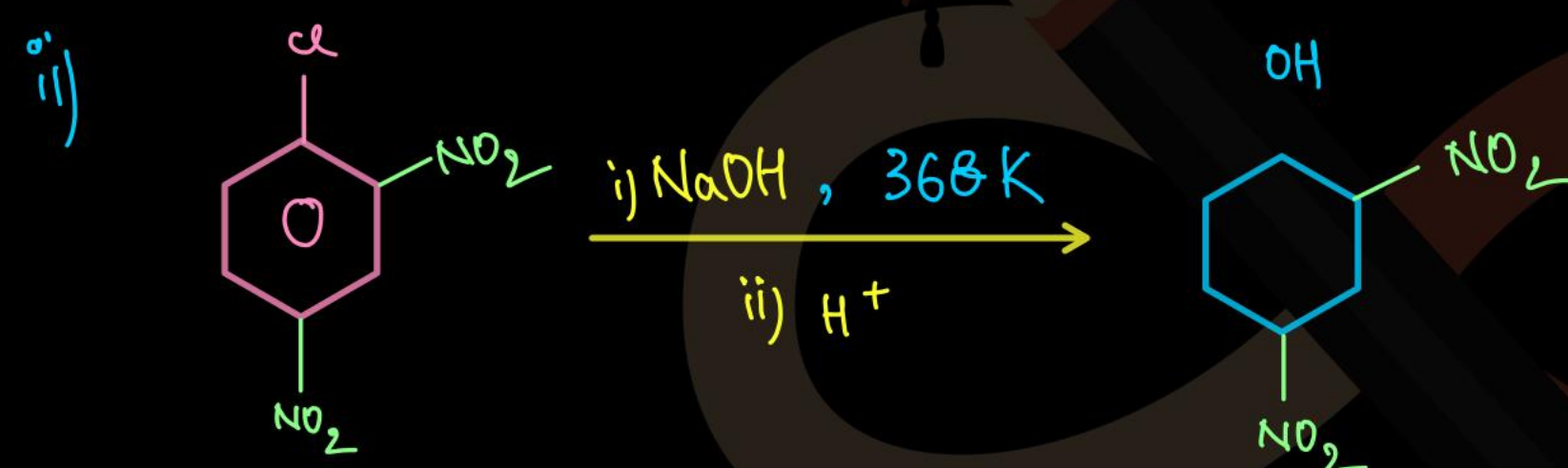
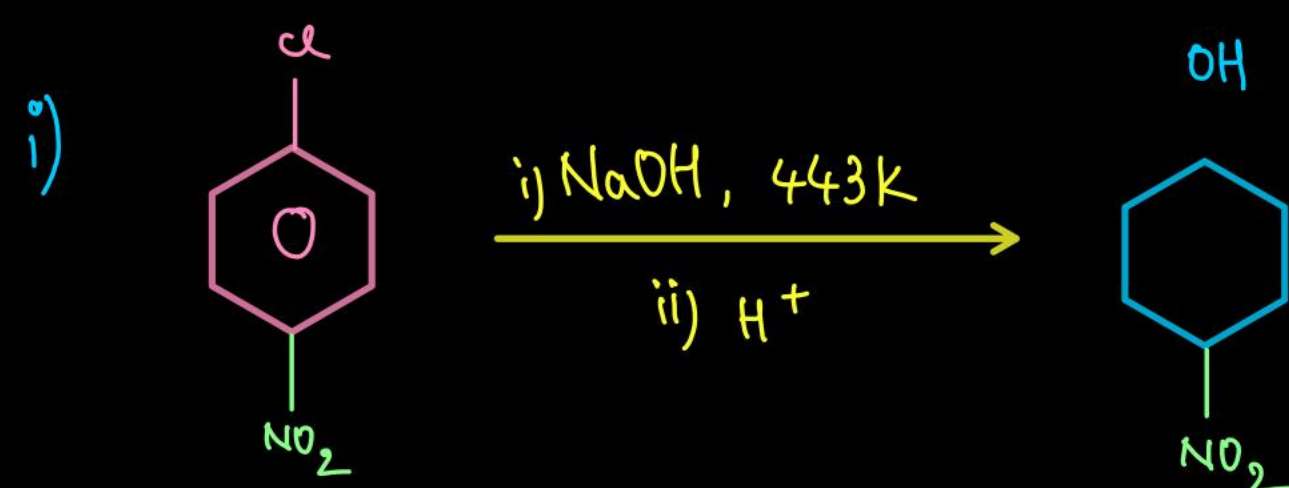
4) Because of possible repulsion :

↳ b/w incoming Nu[⊖] and e[⊖] rich Benzene ring

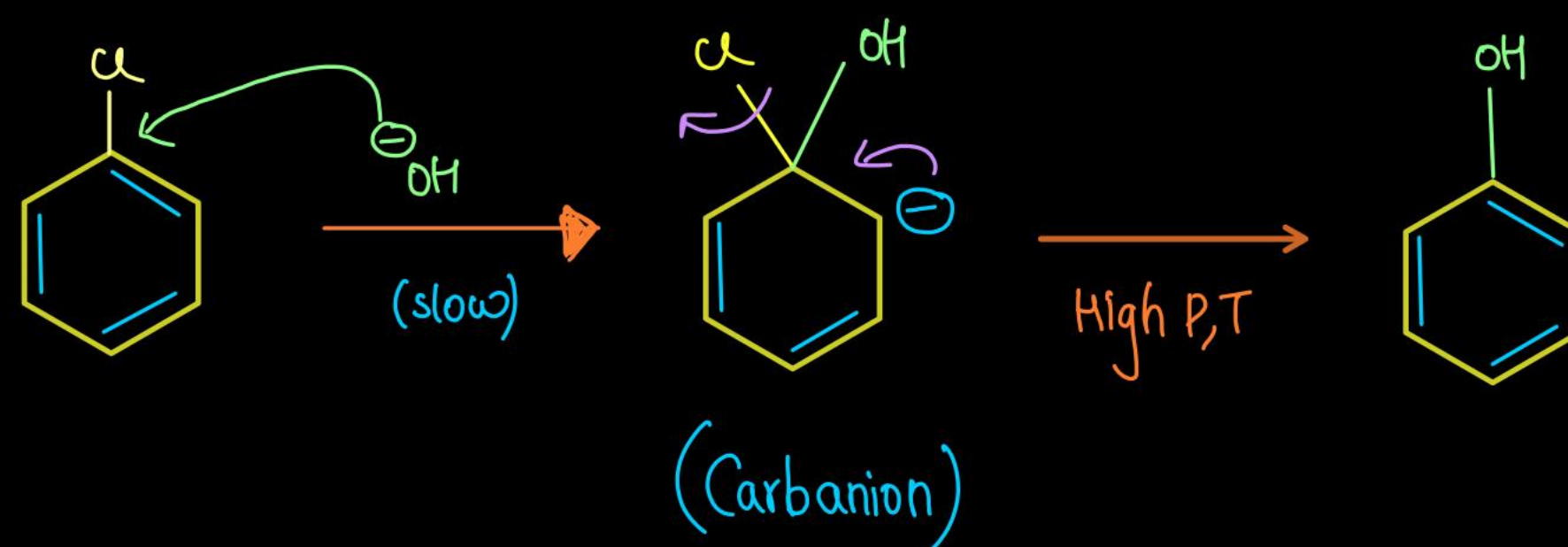
*) Replacement by hydroxyl group :-



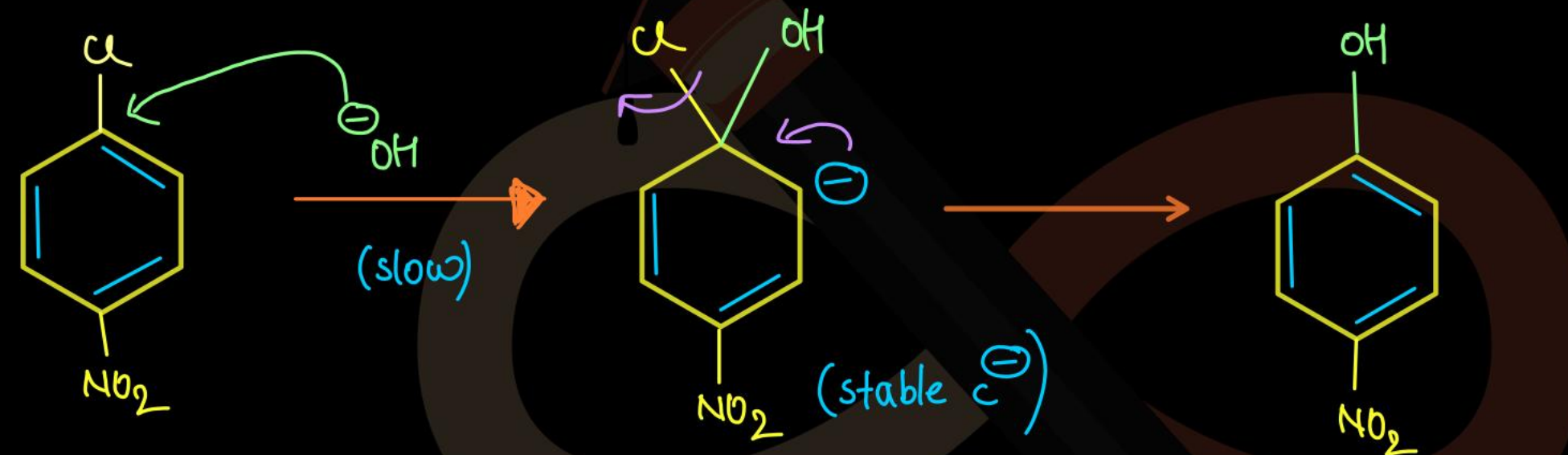
2) If nitro group is present ortho/para position



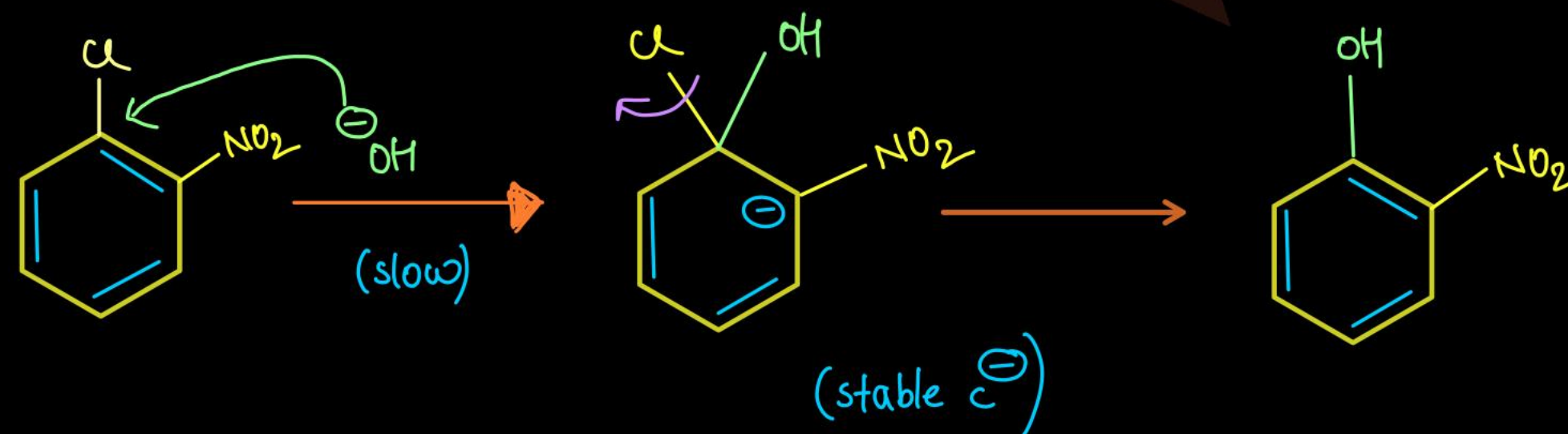
Mech:-
(Ar SN²)

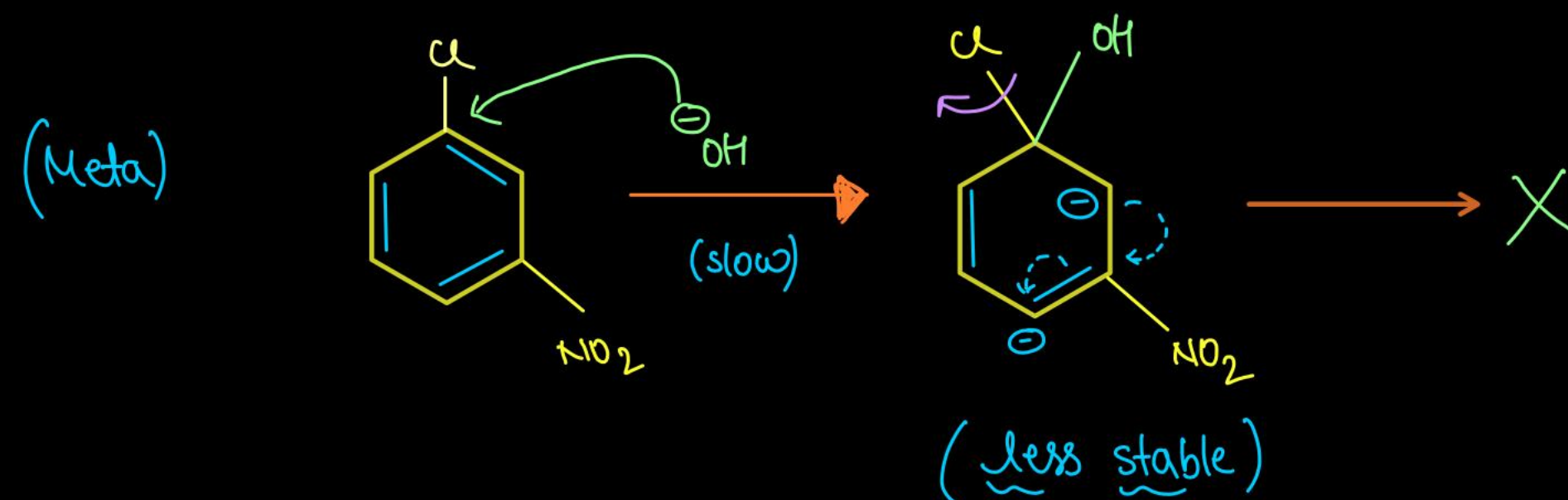


(para)



(ortho)

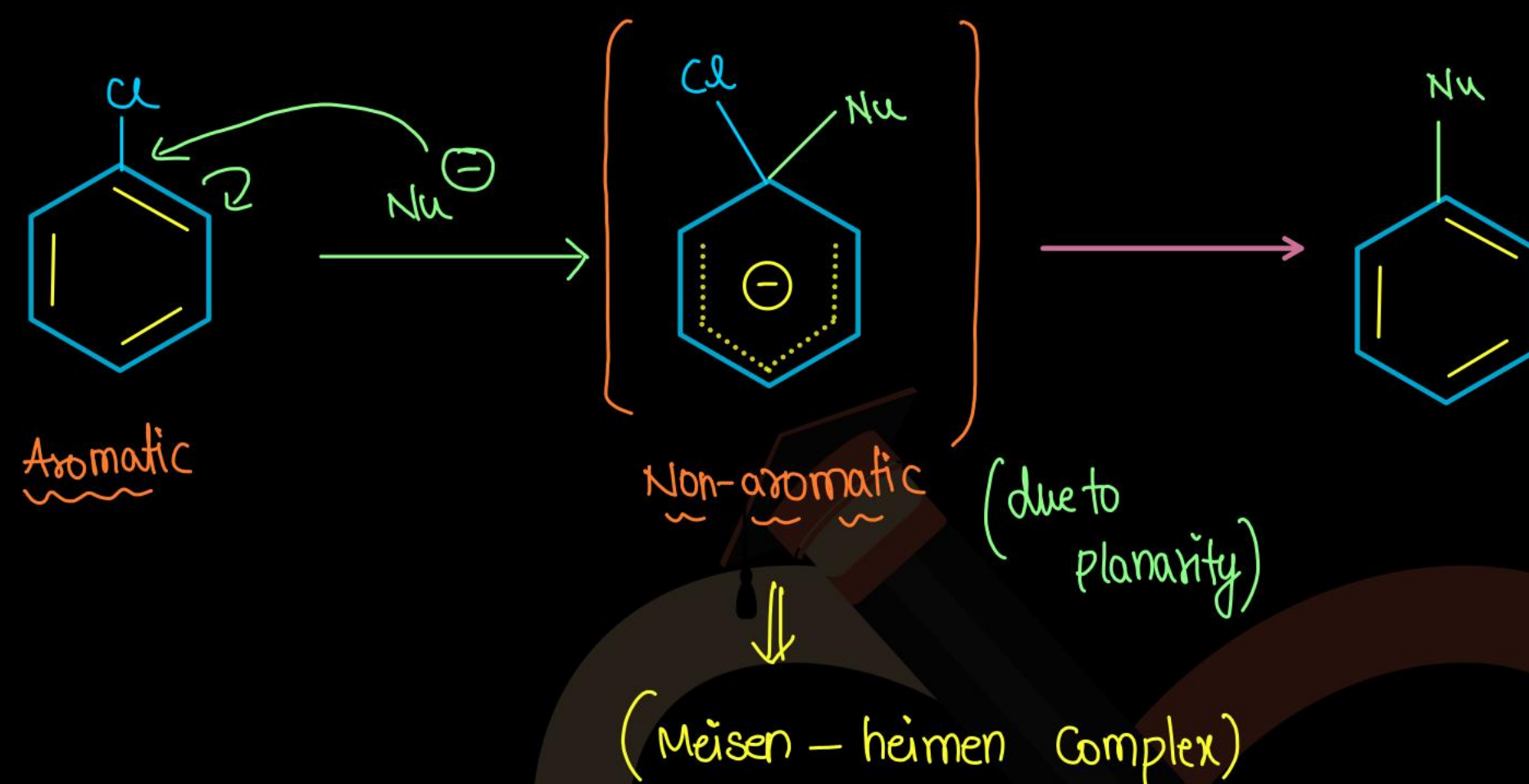




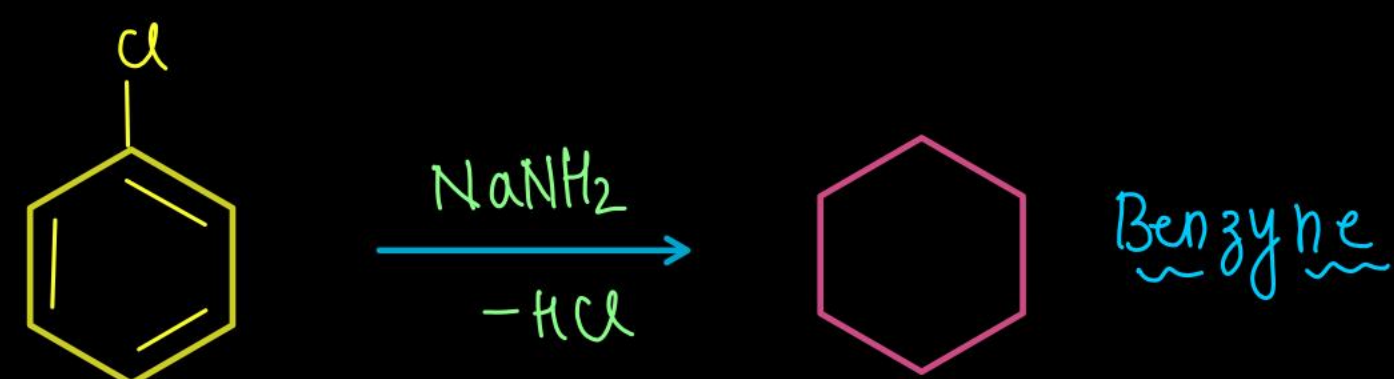
Important points :-

- 1) 2 step rxn
- 2) $C^{\ominus}$ intermediate
- 3) $r = k [Ph-Cl] [OH^-]$ (2nd order)
- 4) rate $\propto$ no. of NO_2 groups at (o,p)
 $\downarrow$ same, then (o > p)
- * 5) R.O.R : $Ar-F > Ar-Cl > Ar-Br > Ar-I$
- 6) rate $\propto$ -M & -I effect
- 7) Resonance hybrid is called Meisen-heimer complex

* Ar SN_2 (Addition-Elimination)



* Elimination-Addition (Benzynes)



Difference b/w SN^1 & SN^2 & ArSN^2

SN^1

- 1) 2 step rxn
- 2) $\text{C}^\oplus$ is formed
- 3) R.O.R:
 $\text{R-I} > \text{R-Br} > \text{R-Cl}$
- 4) rate $\propto$ leaving ability of LG
- 5) Product depends on $\text{C}^\oplus$ stability

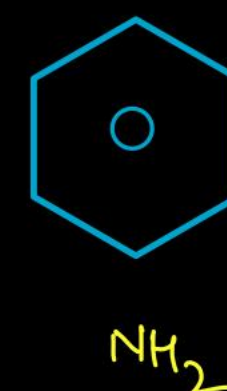
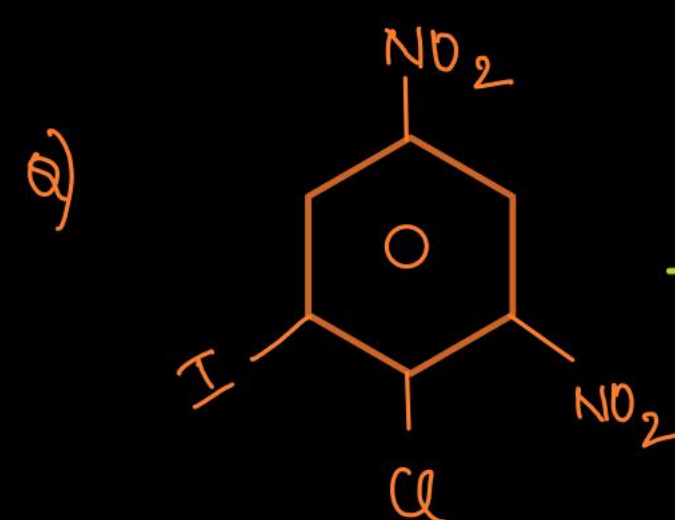
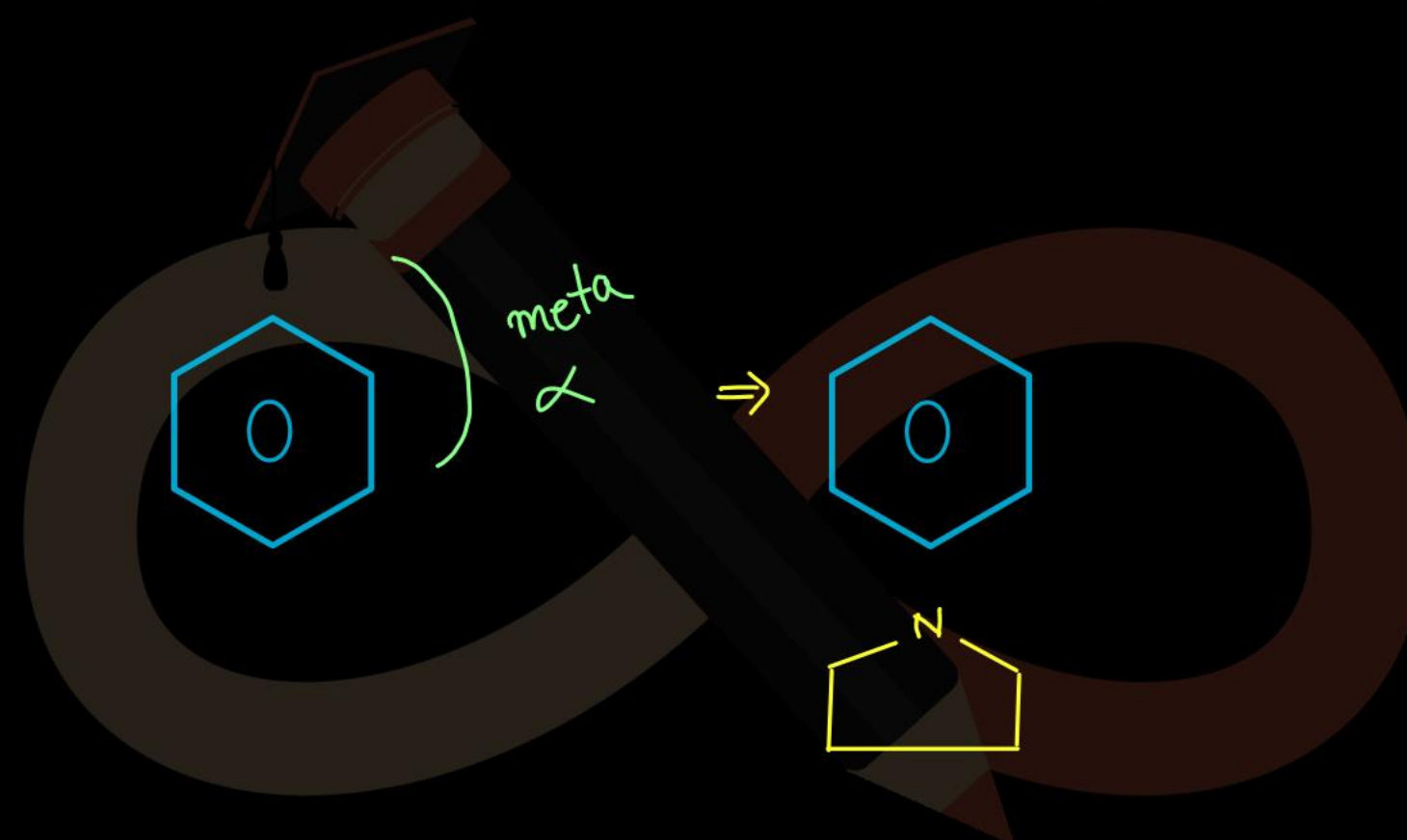
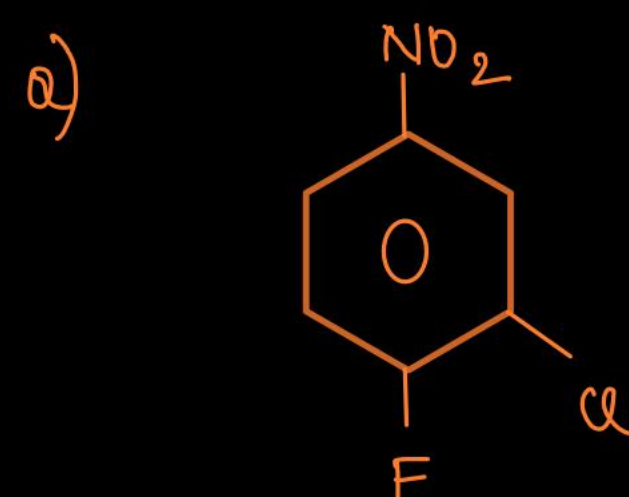
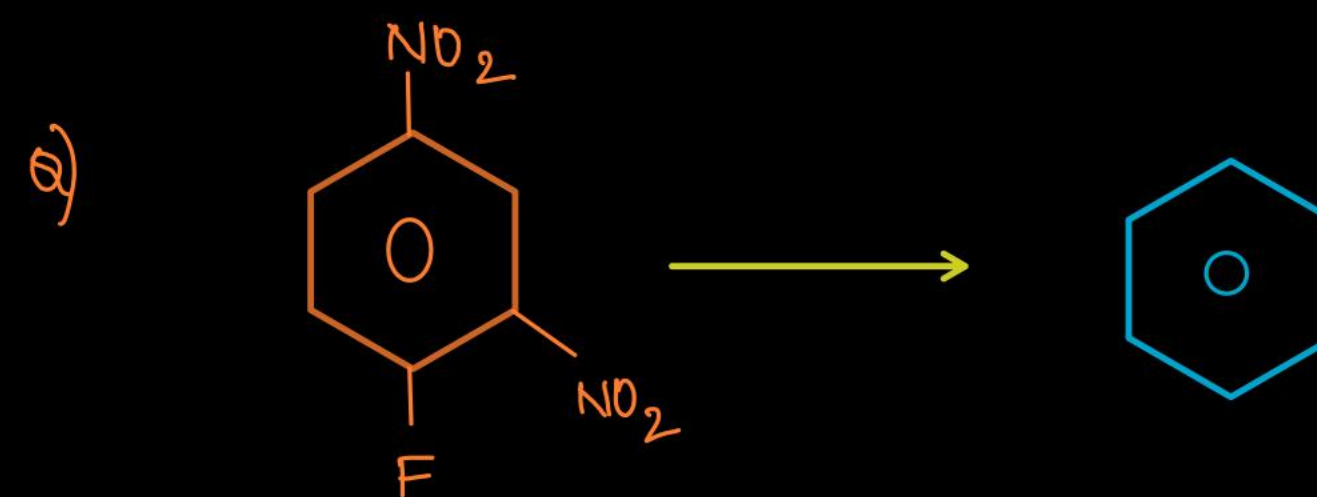
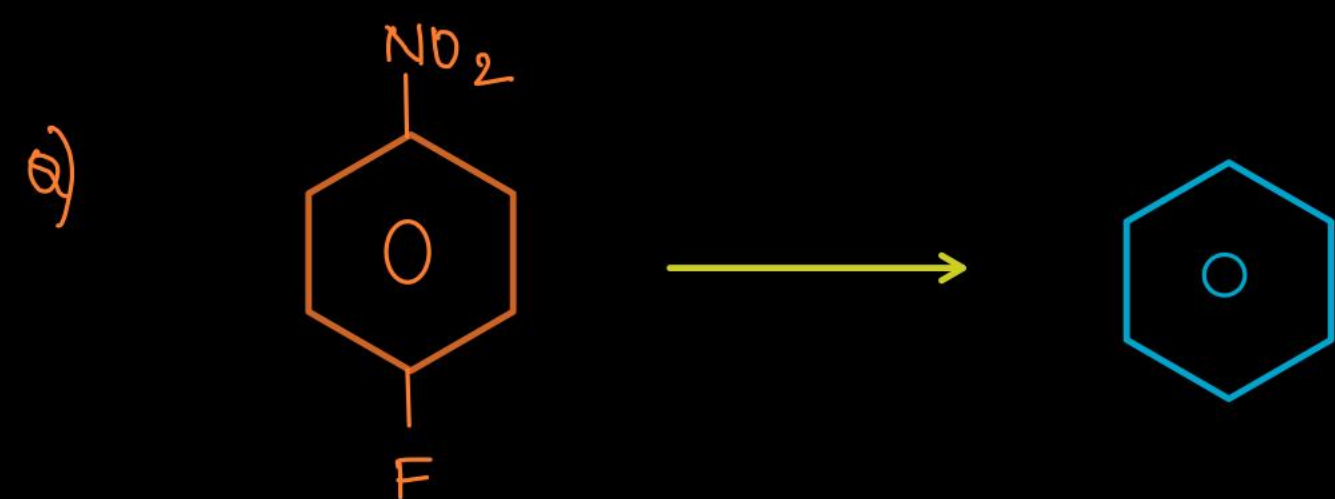
SN^2

- 1) 1 step rxn
- 2) TS is formed
- 3) R.O.R :
 $\text{R-I} > \text{R-Br} > \text{R-Cl}$
- 4) rate $\propto$ leaving ability of LG

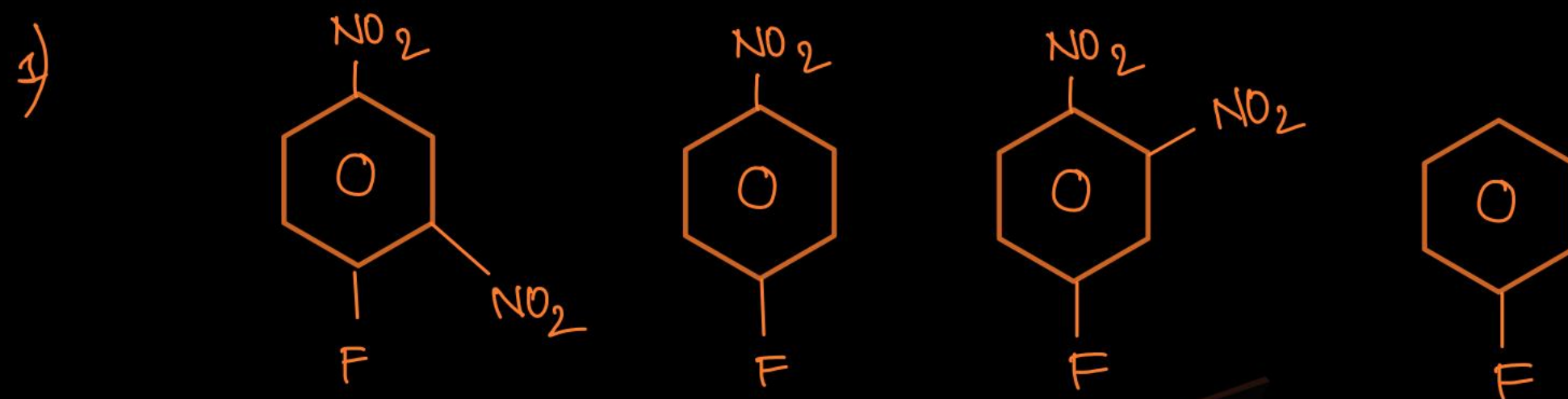
ArSN^2

- 1) 2 step rxn
- 2) $\text{C}^\ominus$ is formed
- 3) R.O.R:
 $\text{Ar-F} > \text{Ar-Cl} > \text{Ar-Br} > \text{Ar-I}$
- 4) rate $\propto$ -M, -I effects $\uparrow$ stability of $\text{C}^\ominus$
- 5) Product depends on $\text{C}^\ominus$ stability

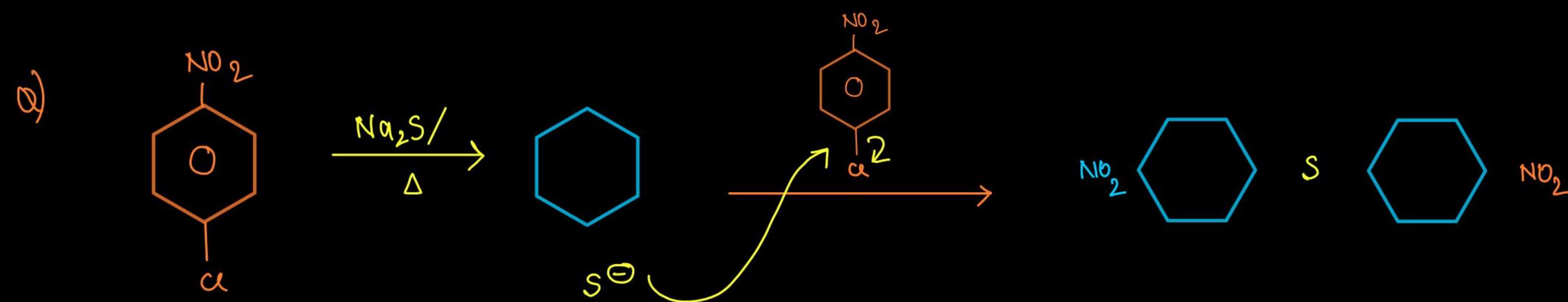
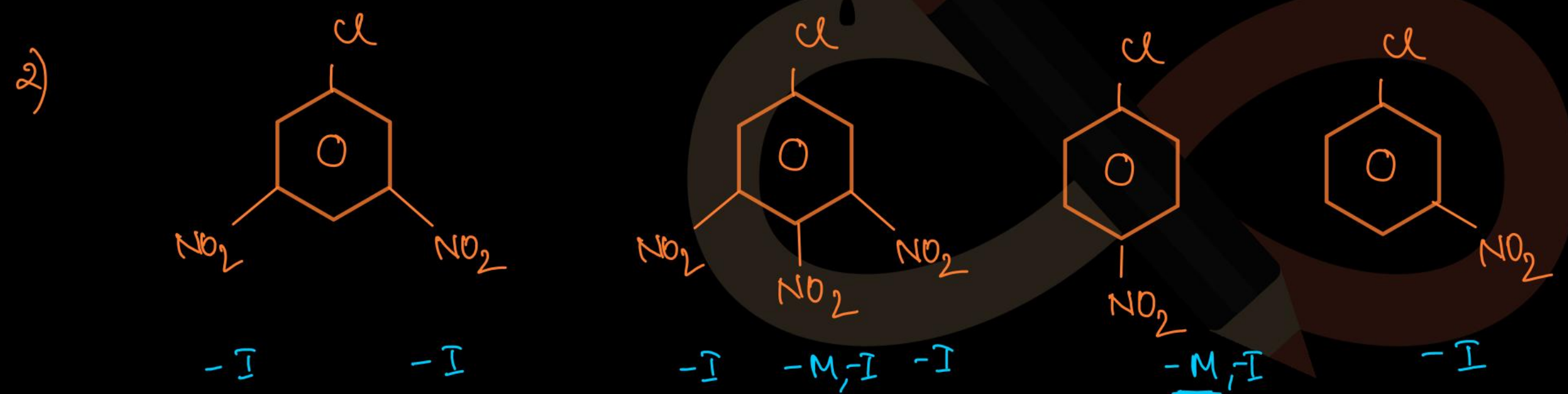
Practice :-



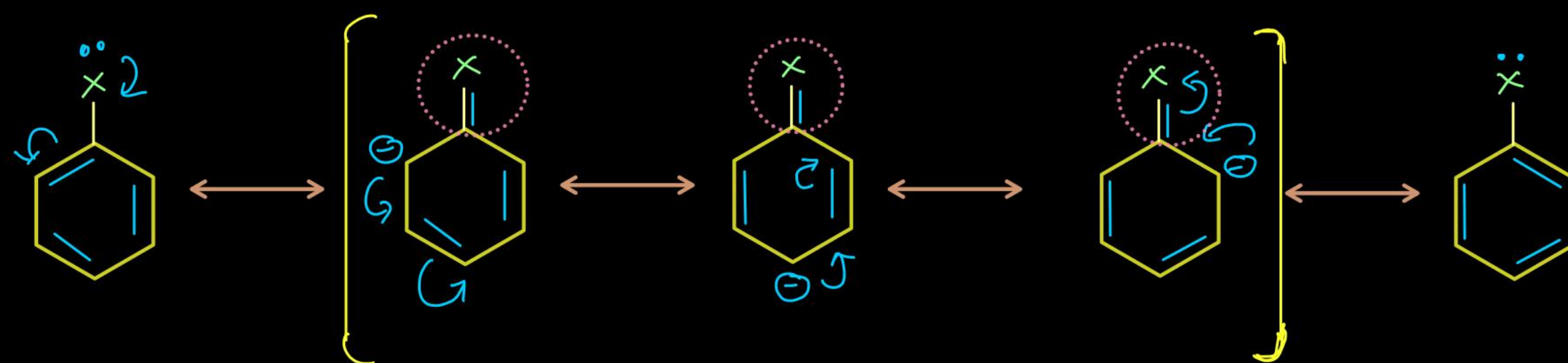
Q) Compare R.O.R of ArSN²:



(∵ rα -I, -M & at o,p)

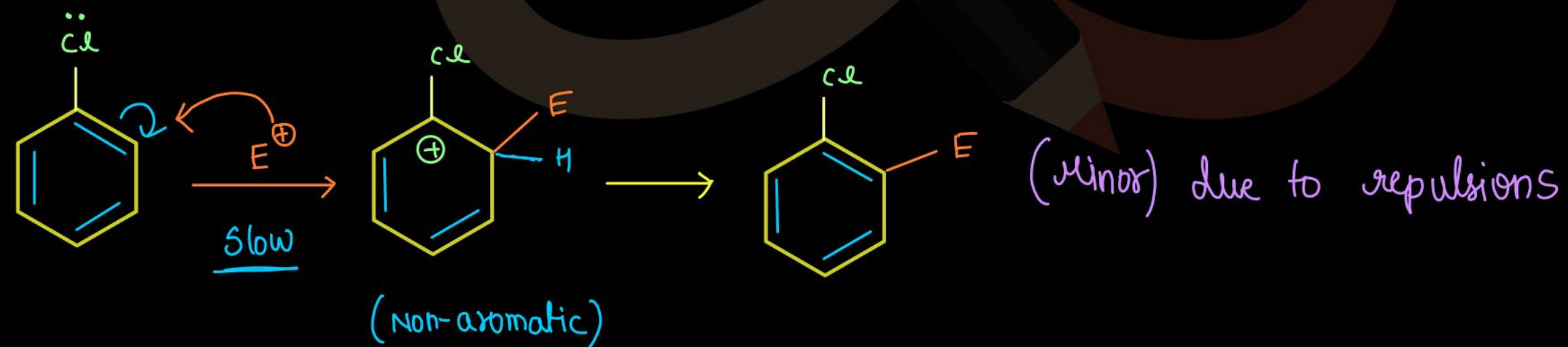


Electrophilic Substitution Rxn's :- (ESR)

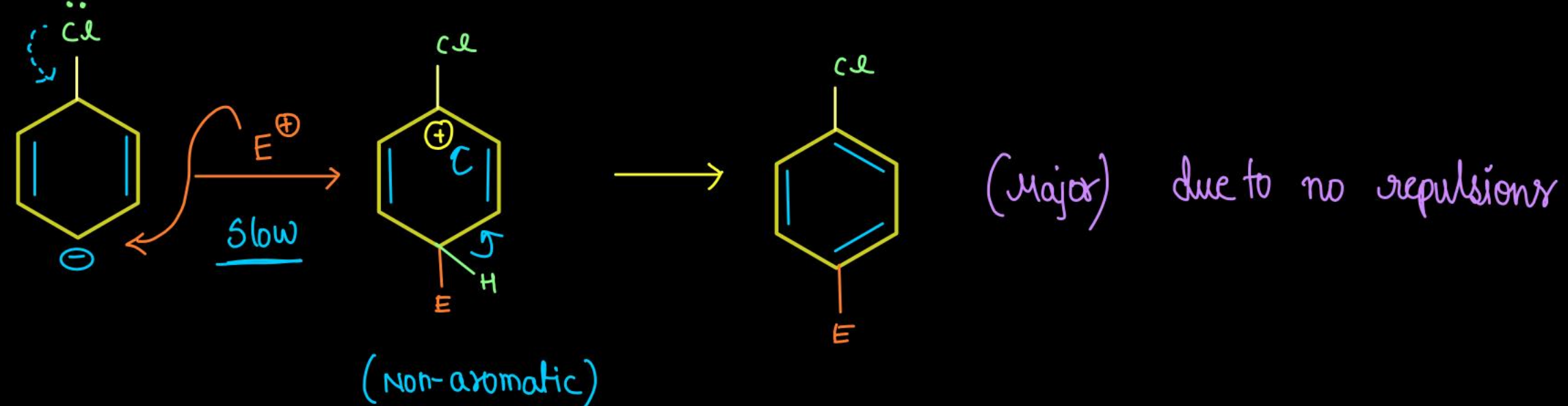


Mechanism:

i) ortho



ii) para



X is (Ortho-para) directing Gr.

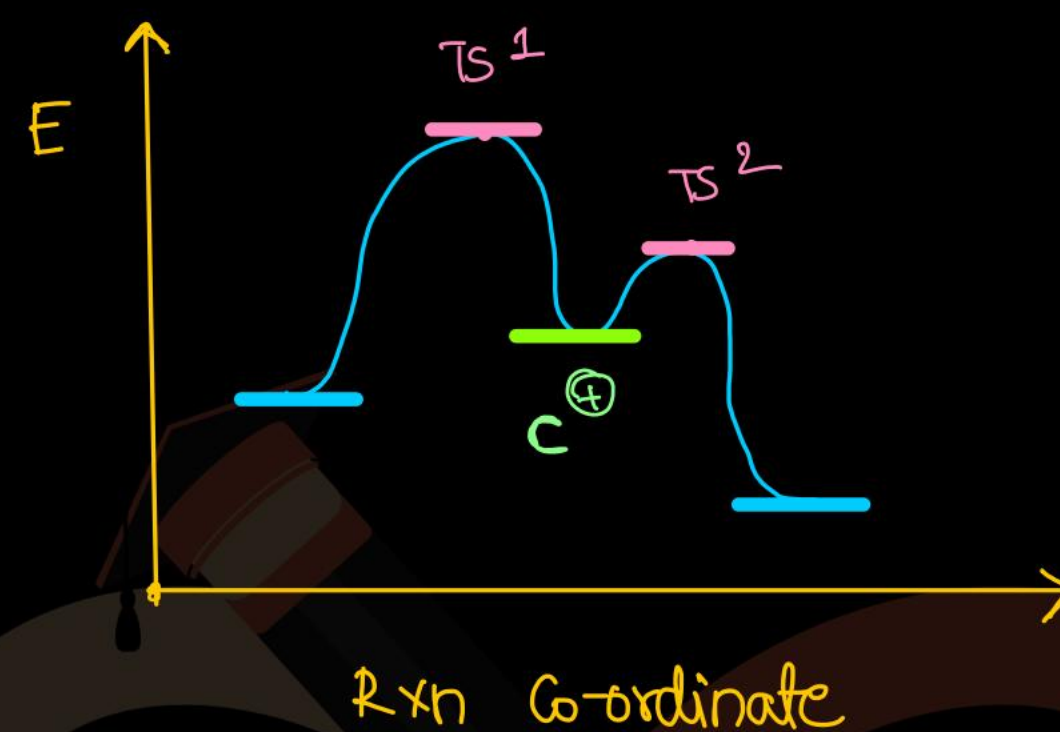
* Important points

1) 2 step rxn

2) Carbocation is formed

3) R.O.R $\propto$ Stability of c^+

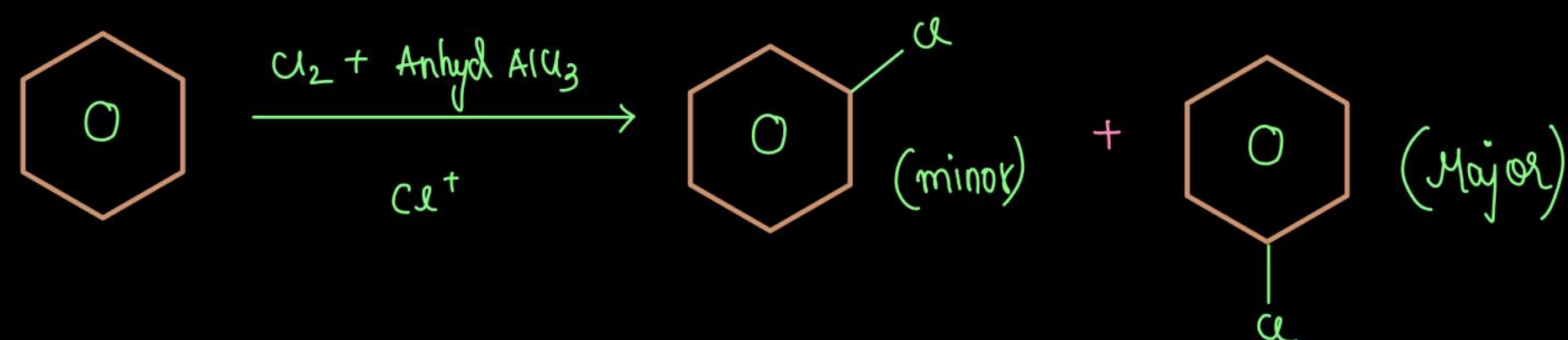
4) Energy profile diagram



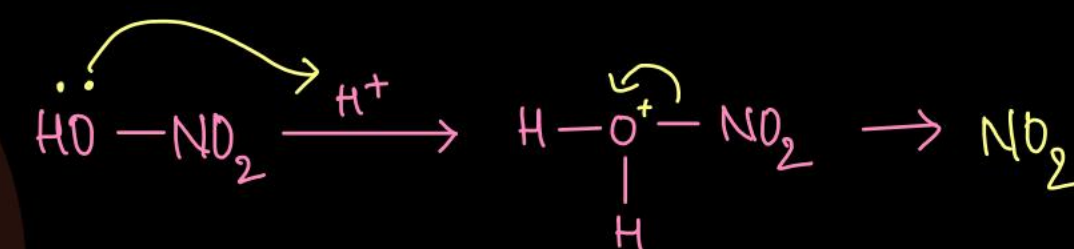
5) Resonance hybrid is called Wheland Intermediate (σ -Complex)



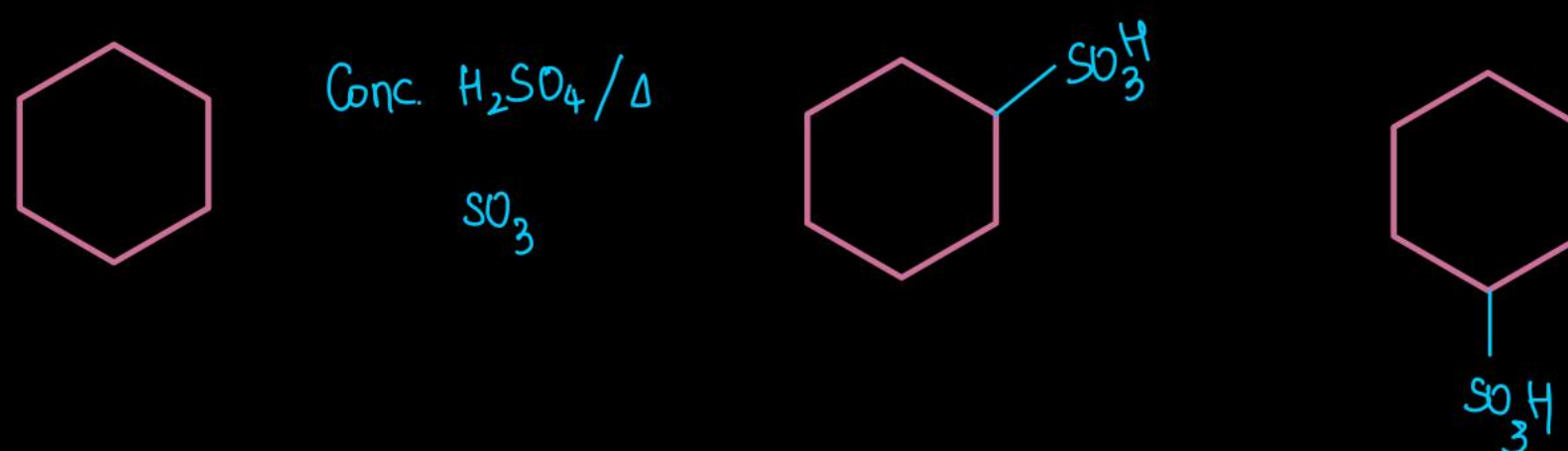
① Chlorination :-



② Nitration :-

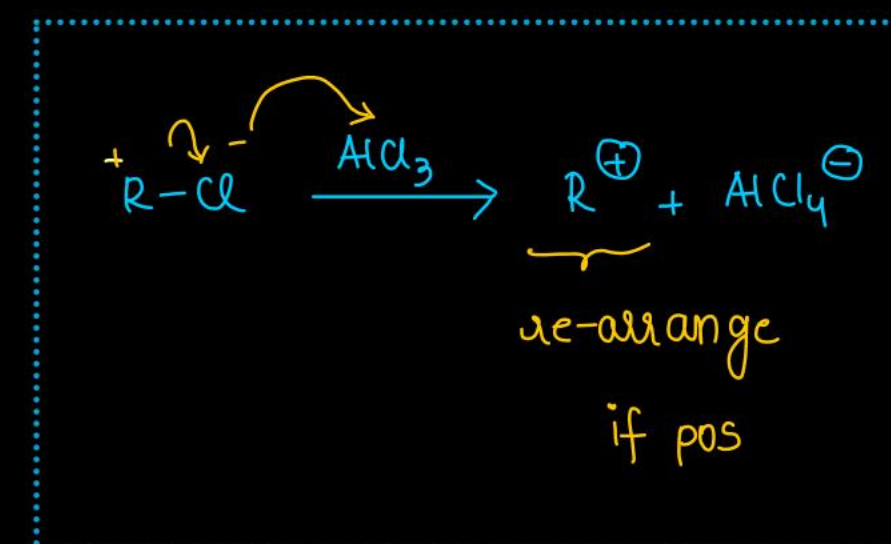
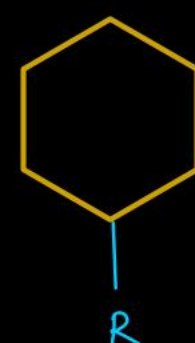
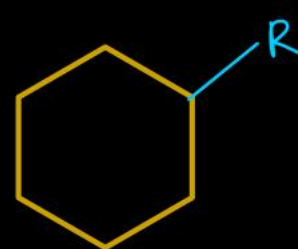
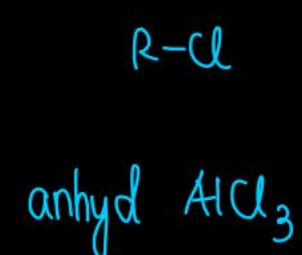
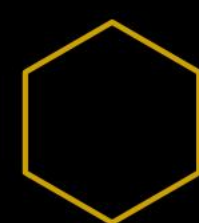


③ Sulphonation

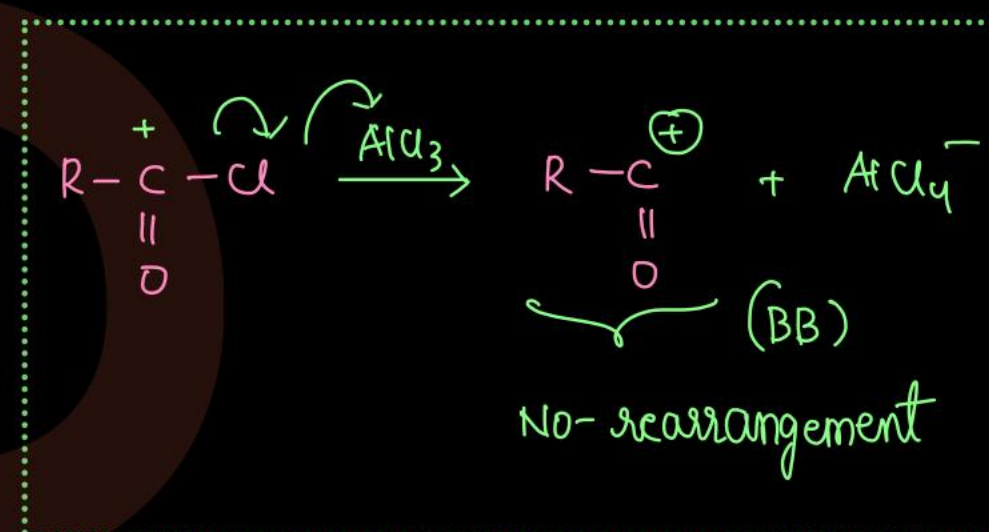
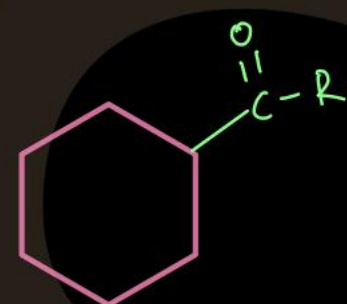
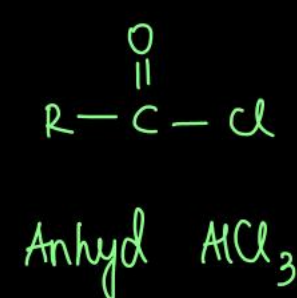
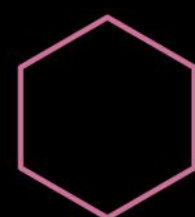


④ Friedal craft reaction

a) alkylation

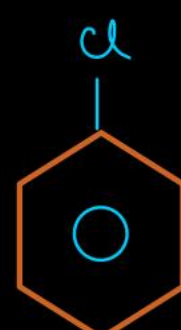


b) acylation



Practice :-

* a) Compare R.O.R towards ESR



-I > +M



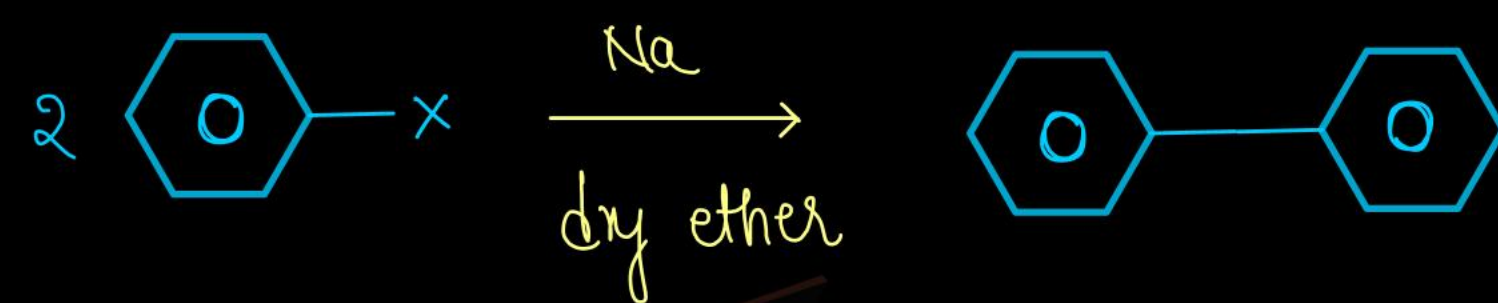
+M, +I

Ⓐ is deactivating grp

Hence, Ⓒ > Ⓐ > Ⓑ

Rxn with metals :-

1) fittig rxn's



ulman rxn



2) klutz fittig rxn :

