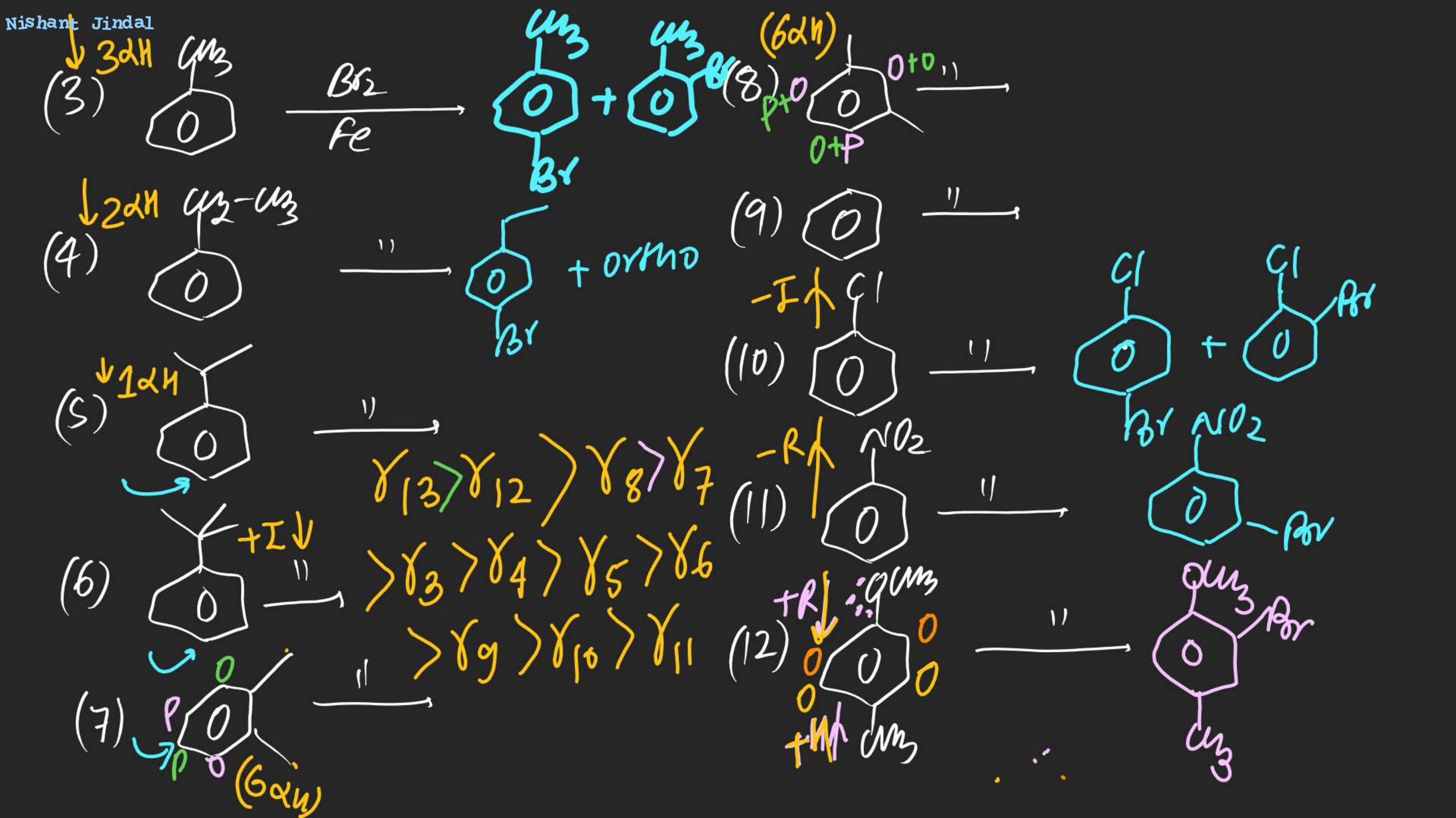
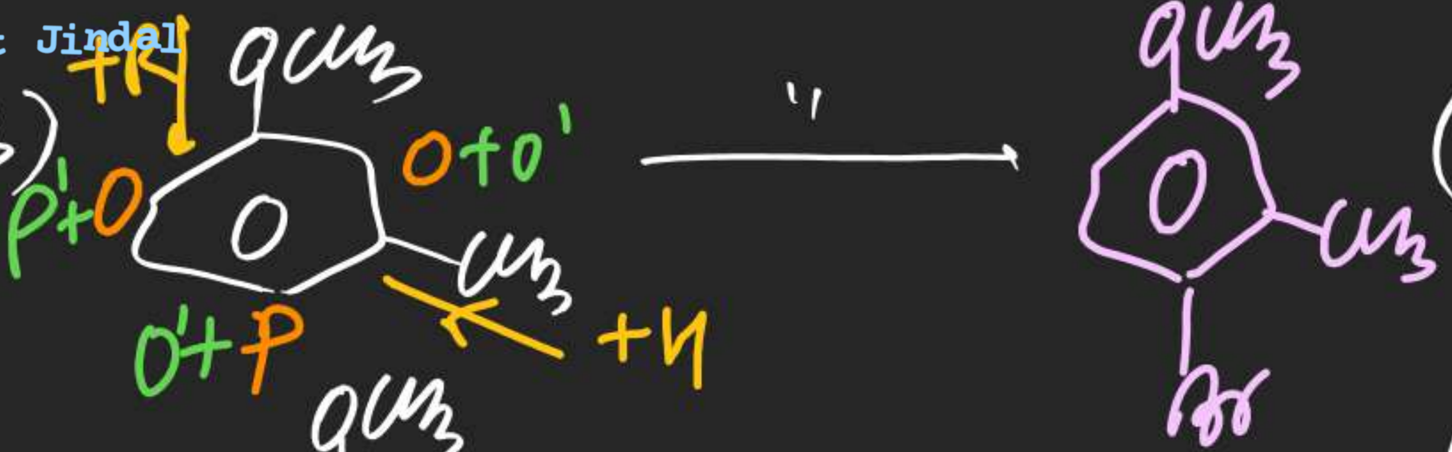
Nishant Jindal

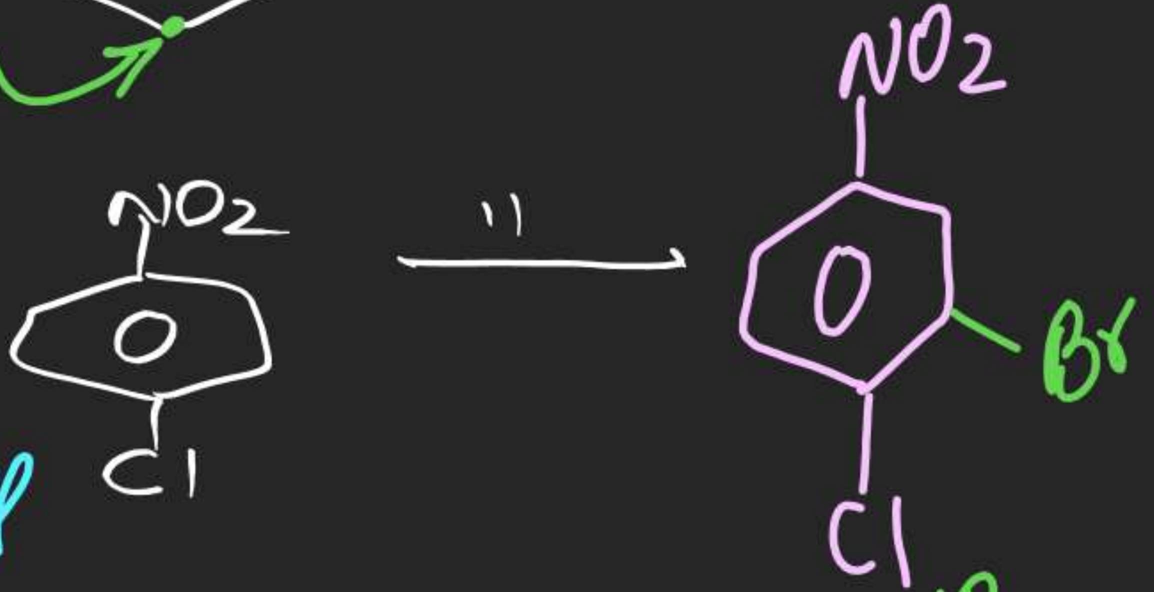


(13)

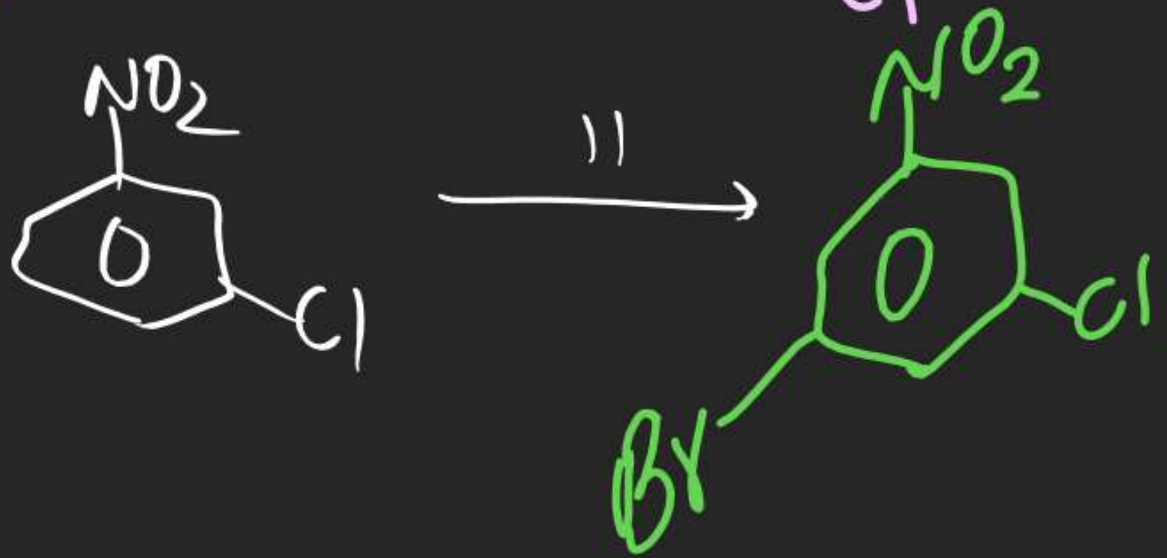


(14)

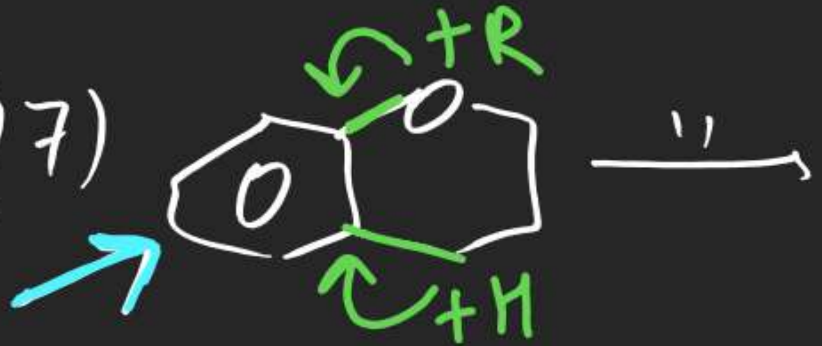
m.E.W
(15)



m.Imp
(16)

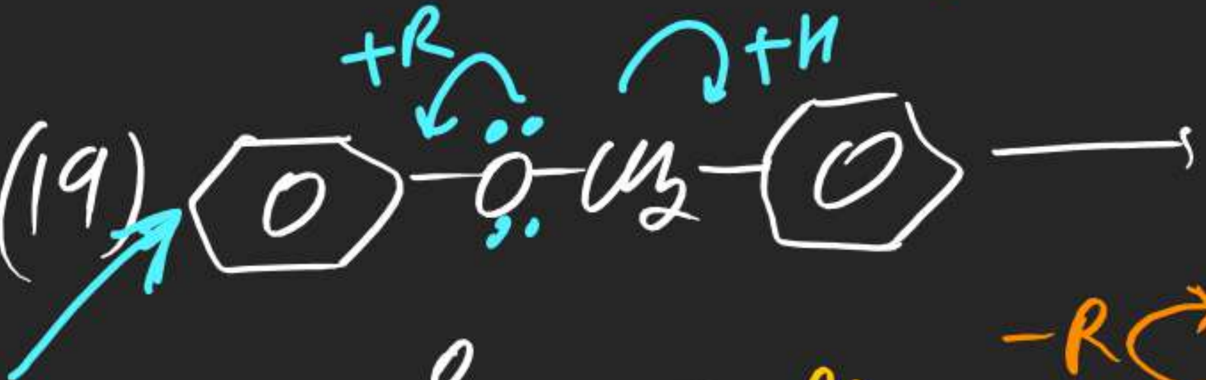


(17)

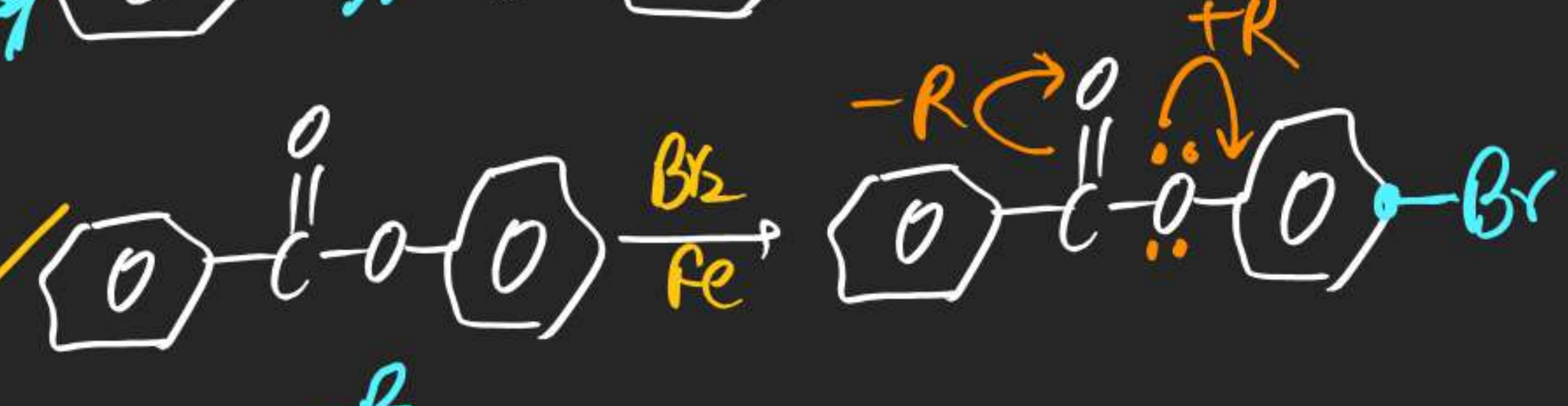


(18)

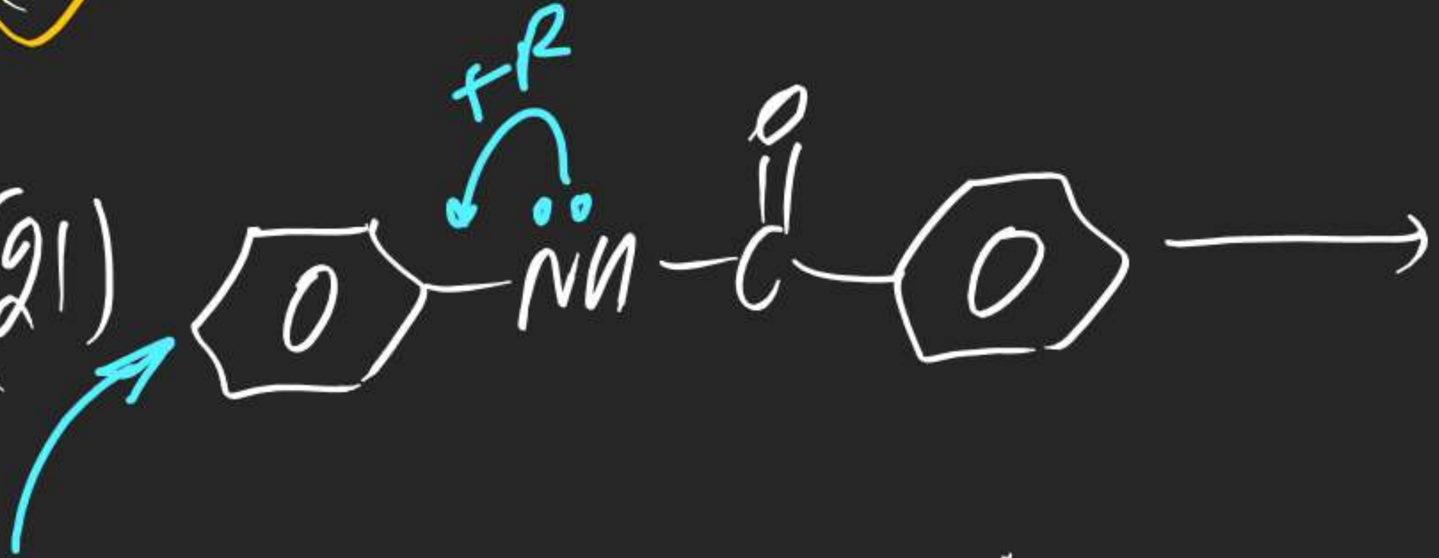
(19)



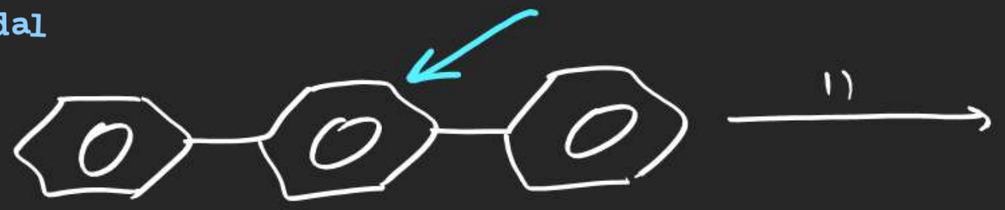
(20)

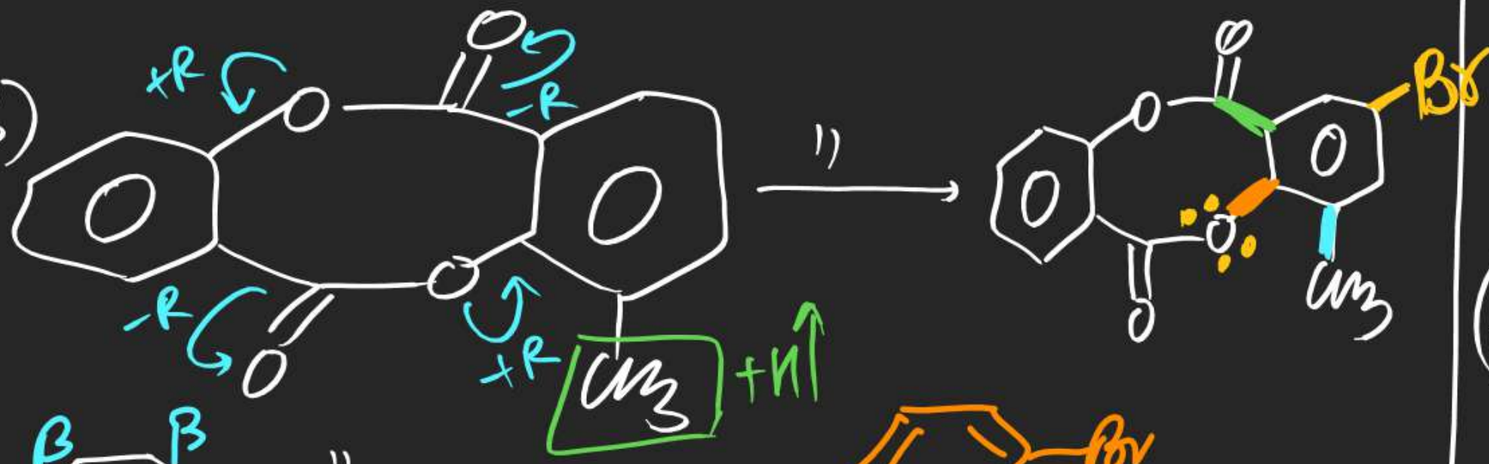


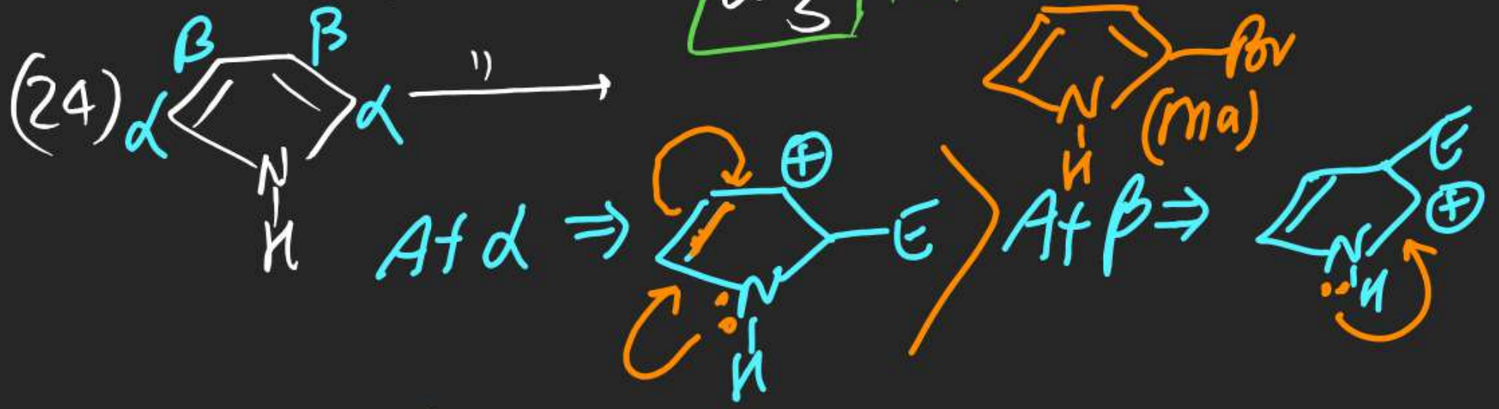
(21)

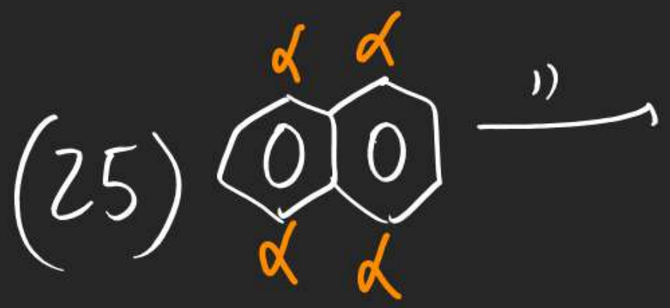


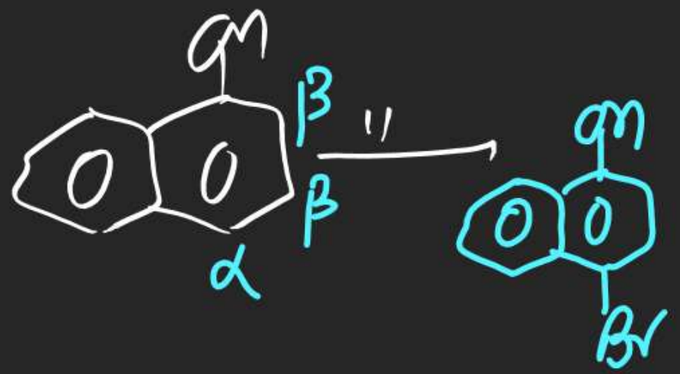
Nishant Jindal

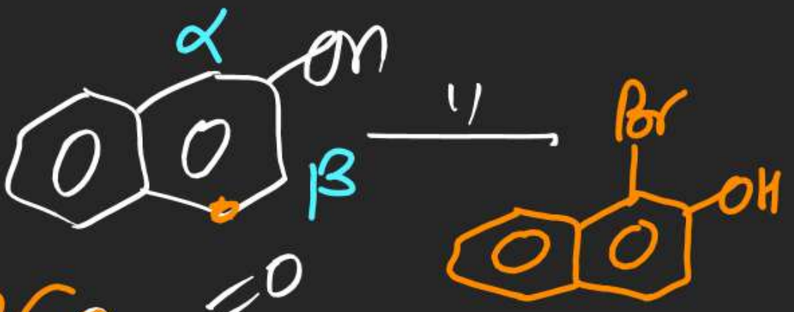
(22) 

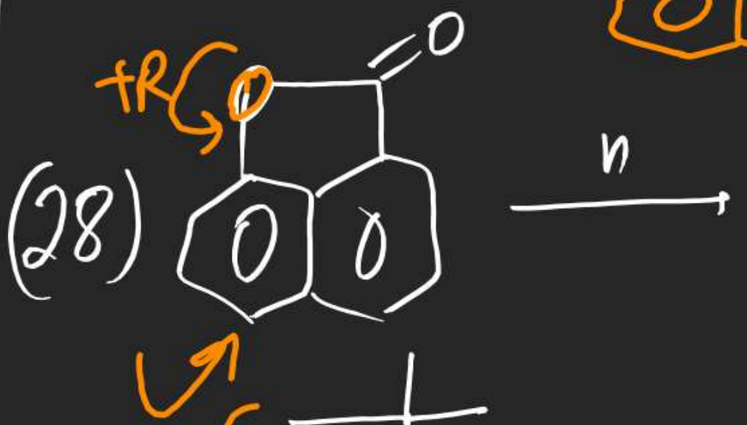
(23) 

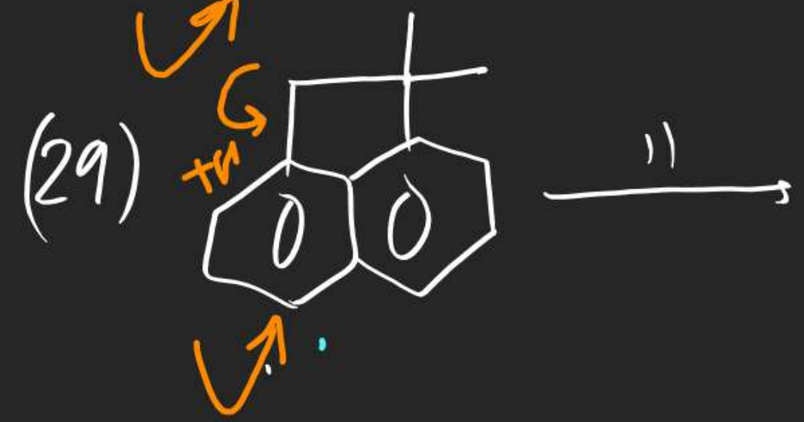
(24) 

(25) 

(26) 

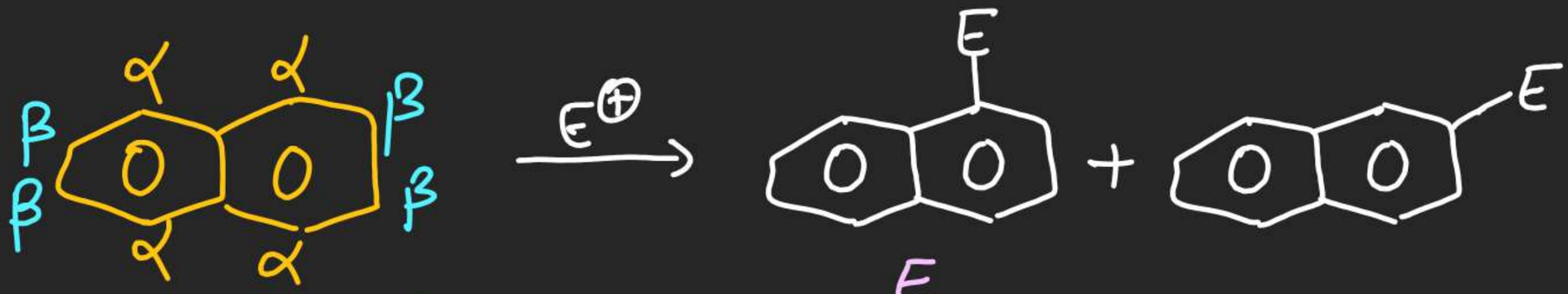
(27) 

(28) 

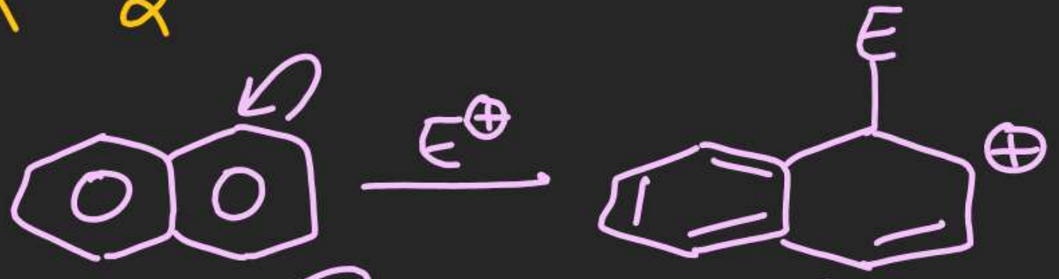
(29) 

Nishant Jindal

Soln:

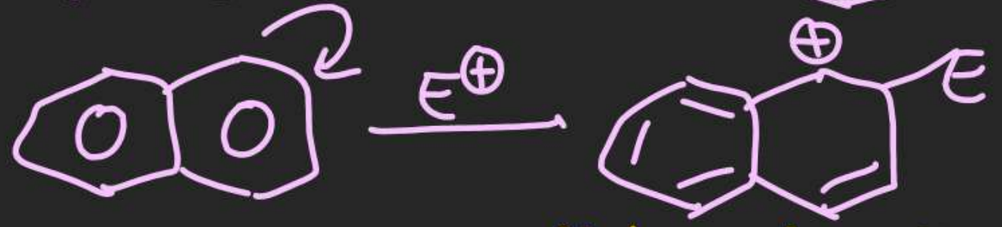


At α :



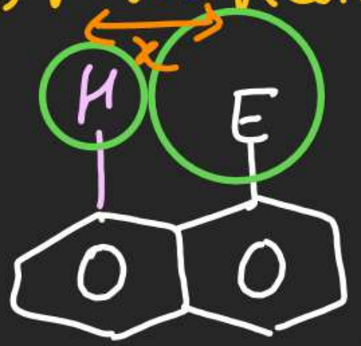
(7 RS) (more stable)

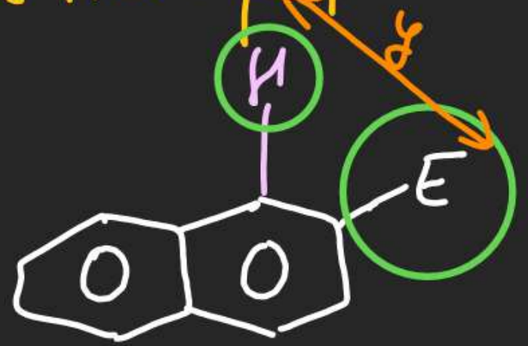
At β :



(6 RS) (less stable)

Note (i) α position of napthlene is more Reactive than β position of napthlene.



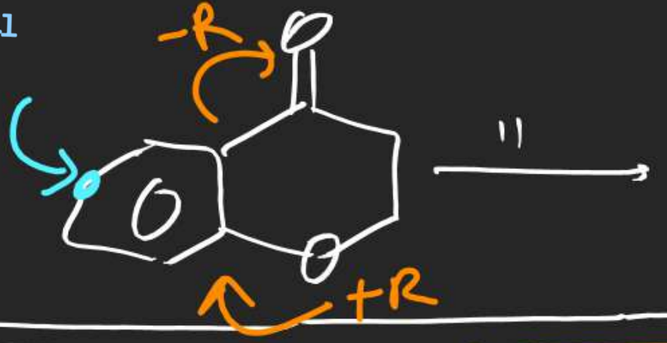


(y > x)

(ii) β-Substituted Napthlene is more stable than α-Substituted Napthlene.

Nishant Jindal

(30)



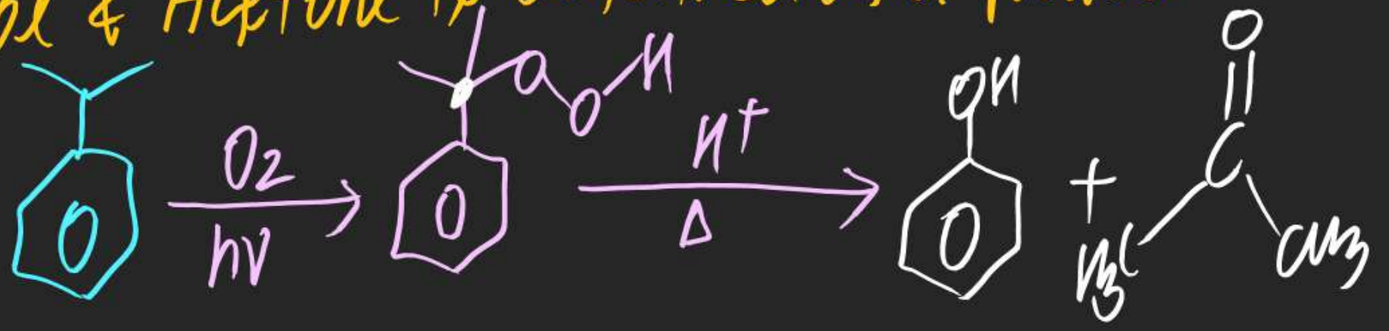
Reactions of phenol

(#) Preparation of phenol :-

M.J.U.P

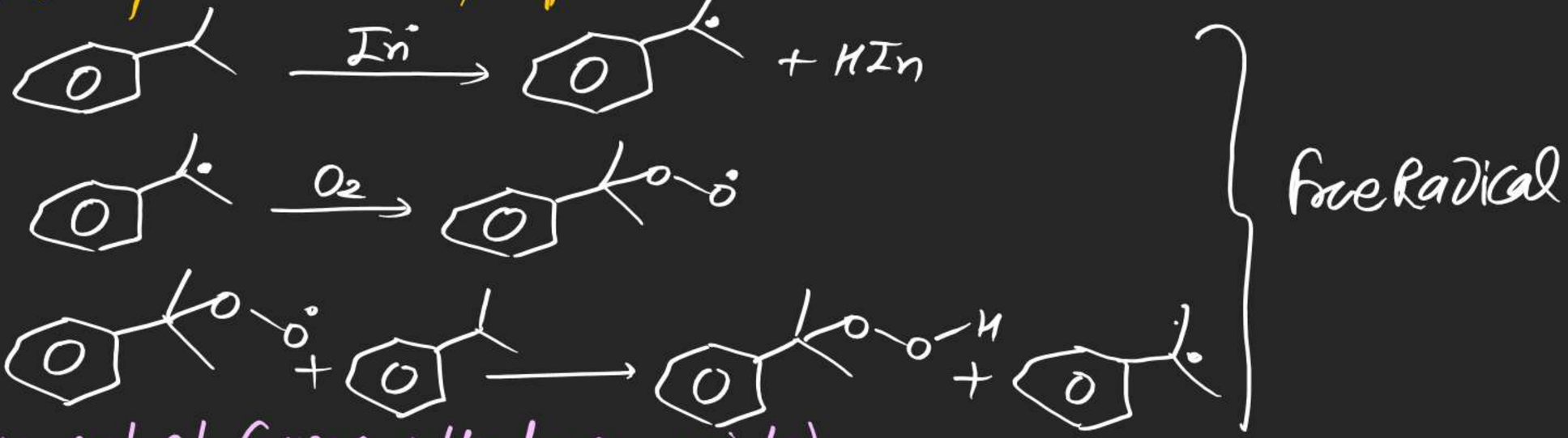
(1) Cumene Hydroperoxide Rearrangement :-

⇒ In this Rearrangement Cumene Hydroperoxide is treated with H_2SO_4/Δ so that phenol & Acetone is obtained as a product.

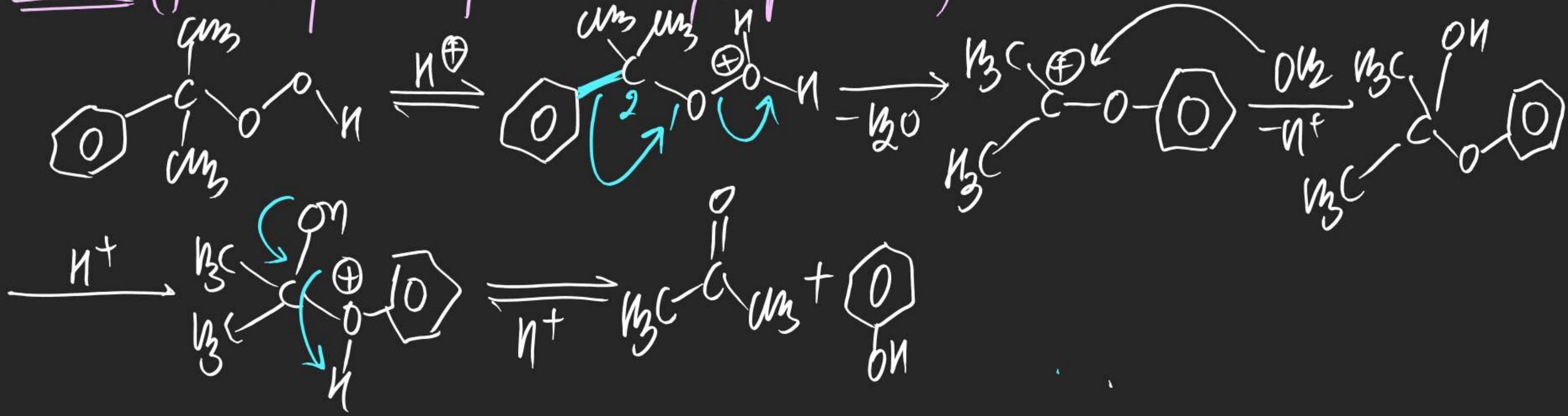


Nishant Jindal

Mechⁿ (Formation of Cumene Hydroperoxide)



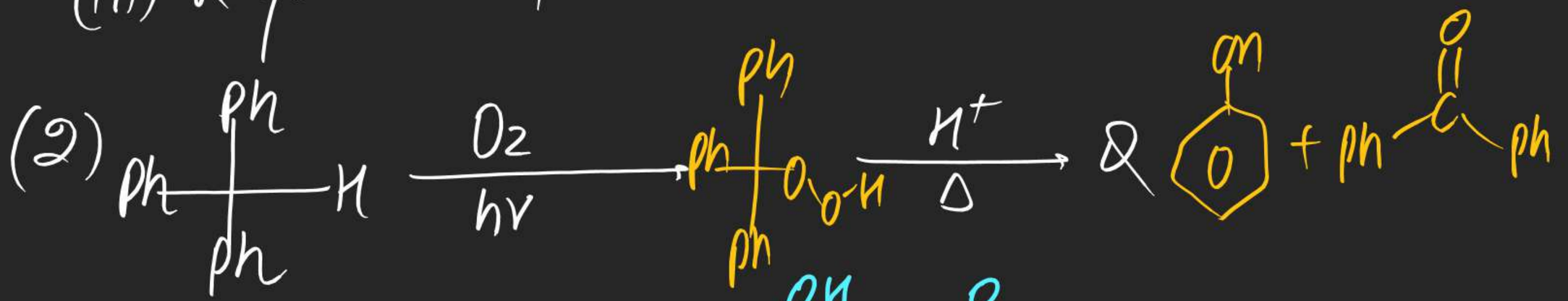
Mechⁿ (for Rearrangement of Cumene Hydroperoxide)

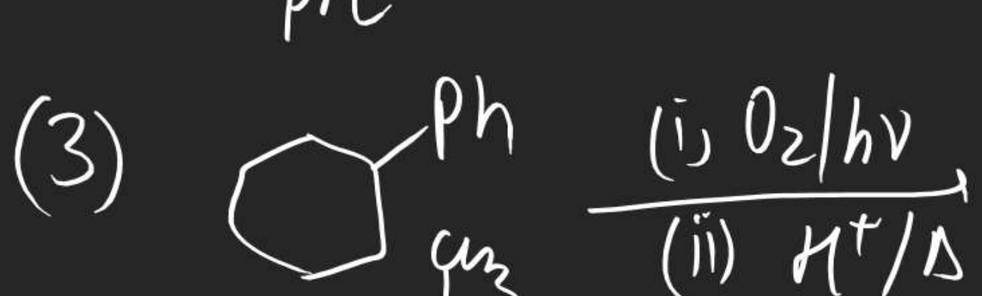


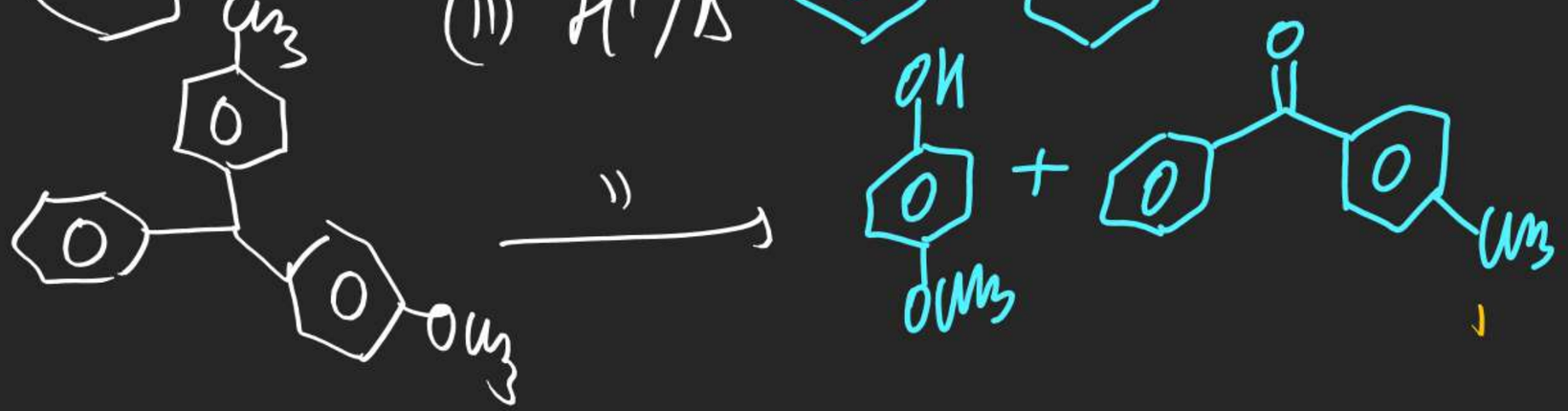
Note (i) Free Radical is formed duiy formation of Cumene Hydroperoxide

(ii) Duiy Reagent of Cumene Hydroperoxide Carbocation intermidiate

(iii) Rearrangement step is 1,2-shift

(2) 

(3) 

(4) 

Nishant Jindal

Note (i) For KOH

$T < 60^\circ C$ — para > ortho [To avoid steric factors]

$60^\circ C \leq T < 160^\circ C$ — ortho > para [due to chelate formation]

$T \geq 160^\circ C$ — para > ortho [chelation destroy]

(ii) **At T = 50°C**

LiOH
NaOH
KOH

para > ortho (universally large size of $Li^{\oplus}$ hydrated)
ortho > para (chelate formation)
para > ortho

(3) 

$\xrightarrow[KOH]{CO_2}$

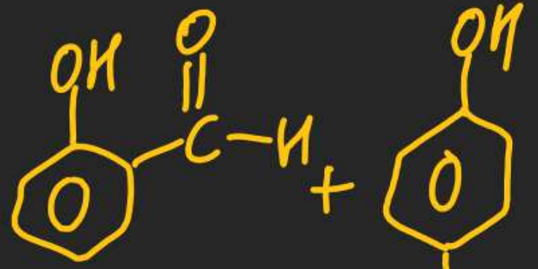
(4) 

$\xrightarrow{\quad\quad}$

M.M.I UP

(#) Reimer Tiemann's Rxn:

⟹ In this Reaction formylation of phenol is carried out By alkaline chloroform Solution.

(1)  + $CHCl_3$ + 3NaOH ⟶ 

o-Salicyldehyde

p-Salicyldehyde

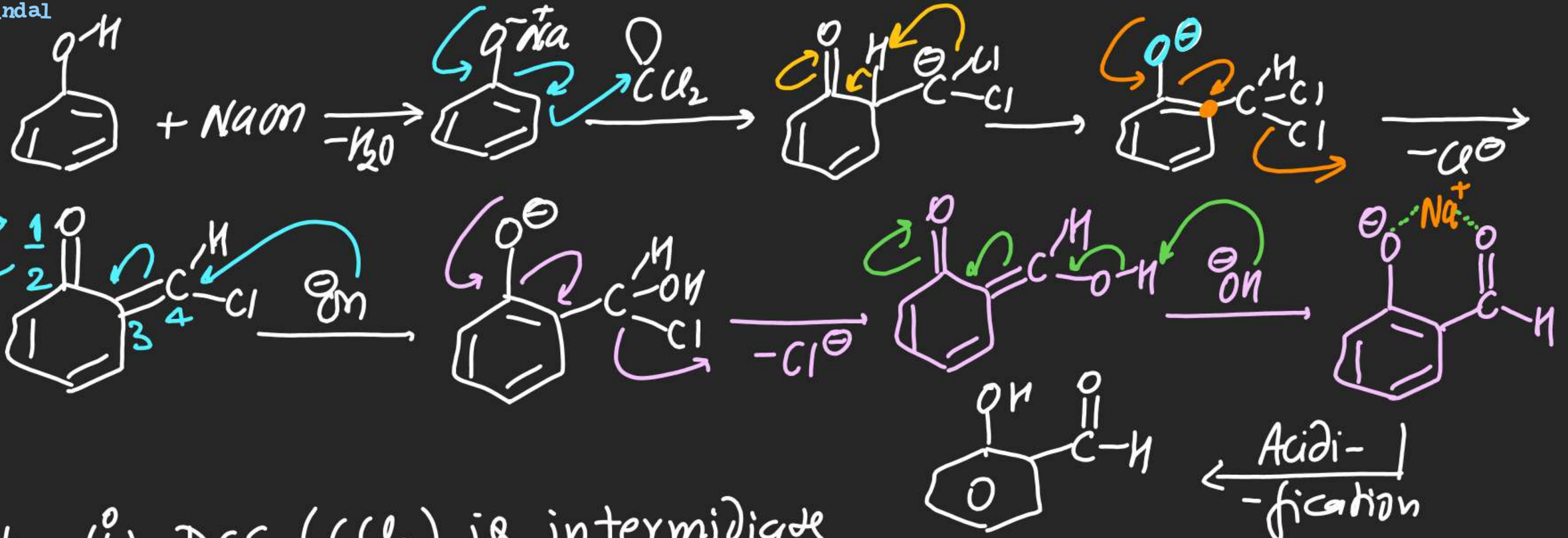
Mechⁿ: $H-CCl_3 + NaOH \longrightarrow Na^{\oplus}\overset{\ominus}{C}Cl_3 + H_2O$

$Na^{\oplus}\overset{\ominus}{C}Cl_3 \rightleftharpoons NaCl + :CCl_2$ (DCC)

(Dichloro carbene)

∴

Nishant Jindal



Note (i) DCC (CCl_2) is intermidiate

(ii) ortho product dominates over para product due to

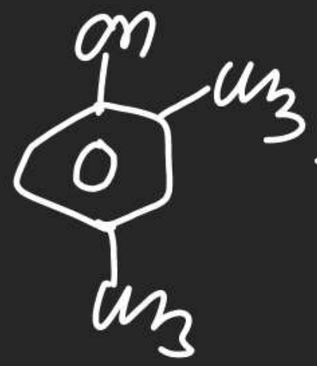
(a) Two ortho position over One para

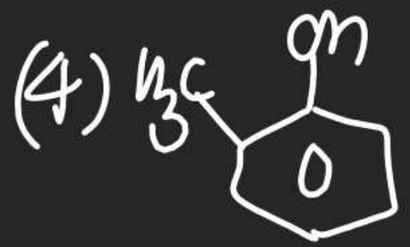
(b) Chelation at ortho position.

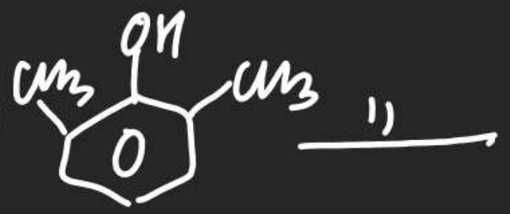
$$\left(\frac{O}{P}\right)_{NaOH} > \left(\frac{O}{P}\right)_{KOH} > 1$$

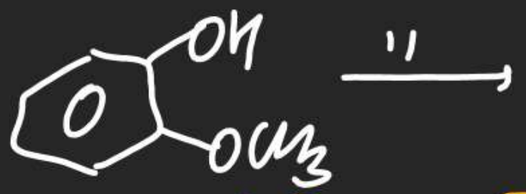
(iii) Para Product dominates when One or Both ortho is subst.

(2)  + $CHCl_3$ + NaOH ⟶

(3)  $\xrightarrow[NaOH]{CHCl_3}$

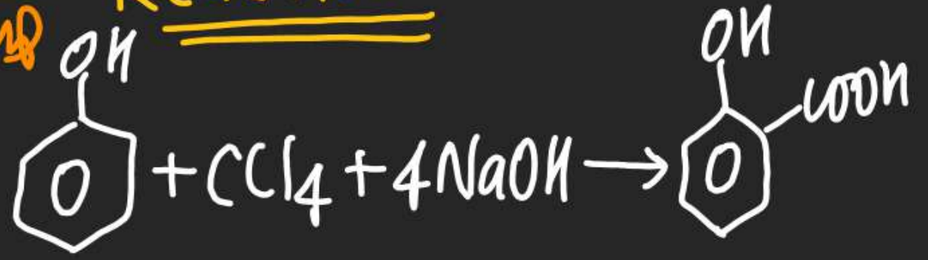
(4)  ⟶

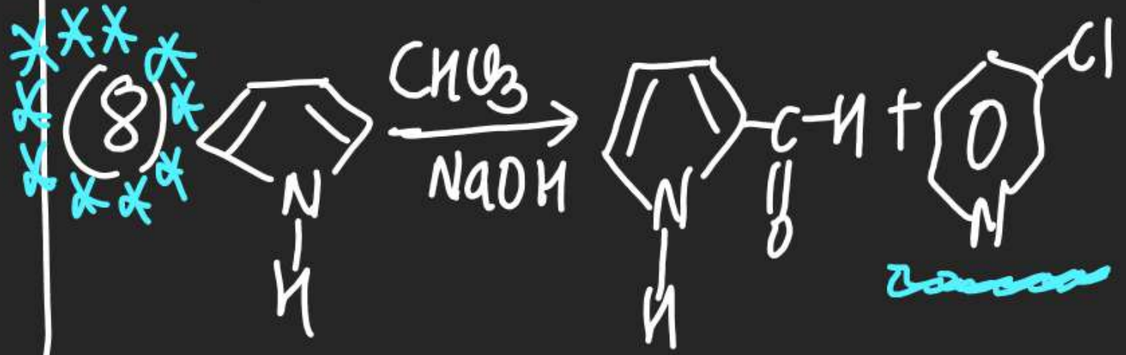
(5)  ⟶

(6)  ⟶

(#) Abnormal Reimer Tiemann Reaction

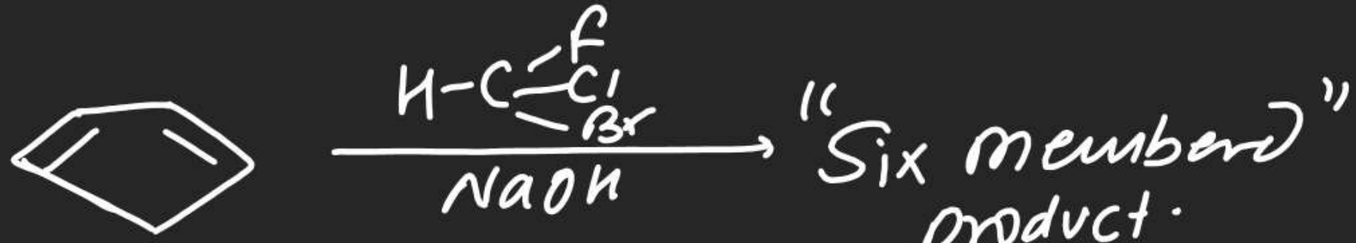
M.M.Imp

(7) 

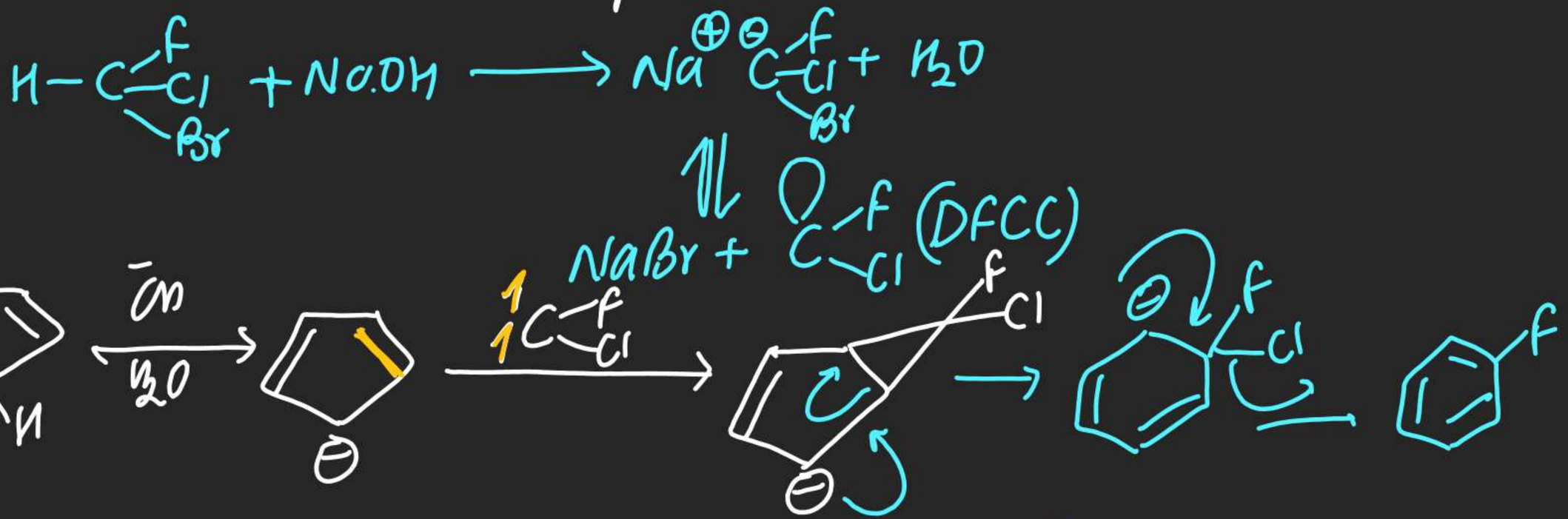
(8) 

Nishant Jindal

(9) 

(10) 

Soln:

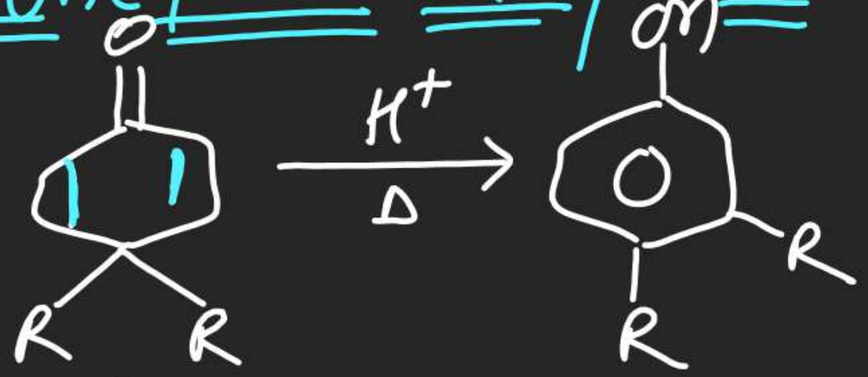


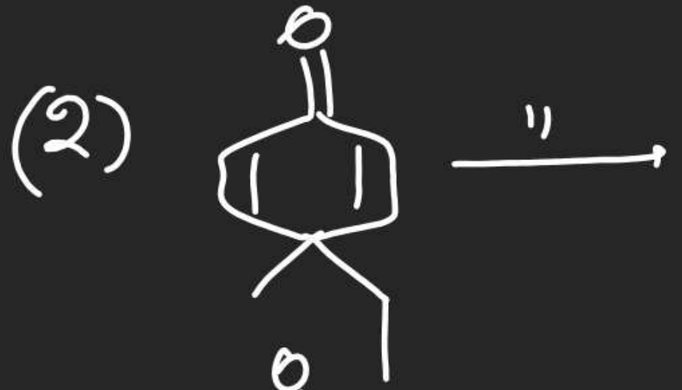
∴

Nishant Jindal

(#) Aromatic Reagents :-

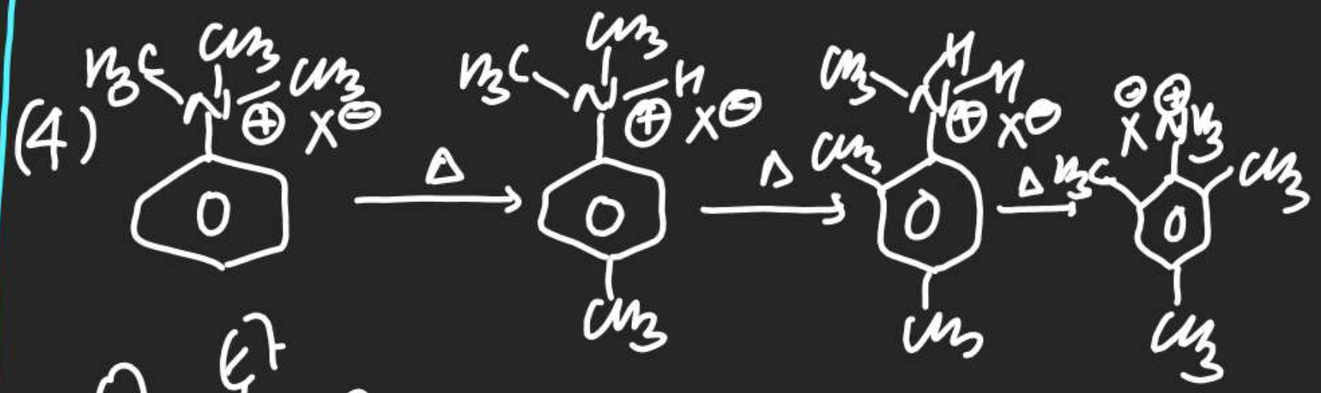
Dienone Phenol Reagent :-

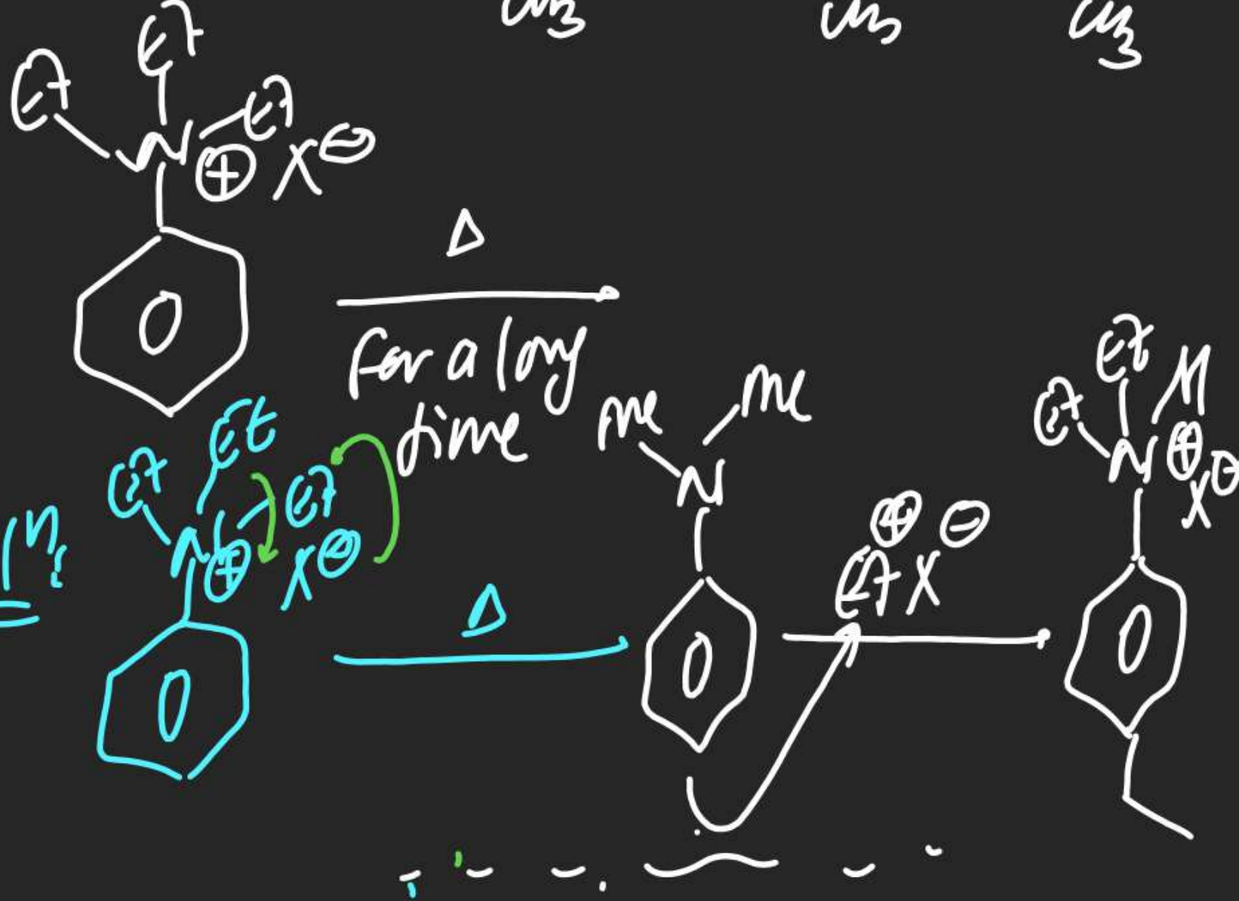
(1) 

(2) 

(3) 

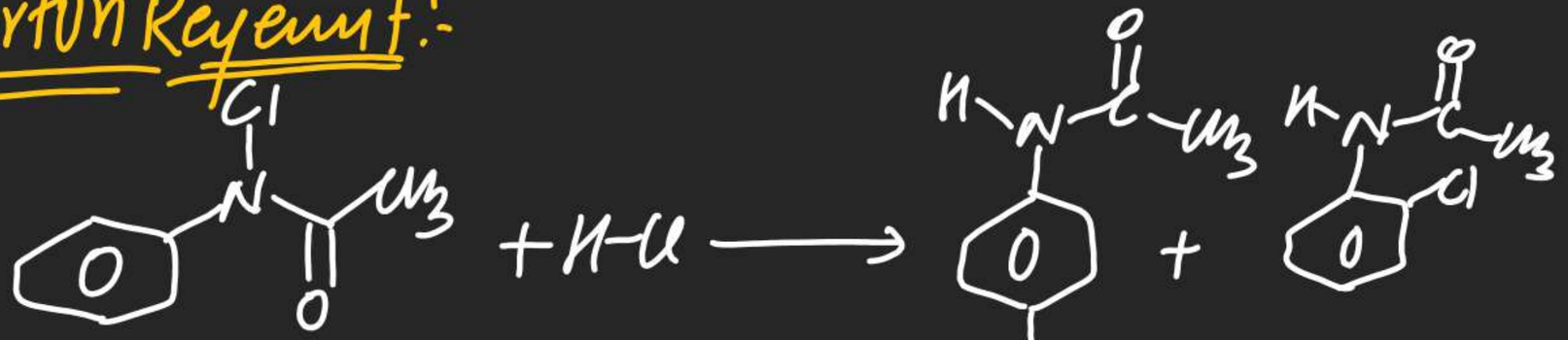
(#) Hofmann Mauribus Reagent

(4) 

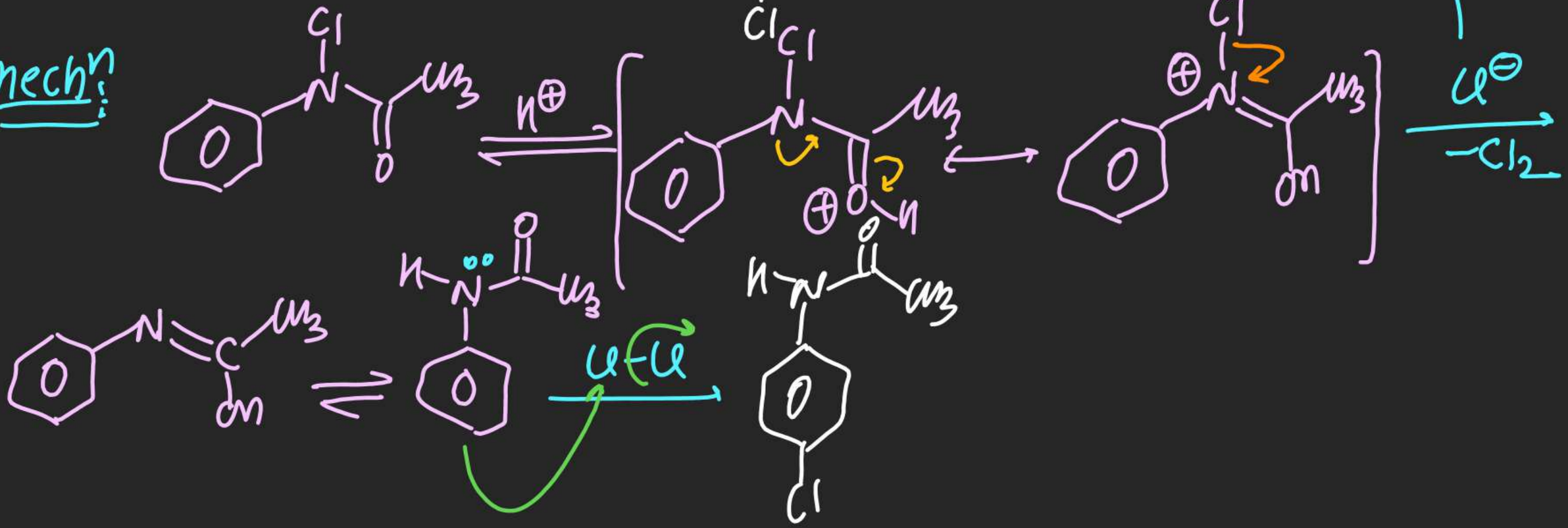
(5) 

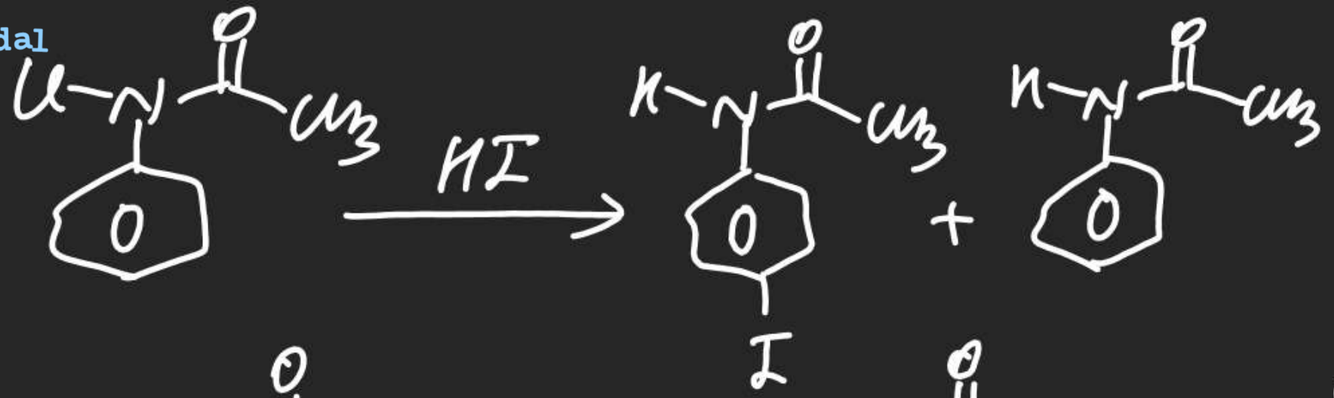
(#) ortho Rearrangement :-

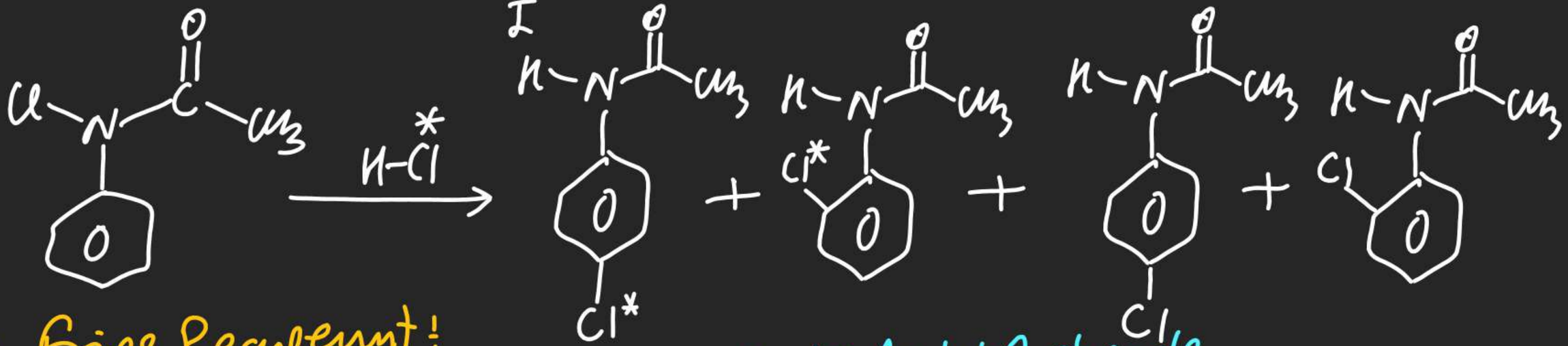
(6)



mechn :

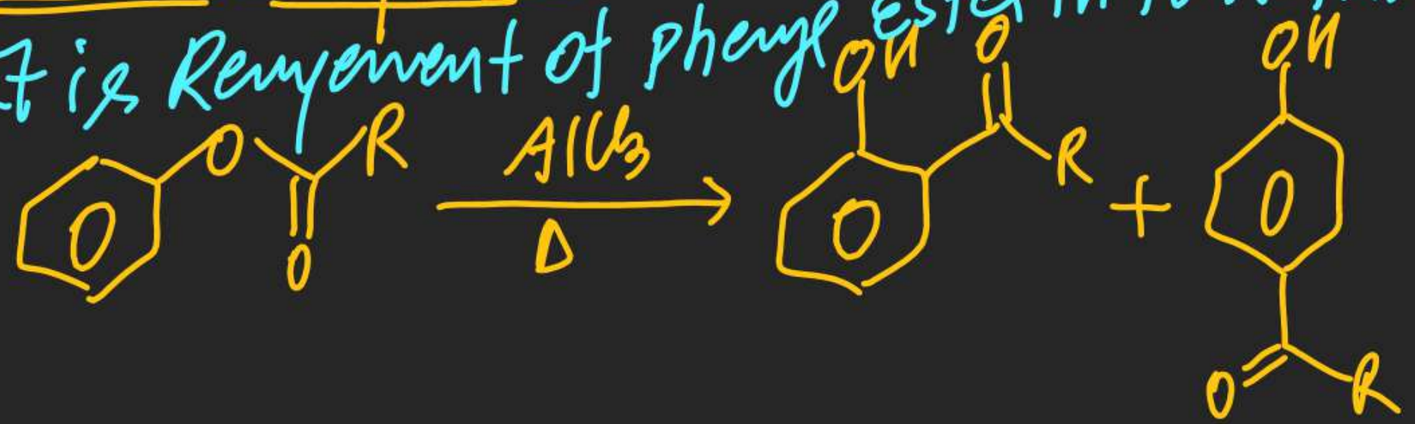


(7) 

(8) 

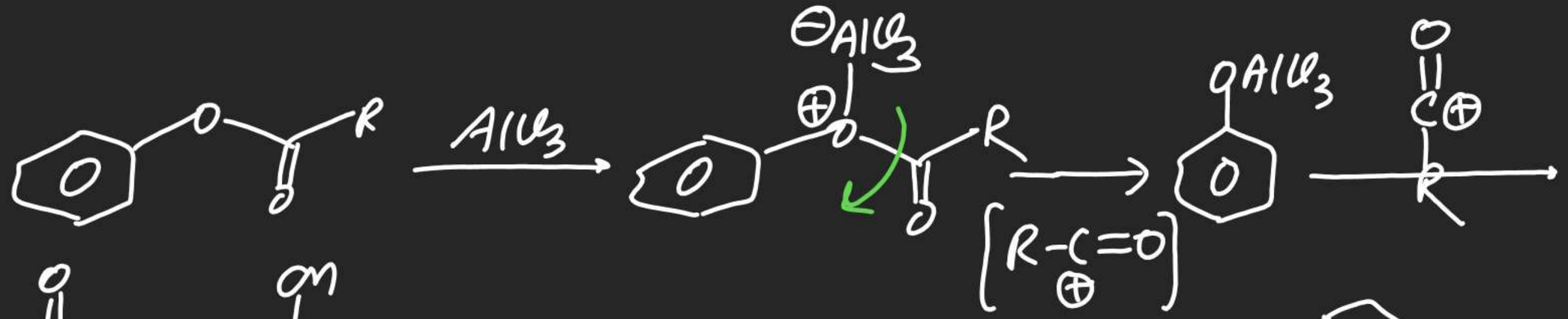
(#) **Fries Rearrangement:**

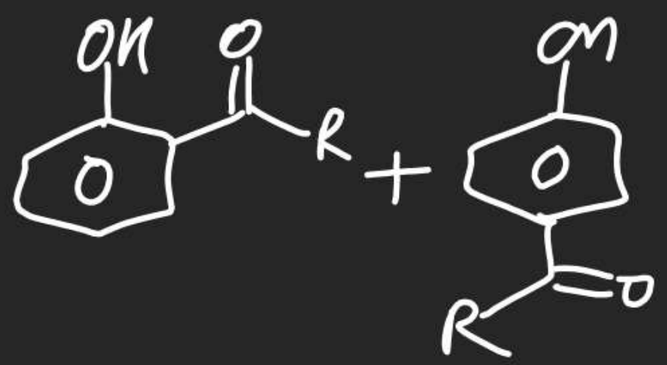
⇒ It is Rearrangement of phenyl Esters in to Acylated phenols.

(9) 

Nishant Jindal

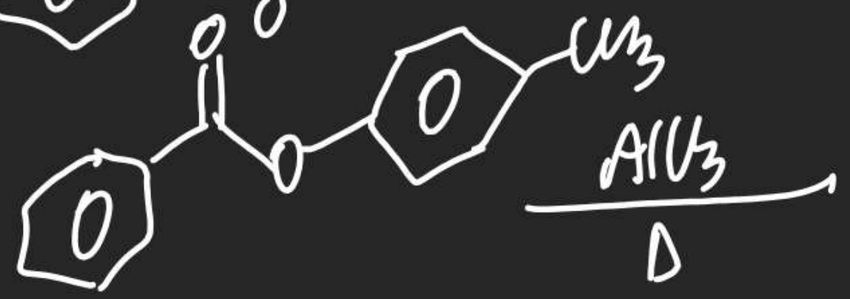
Mechⁿ:



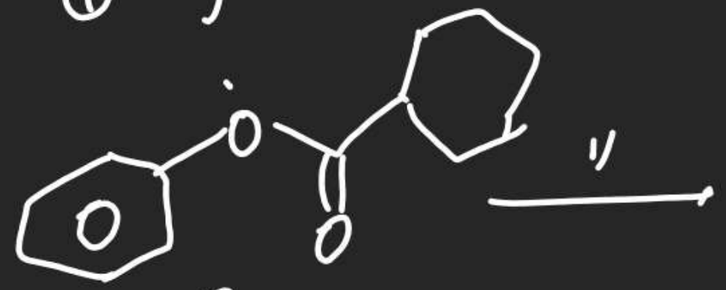


(10)

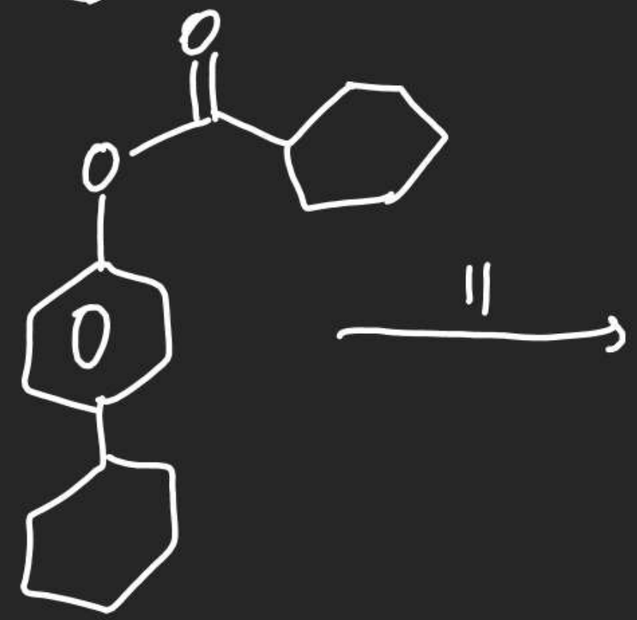
(11)



(12)

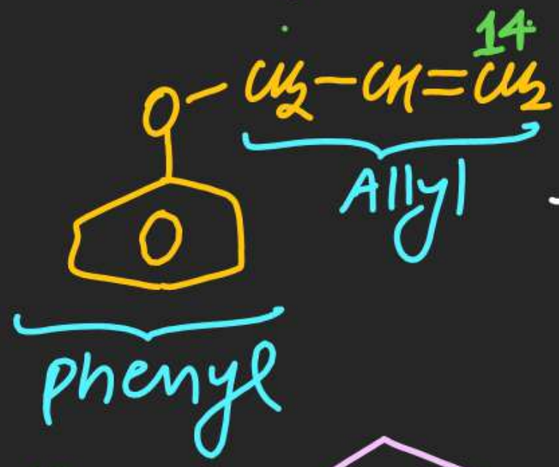


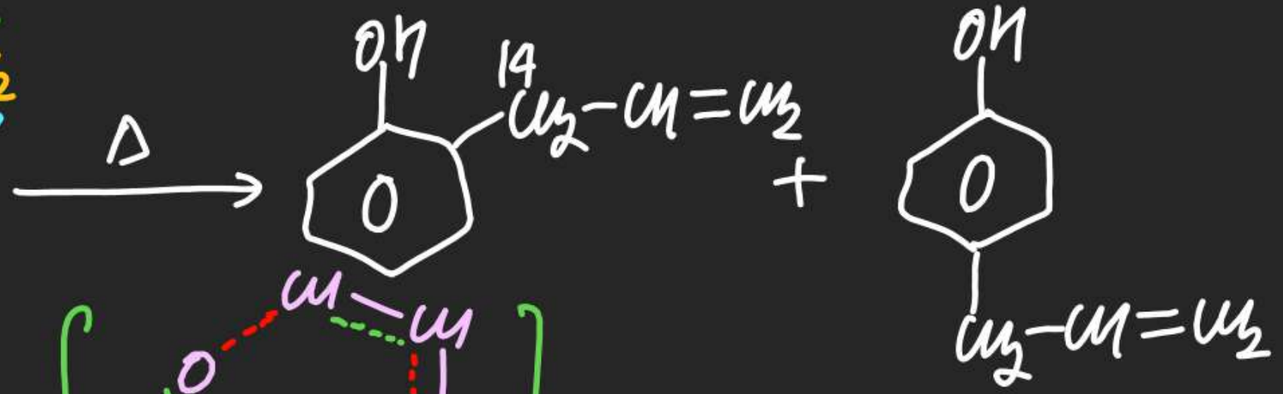
(13)



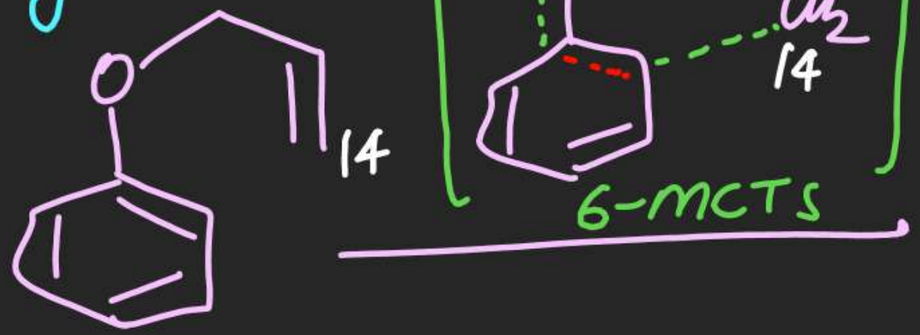
(H) Claisen Rearrangement :-

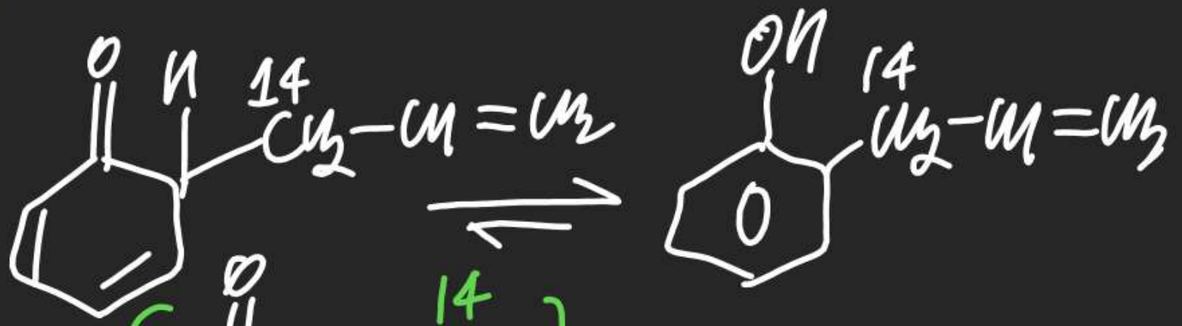
(14)

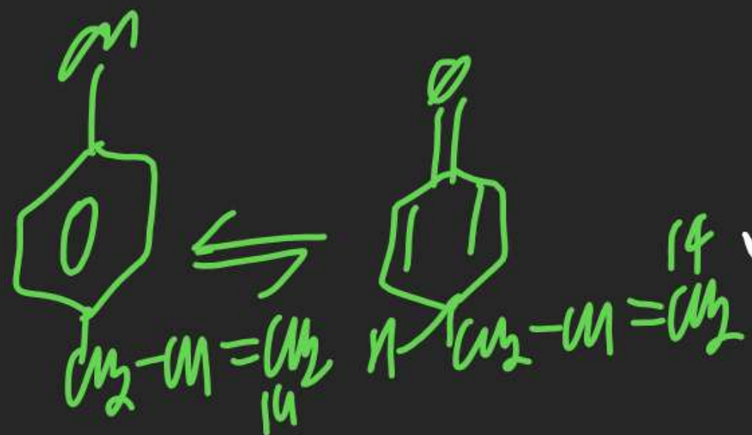


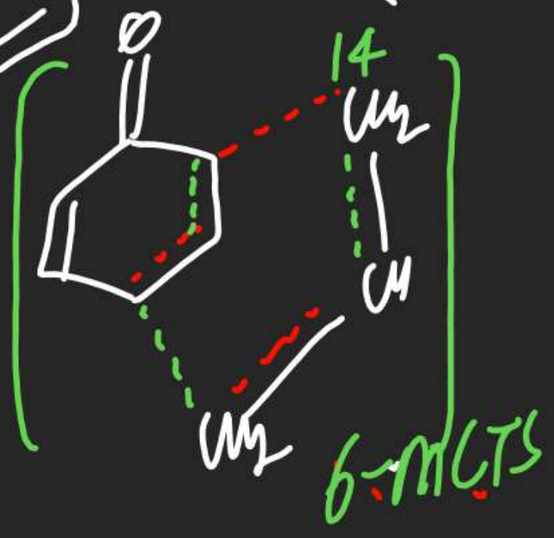


Mech?







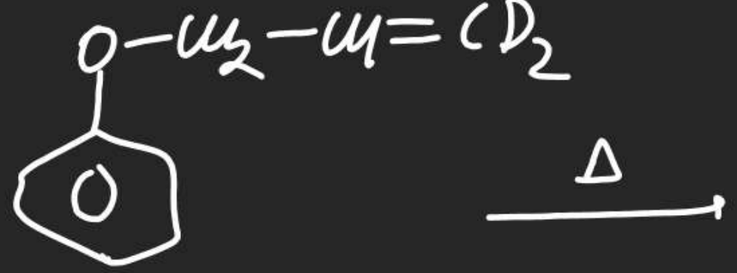


Note (i) 6-MCTS involved

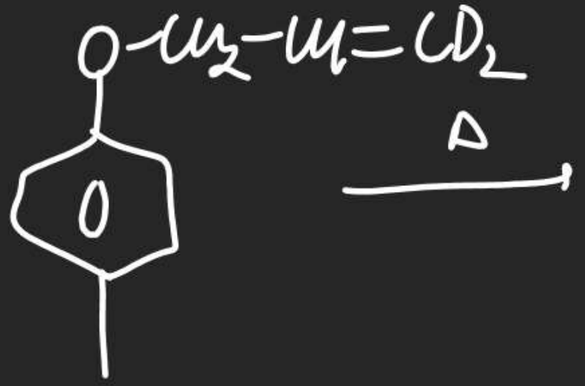
(ii) ortho product dominates over para

(iii) para product obtained only when Both ortho is Substituted.

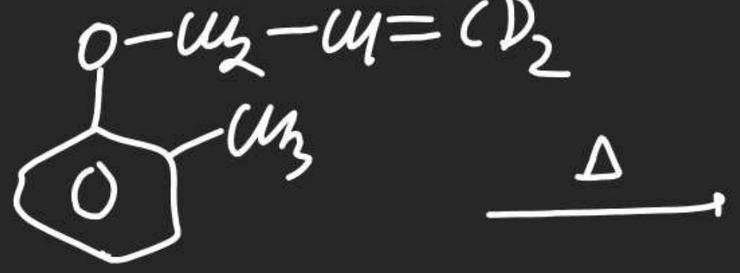
(15)



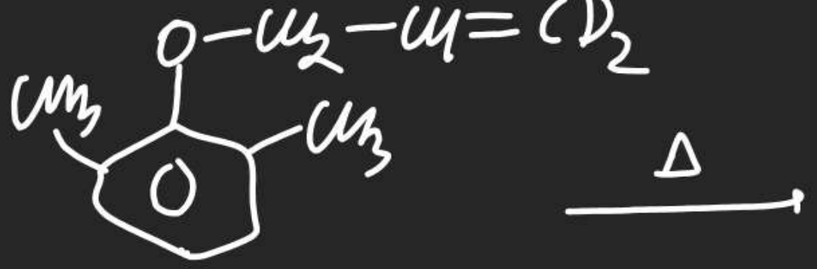
(16)



(17)

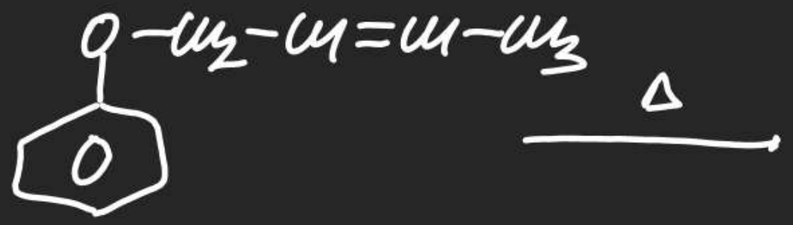


(18)



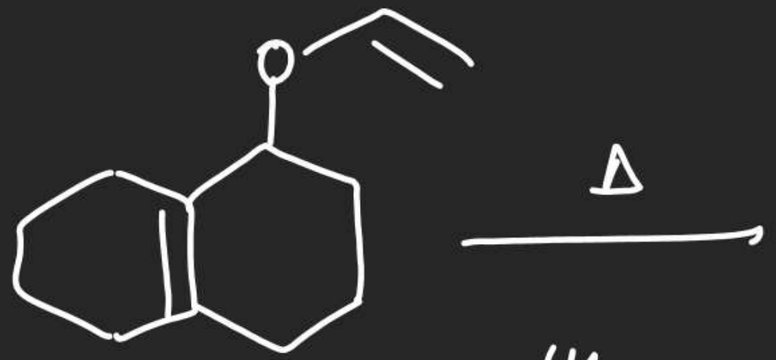
Nishant Jindal

(19)

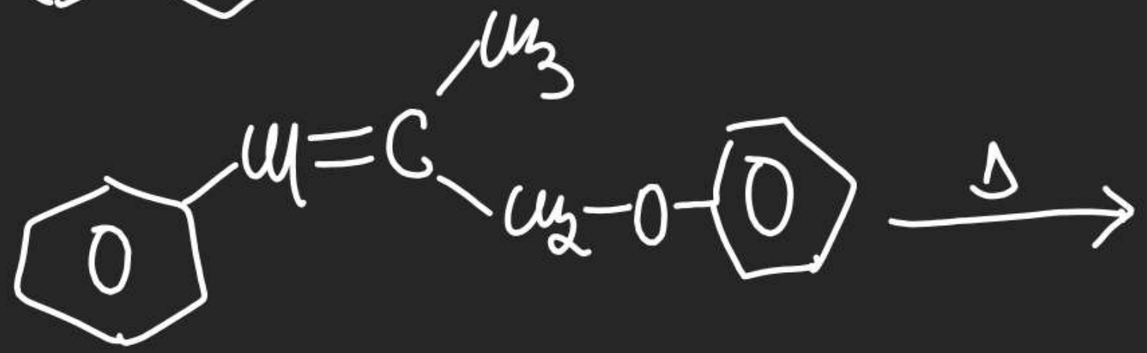


(20)

(21)



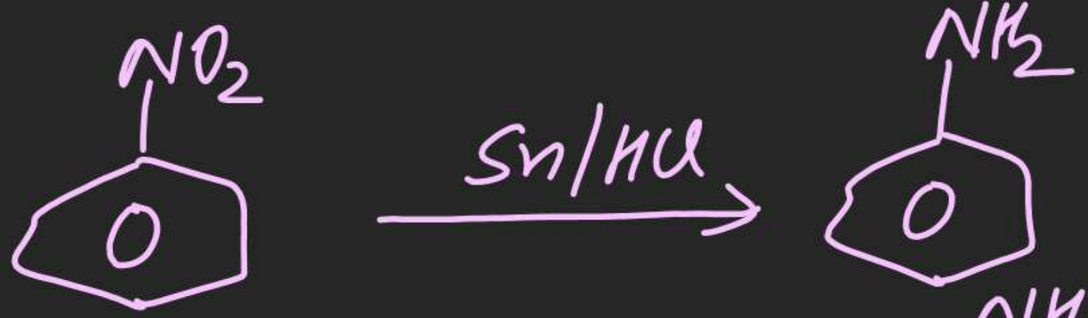
(22)



Nishant Jindal

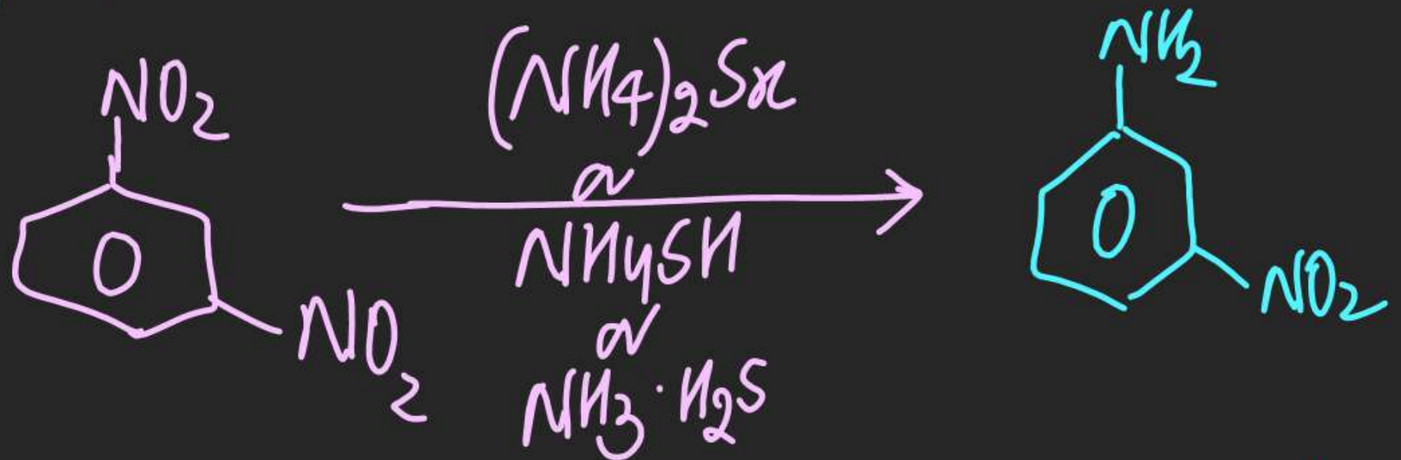
(#) Reduction of Nitro Benzene :-

IUP (1)



IUP (2)

MMIUP (3)



Nishant Jindal

Bio Molecule

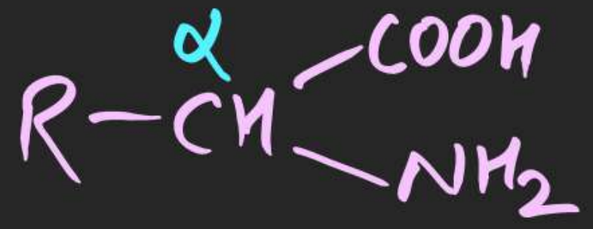
- Amino Acid
- Carbohydrates

Amino Acid

⇒ Bifunctional group Compounds having Amine ($-NH_2$) & Acid ($-COOH$) group.

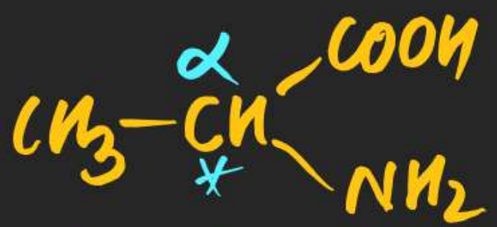
⇒ in this segment we are studying "α" Amino Acid

Nishant Jindal



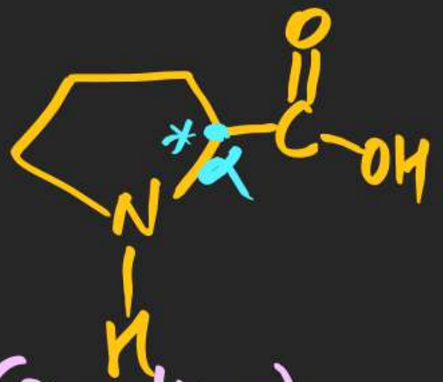
Ex:-

Glycine (Gly)



Alanine (Ala)

Phenyl Alanine



(proline)

Note:- Glycine is only naturally occuring Amino Acid having absence of Chiral Centre.

(#) Classification of Amino Acid:-

(i) On behalf of synthesis:-

(a) Natural Amino Acid ⟹ Amino Acid found in nature.

(b) Synthetic Amino Acid ⟹ man made Amino Acid.

(#) On Behalf of Requirments :-

(a) Essential Amino Acid :-

(b) Semi essential Amino Acid :-

(C) Non essential Amino Acid :-

Nishant Jindal

(#) On Behalf of chemical nature:

Acidic Amino Acid

⇒ when no. of Acidic group (−COOH) is higher than no. of Basic (−NH₂) group.

Neutral Amino Acid

⇒ when no. of Acidic group (−COOH) is equal to no. of Basic (−NH₂) group.

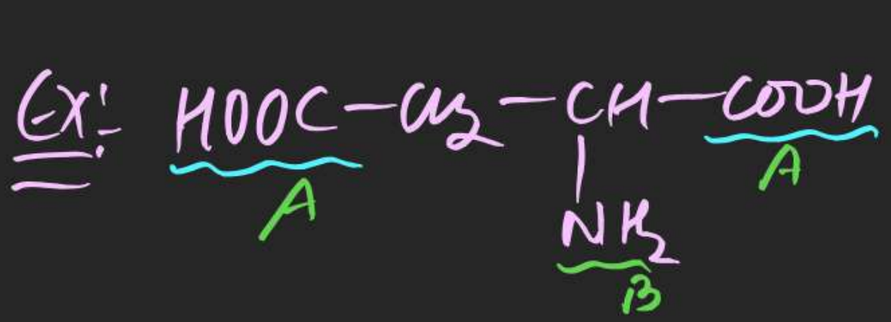
Basic Amino Acid

⇒ when no. of Acidic group (−COOH) is lesser than no. of Basic (−NH₂) group.

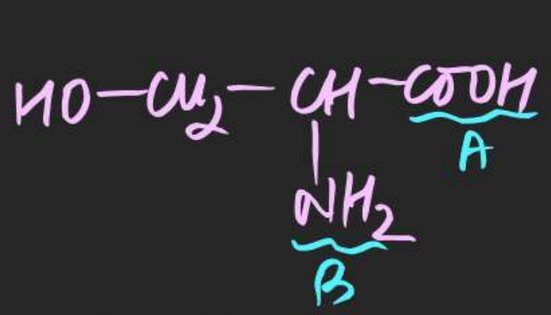
Note: Groups −OH / Phenol / Amide / −SH are neither considered Acidic nor Basic while deciding chemical nature of Amino Acid.

Nishant Jindal

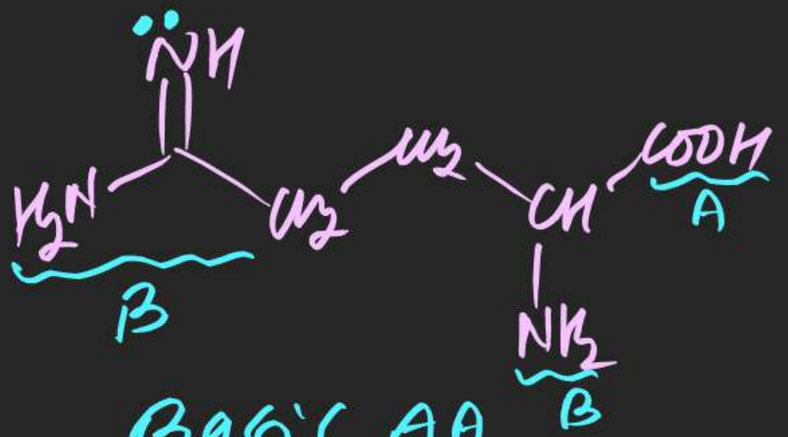
Ex:



Acidic AA



Neutral AA



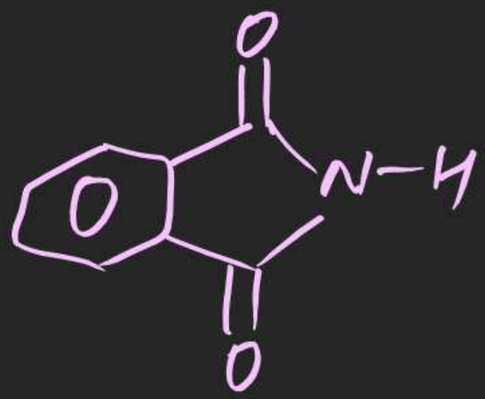
Basic AA

Note: Proteins are polymers of Amino Acid

"n" Amino Acid —Polymerise→ "Protein"

(#) Method of Preparation :-

(1)

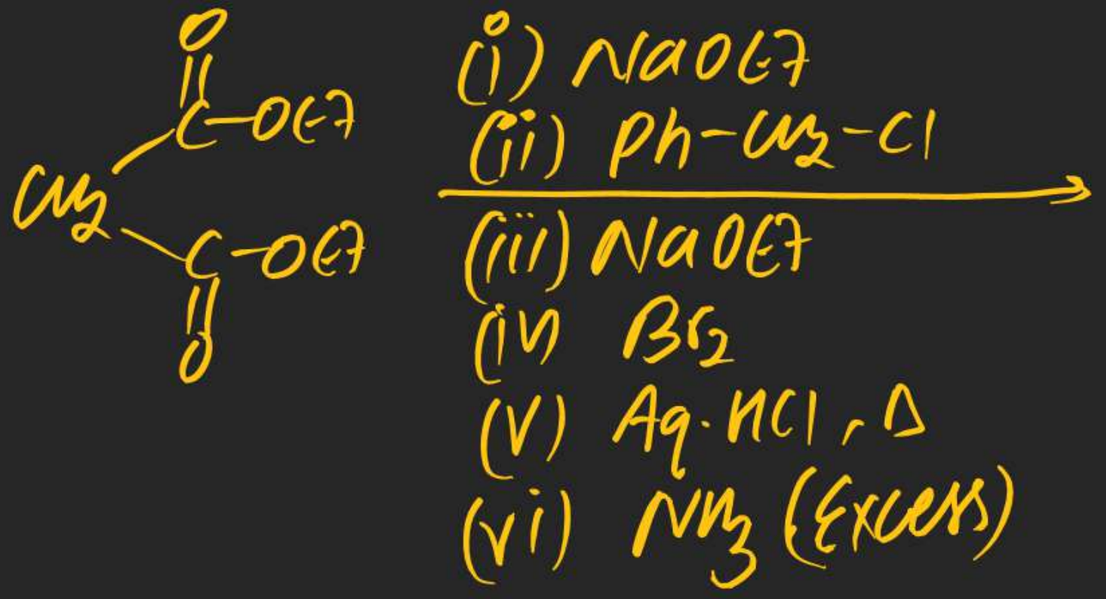


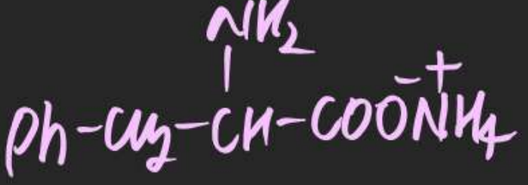
$\xrightarrow[\text{(ii) } CH_3-CH_2-COOEt]{\text{(i) KOH}}{\text{(iii) Aq. HCl}}$

(2) $CH_3-CH_2-COOH \xrightarrow[\text{(ii) } NH_3 \text{ (excess)}]{\text{(i) Red P/Br}_2}$

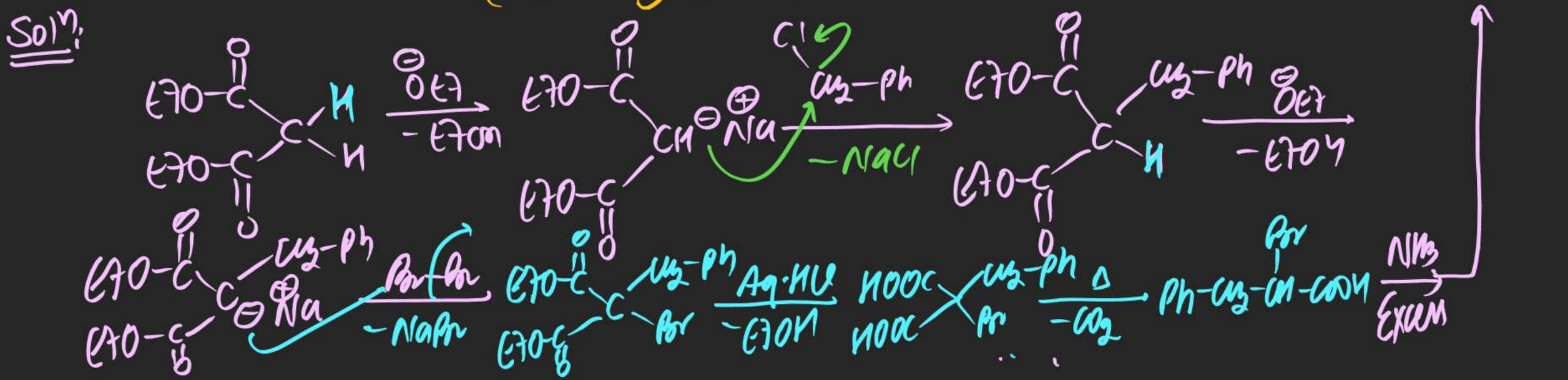
Nishant Jindal

(3)





Soln:



Nishant Jindal

(4) $R-C(=O)-H$ $\xrightarrow[\text{(ii) } HCN/NaCN]{\text{(i) } NH_3}$ $\xrightarrow[\text{(iii) } H_3O^{\oplus}]{}$

(5) $CH_3-C(=O)-OH$ $\xrightarrow[\text{(ii) } DMSO, NaHCO_3]{\text{(i) } Red\ P/Br_2}$ $\xrightarrow[\text{(iii) } NH_3]{}$ $\xrightarrow[\text{(iv) } NaBH_4 (Excess)]{}$

Nishant Jindal

(#) Amino Acid Exist as a Zwitter ion / Dipolar Ion :-

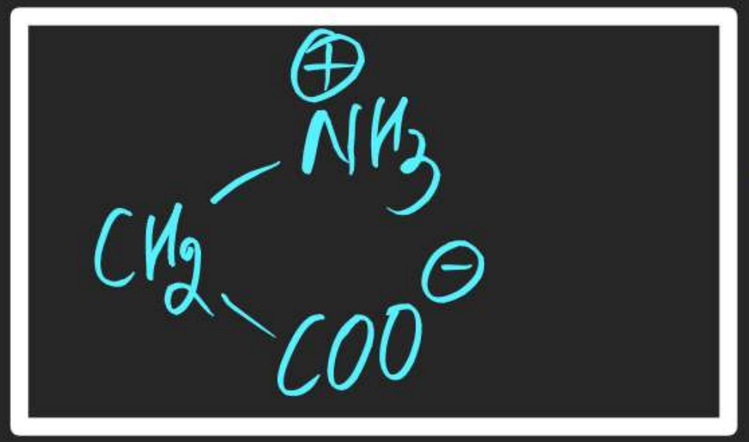
$\Rightarrow$ For Glycine Contains $K_a = 1.6 \times 10^{-10}$ & $K_b = 2.5 \times 10^{-12}$

which suggest that $CH_2(NH_2)-COOH$ $K_b \simeq 10^{-4}$ $K_a \simeq 10^{-5}$

is not correct Representation of Glycine these values suggest us that

$K_a(\overset{\oplus}{N}H_3) \simeq 10^{-10}$ $K_b(-COO^{\ominus}) \simeq 10^{-12}$

& Exist as Zwitter ion



Zwitter ion

Nishant Jindal

(#) **Electrophoresis**:- movement of charge particle under influence of electric field is known as electrophoresis.

If Particle nature is

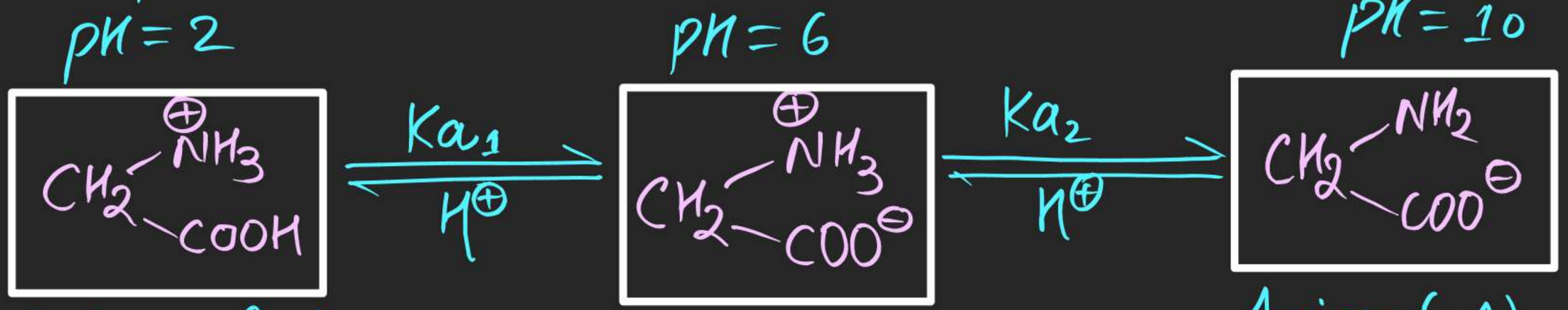
⇒ Cationic $pH < pI$ — movement towards Cathode

⇒ Zwitter ion $pH = pI$ — No net movement

⇒ Anionic $pH > pI$ — movement towards Anode

Nishant Jindal

(#) Glycine structure:



$pH < pI < pH'$

$$Ka_1 = \frac{[H^+][ZI]}{[cation]} \longrightarrow (i)$$

$$Ka_2 = \frac{[H^+][Anion]}{[ZI]} \longrightarrow (ii)$$

From eq^n (i) & (ii)

$$Ka_1 \times Ka_2 = [H^+]^2 \frac{[A]}{[C]}$$

$$\Rightarrow \log Ka_1 + \log Ka_2 = 2\log[H^+] + \log\frac{[A]}{[C]}$$

$$\Rightarrow pKa_1 + pKa_2 = 2pH + \log\frac{[C]}{[A]}$$

Nishant Jindal

$$pH = \frac{pKa_1 + pKa_2}{2} - \frac{1}{2}\log\frac{[C]}{[A]}$$

at $pH = pI \Rightarrow [C] = [A]$

$$pI = \frac{pKa_1 + pKa_2}{2}$$

(#) Isoelectric point (pI)

$\Rightarrow$ A pH at which no net movement of charge particle takes place.

$pH = pI$

- (*) No movement
- (*) No electrophoresis
- (*) AA wd exist as ZI
- (*) $[C] = [A]$

Nishant Jindal

Ex: lowest pH

$$AA \underset{}{\overset{Ka_1}{\rightleftharpoons}} AA' \underset{}{\overset{Ka_2}{\rightleftharpoons}} AA'' \underset{}{\overset{Ka_3}{\rightleftharpoons}} AA'' \underset{}{\overset{Ka_4}{\rightleftharpoons}} AA''$$

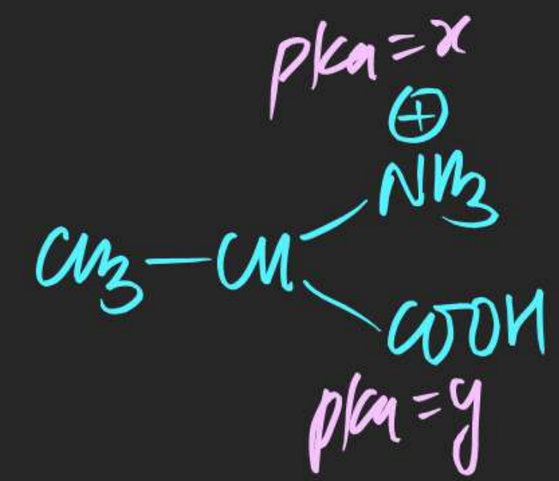
$+2 \quad +1 \quad 0 \quad -1 \quad -2$

$+2$ ✓

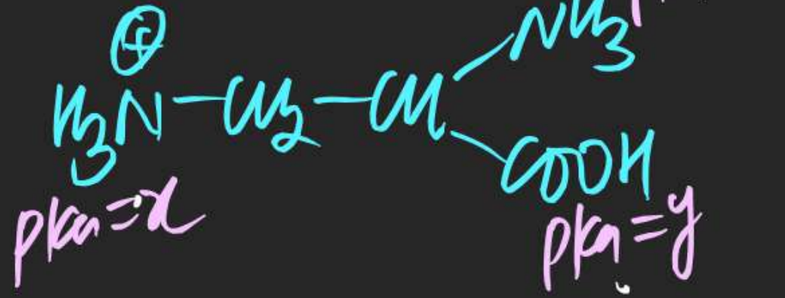
$+1$

$$pI = \frac{pKa_2 + pKa_3}{2}$$

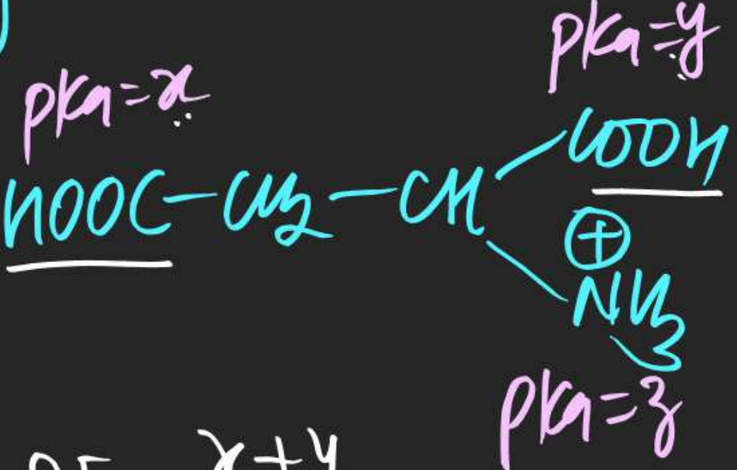
Ex:



$$pI = \frac{x+y}{2}$$



$$pI = \frac{x+y}{2}$$



$$pI = \frac{x+y}{2}$$

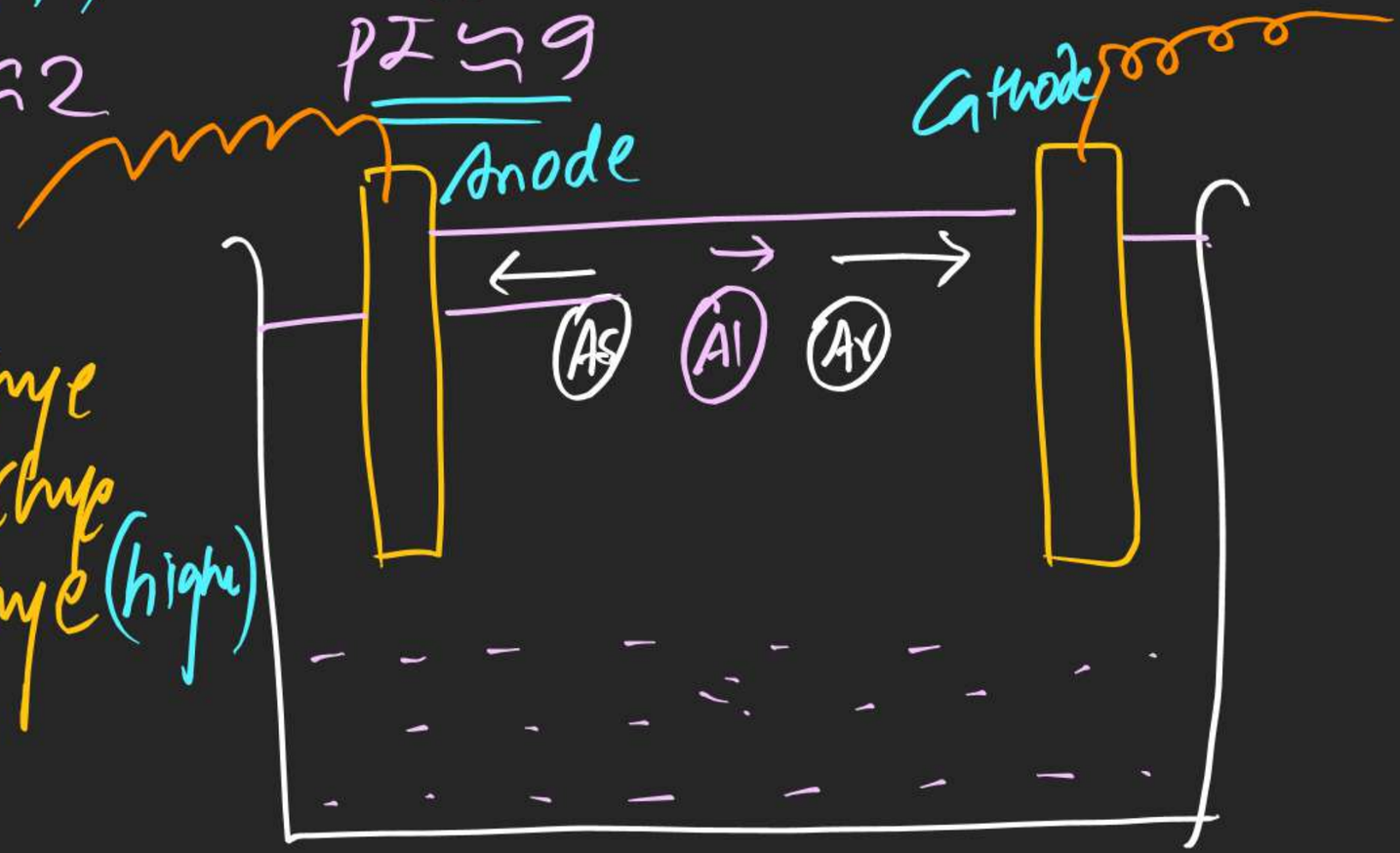
Nishant Jindal

(#) How Can we separate Ternary mixture of

Alanine (Neutral AA) pI ≒ 6 , Aspartic Acid (Acidic AA) pI ≒ 2 , Arginine (Basic AA) pI ≒ 9

Soln:

At pH = 5 Alanine (+)ve charge
Aspartic acid (−)ve charge
Arginine (+)ve charge (high)

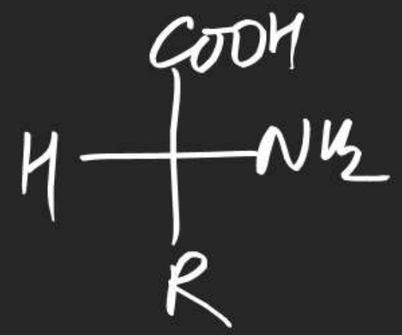


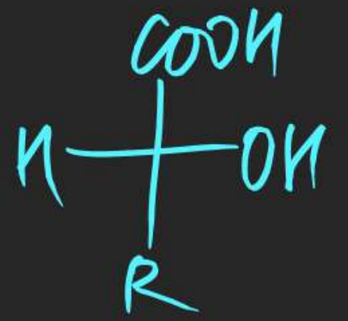
Nishant Jindal

(#) Rxn shown By Amino Acid :

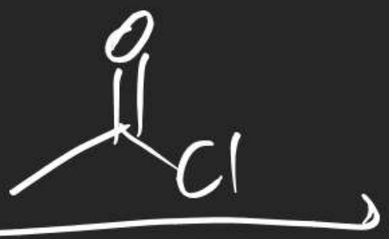
⇒ Due to $-NH_2$ group :

N.F.G

(1) 

$\xrightarrow{NaNO_2/HCl}$ 

(Simple product due to Nap of $-COO^{\ominus}$)

(2))) $\xrightarrow{NOCl}$ 

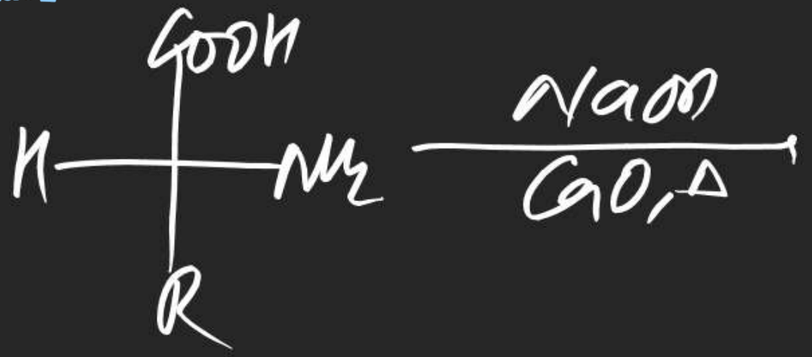
(3)))

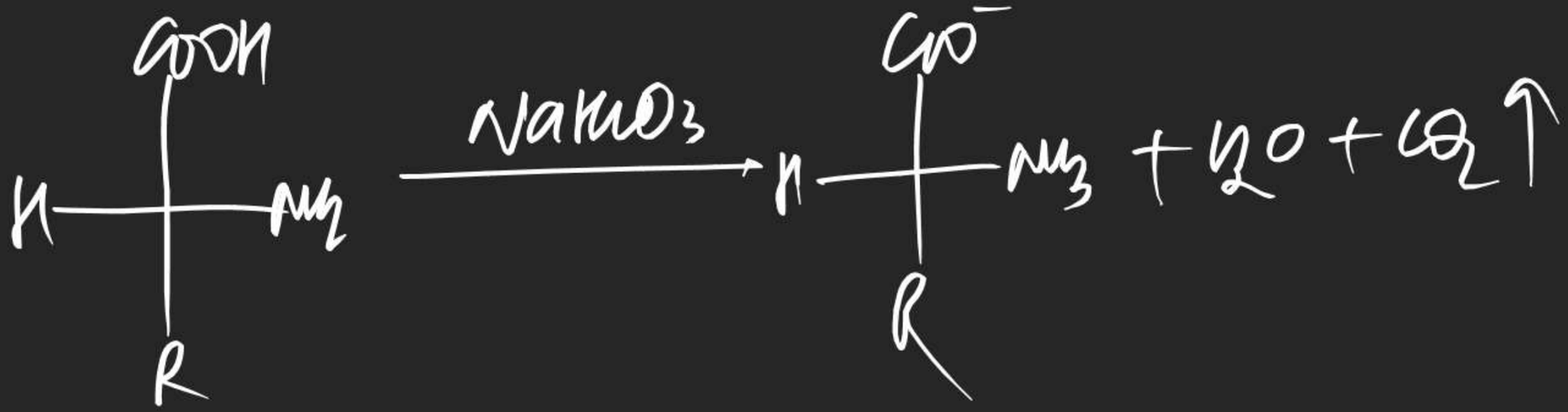
(4) 

(#) Rxn due to –COOH group :

(5) 

(6) 

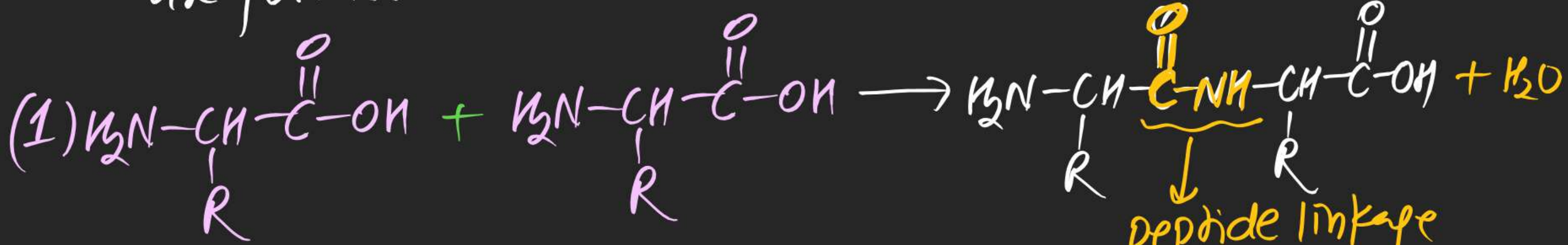
(7) 

(8) 

Nishant Jindal

Peptide

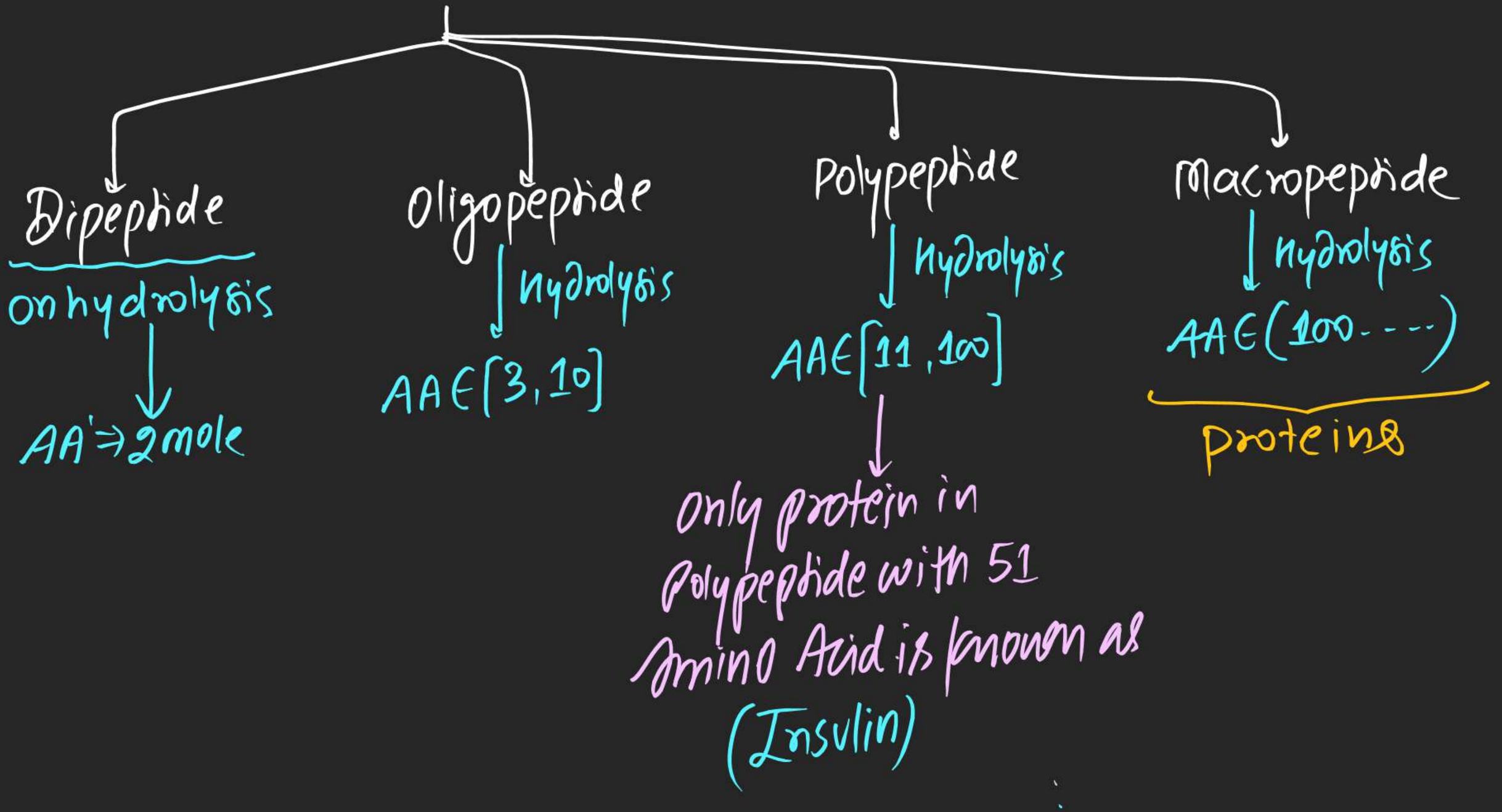
$\Rightarrow$ when two or more than Amino Acids get condensed then peptides are formed.

(1) 

(*) Dipeptide

(#) Classification of peptides: peptides are classified as

Nishant Jindal



Nishant Jindal

Ex: Find All possible peptides in following cases

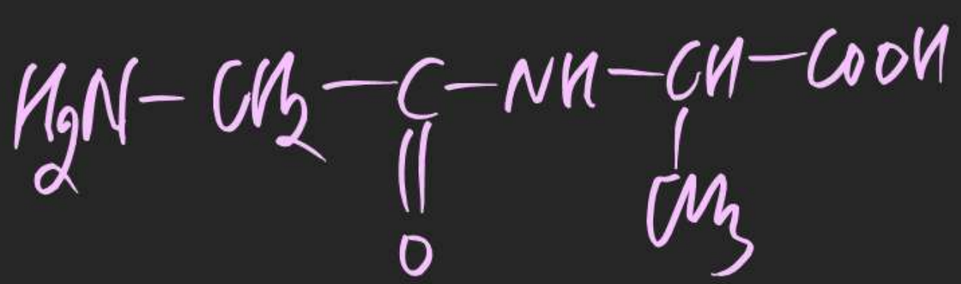
		Dipeptide	Tripeptide	Polypeptide
(i)	Glycine	Gly-Gly 1^2	Gly-Gly-Gly 1^3	...Gly-Gly-Gly... 1^n
(ii)	Glycine & Alanine	Gly-Gly, Gly-Ala, Ala-Gly, Ala-Ala 2^2	2^3	2^n
(iii)	Glycine, Alanine, Valine	3^2	3^3	3^n

Nishant Jindal

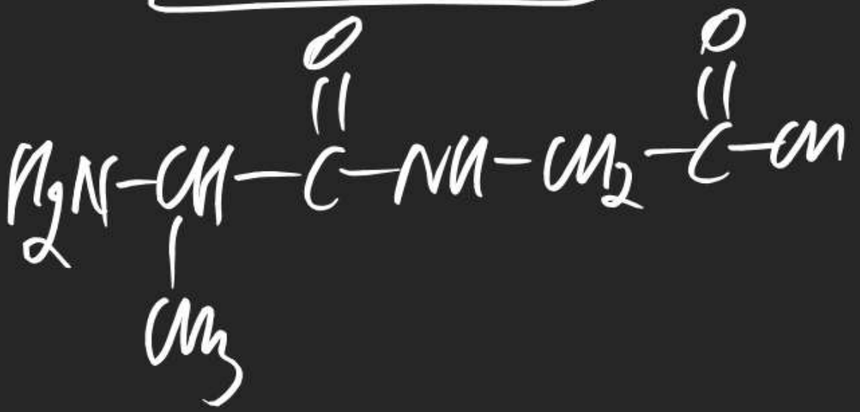
(#) Naming of peptide:-

AA with free NH_2 is written first

Ex:- Dry structure of **Gly-Ala**

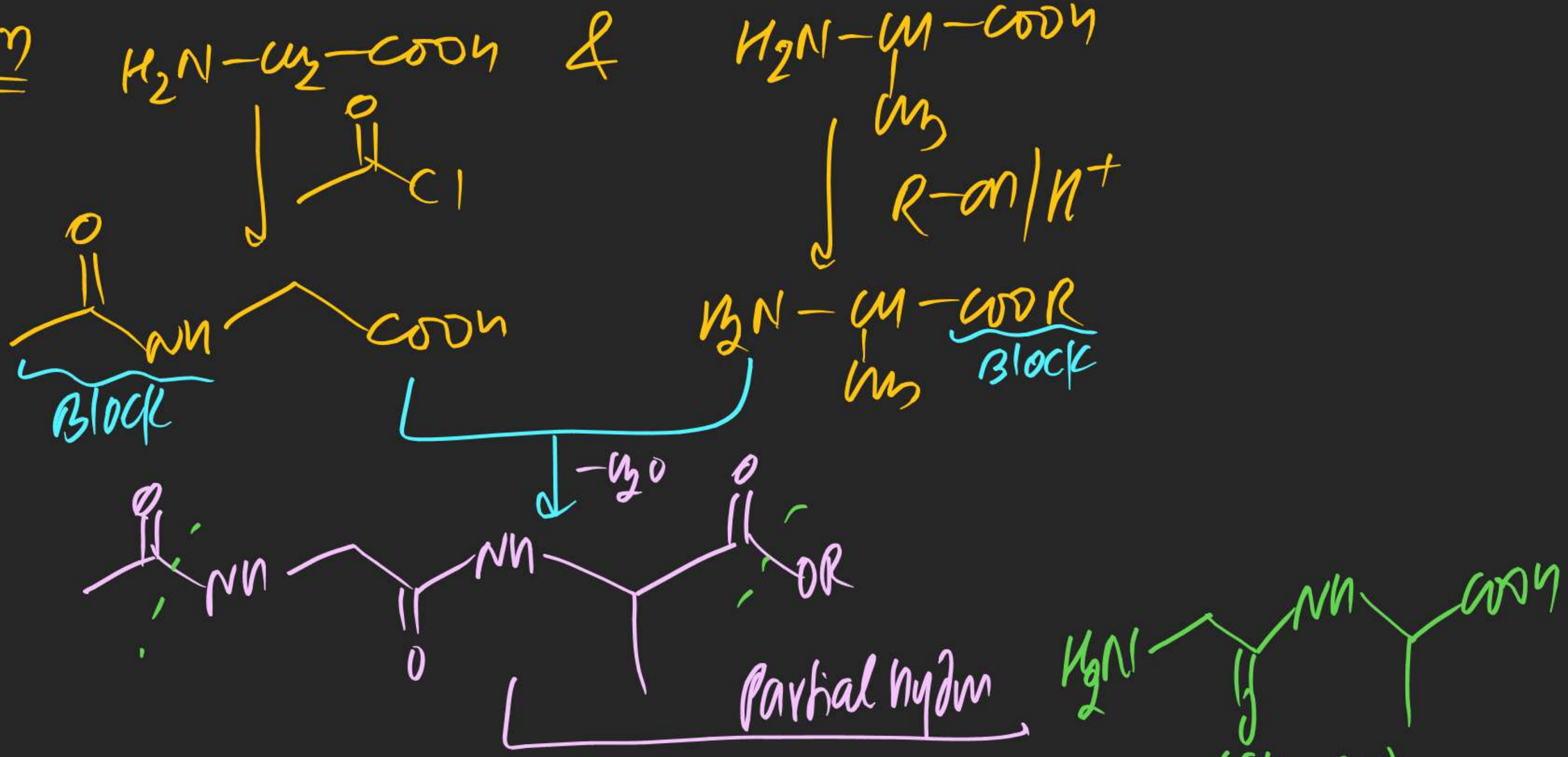


Ala-Gly



Nishant Jindal

Ex! How can we prepare Exclusively (Gly-Ala)

Soln 

(#) Str. of Proteins — Fibrous, Globular

(a) Primary

(b) Sec.

(c) Tert.

(d) Quat.