

# General Organic Chemistry

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Inductive effect :- (Permanent)

\*) operate to  $\sigma$  bond

\*) partial displacement of  $e^-$

+I effect :- Electron donating



-I effect :- Electron withdrawing



\*)  $-OCH_3$  is -I group

Applications :-

Acidic strength :-  $\propto -I \propto \frac{1}{+I}$

distance > Number > Power



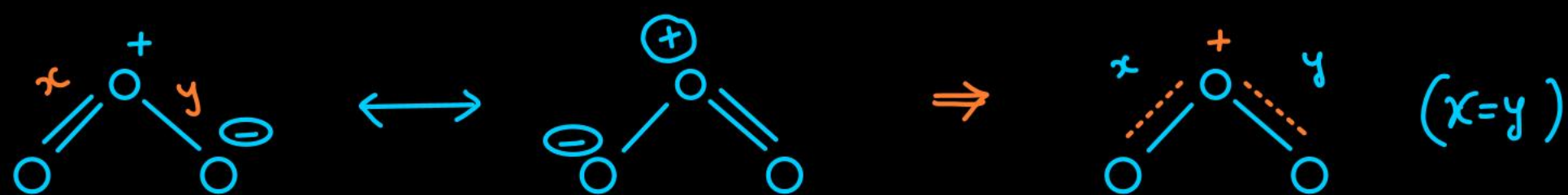
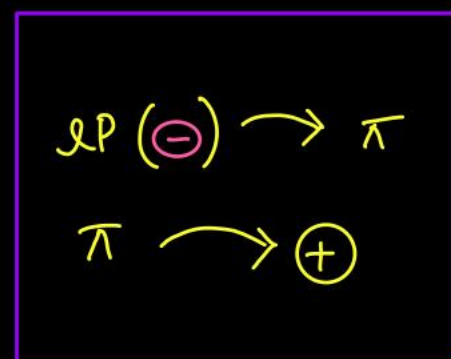
Stability of carbocation  $\propto +I \propto \frac{1}{-I}$

free radical  $\propto$  " "

Carbanion  $\propto -I \propto \frac{1}{+I}$

Resonance :-

(Permanent)



\* All participating atoms must be in same plane (planarity)



Stability

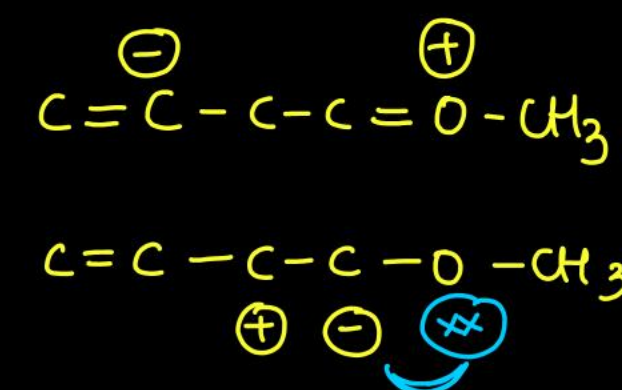
- 1> Uncharged > charged
- 2> More no. of '=' bonds
- 3> Octet
- 4> More Electronegative ; more -ve charge (L → R)  
Bigger size ; more -ve charge (T → B)



6> ↓ Similar charges on adj atoms

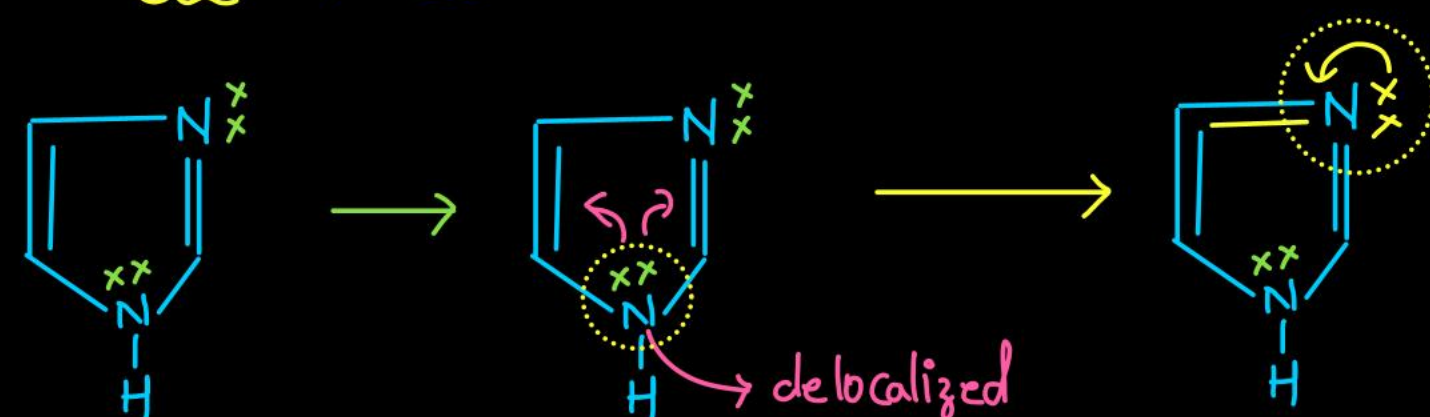
⇒ ↓ Charge Separation

}

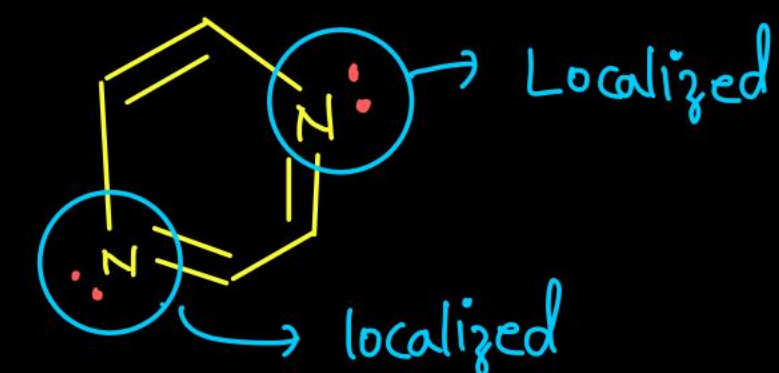


Seems like  $B > A$   
but  $B < A$

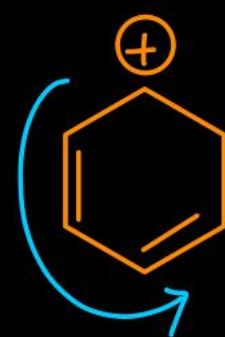
\* Localized & de-localized LP



but  $=N=$  is not possible hence it is localized.



\* Extended Cong



Cross Cong

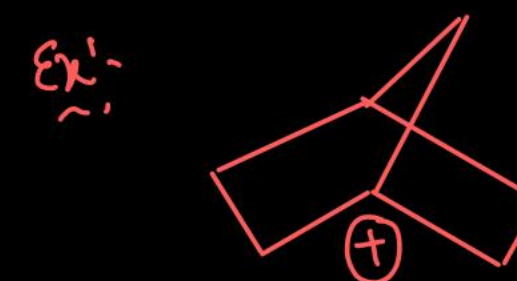


Bredt's rule :-

\* Bridged Carbon  $\rightarrow$   $\oplus$  charge /  $\pi$  bond  $\times$



Not possible



} unstable

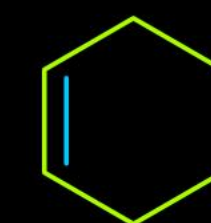
Aromaticity :

- 1) Cyclic
- 2) Conjugation
- \* 3) Planar

If atleast any 1  
Cond is failed

Non-aromatic

Ex:-



Alcyclic

- 1) ✓
  - 2) ✗
- No conjugation

4) Huckel's rule

Aromatic

$(4n+2) \pi e^-s$

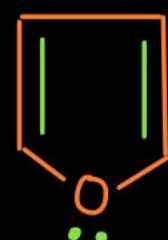
Anti-aromatic

$(4n) \pi e^-s$

Stability :-

Aromatic > Non-aromatic > Anti-aromatic

Ex:-



$6\pi$   
Aromatic

\*)



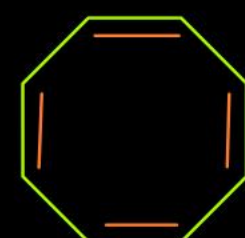
$4\pi$   
Anti-aromatic

$sp^2$  vacant p

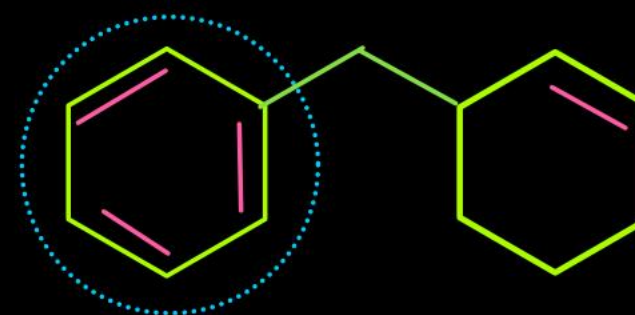
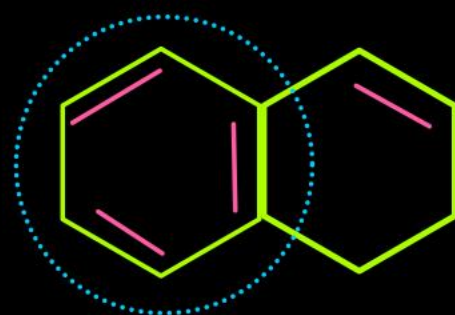


$6\pi$   
Aromatic

localized sp



Non-planar  
Non-aromatic



Aromatic due to presence of Benzene ring

\*) Mesomeric effect



+M : Electron donating



\*)  $\text{OCH}_3$  is +M group

-M : Electron withdrawing



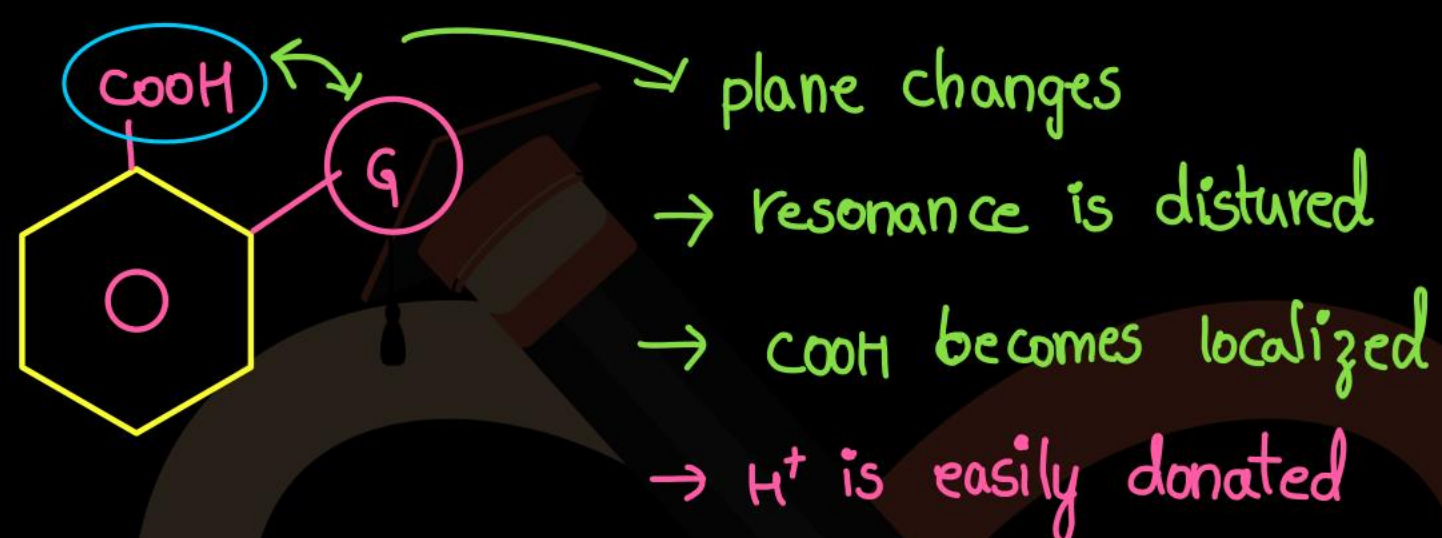
Note:-

1) M effect does not operate on Meta position

2)  $+M > -I$  ( $-OH, -NH_2, -OR \dots -OCH_3$ )

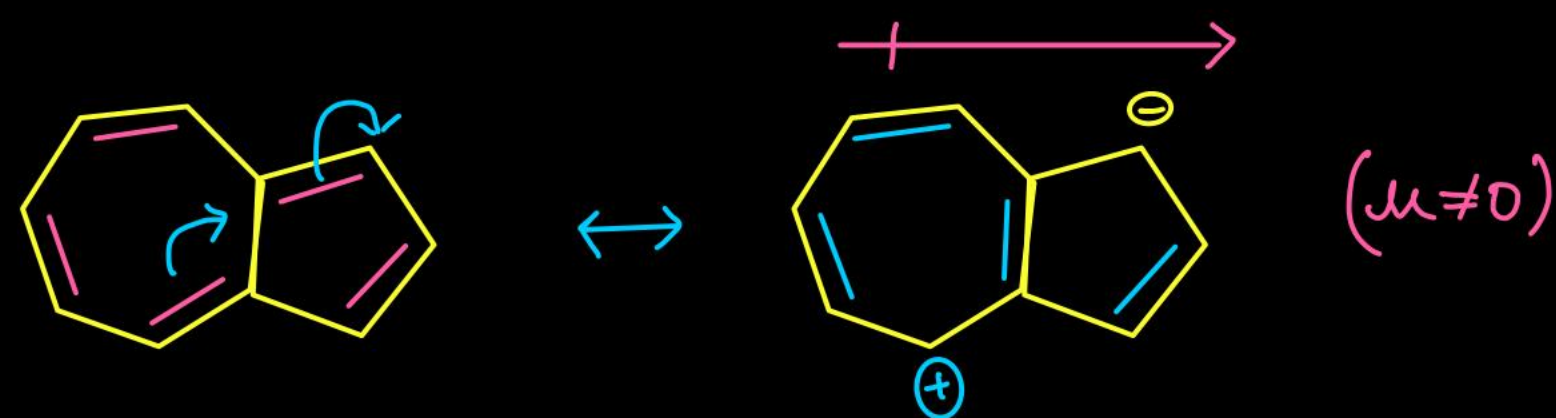
3)  $+M < -I$  ( $-X$ )

4) Ortho effect :



$\left( G \neq H, -OH, NH_2 \right)$   
CN

dipole moment :-



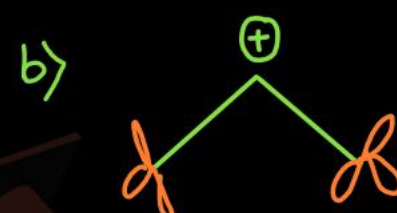
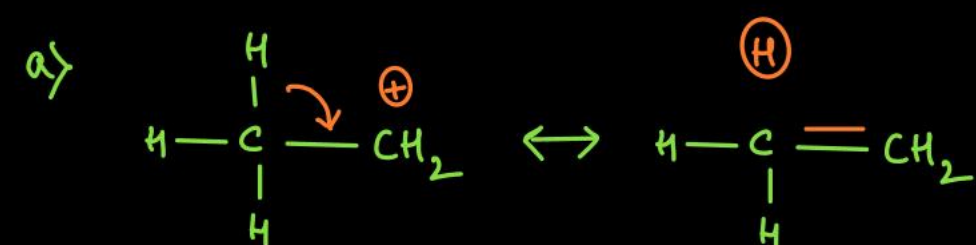
Azulene

Hyperconjugation: \*)  $\alpha$ -C  $sp^3$ , \*)  $\alpha$ -H  $\checkmark$  (No bond resonance)

Applications :- \*)  $R > H > I$

1) Stability of  $\text{C}^+$ ,  $\propto$  (No. of HCS)

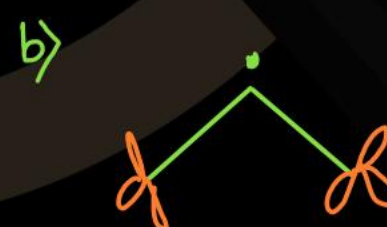
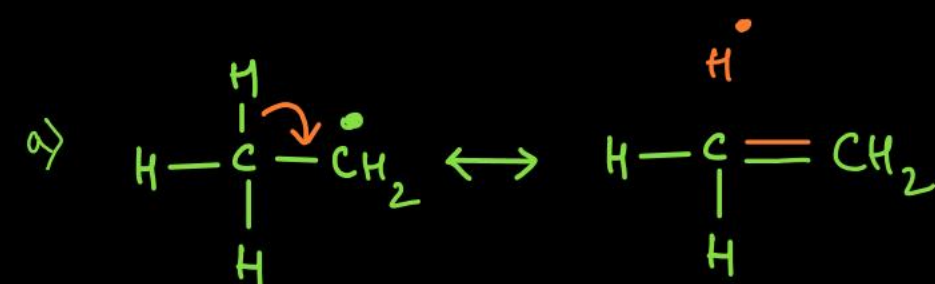
\*)  $\sigma$  - vacant p



(6)  $\alpha$ H  $\Rightarrow$  6 HCS

2) Stability of  $\text{C}^\bullet$ ,  $\propto$  (No. of HCS)

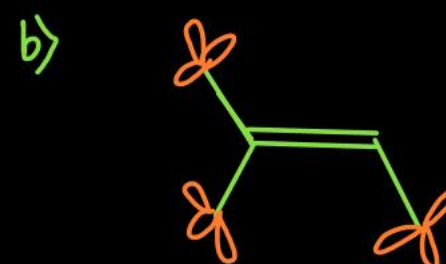
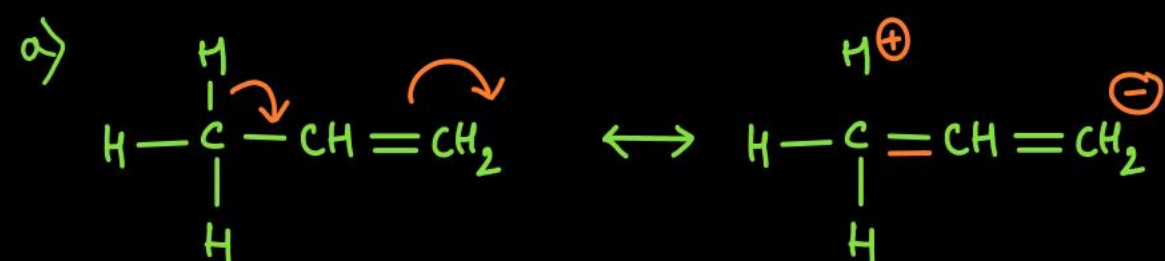
\*)  $\sigma$  - half filled p



(6)  $\alpha$ H  $\Rightarrow$  6 HCS

3) Stability of alkenes  $\propto$  (No. of HCS)

\*) ( $\sigma$ - $\pi^*$ ) overlapping

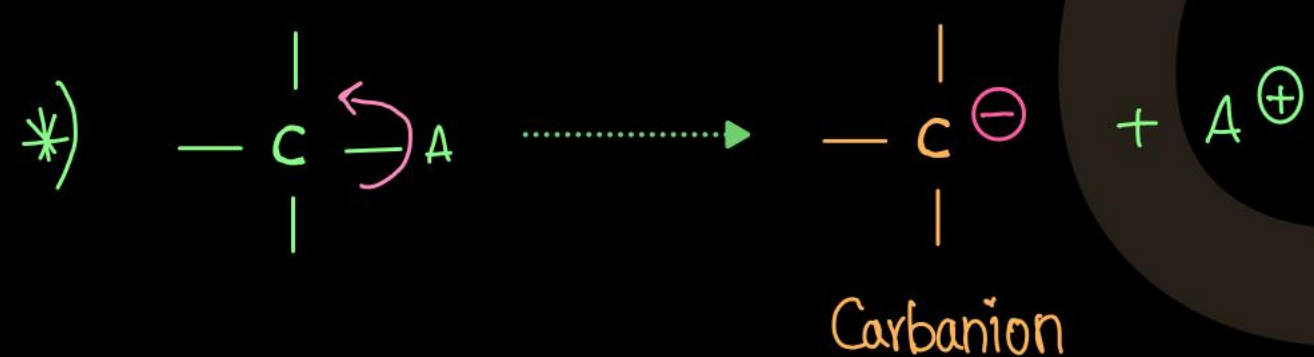


(9)  $\alpha$ H  $\Rightarrow$  9 HCS

## \* Reaction Intermediates :

Bond fission/cleavage :

i) Heterolytic : { Ionic / heteropolar / Polar rxn's }

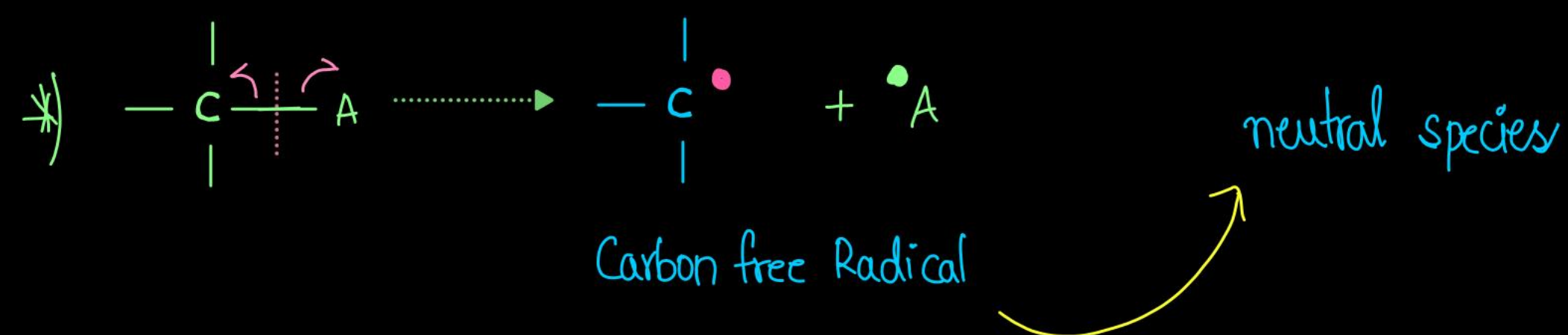


Note:-

Electrophile :  $e^-$  deficient :  $\text{C}^+$   $6e^-$

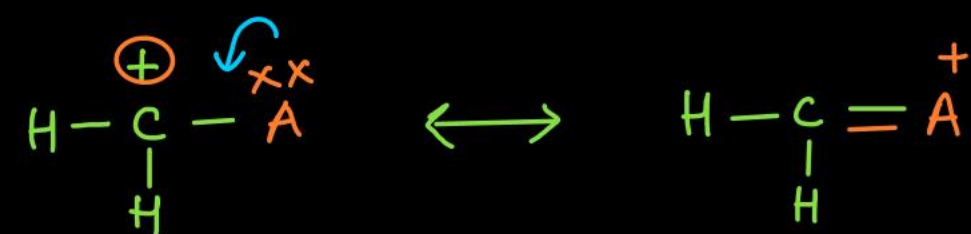
Nucleophile :  $e^-$  rich :  $\text{C}^-$   $8e^-$

ii) Homolytic : (free radical / homopolar / non-polar rxn's)

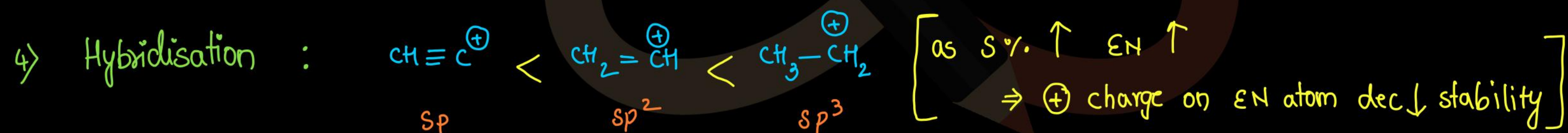
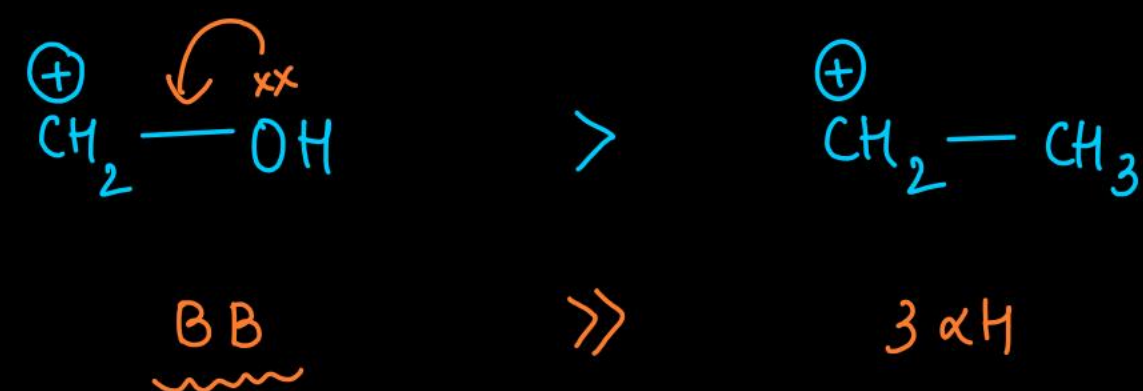


## Stability of Carbocation :-

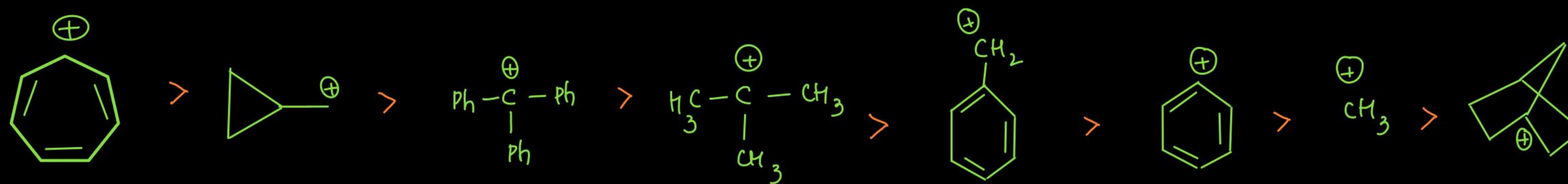
### 1) $\alpha$ -effect (Back-Bonding)



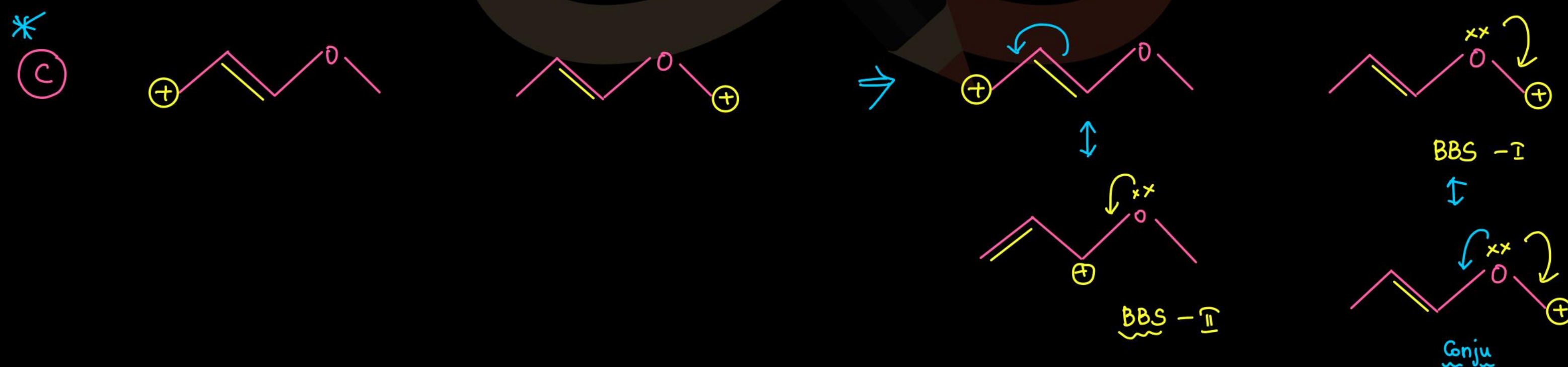
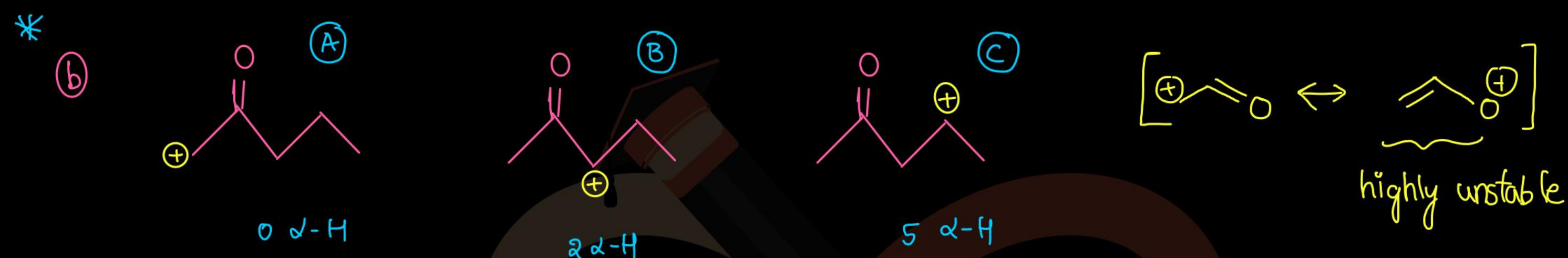
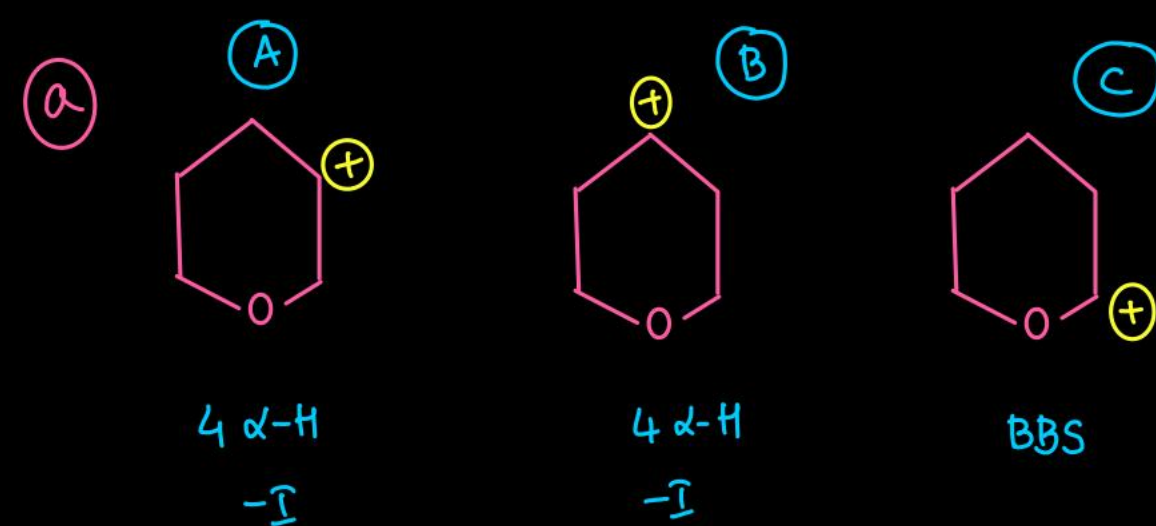
Ex:-



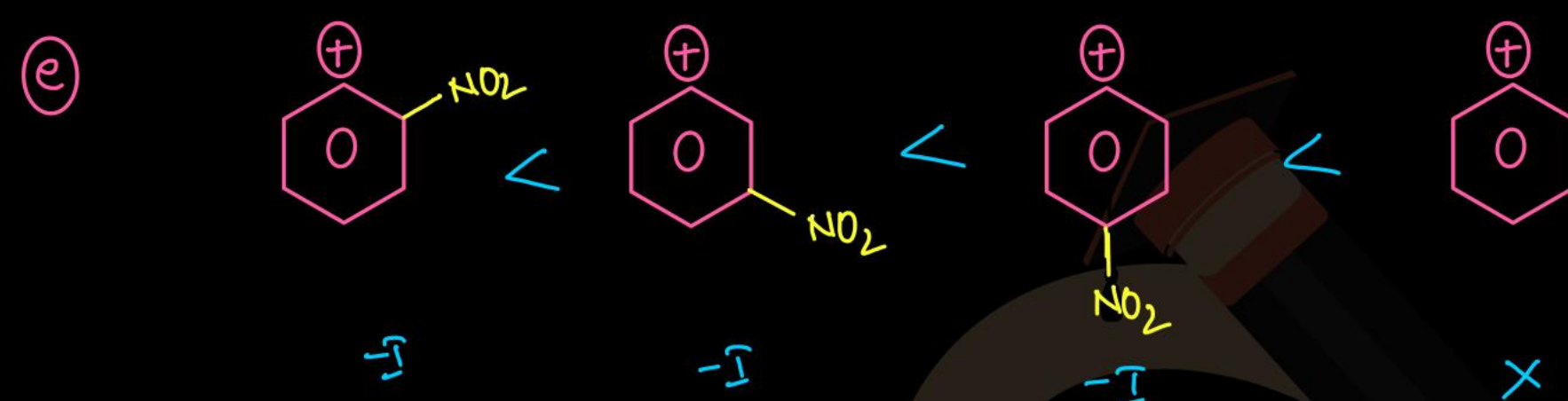
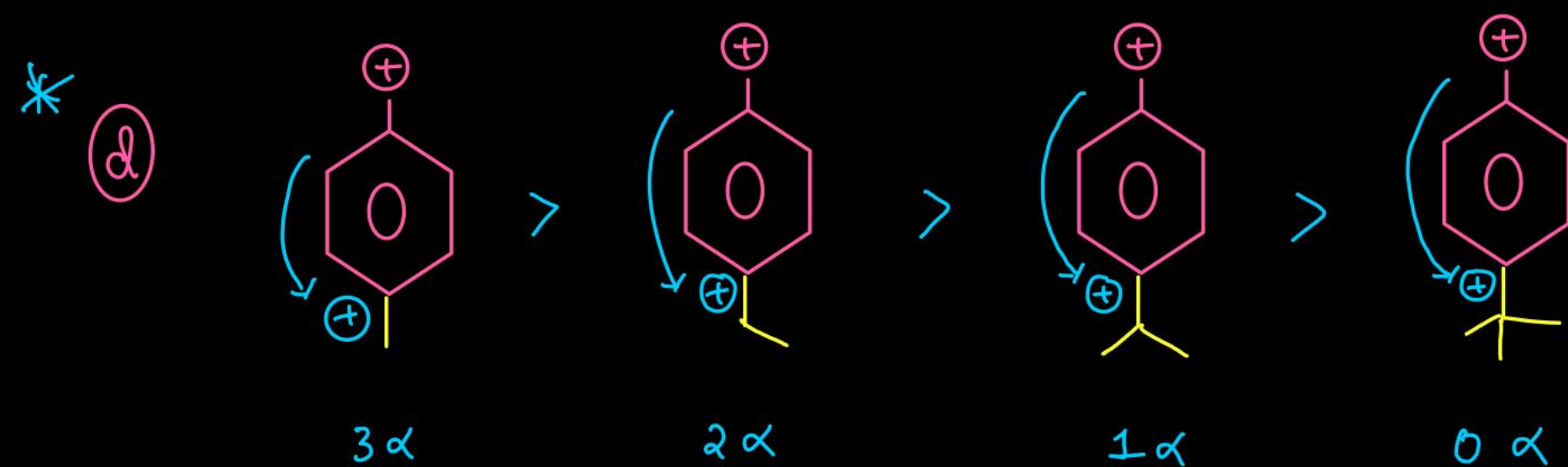
### 5) Order



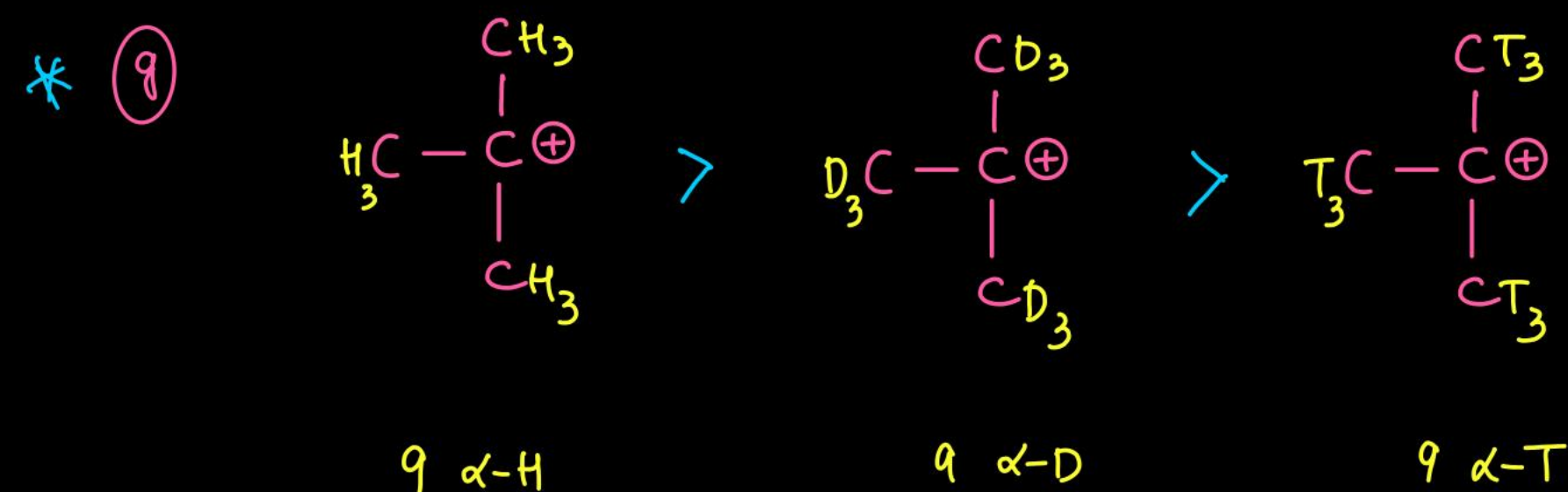
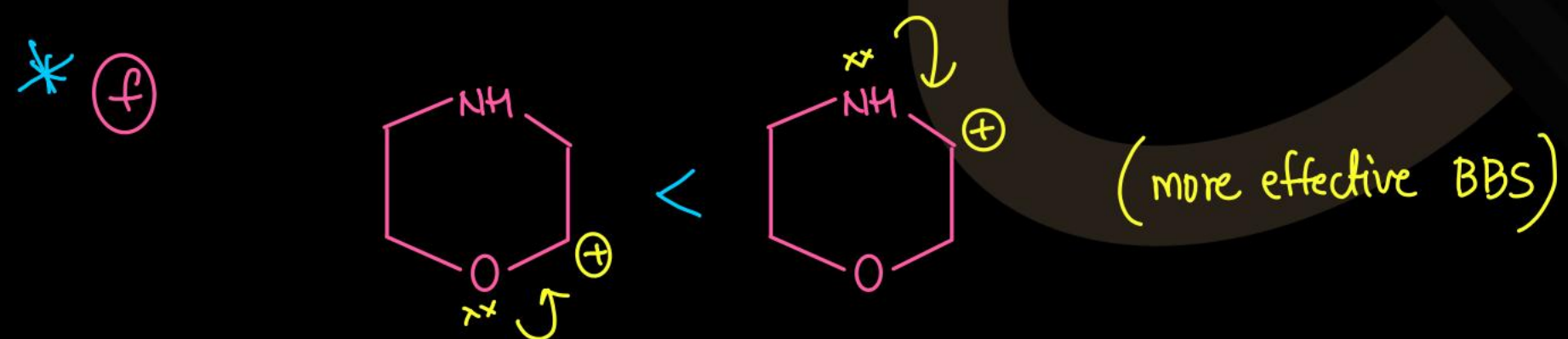
Practice:



BBS-II is more effective than BBS-I



{ No resonance if  $\oplus$  charge is on the ring }



BE:  $C-H < C-D < C-T$

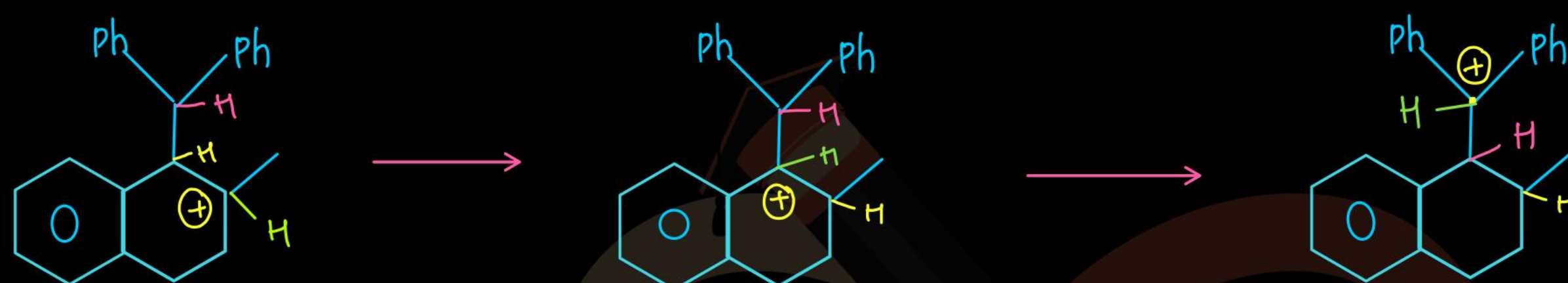
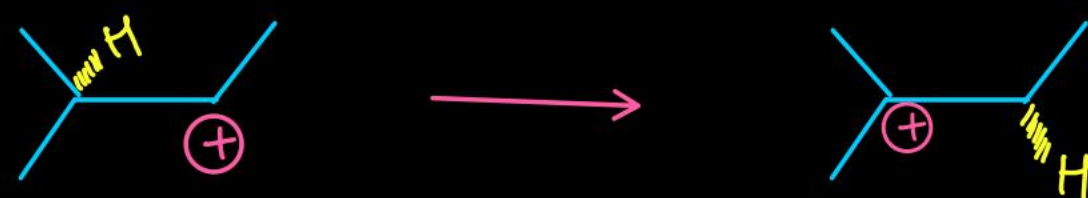
$\therefore$  B.E  $\downarrow$  H - gets released easily

for HCs we need H

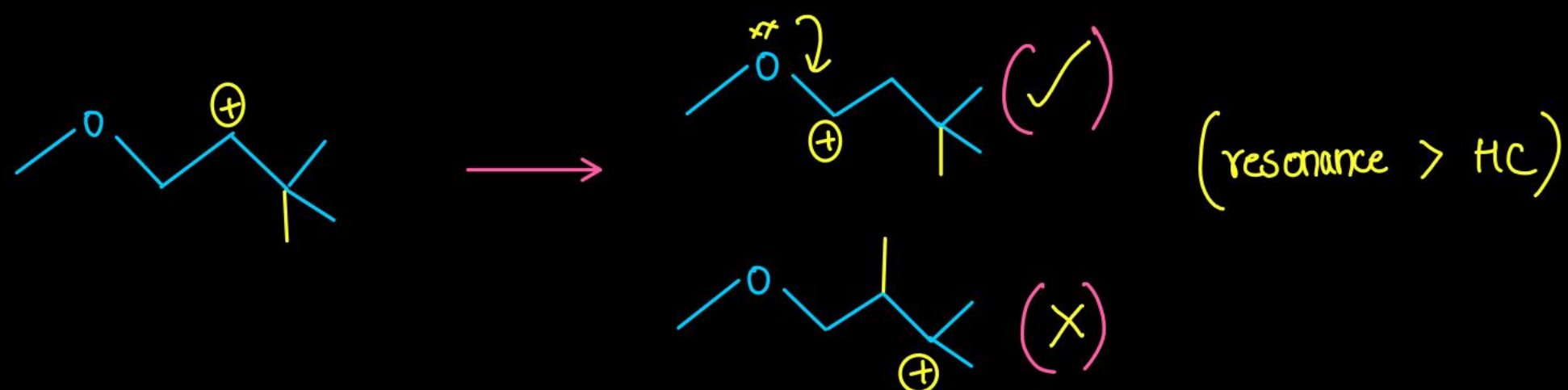
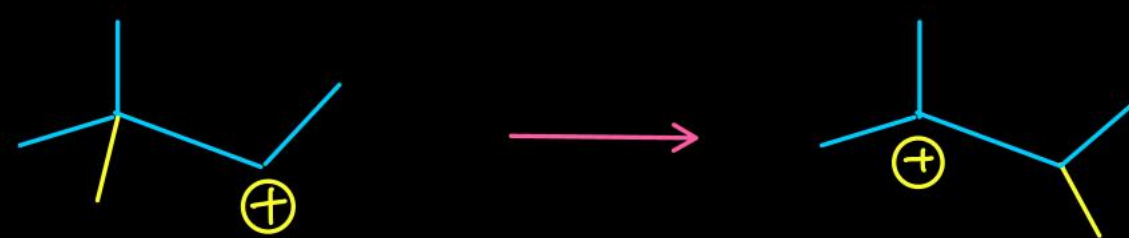
$\Rightarrow$  so (A) > (B) > (C)

## Re-arrangement of Carbocation :-

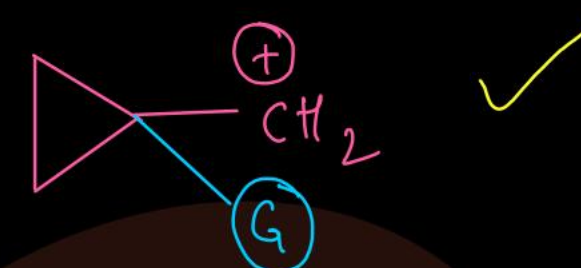
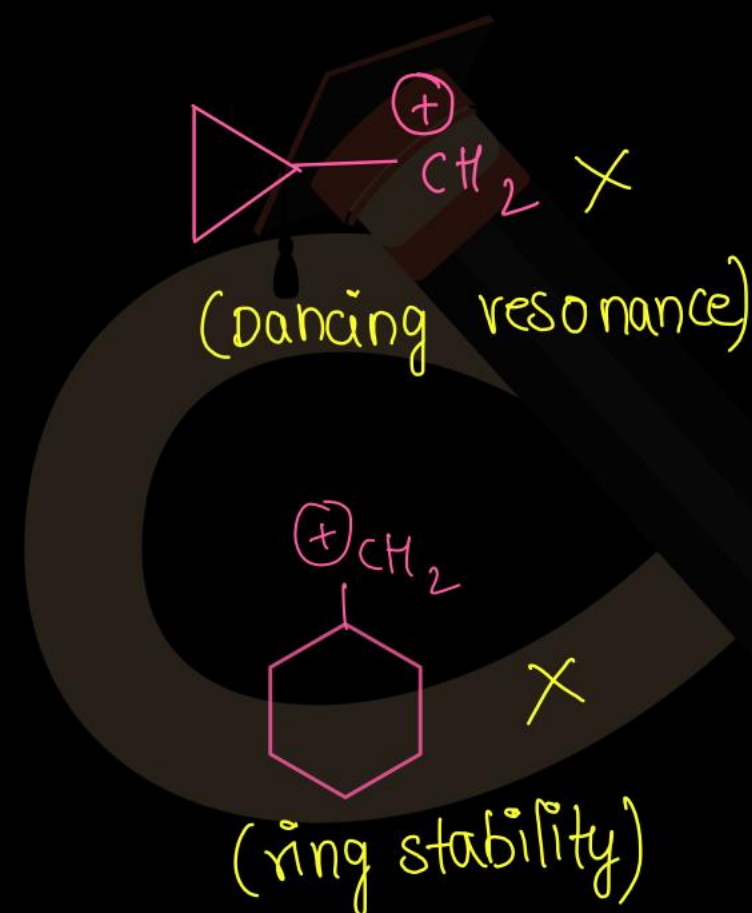
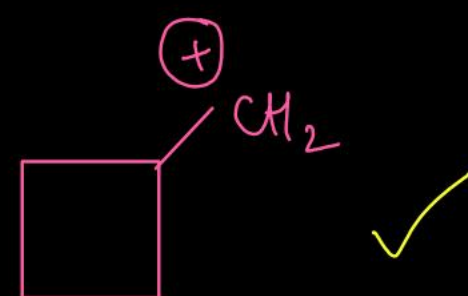
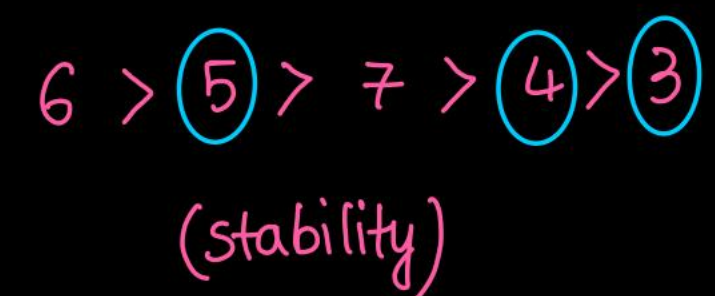
### 1) 1,2-hydride shift



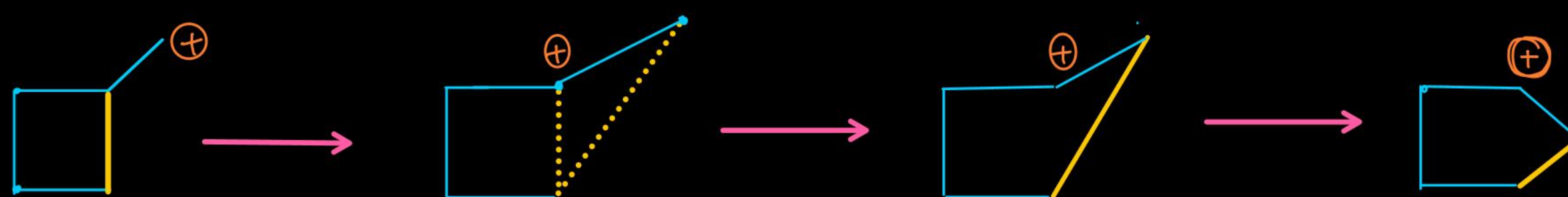
### 2) 1,2-methyl shift

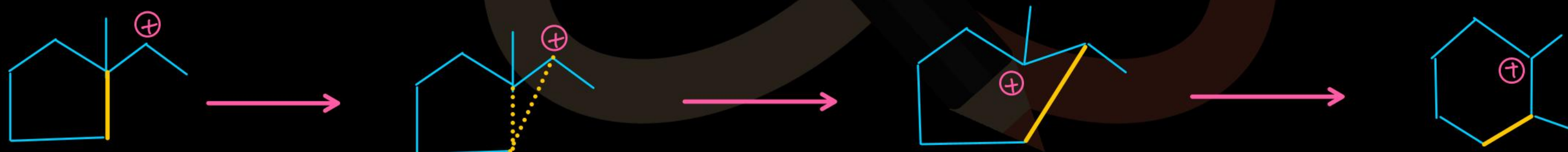
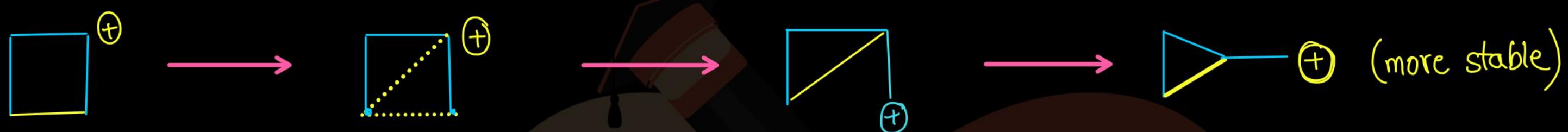
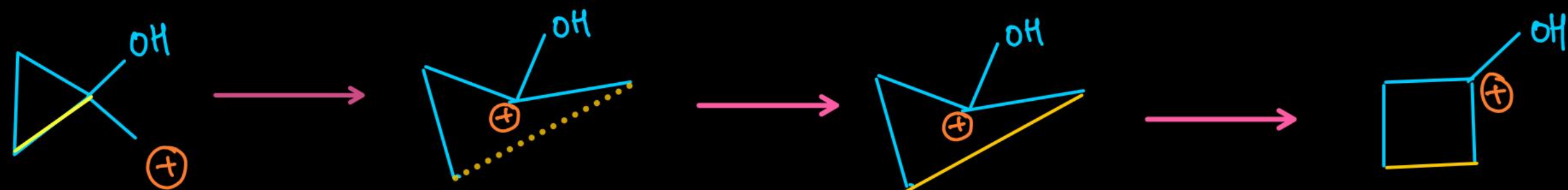


# Ring Expansion (bond shift)



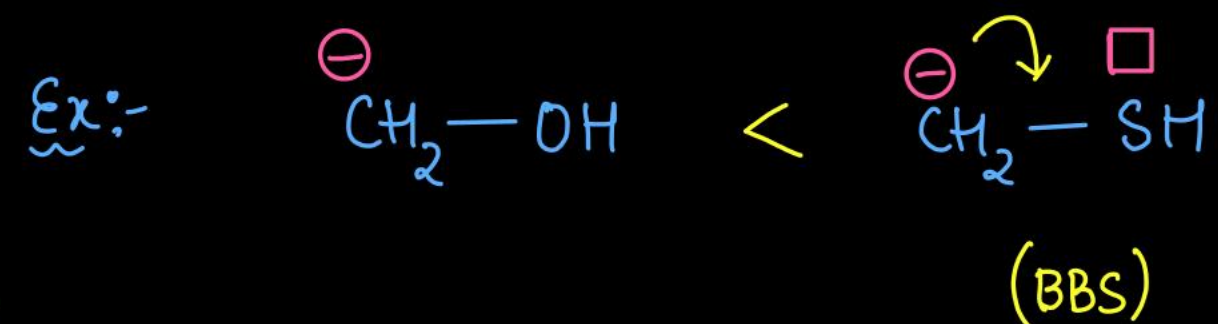
G = OH, Me





## Stability of Carbanion

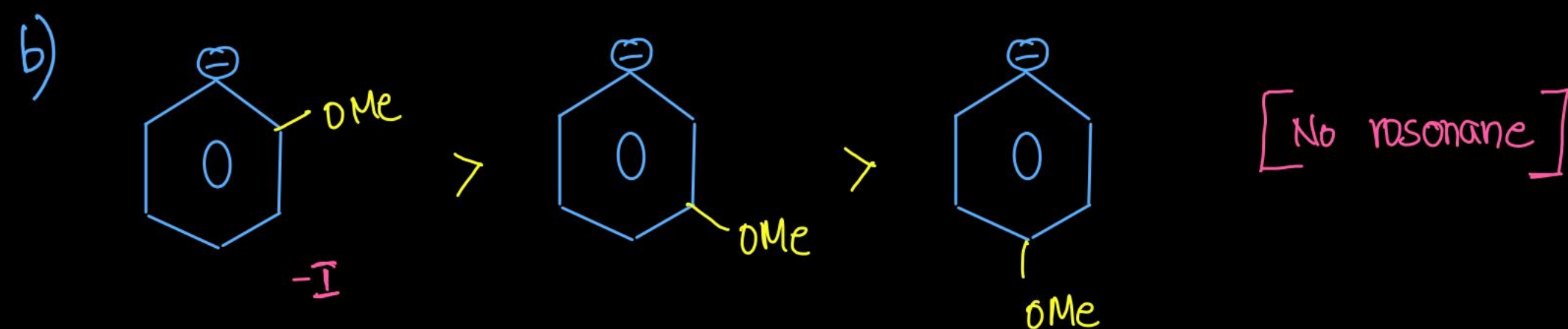
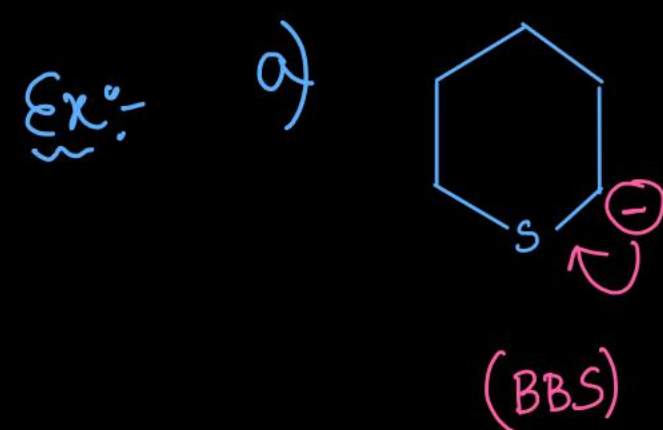
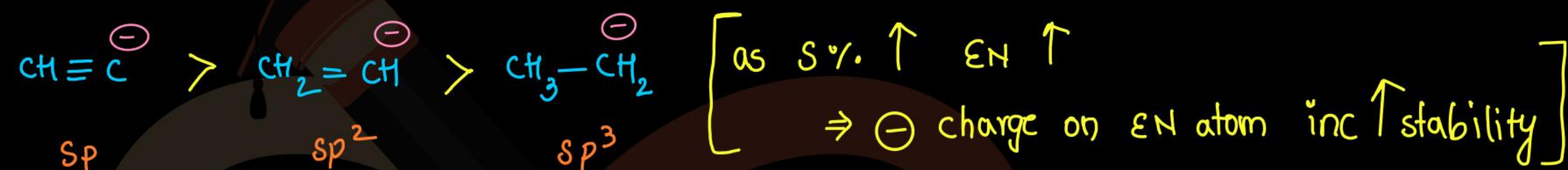
1)  $\alpha$ -effect (BBS)

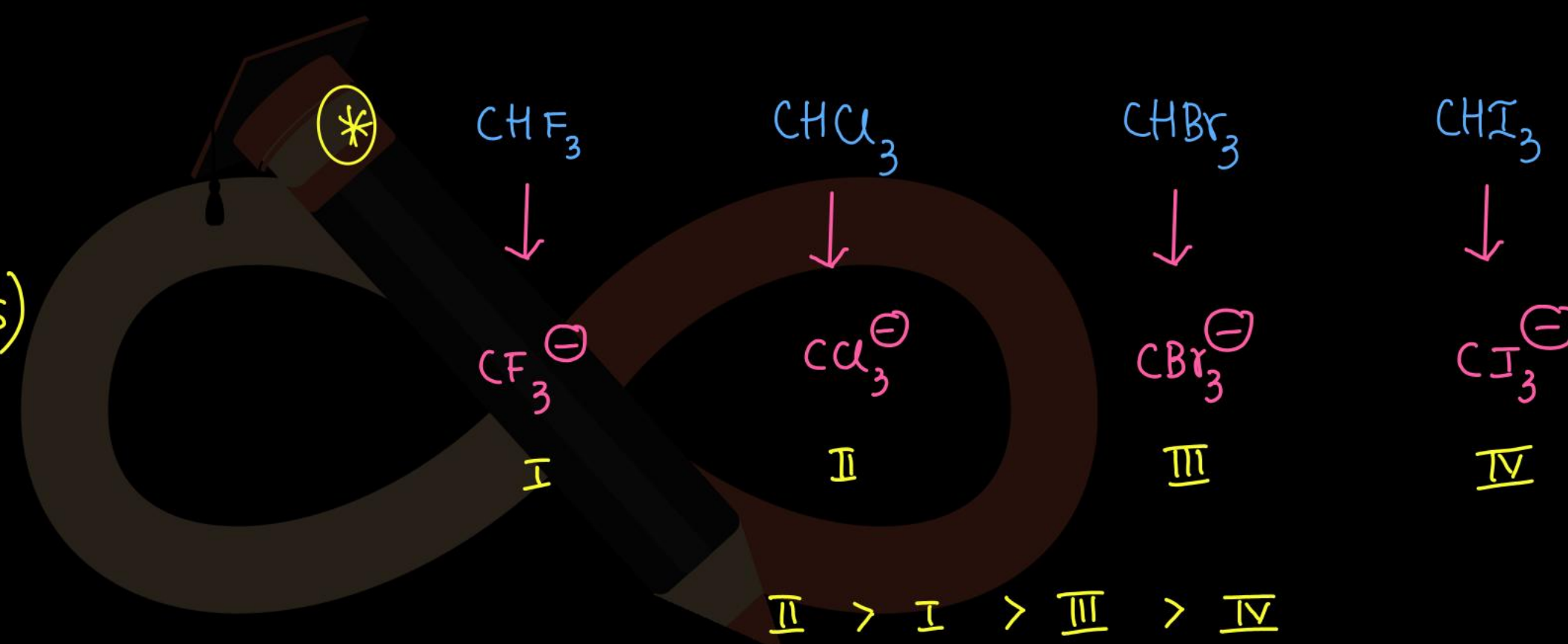
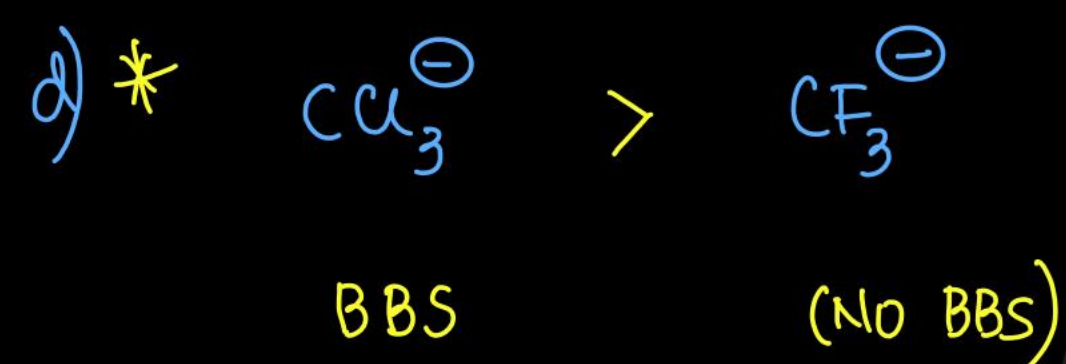
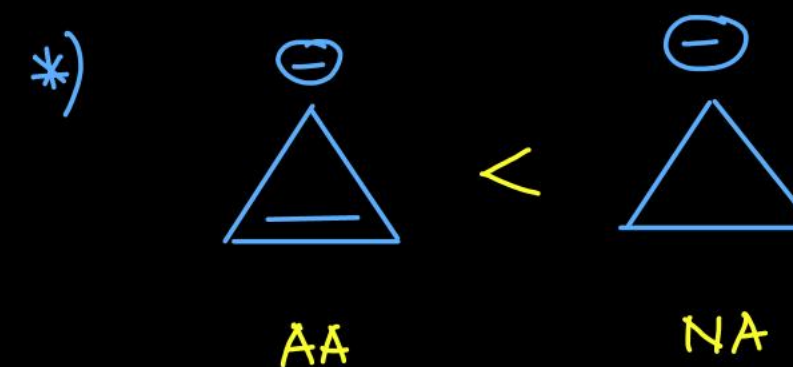
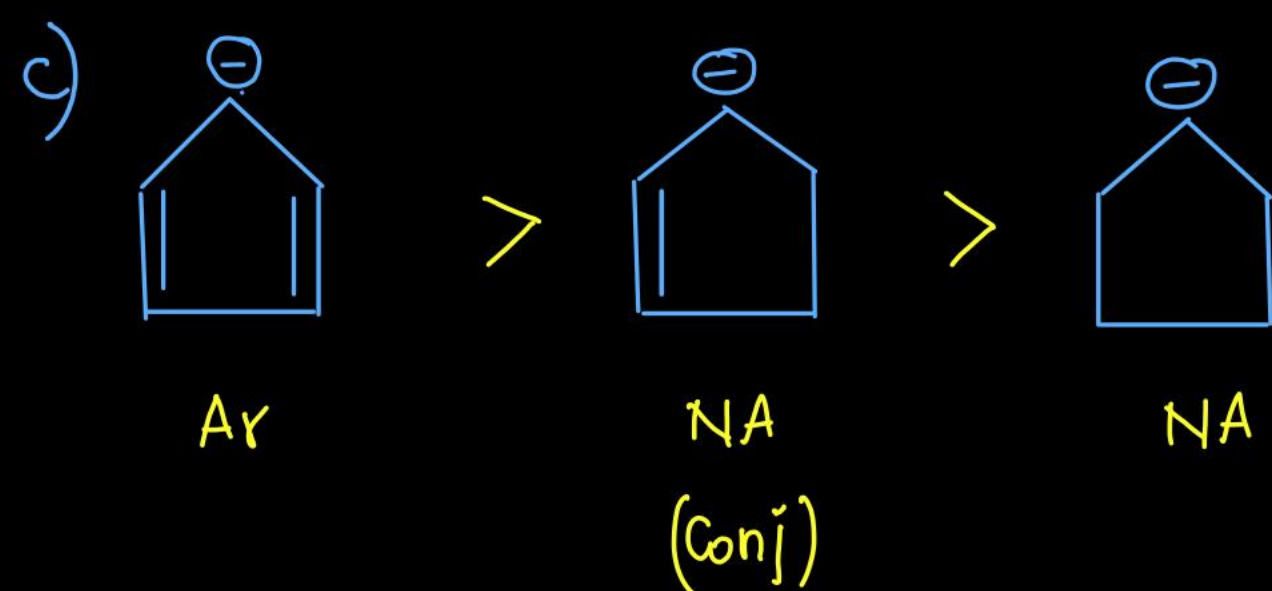


2)  $\text{BBS} > \text{Ar} > \text{M} > \text{H} > \text{I}$

3)  $\alpha$   $-\text{M}, -\text{H}, -\text{I}$

4) Hybridisation





Stability of free radical :-

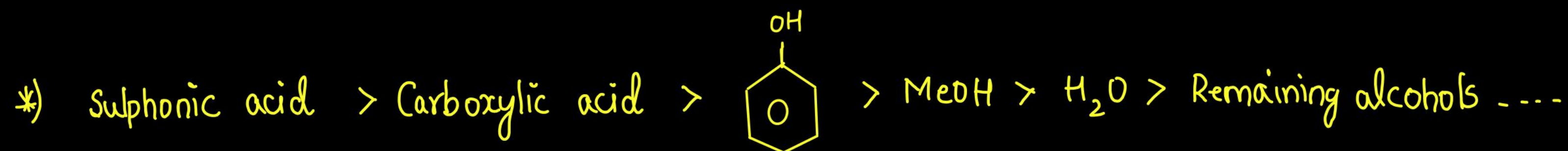
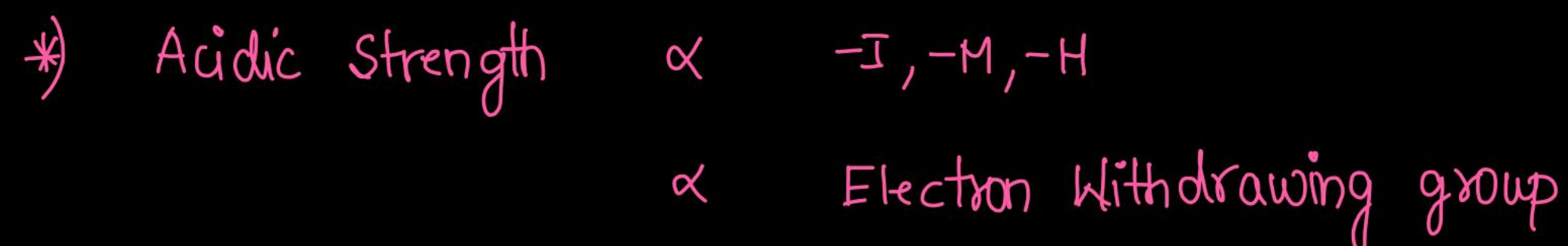
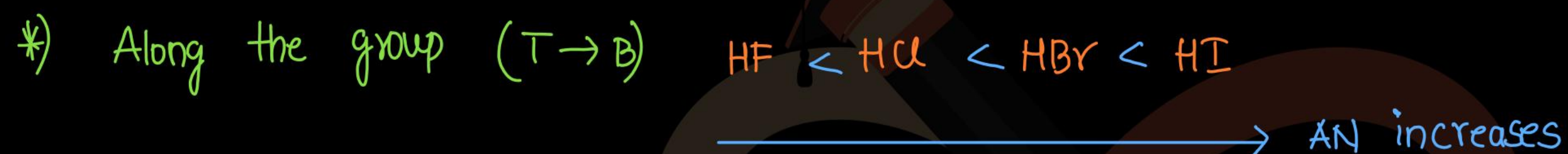
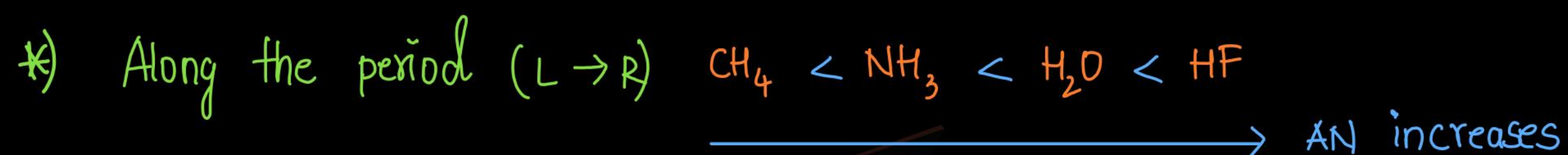
1) M > H > I \* (No Ar, BBS)

2) Stability  $\propto$  +I, +M, +H

3) Hybridisation

## Acidic Strength :

\*  $\propto K_a \propto \frac{1}{pK_a}$



## Acidic Nature in phenols

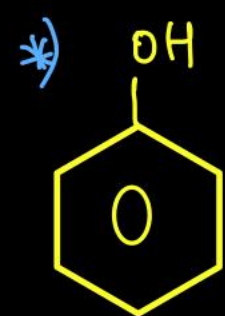
I>



$\text{NO}_2$

-I

-M



$\text{Cl}$

-I

+M



$\text{CH}_3$

+I

+M



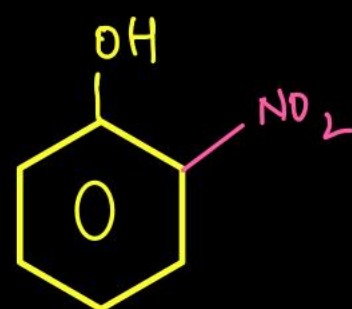
$\text{OCH}_3$

-I

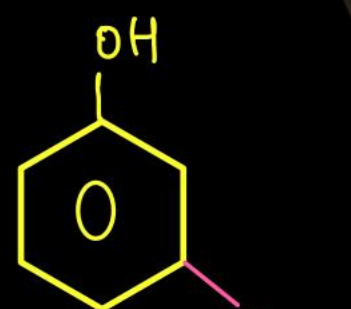
+M



\* II>



-I, -M



-I

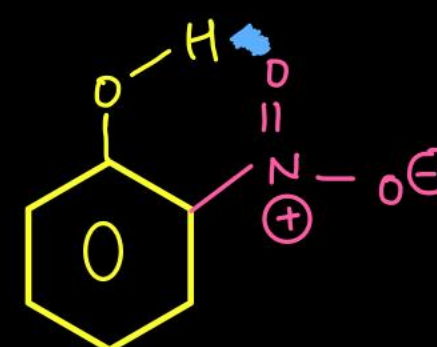


$\text{NO}_2$

-I, -M

Expected :  $o > p > m$

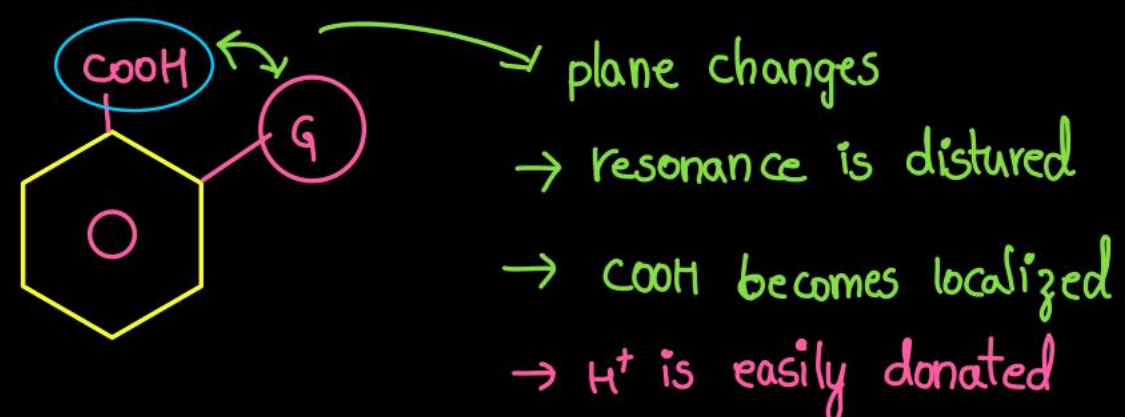
but, reality :  $p > o > m$  { due to H-bonding }



(It is not so easy to donate H due to this  $p > o$ )

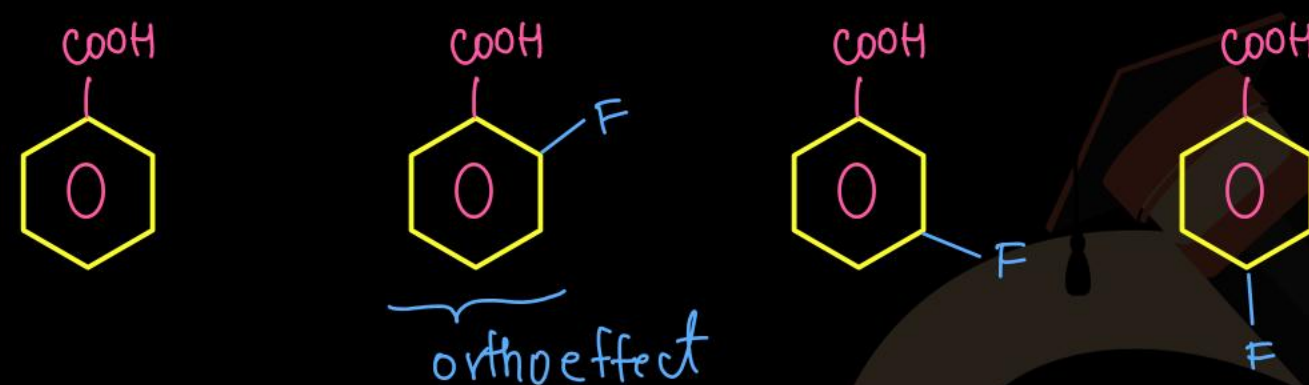
# Acidic Nature in Benzoic acid

\* Orthoeffect :-



$(G \neq H, -OH, NH_2, CN, D, T)$   $G$  can be  $+I/-I$   
 ↓ irrespective of nature

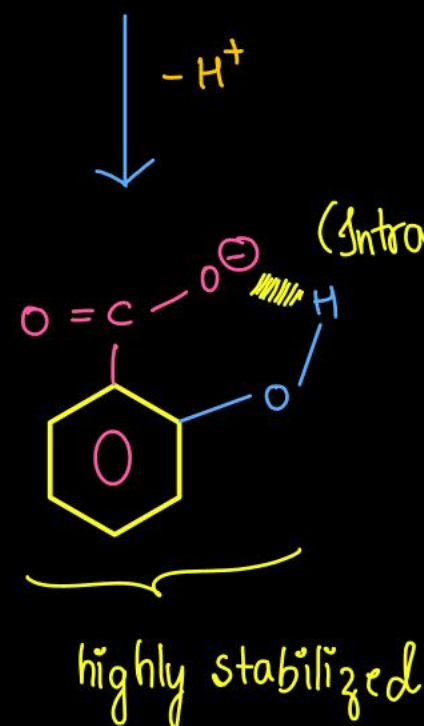
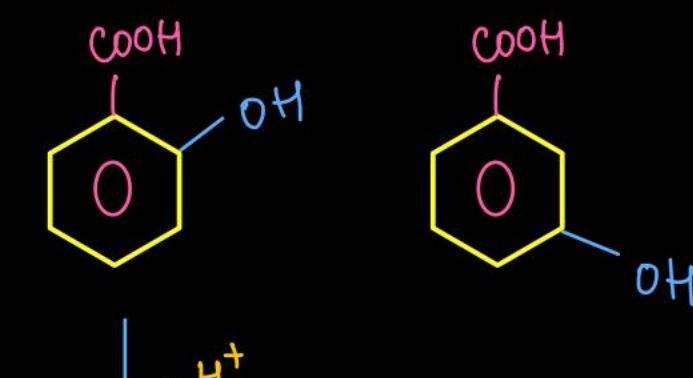
I>



II > III > IV > I

[do not consider H-bond here, only ortho]

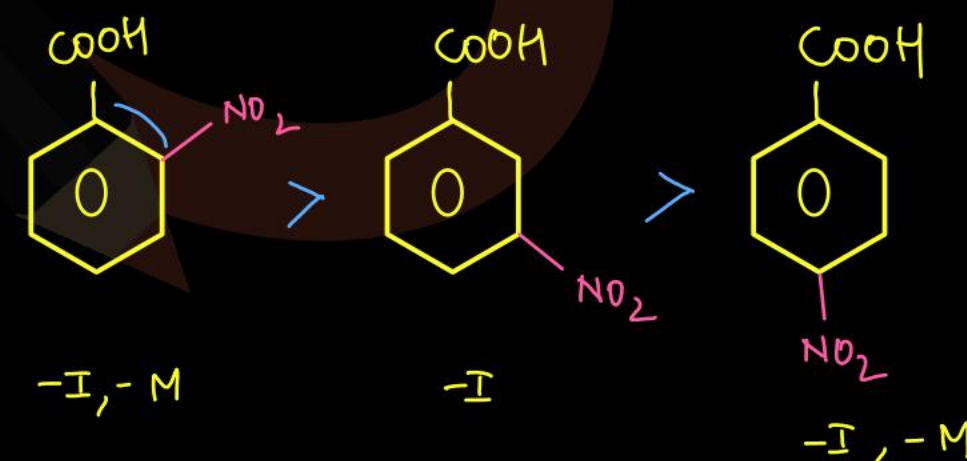
II>



⇒

O > m > p

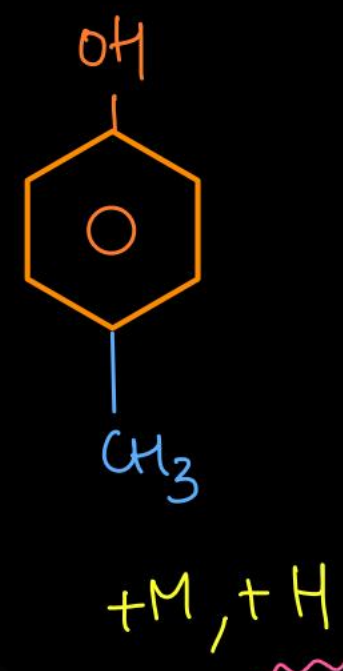
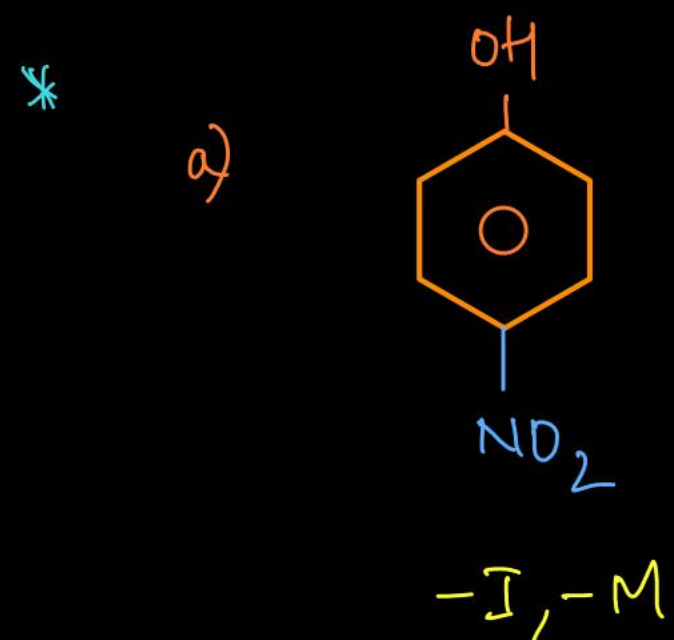
III>



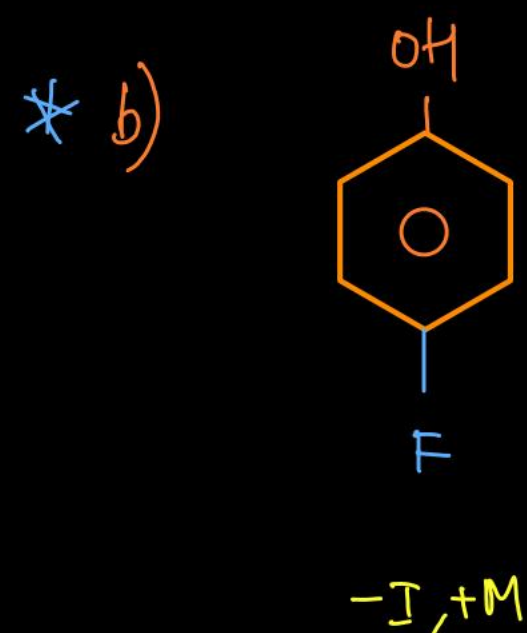
O > m > p (ortho effect)

\*) H-bond may inc/dec acidic strength  
 in benzoic acids & phenols

# Acidic strength practice

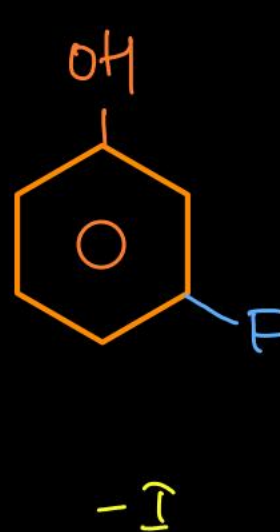
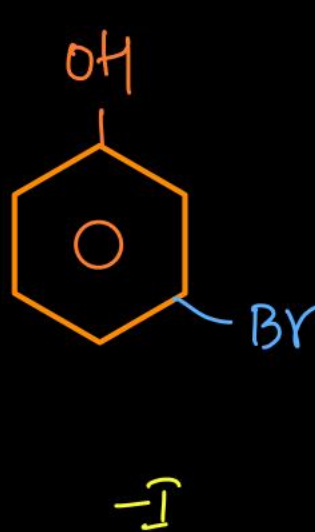
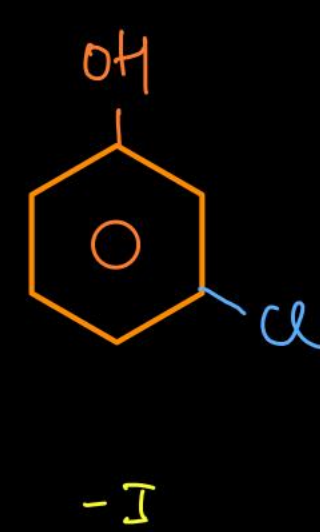
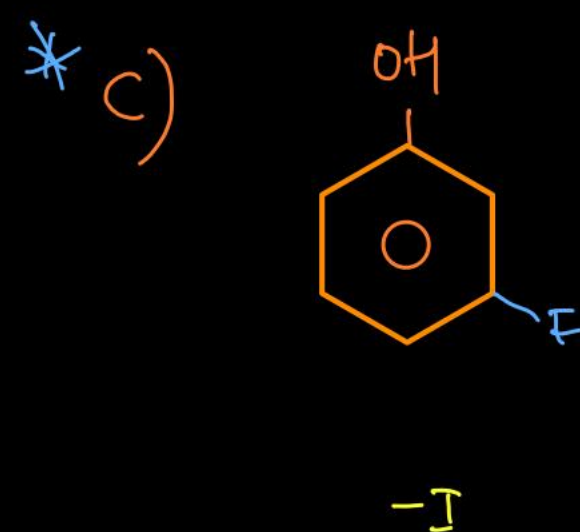


$$\Rightarrow (\text{I} > \text{III} > \text{II})$$



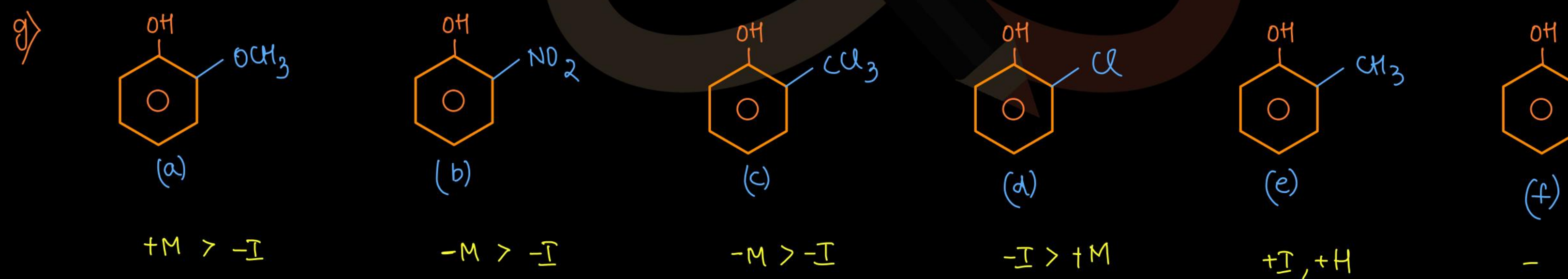
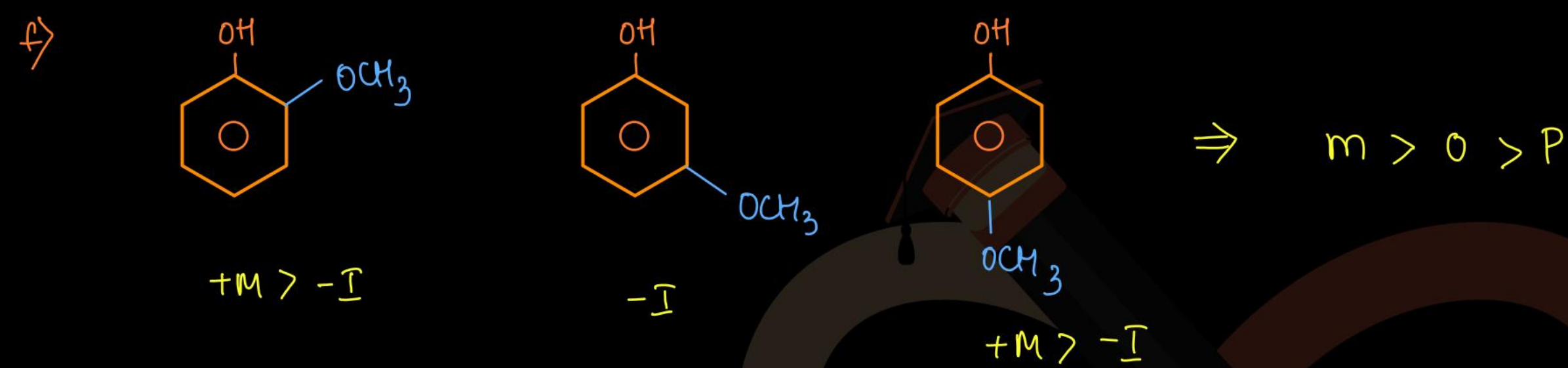
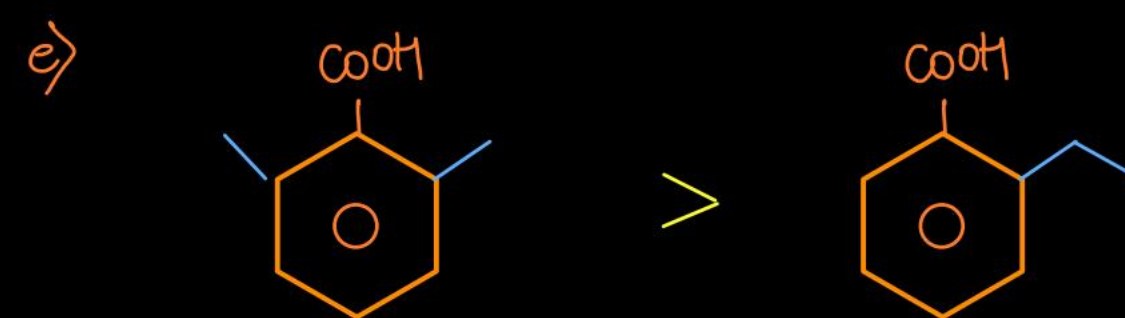
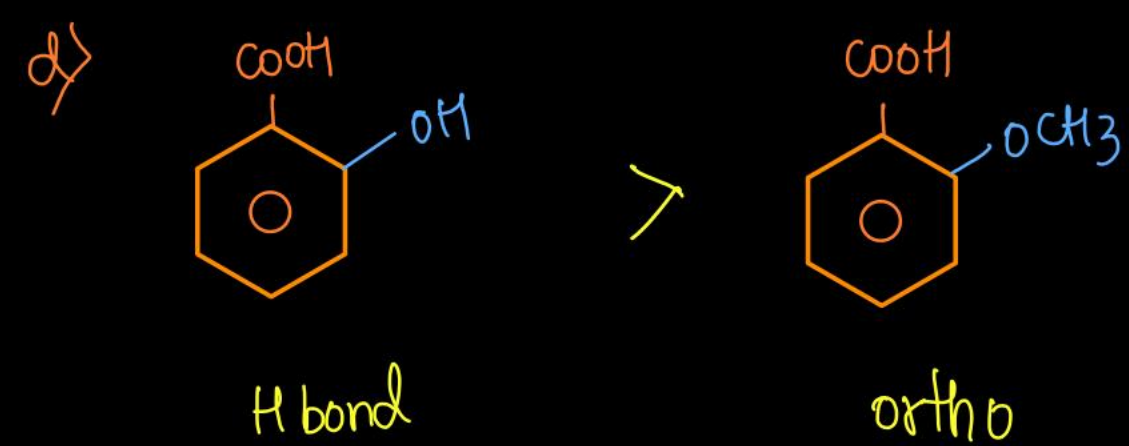
Expected:  $\text{I} > \text{II} > \text{III} > \text{IV}$

but  $\text{I} < \text{II} < \text{III} < \text{IV}$   
(due to +M)



$$\text{I} > \text{II} > \text{III} > \text{IV}$$

(only -I)



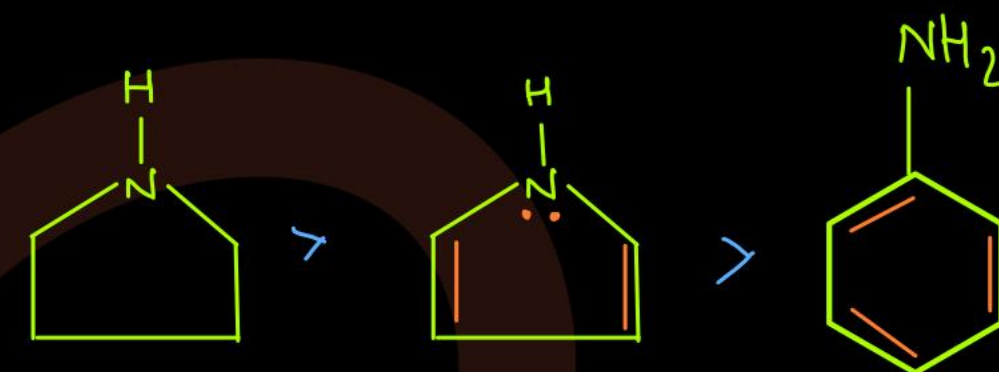
## Basic Nature :

$$*) \text{ B.N} \propto K_b \propto \frac{1}{pK_b}$$

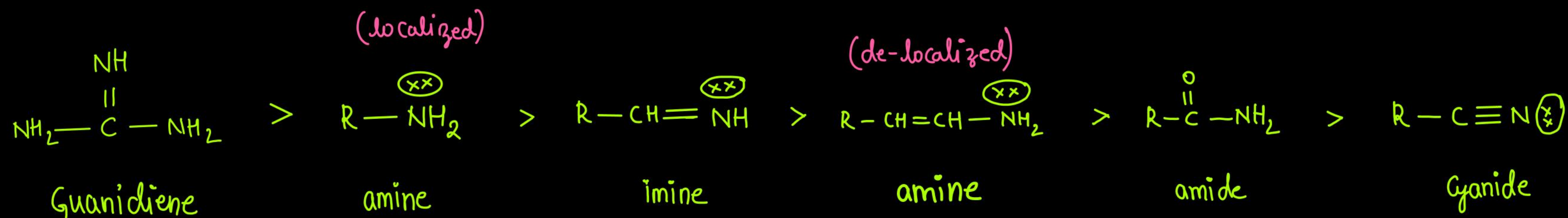
\*) Lewis base :  $e^-$  pair donor

\*) Basic strength  $\propto +I, +M$   
 $\propto$  Electron releasing group

\*) availability of LP  $\Rightarrow$  localized > de localized



## Nitrogenous Bases :-

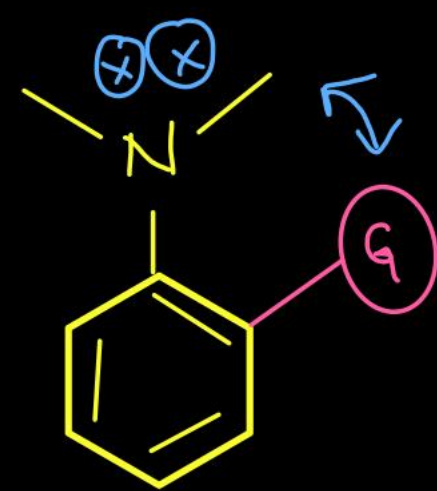


\* Amines :-  $\Rightarrow 3^\circ > 2^\circ > 1^\circ > \text{NH}_3$

$\Rightarrow$  Aliphatic  $>$  aromatic (localized  $>$  delocalized)

SIR effect (same like ortho effect in acids)

$\rightarrow$  due to SIR effect, BS of o-subst  $2^\circ, 3^\circ$  amines inc  $\uparrow$



$\rightarrow$  plane changes  
 $\rightarrow$  resonance is distured  
 $\rightarrow$   $\text{xx}$  becomes localized  
 $\rightarrow$  LP is easily donated

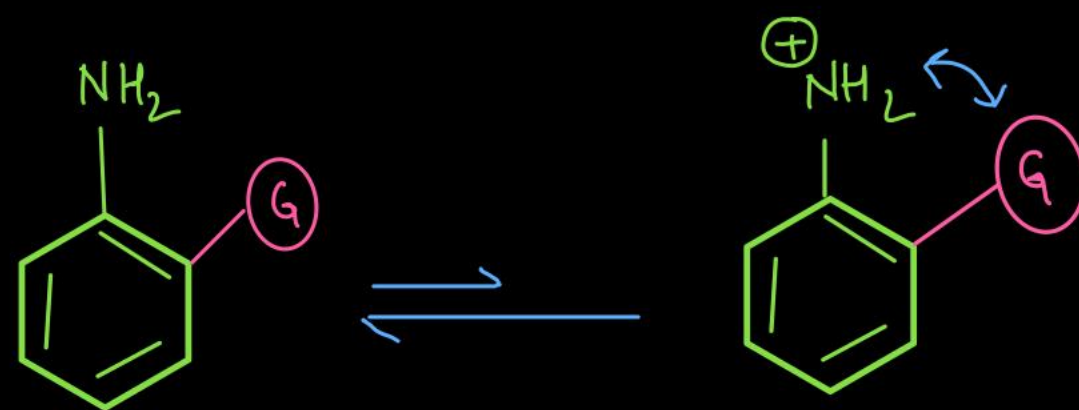
\* SIR effect

$\Rightarrow$  In  $1^\circ$  amines Basicity  $\downarrow$

$\Rightarrow$  In  $2^\circ/3^\circ$  amines Basicity  $\uparrow$

$\Rightarrow$  In acids, AN  $\uparrow$

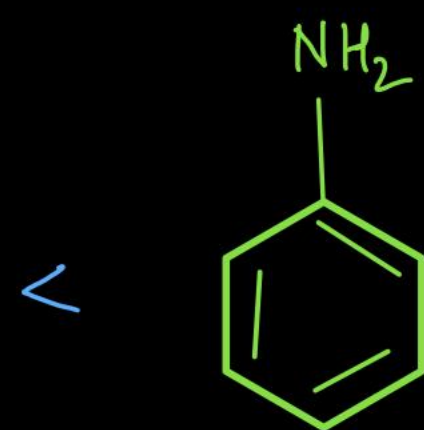
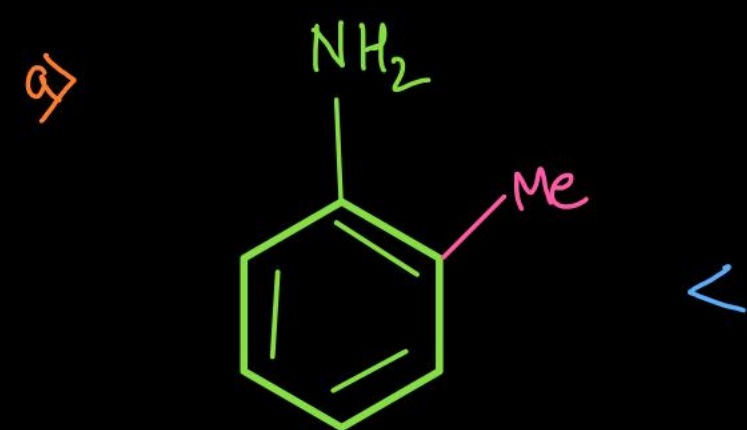
SIP effect :



becomes unstable

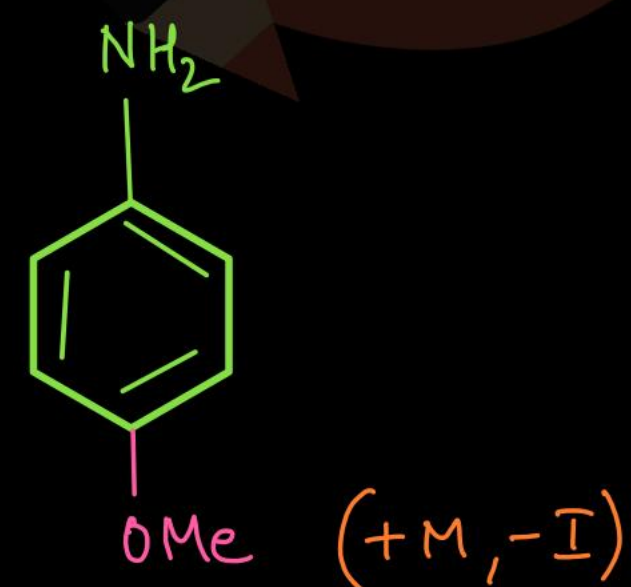
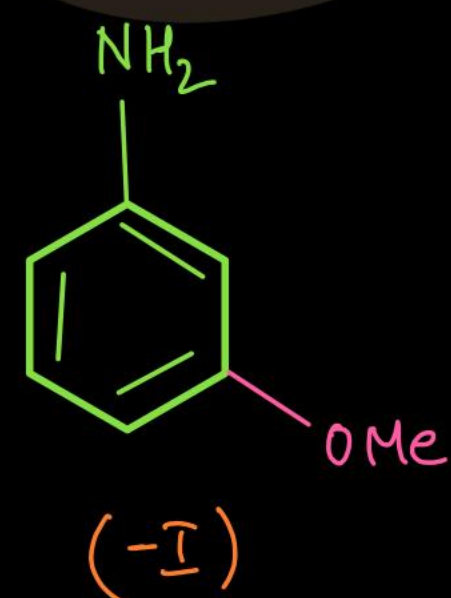
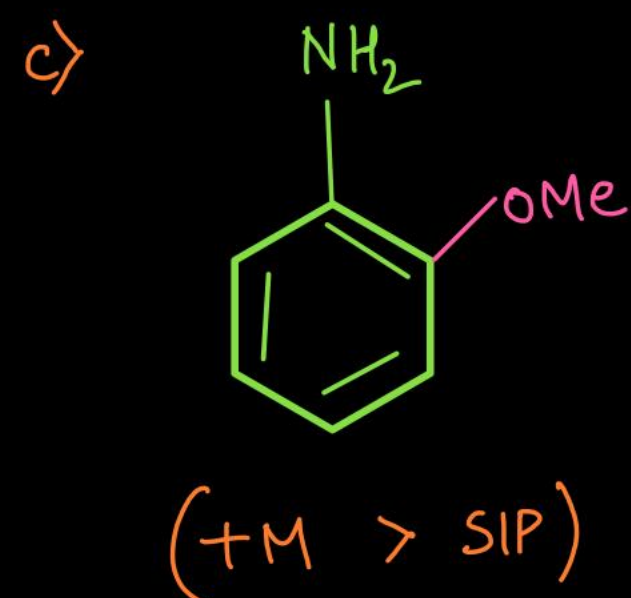
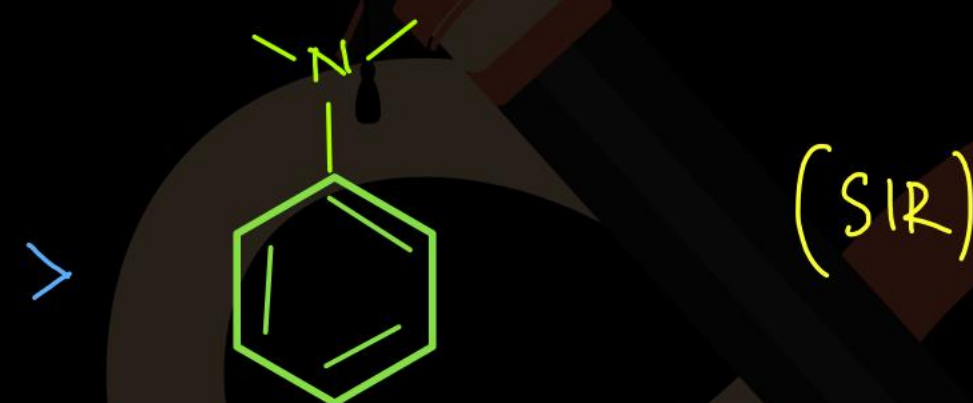
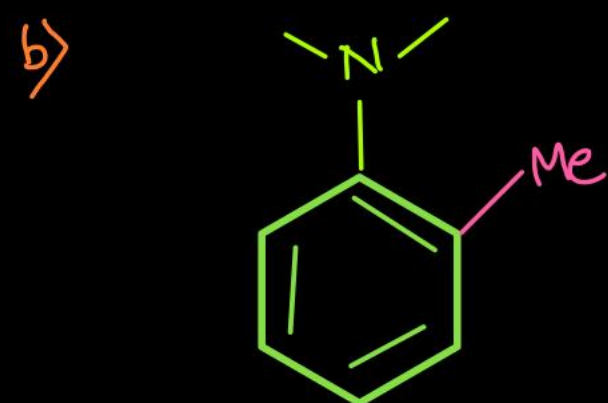
so tends in back direction

## Basic strength Practice :



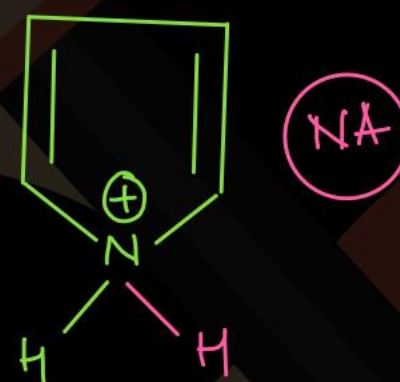
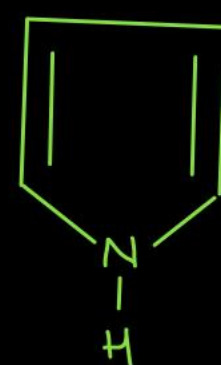
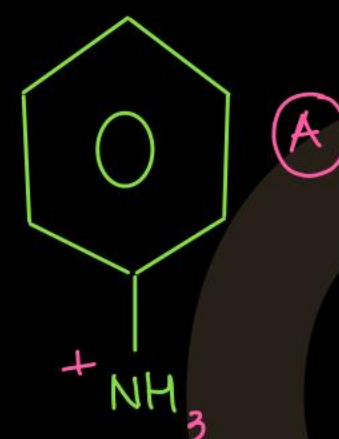
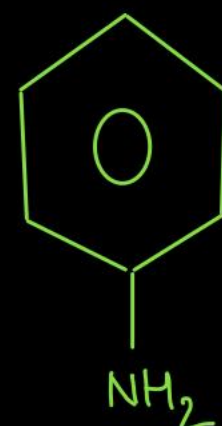
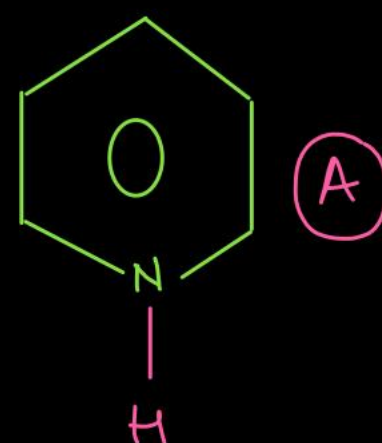
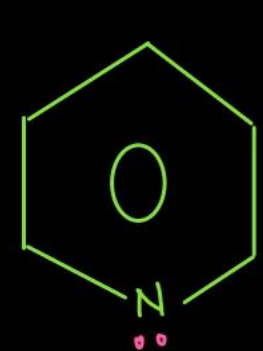
Expected I > II (due to +I)

reality :- I < II (due to SIP)



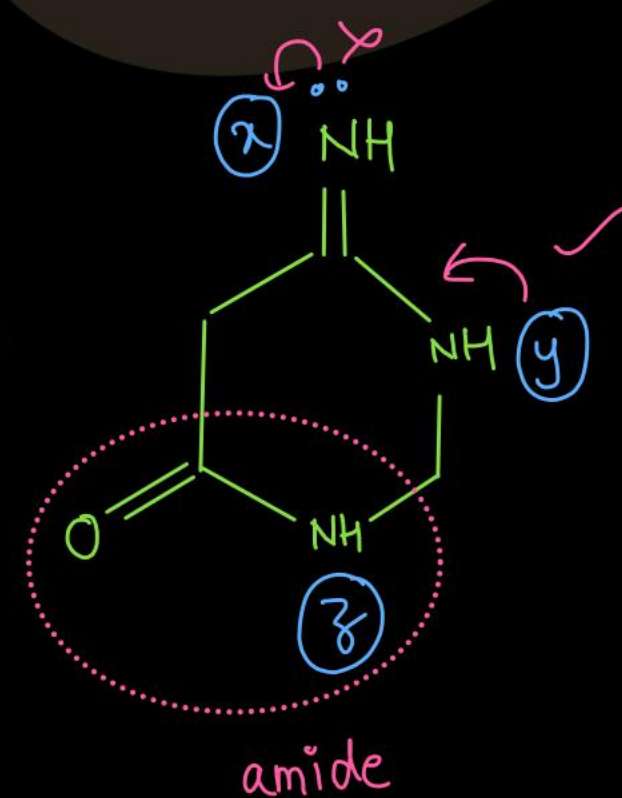
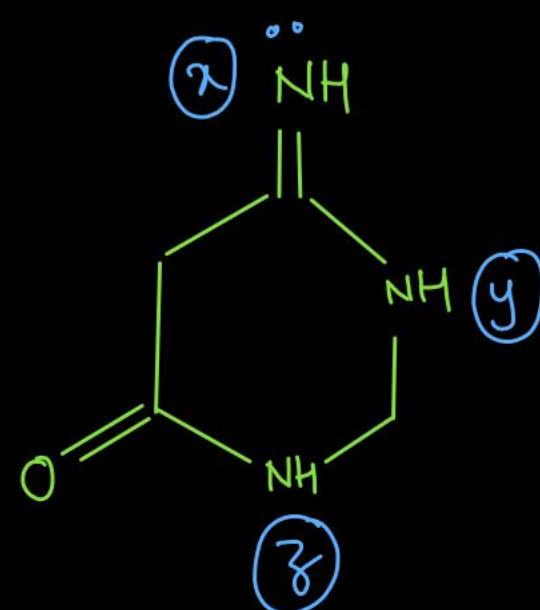
$\Rightarrow P > O > m$

ds

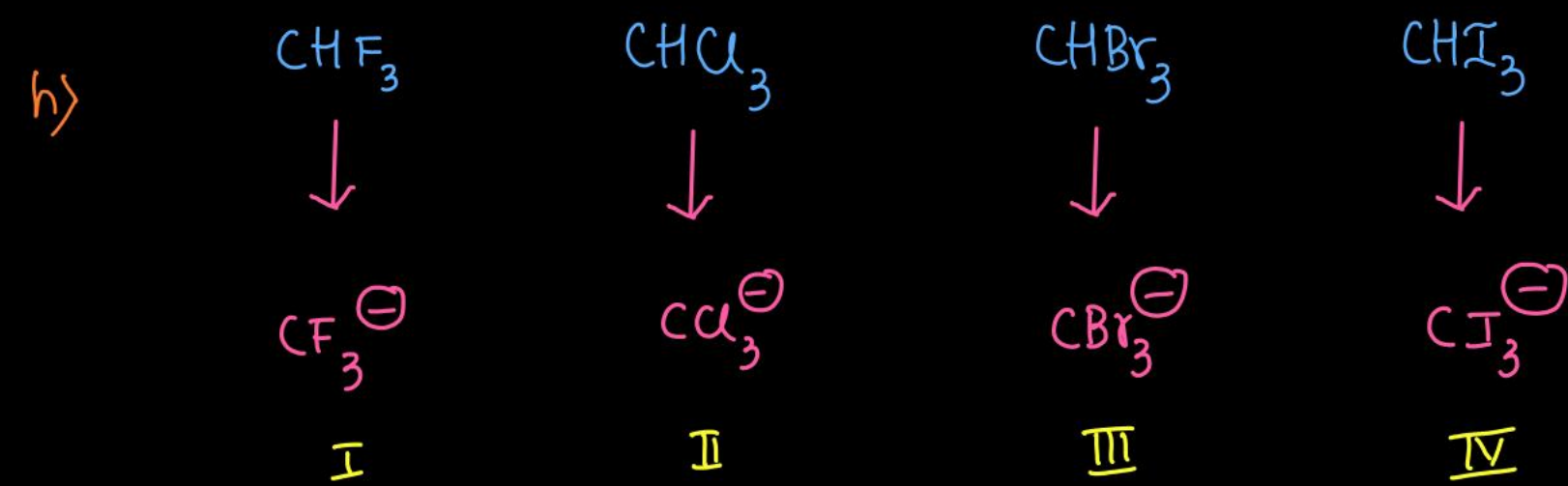
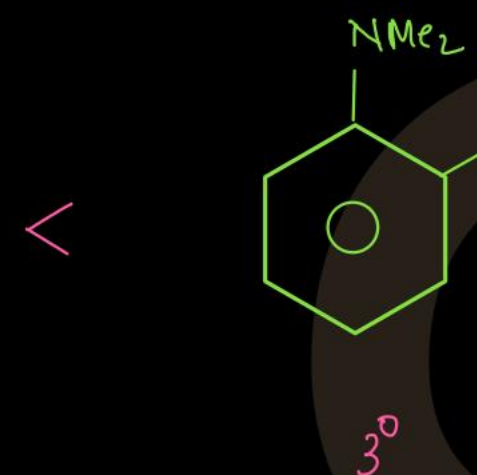
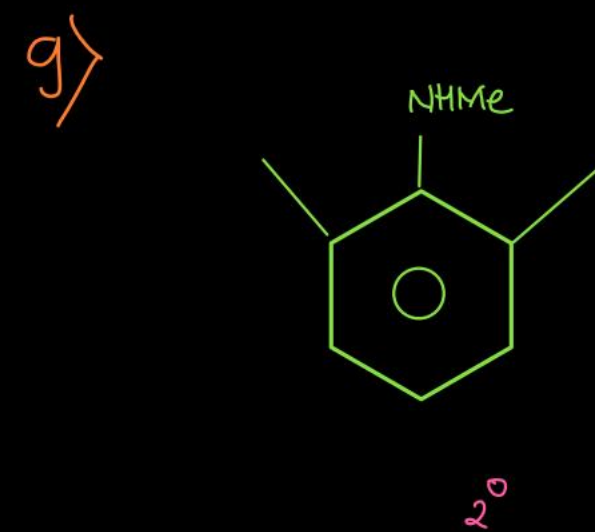
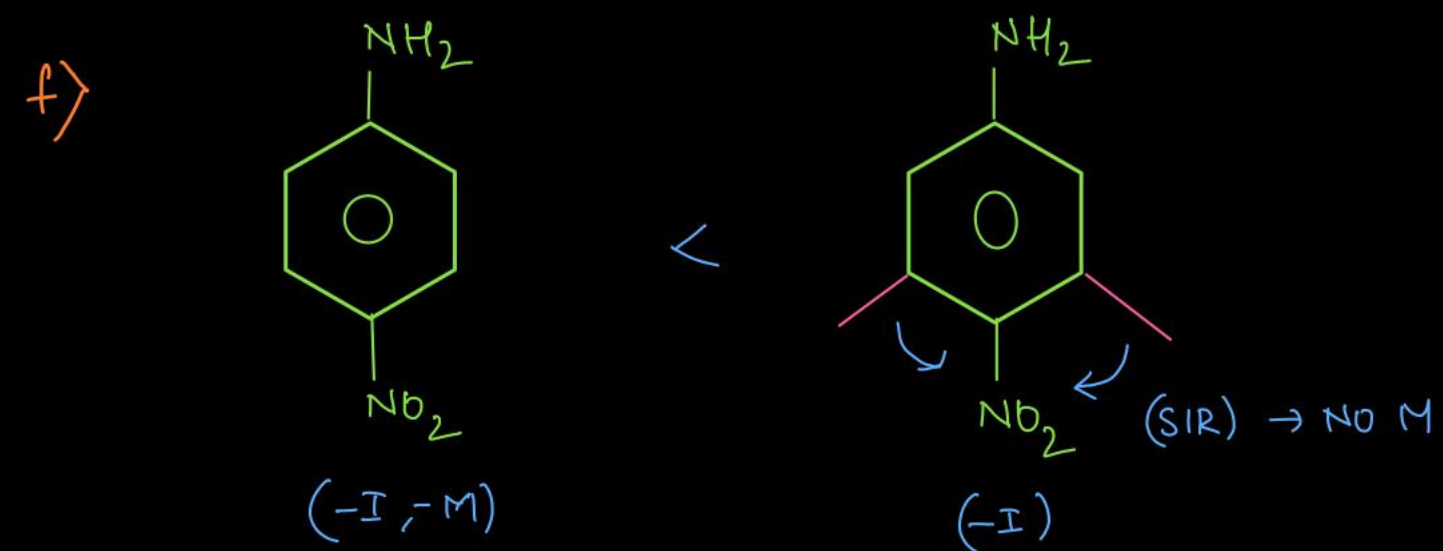


(a) > (b) > (c)

e)



$\Rightarrow$  (2) > (y) > (z)

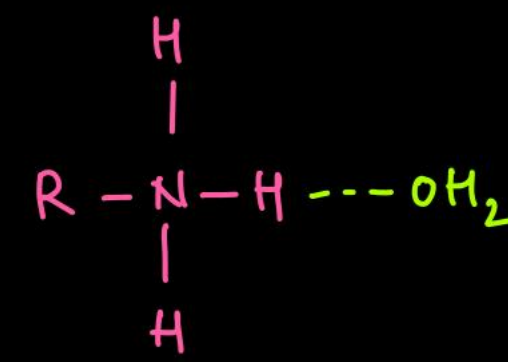
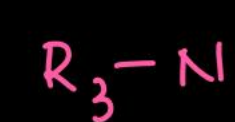
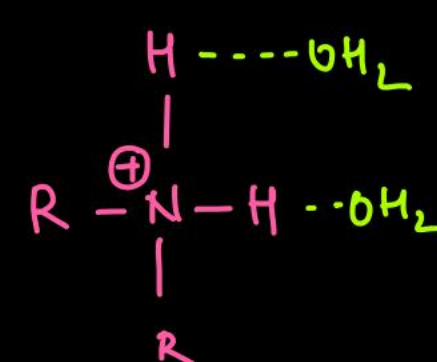
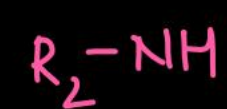
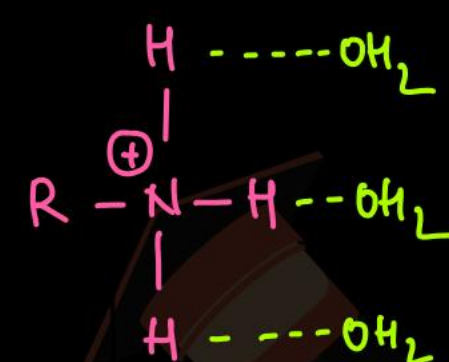
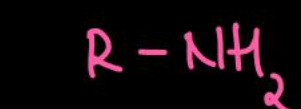


Effect of H-bond :-

\* In aqueous state

$\Rightarrow$  solvation :  $1^\circ > 2^\circ > 3^\circ$

but +I :  $1^\circ < 2^\circ < 3^\circ$



final:

$R = Me$        $2^\circ > 1^\circ > 3^\circ$       (213)

$R = Eth$        $2^\circ > 3^\circ > 1^\circ$       (231)

} In aq. medium

$R = Me$        $3^\circ > 2^\circ > 1^\circ$       (321)

$R = Eth$        $3^\circ > 2^\circ > 1^\circ$       (321)

} Gaseous state

## Boiling & Melting points :-

\* Hydrocarbons : MP  $\rightarrow$  irregular

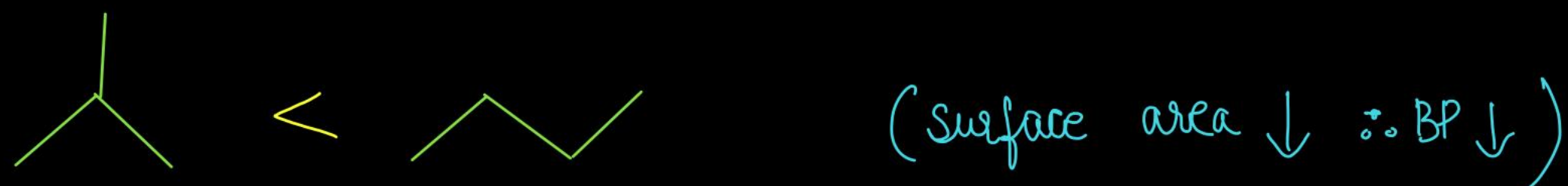
### Boiling point

a) As no. of C  $\uparrow$  , BP  $\uparrow$



b) In isomeric alkanes,

as branching increases  $\uparrow$  , BP  $\downarrow$



\* Halo alkanes :-

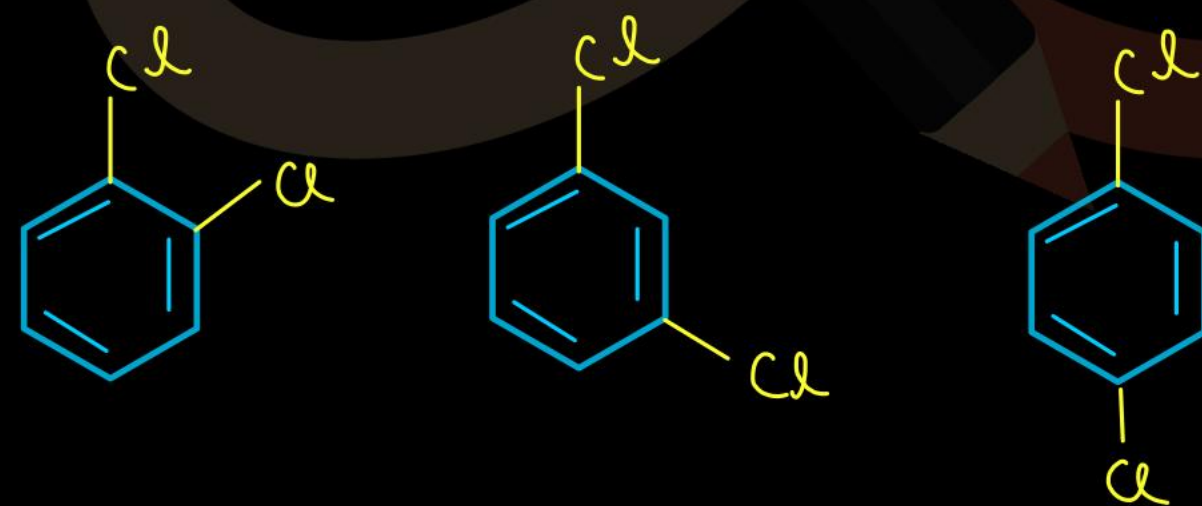
→ Higher than hydrocarbons of similar mol wt.

B.P :-  $R-I > R-Br > R-Cl > R-F$

\*  $H-F > HI > HBr > HCl$  (H-bond in HF)

α / branching

\* Halo arenes :-



B.P/K      453

446

448

(o > p > m)

M.P/K      256

249

324

(m > o > p)

\* Alcohols, phenols

→ B.P : higher than hydrocarbons, alkyl halides, ethers  
of comparable masses

\*  $B.P \propto \text{no. of carbons}$

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

\* High B.P are due to Intermolecular H bond

\* ethers

→ B.P : less than alcohols but comparable to hydrocarbons

\* Aldehydes & ketones

B.P :- Higher than hydrocarbons of comparable wt.

It is due to weak molecular association by dipole-dipole interactions.

\* Lower than Alcohols due to absence of H bond

\* Carboxylic acids :-

B.P :- Higher than aldehydes & ketones

Higher than Alcohols too

Note :- For comparable molecular sizes

Acids > Alcohols > Aldehydes, ketones > Haloalkanes > Hydrocarbons