

Aromatic Compound

Few Aromatic Compounds:

(1) Benzene 

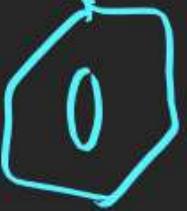
(2) Chloro Benzene 

(3) Toluene 

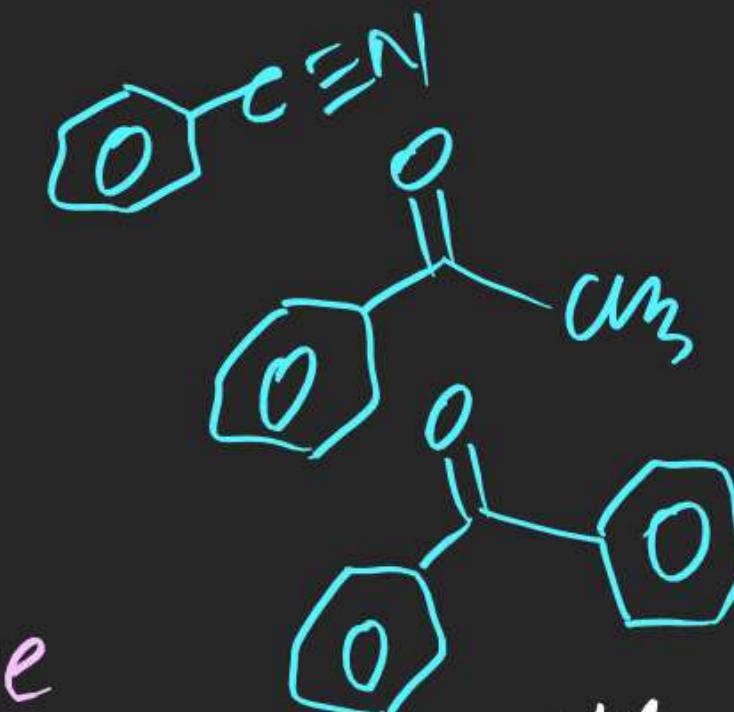
(4) Cumene 

(5) Nitro Benzene
(Oil of mignon) 

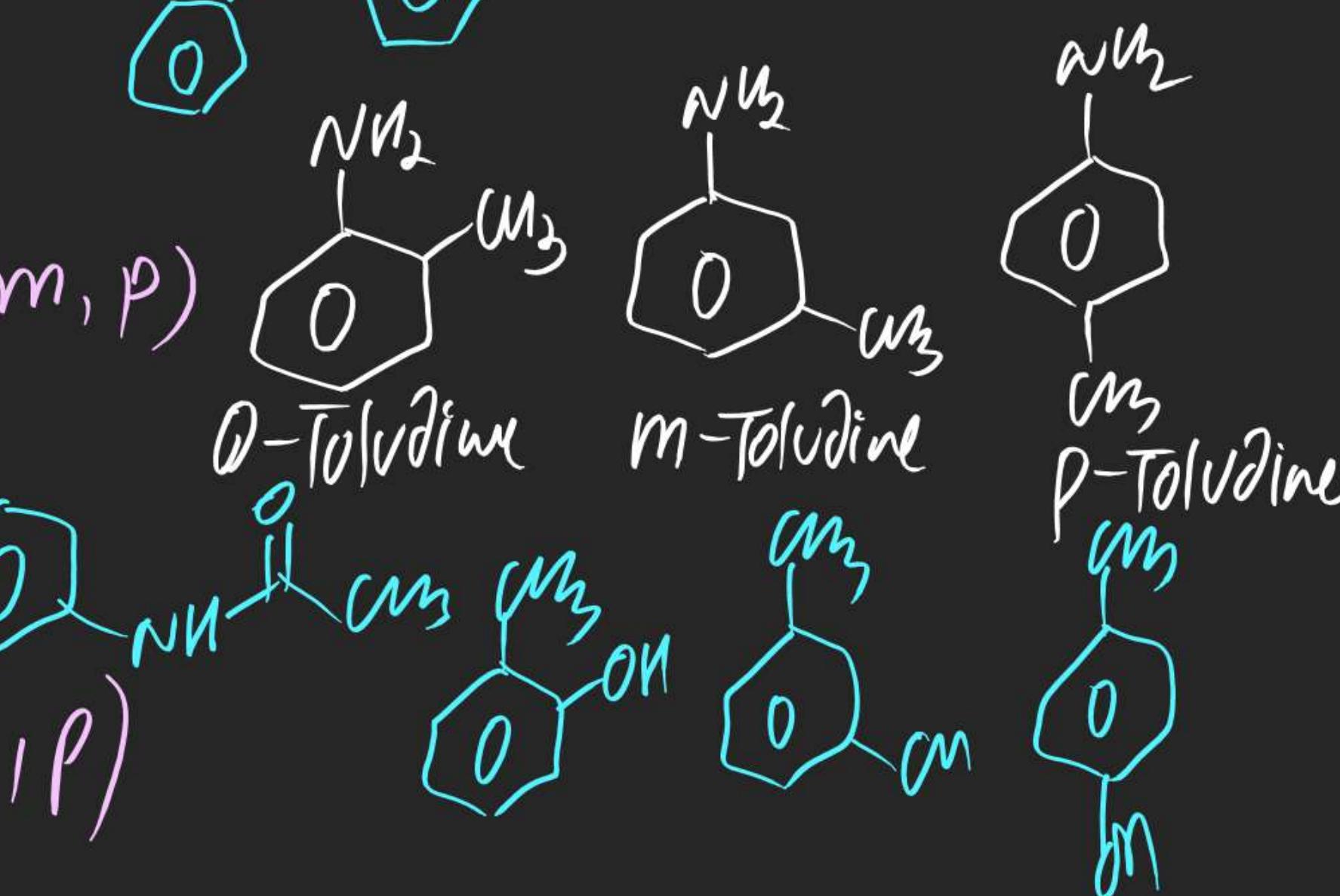
(6) Aniline 

- (7) Benzaldehyde 
- (8) Benzoic Acid (white crystalline) 
- (9) Benzene Sulphonic Acid 
- (10) Phenol (Carbolic Acid) 
- (11) Benzene diazonium chloride 

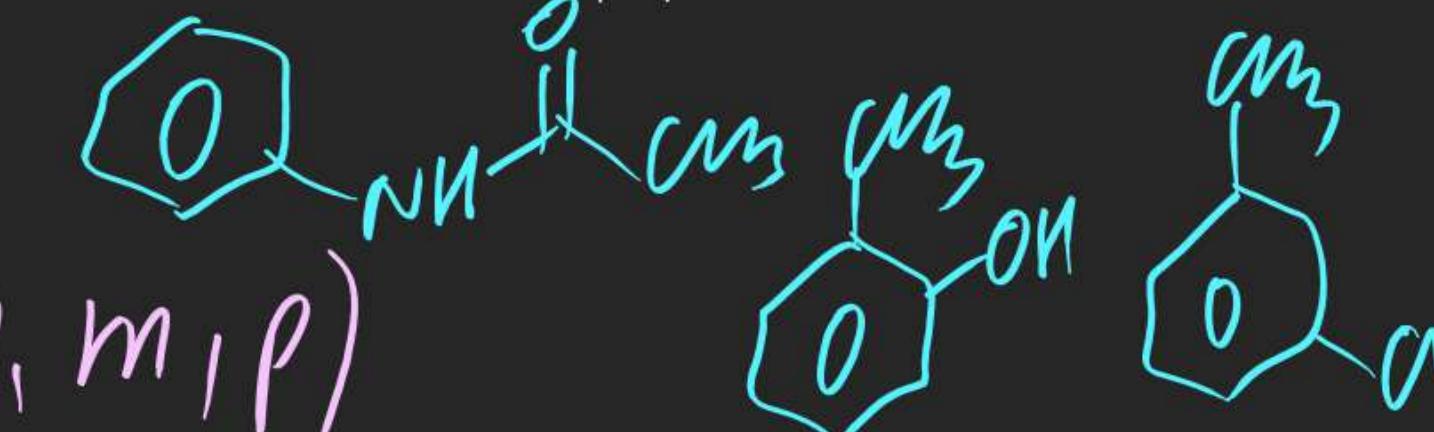
(12) Benzonitrile



(13) Acetophenone



(16) Acetanilide

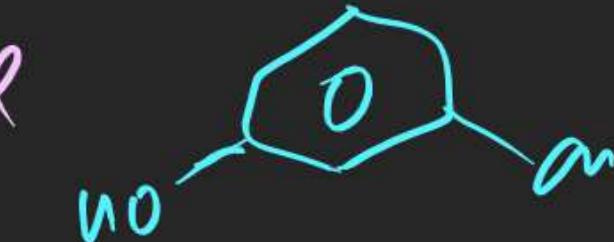


(17) Cresol (o, m, p)

(18) Catechol



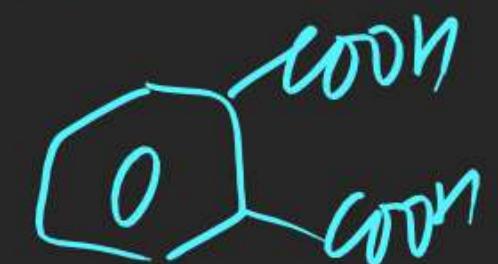
(19) Resorcinol



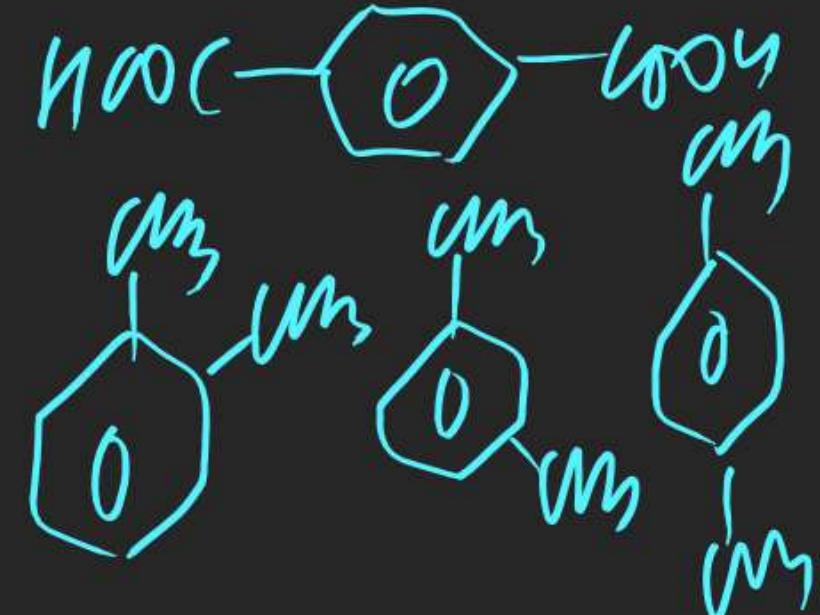
(20) Quinol



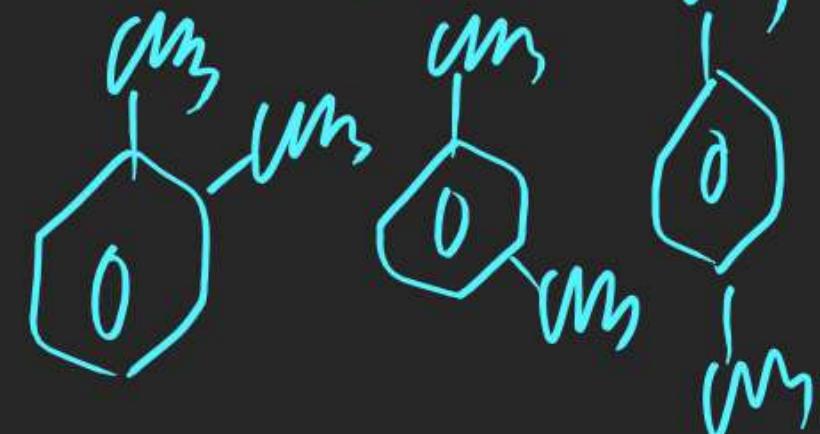
(21) Pthalic Acid



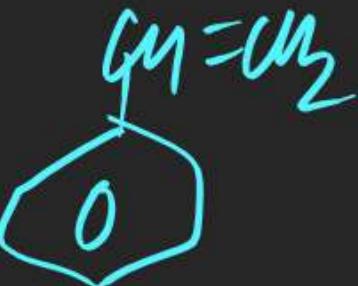
(22) Tel Pthalic Acid



(23) Xylene (o,m,p)



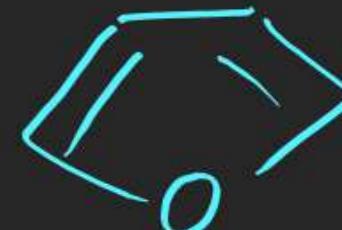
(24) Styrene



(25) Anisole



(26) Furan



(27) Pyrrole



(28) Thiophene

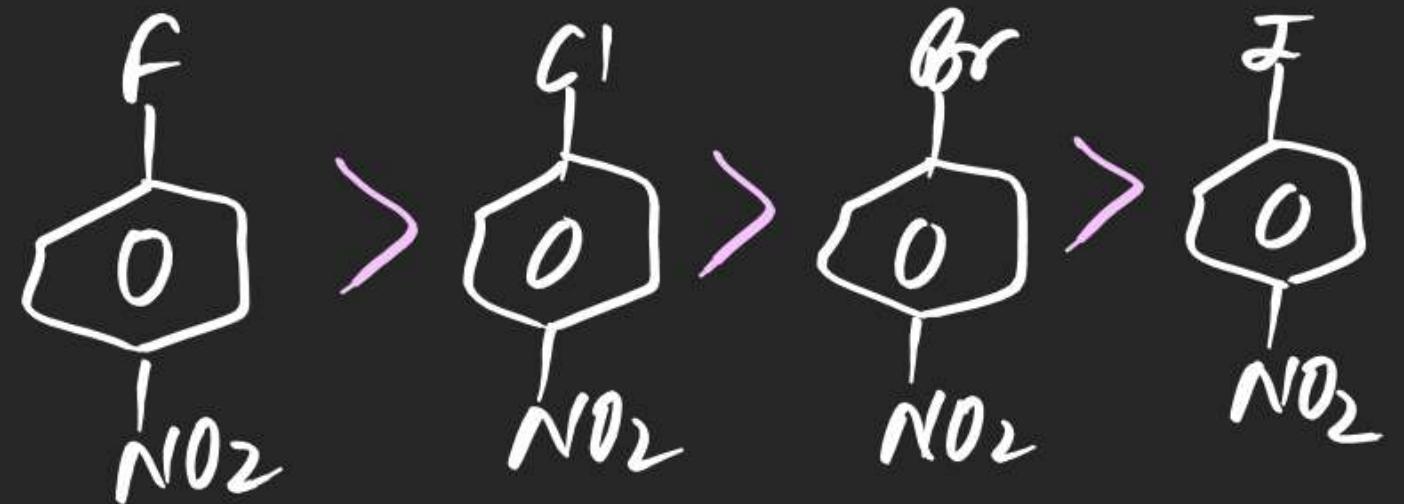


(46) Inorganic Benzene / Borazine / Borazole

(47) Indole

(48) Benzene Hexa Chloride .

(v) Order of rate of S_N^2 -Ar mechⁿ for Ar-X



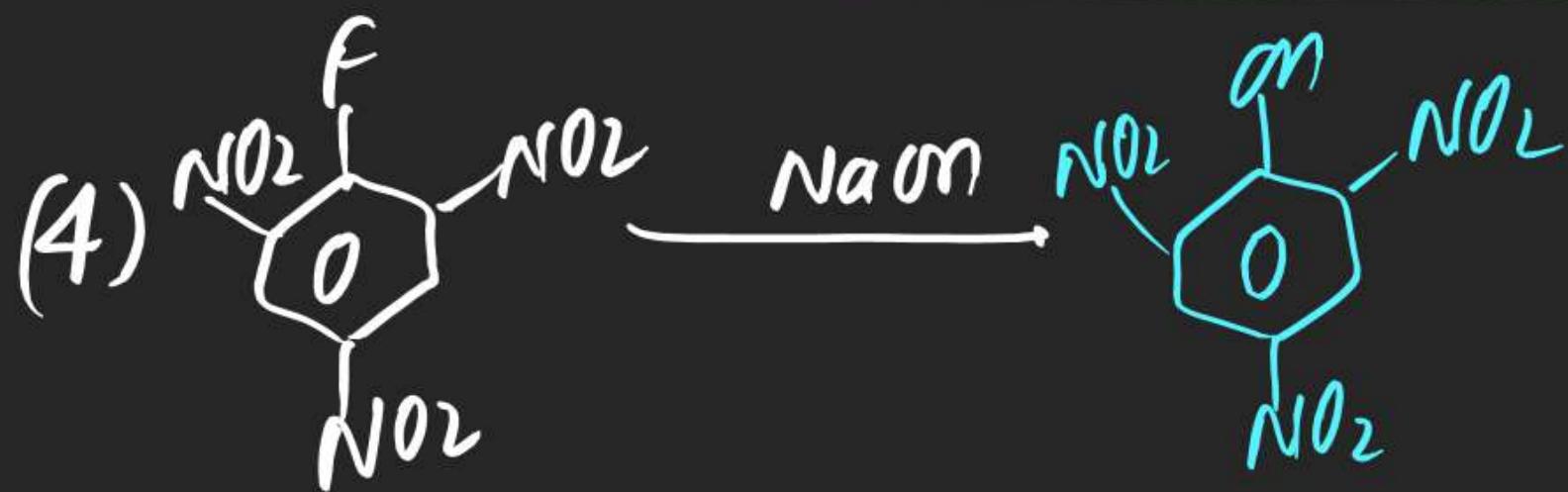
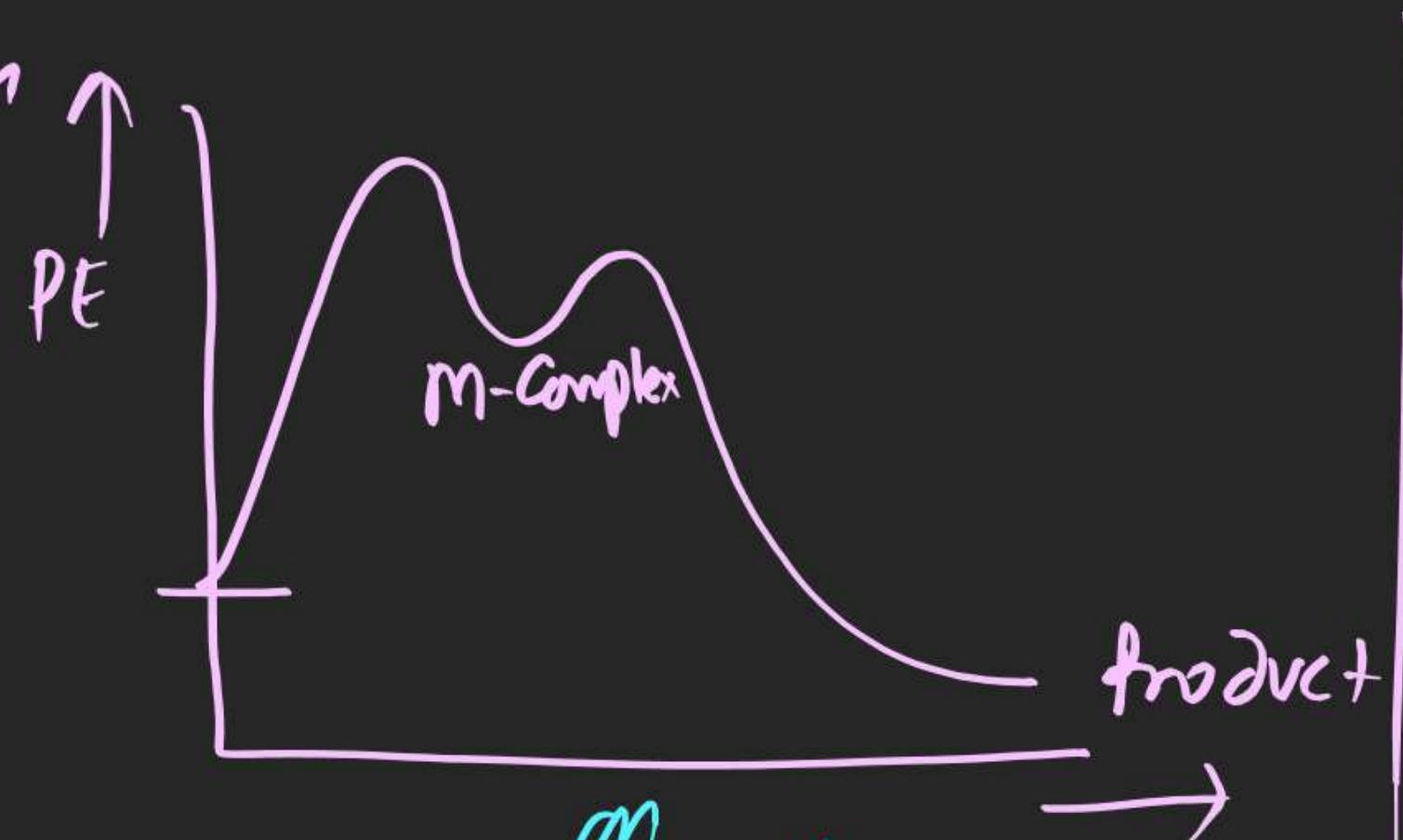
(vi) Breaking of C-X Bond is not involved in γ -def



(viii) II-order

(ix) Bimolecular

(X) P.E Diagnos ↑

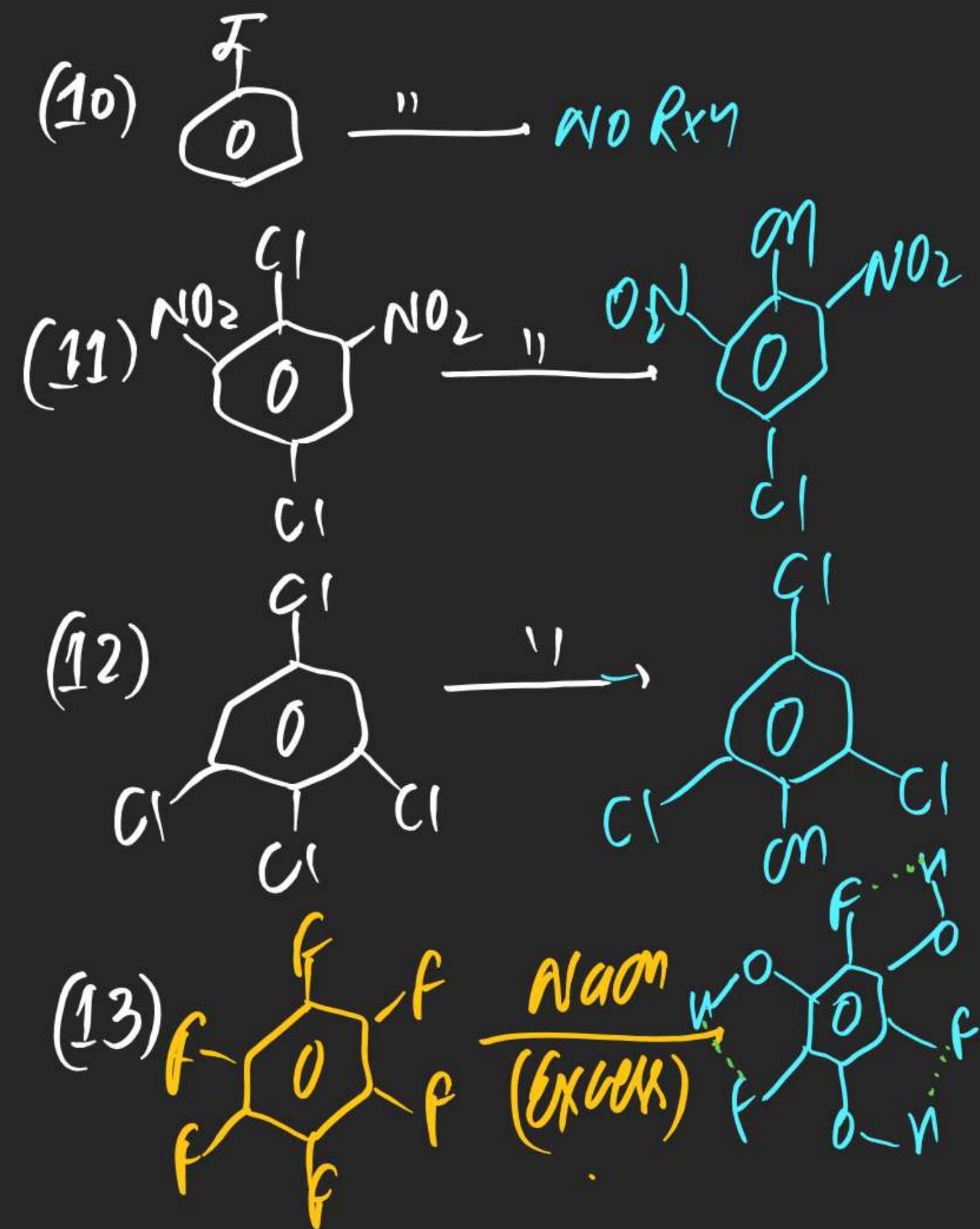
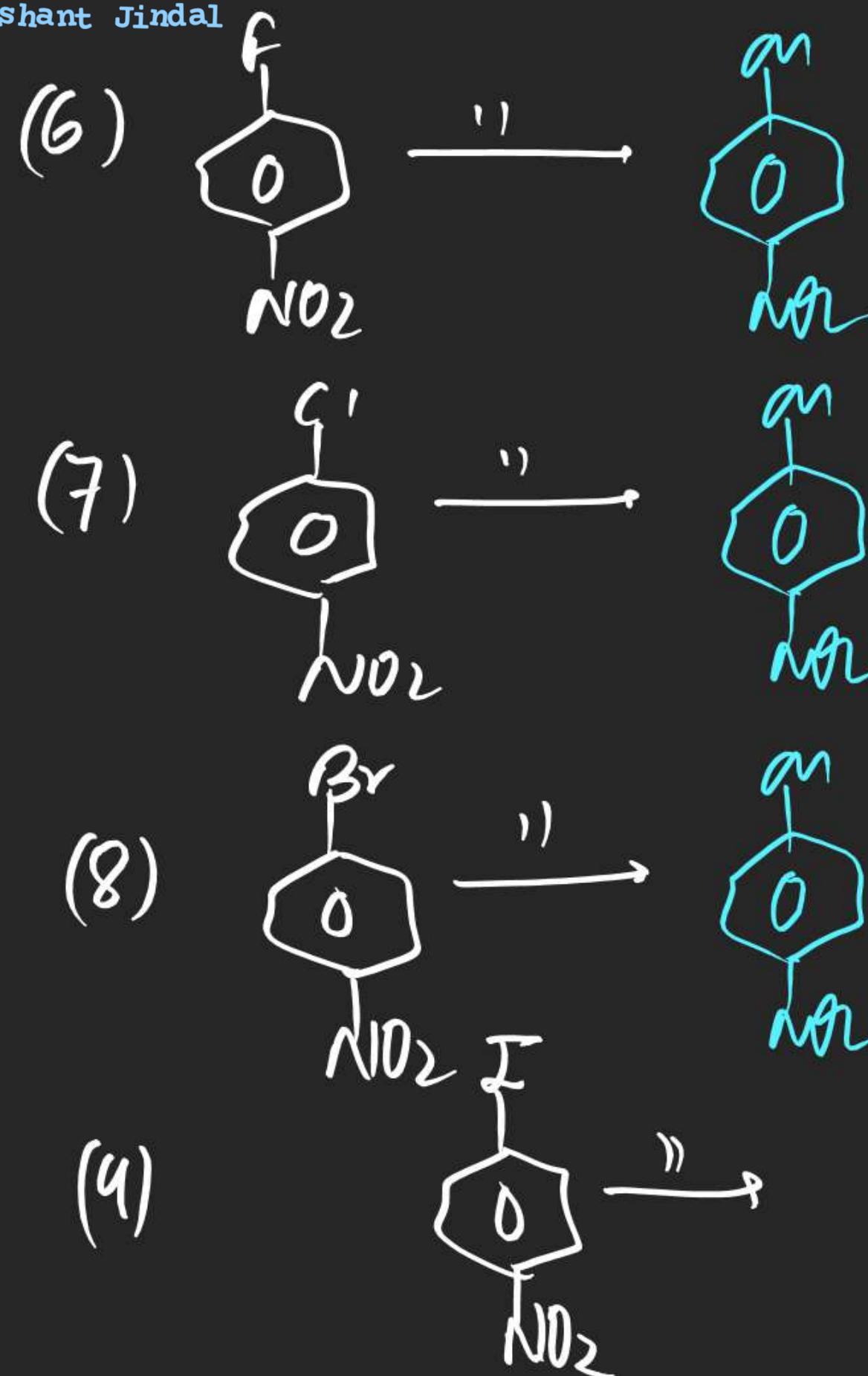
(xi) Two step mechⁿ

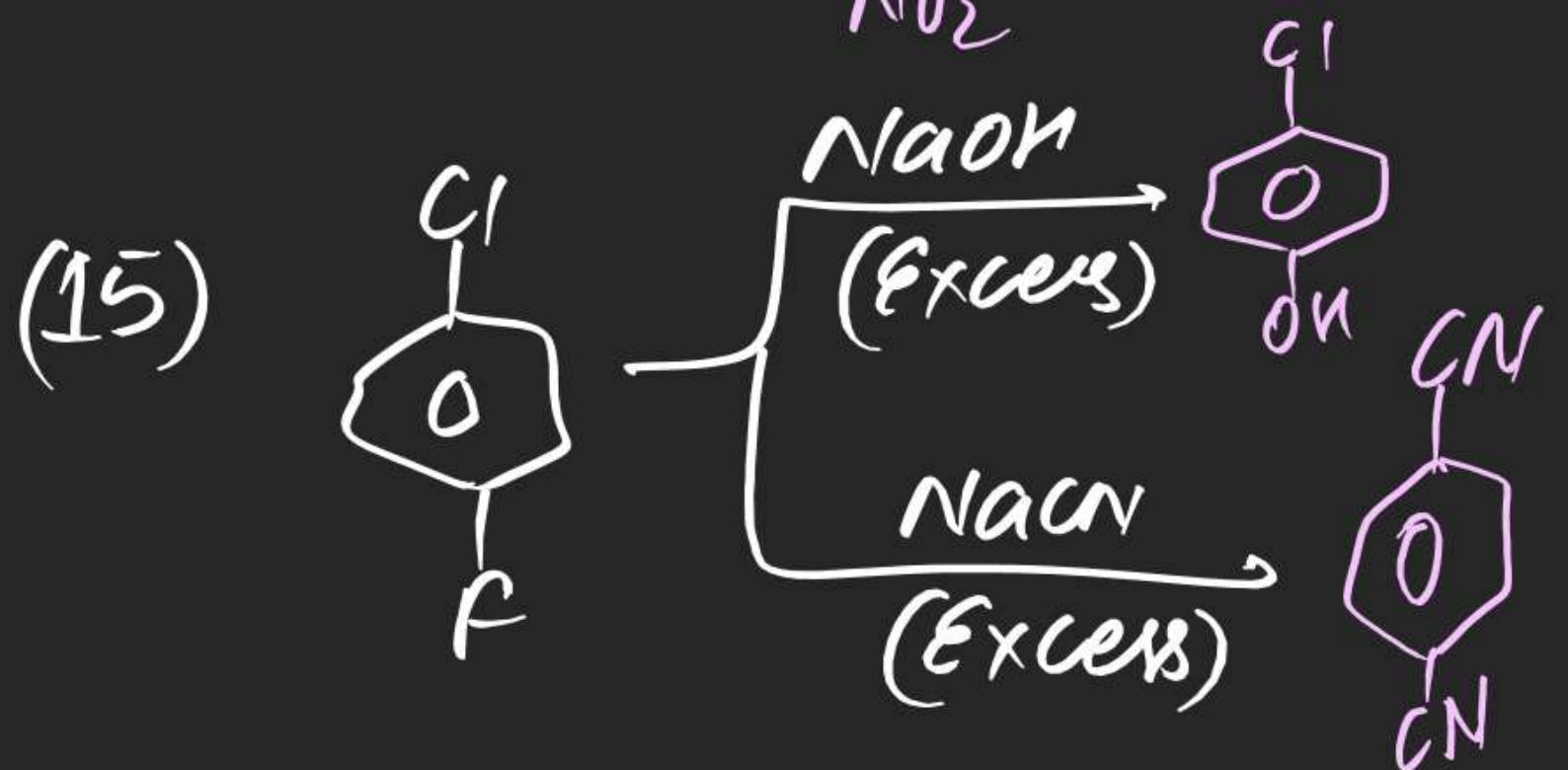
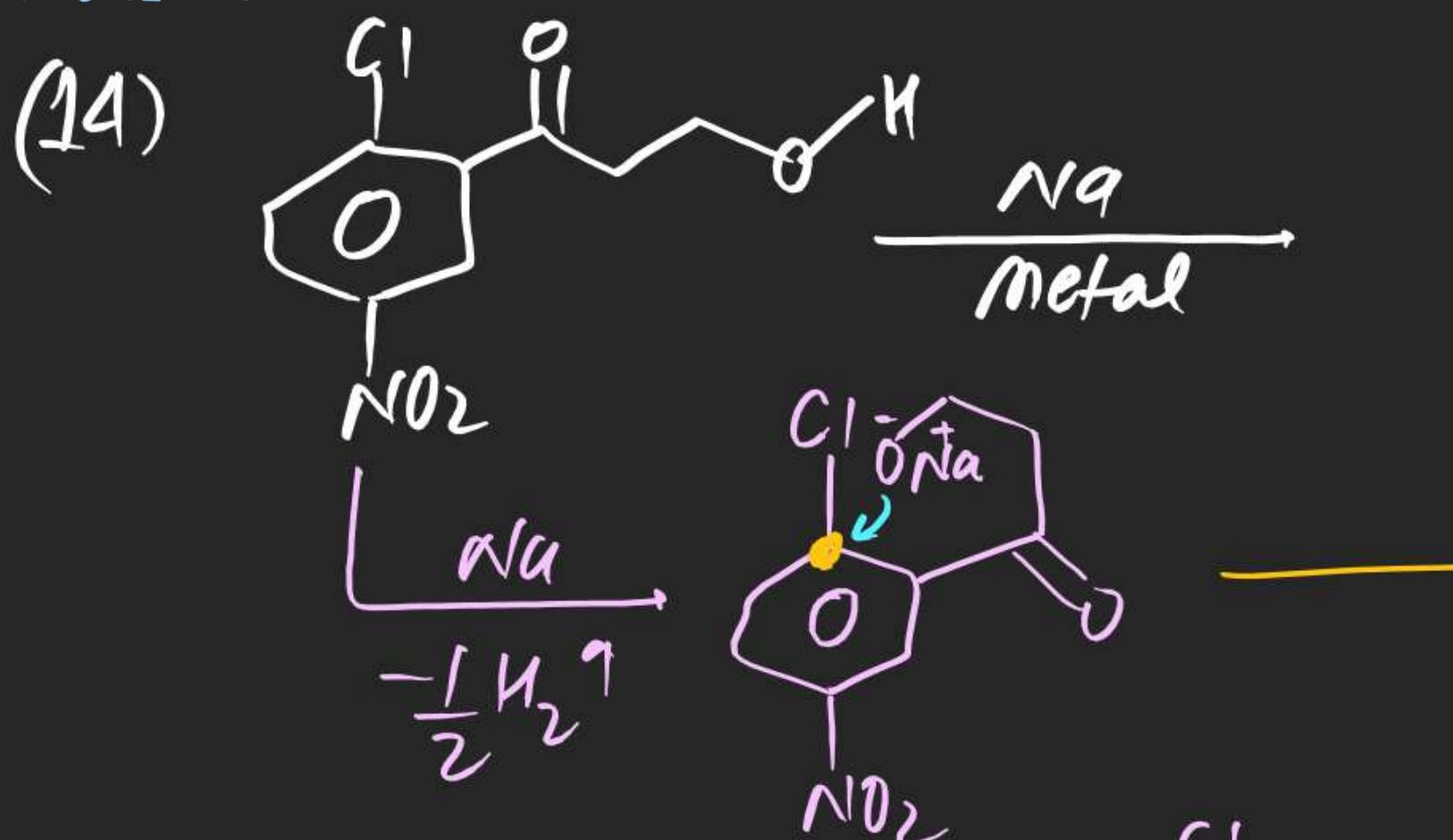
(xii) Rxⁿ is used in POC
To distinguish -NO₂
group.

M-Complex

Red when 3 NO₂
purple — 2 NO₂
yellow — 1 NO₂

Y₄ > Y₅ > Y₆ > Y₇ > Y₈ > Y₉ > Y₁₀

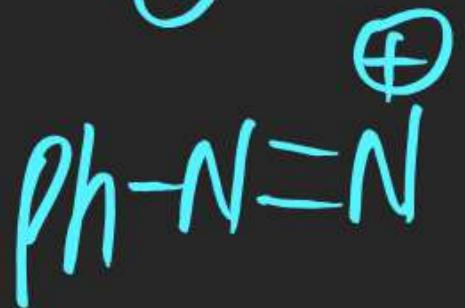
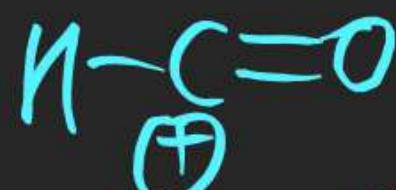
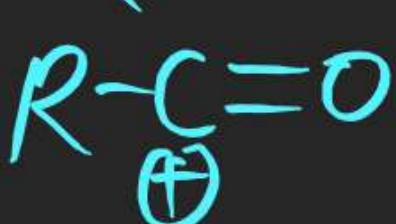
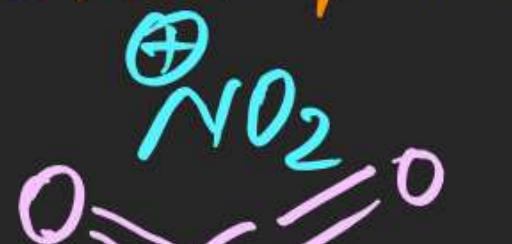




(#) Application of EAS:

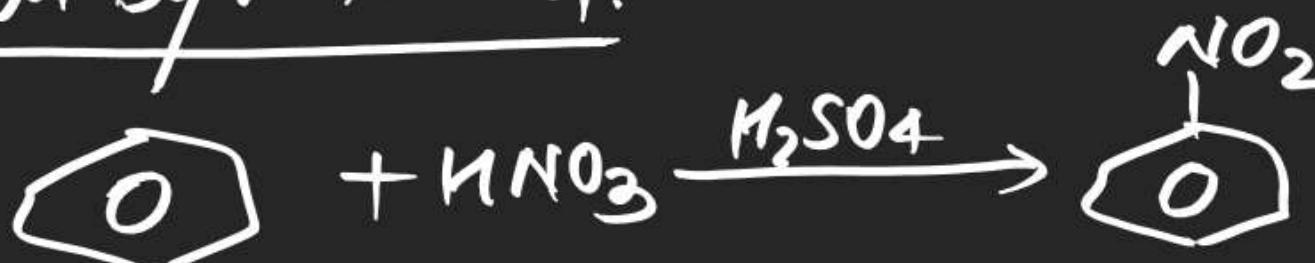
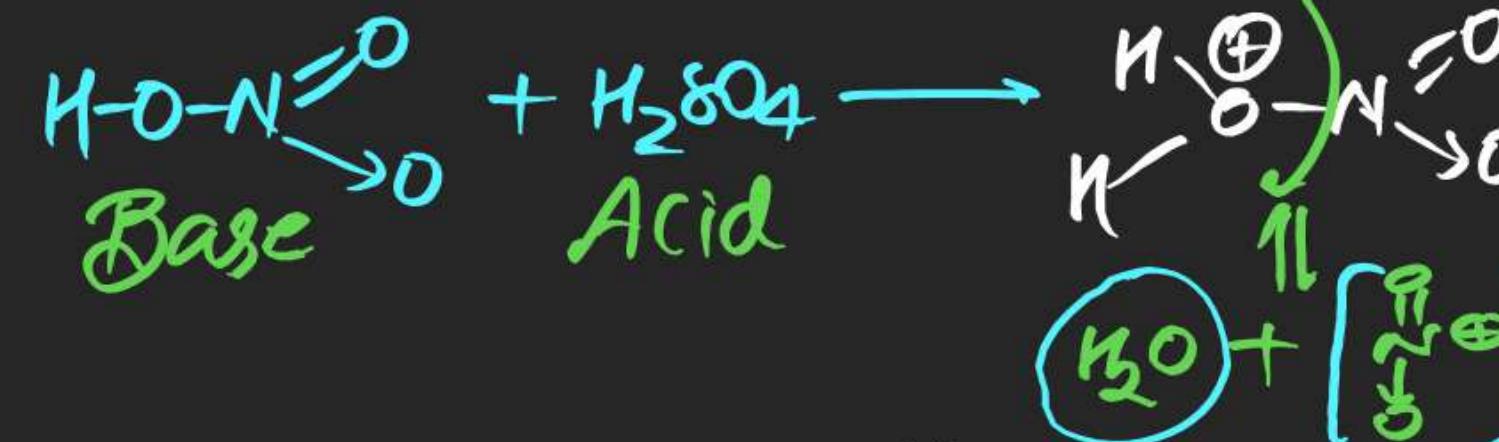
- (i) Nitration of Benzene
- (ii) Sulphonation of Benzene
- (iii) Halogenation of Benzene
- (iv) Alkylation of Benzene
- (V) Acylation of Benzene
- (VI) Formylation of Benzene
- (VII) Coupling RX^n

Electrophile (E^\oplus)



~~Mixture~~Nitration By Mix Acid:-

(2)

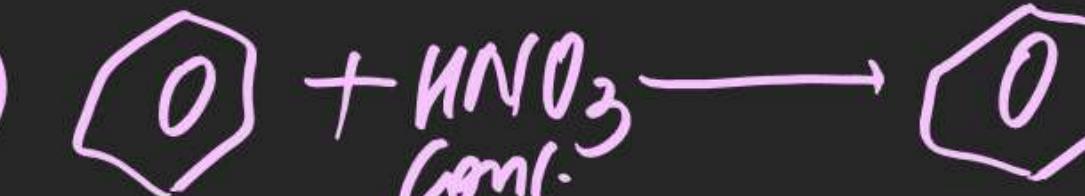
mech?:

Note:- (i) HNO_3 behaves like a Base during nitration of Benzene By Nitration mixture.

(ii) H_2SO_4 is used in generation of NO_2 & it consumes H_2O present in Rxn .

Nitration By Conc. HNO_3 :

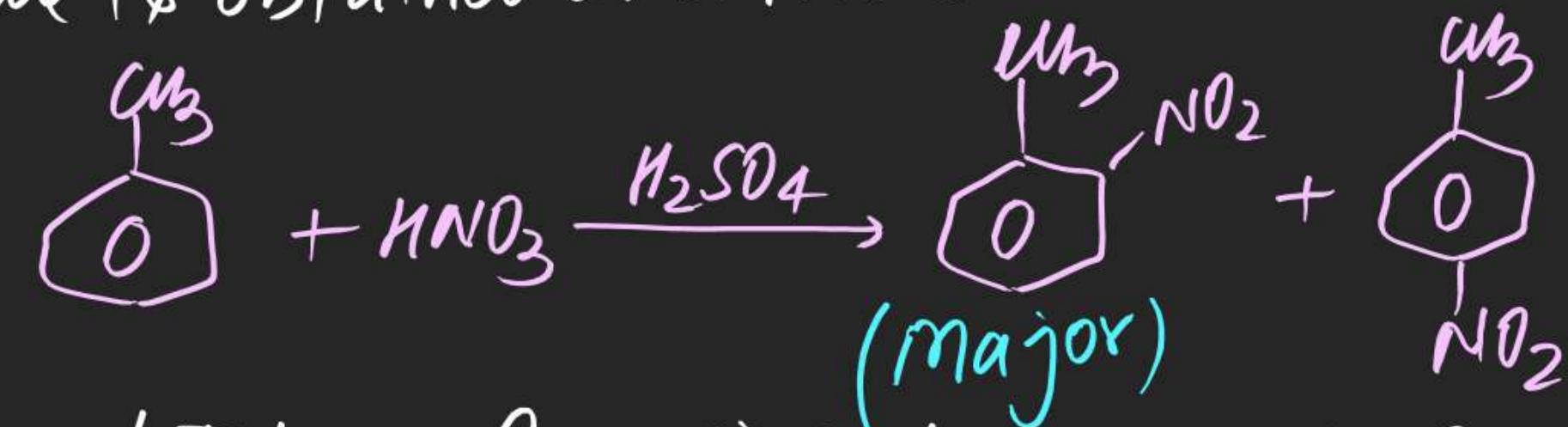
(3)

mech?:

Note (i) *Toluene*

On nitration of Toluene , O-nitro Toluene
Toluene is obtained as a product.

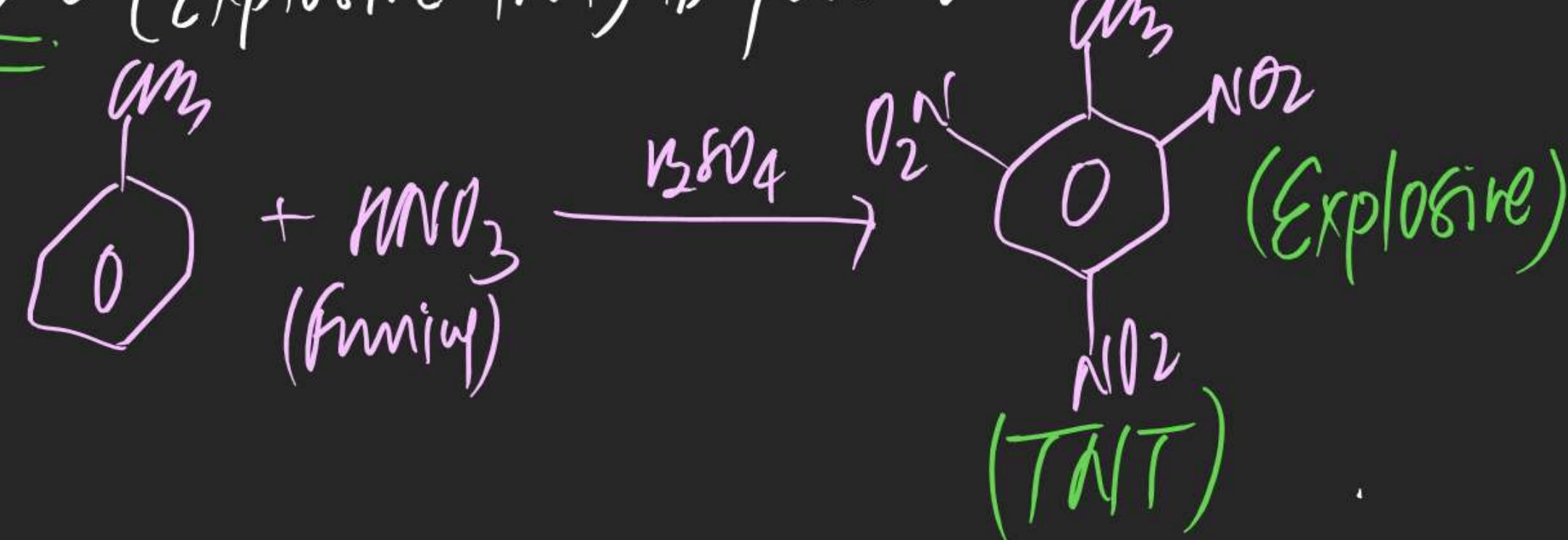
(1)



(ii)

On nitration of Toluene By using fuming HNO_3 & B_2S_0_4 , 2,4,6-Tolu
nitrone Toluene (Explosive TNT) is formed.

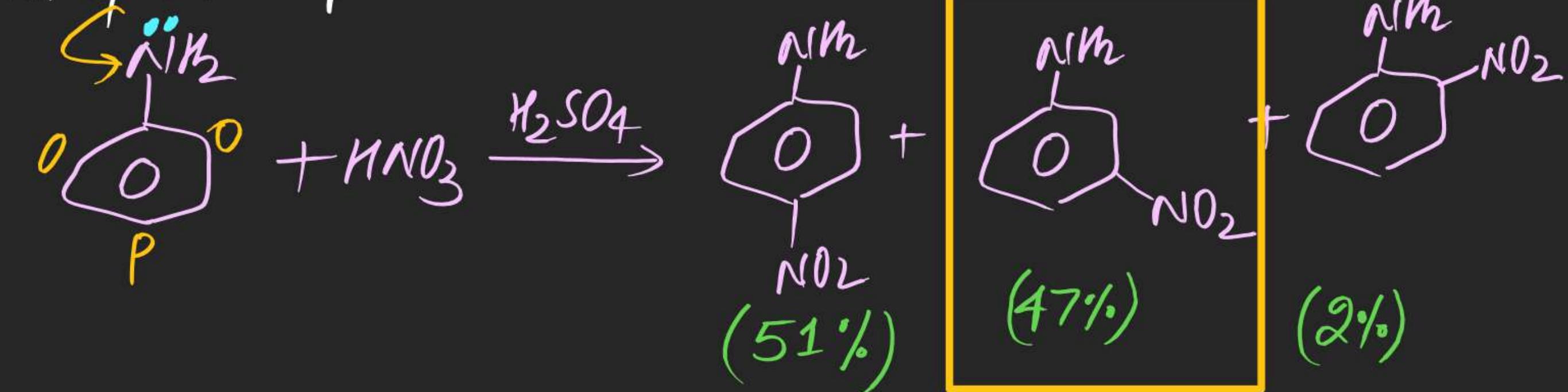
(2)



~~N.P.W.~~

(#) Nitration of Activated Aromatic Compound gives appreciable amount of meta product.

(3)

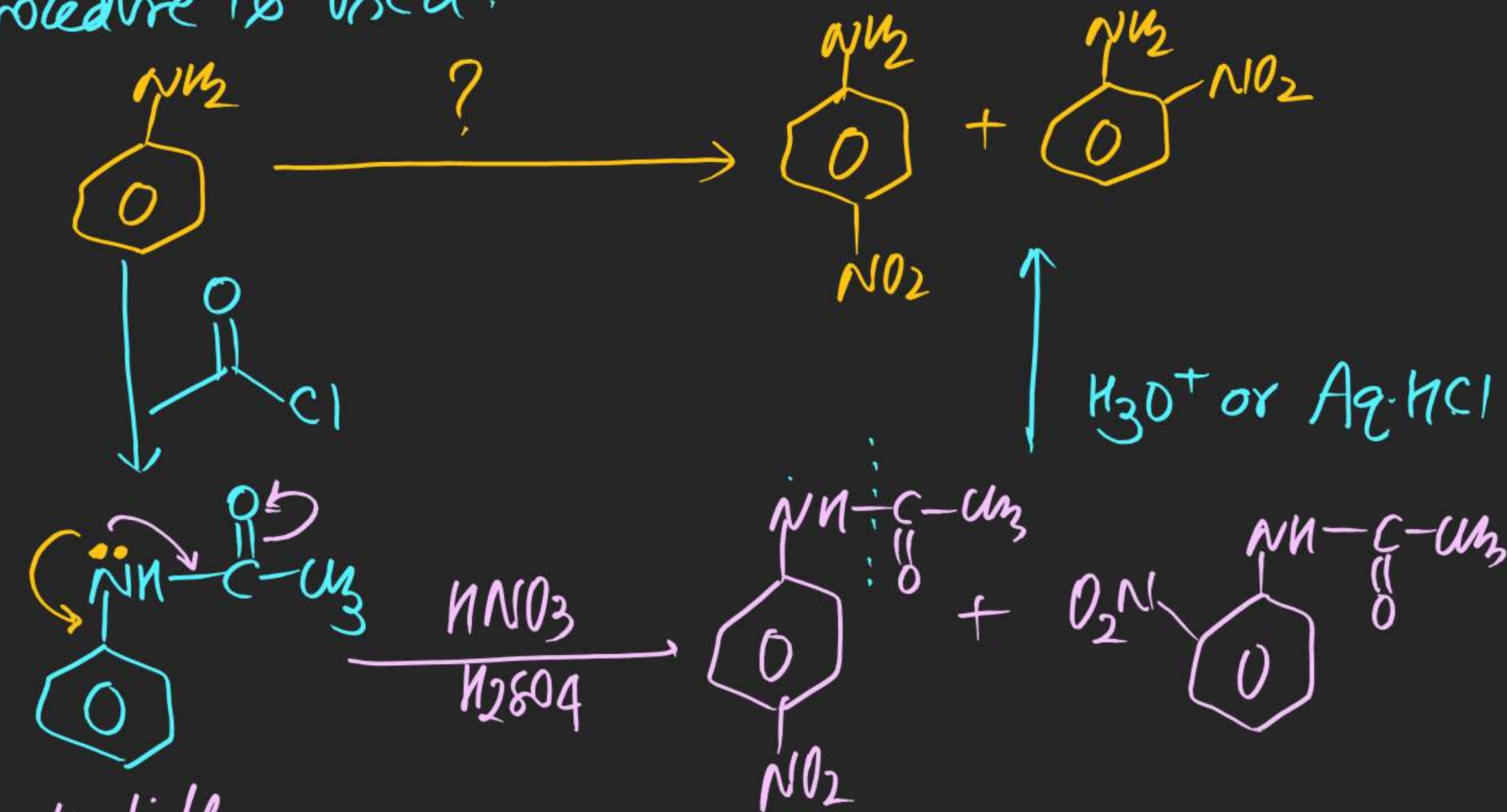


\Rightarrow Formation of 47% meta product can be explained as shown.



~~(#)~~ Direct nitration of highly Activated Compound is not carried out
following procedure is used.

(To avoid
m-product) (4)



Acetanilide
Mod. Activating (O & P)

(#) Sulphonation of Benzene:

→ on Sulphonation of Benzene, Benzene Sulphonic Acid is obtained as a product.

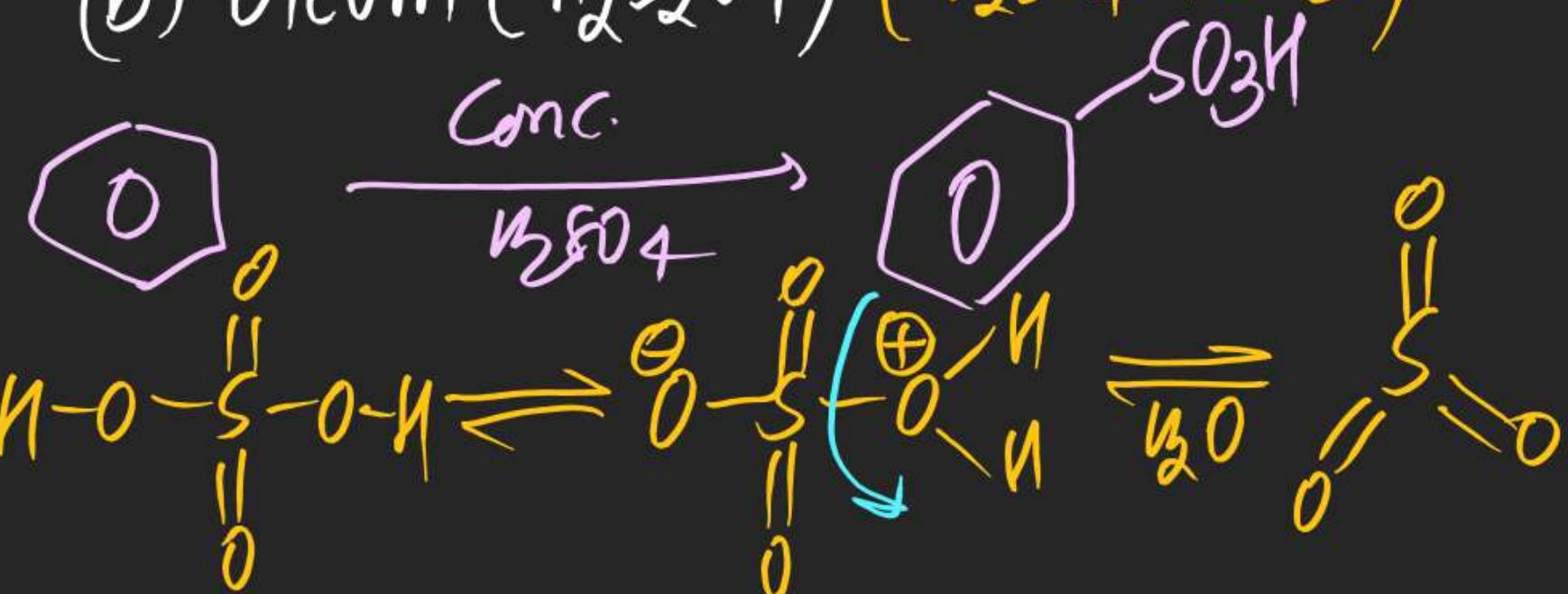


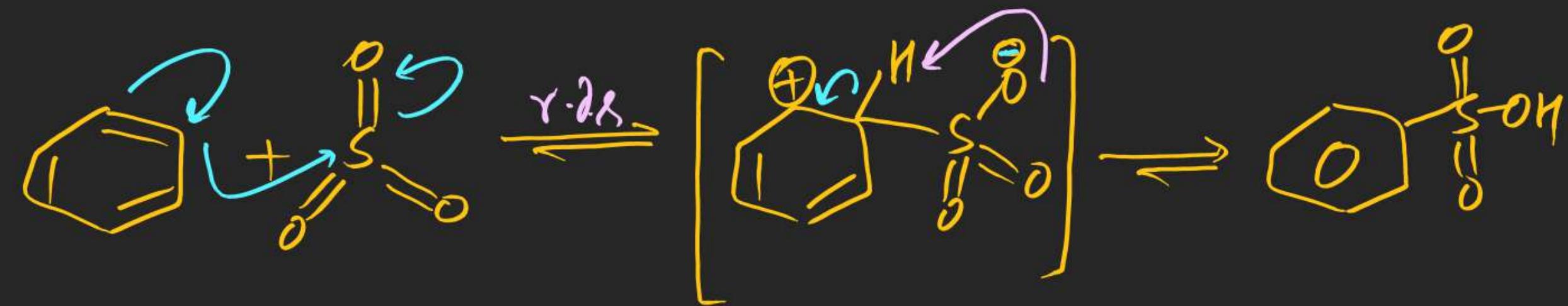
P may be

(a) Conc. H_2SO_4

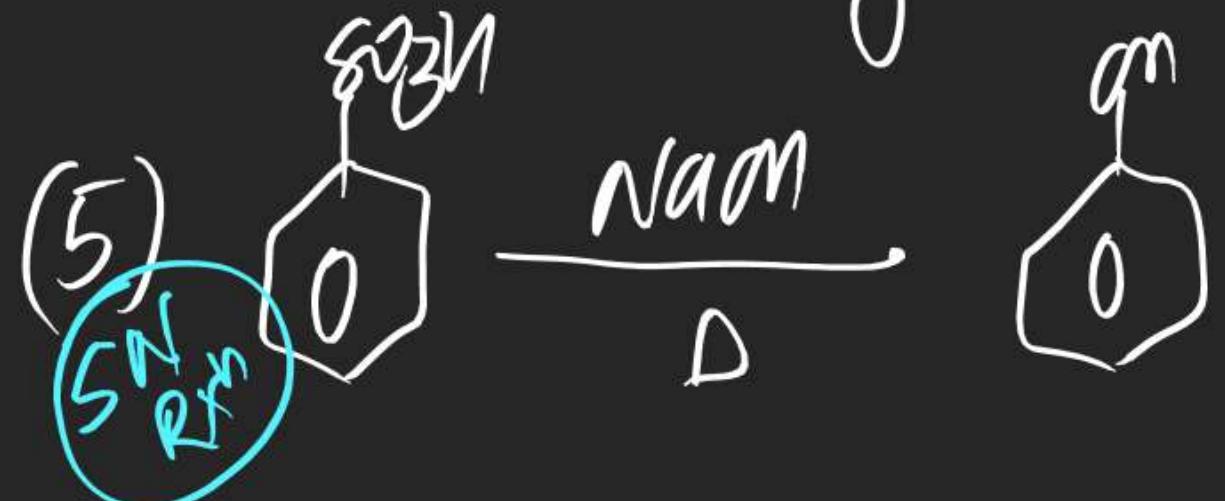
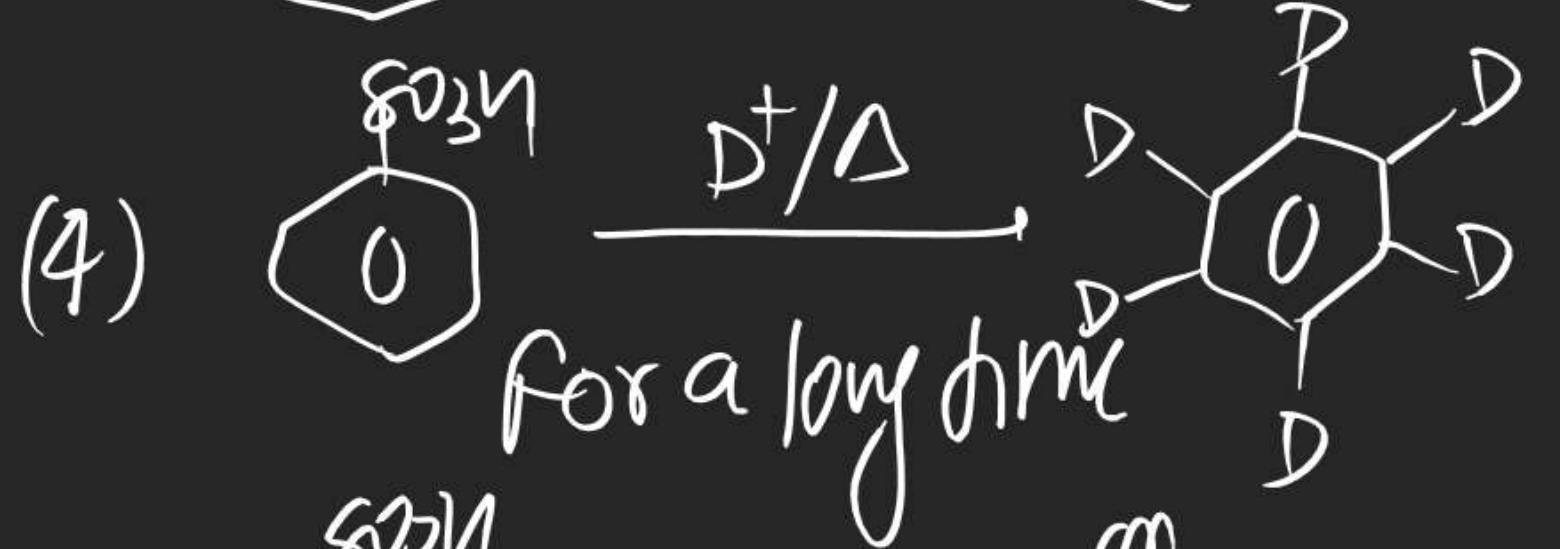
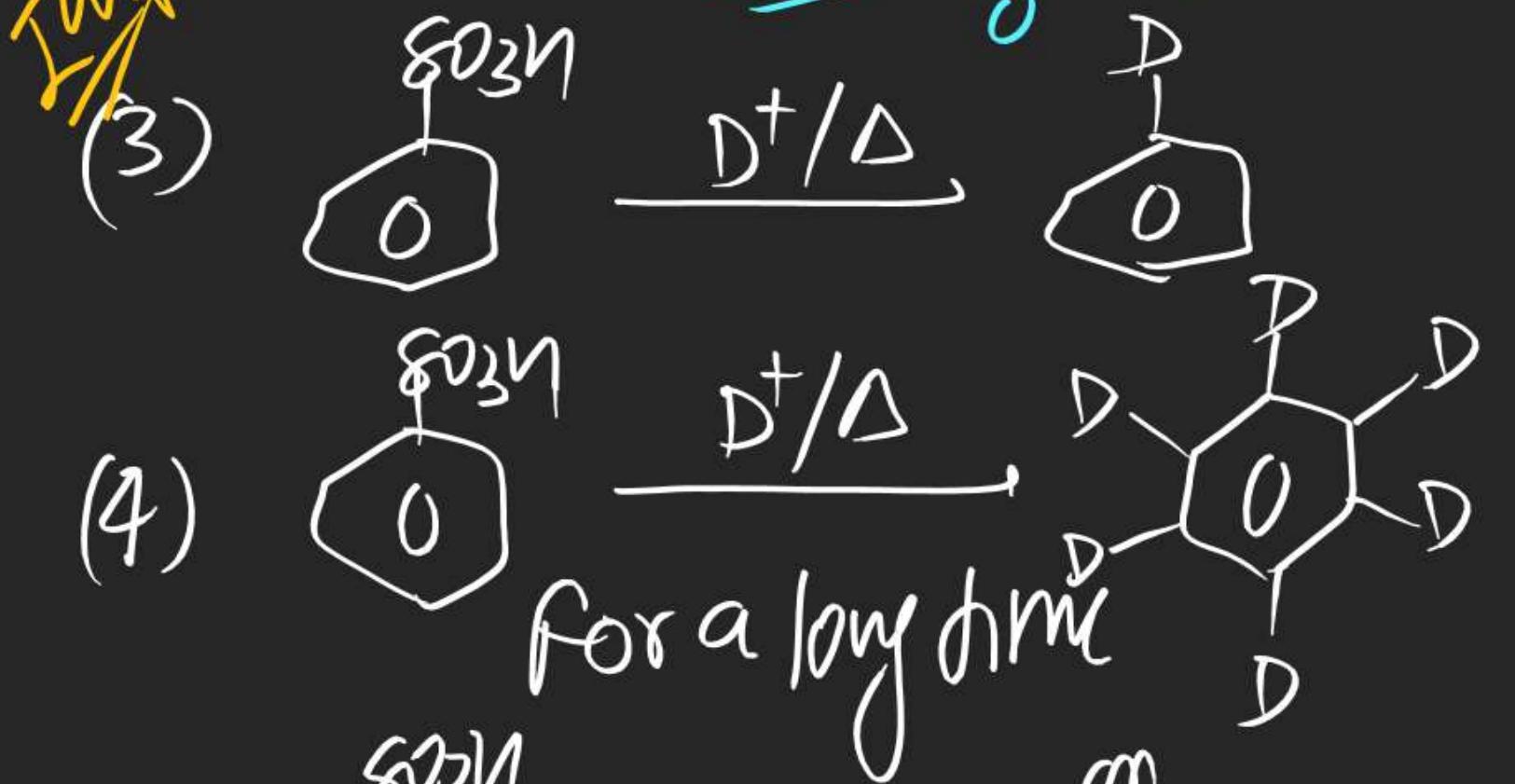
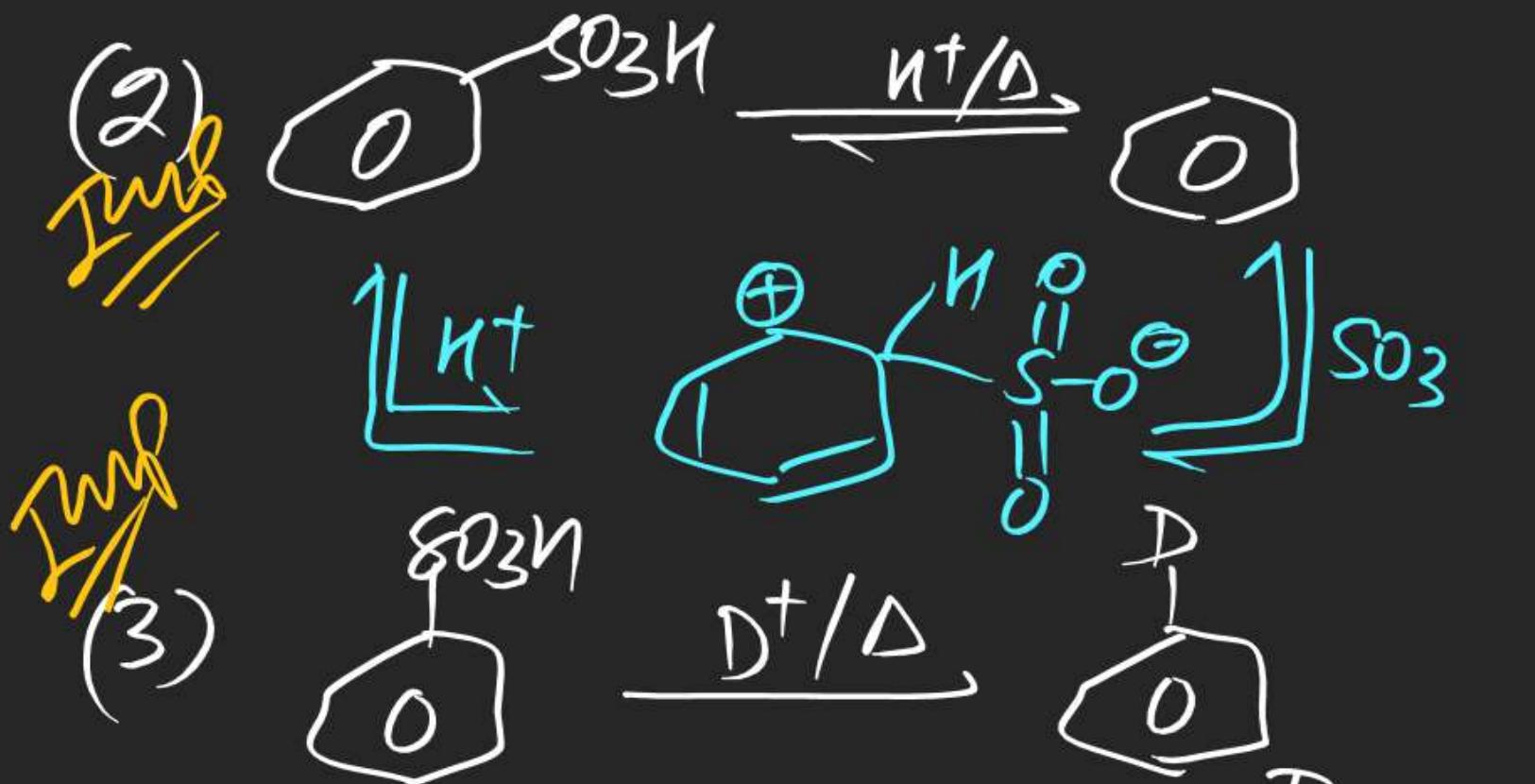
(b) Oleum (HgS_2O_7) ($\text{H}_2\text{SO}_4 + \text{SO}_3$)

(1)





- Note
- (i) δO_2 attacking electrophile
 - (ii) Reversible Rxn
 - (iii) Kinetic isotopic effect observed
 $\gamma_{CH_6} > \gamma_{CD_6} > \gamma_{CT_6}$
 - (iv) No chance of Polysulphonation because product is less electron dense than reactant.
 - (v) Desulphonation can also be carried out.

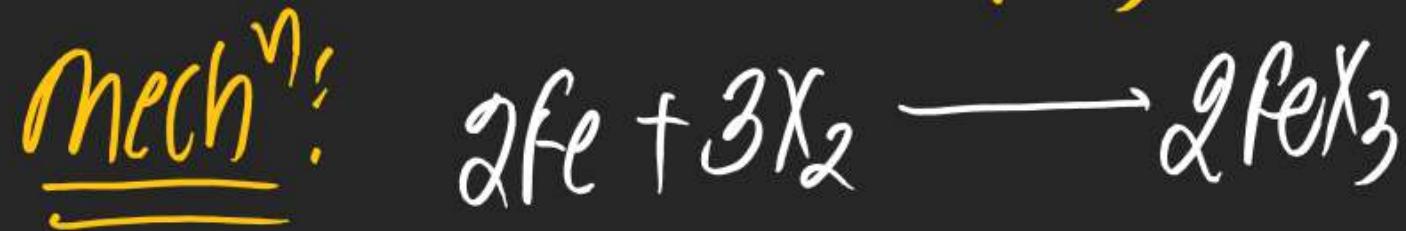
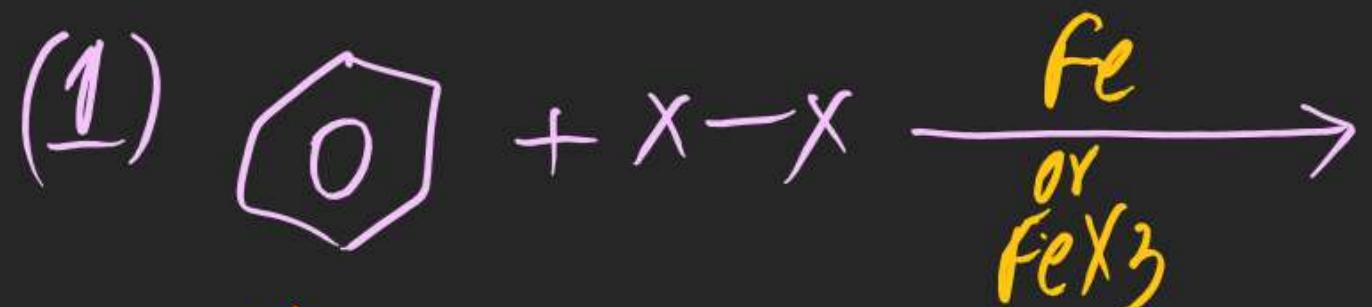


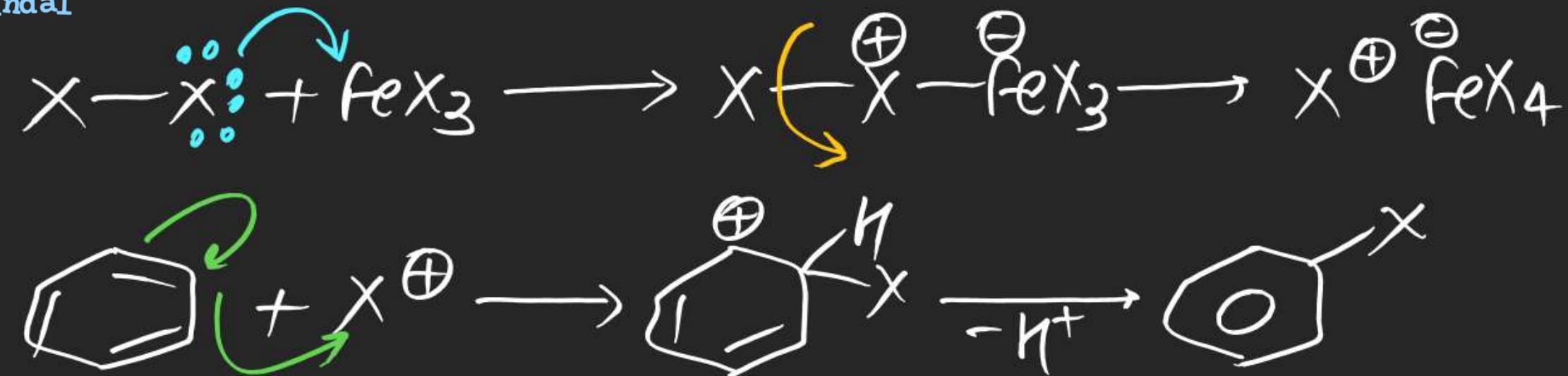
(#) Halogenation of Benzene!

\Rightarrow Benzene on halogenation gives haloBenzene as a Product.



- P may be
- (a) X_2 / Lewis Acid
 - (b) $X-X'$ / Lewis Acid
 - (c)



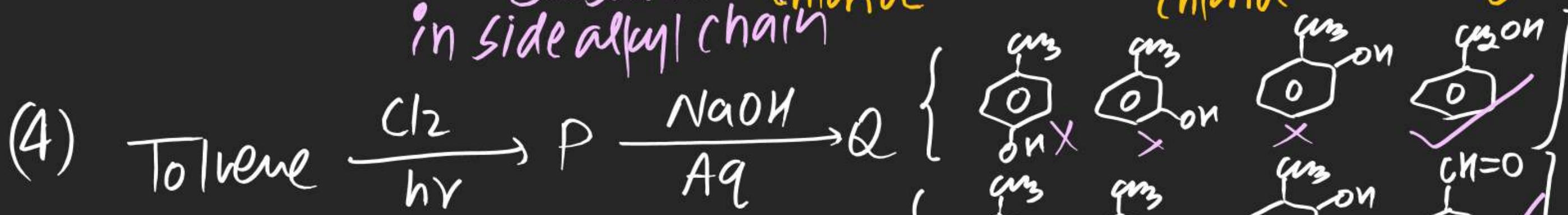
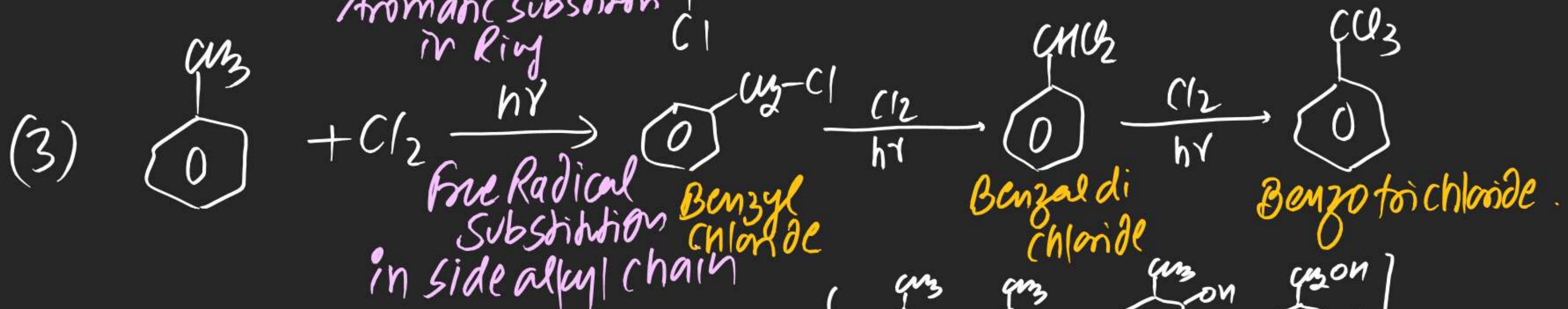
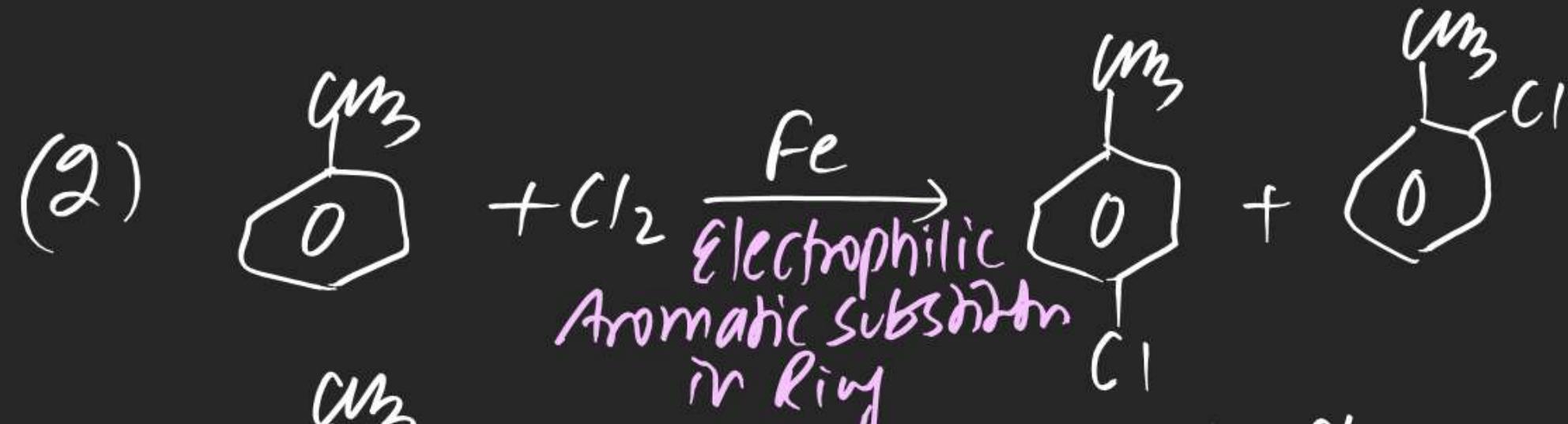


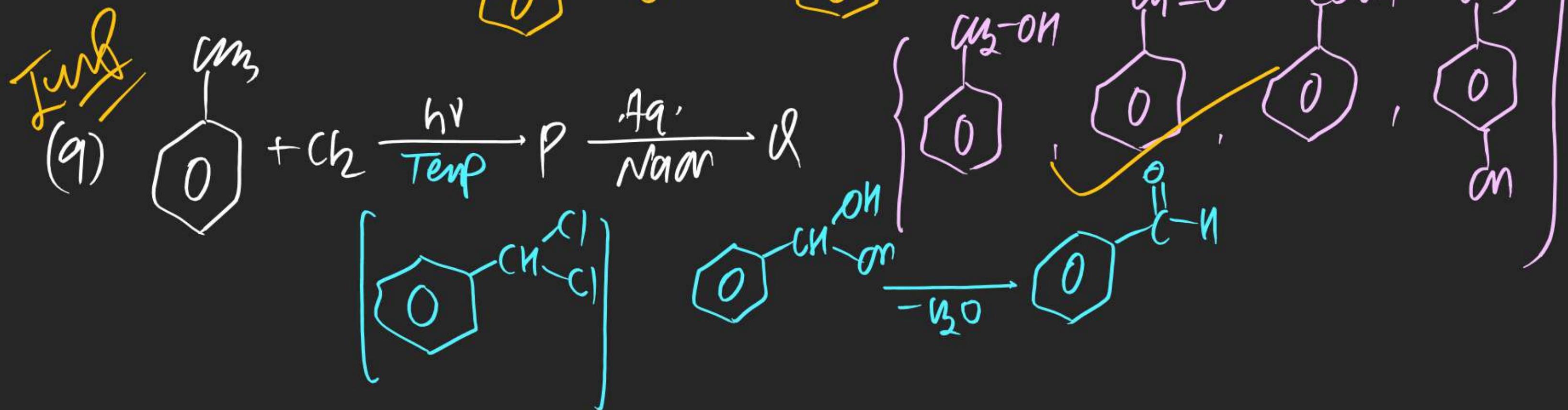
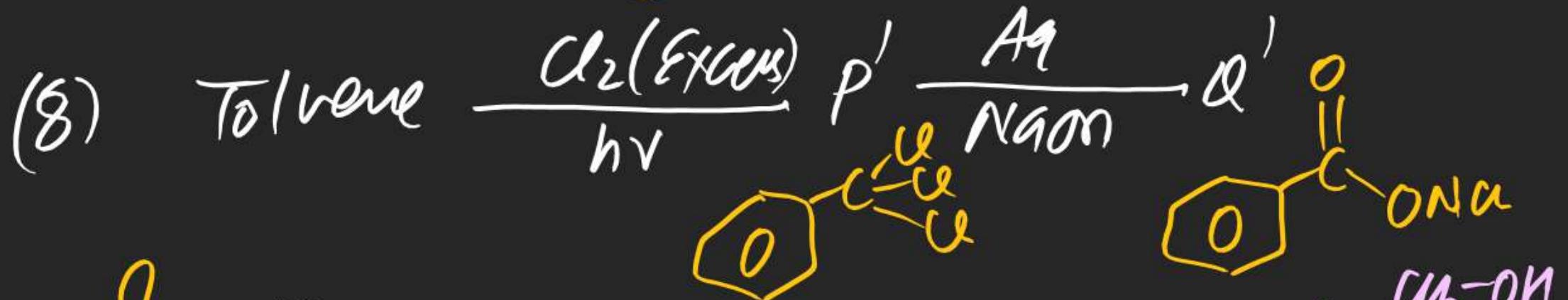
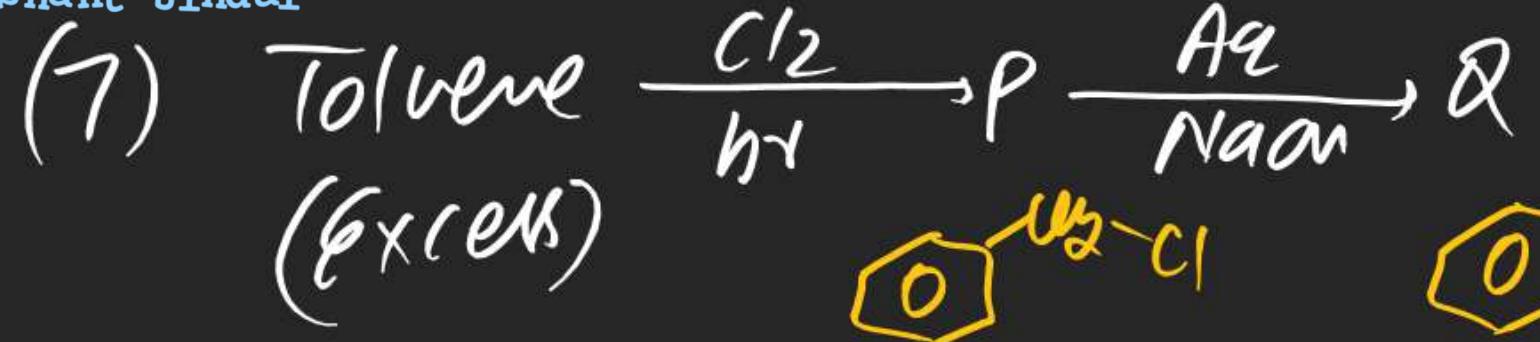
Note (i) attacking electrophile is X^+

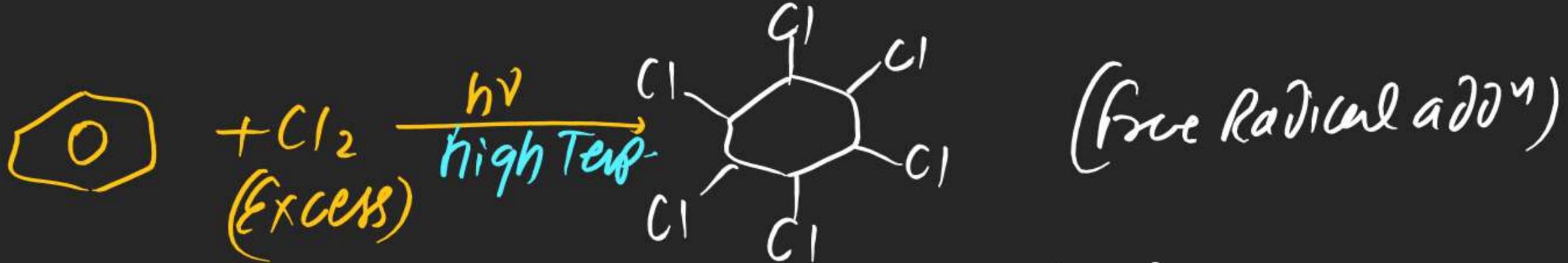
(ii) No chance of polyhalogenides, because product is less electron dense than Reactant.

(iii) Lewis Acid used is known as halogen carrier.

(iv) No halogen carrier is required in case of Activated Aromatic Compounds.





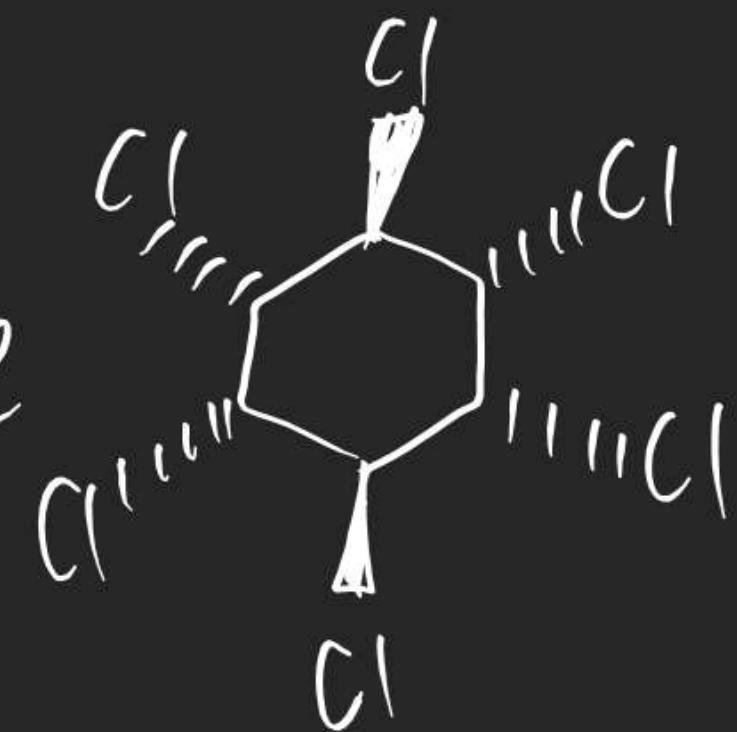
~~M(10)~~

(*) Benzene Hexa chloride

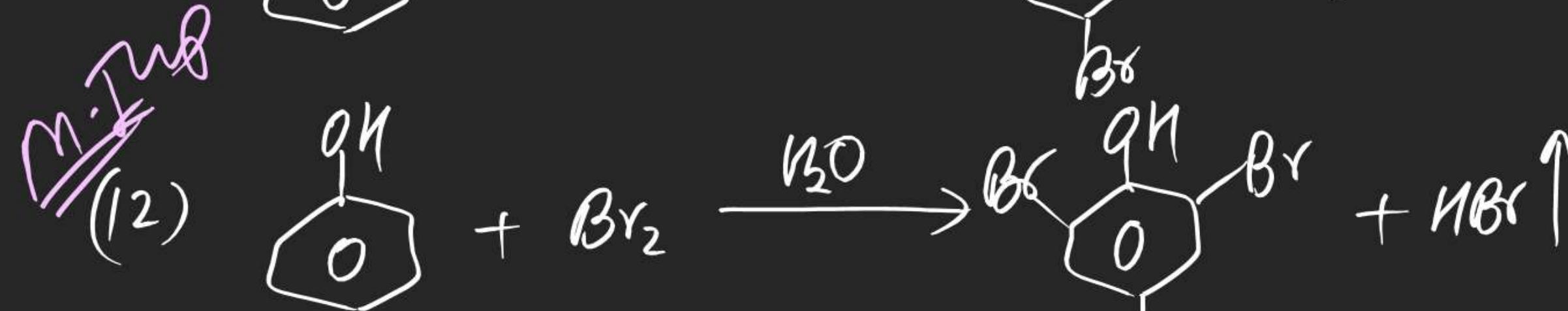
(*) BHC / 666 / lindane

(*) mol. formula (C₆H₆Cl₆)

its γ -isomer is Gammexene

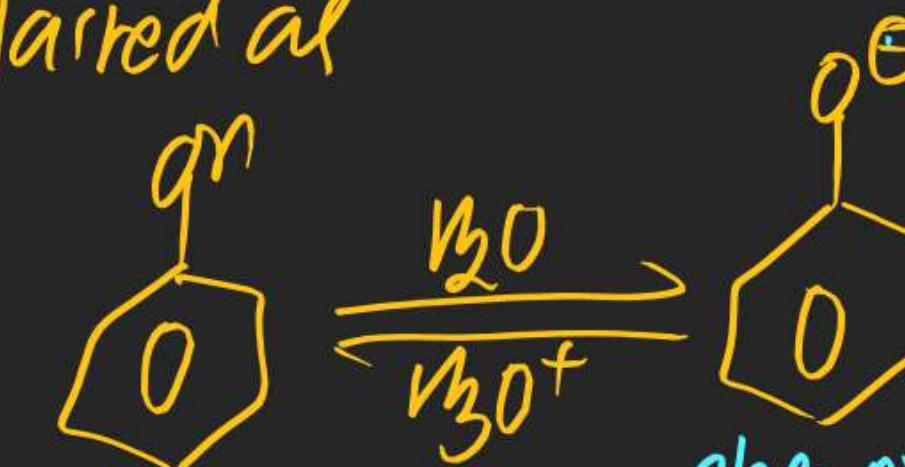


(Insecticide)



white ppt (2,4,6-Tri Bromo Phenol)

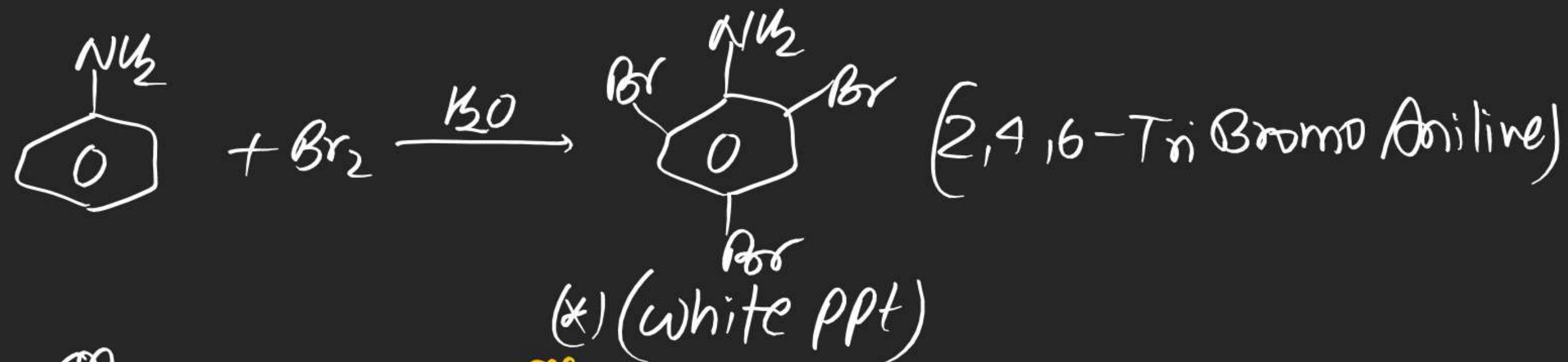
It can be explained as



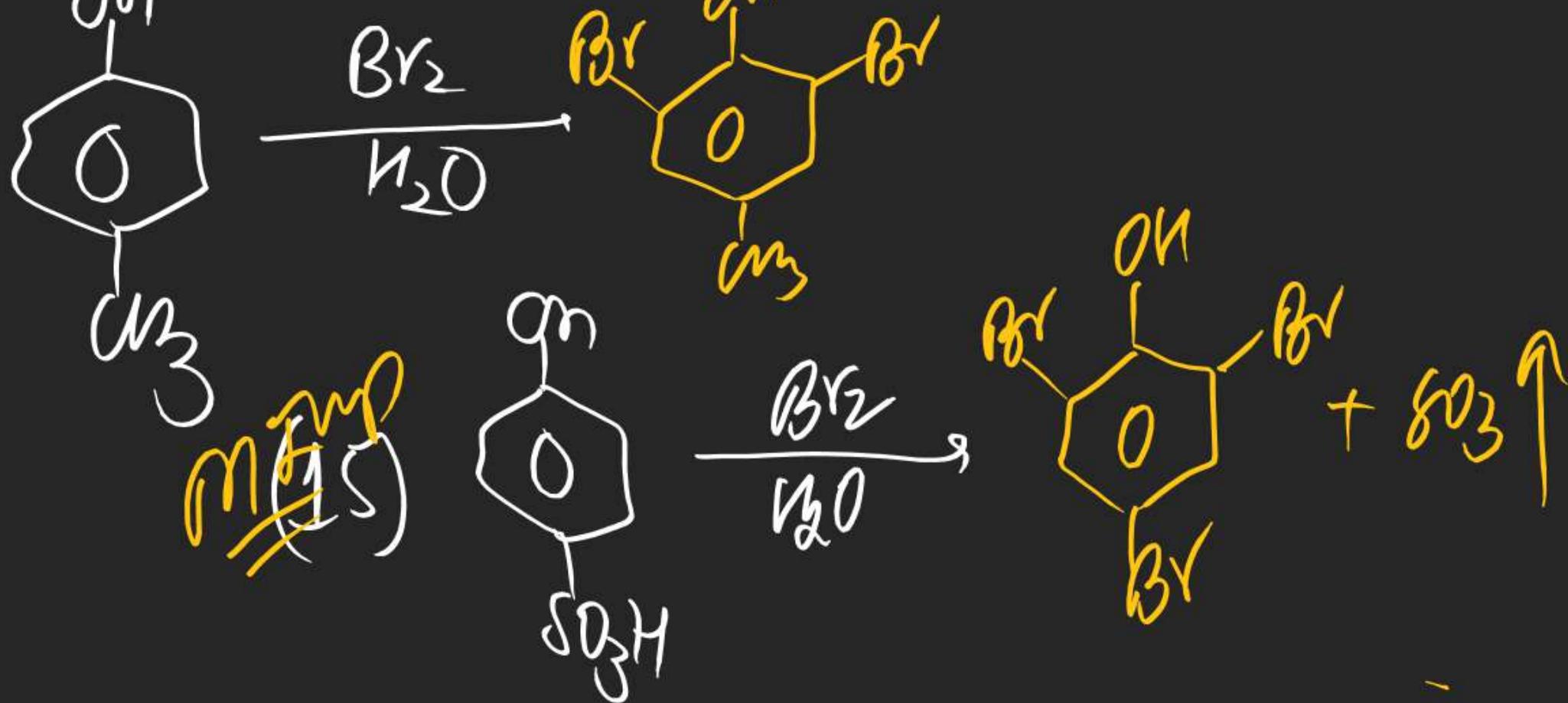
phenoxide ion
(highly Activated) hence poly halogenation takes place

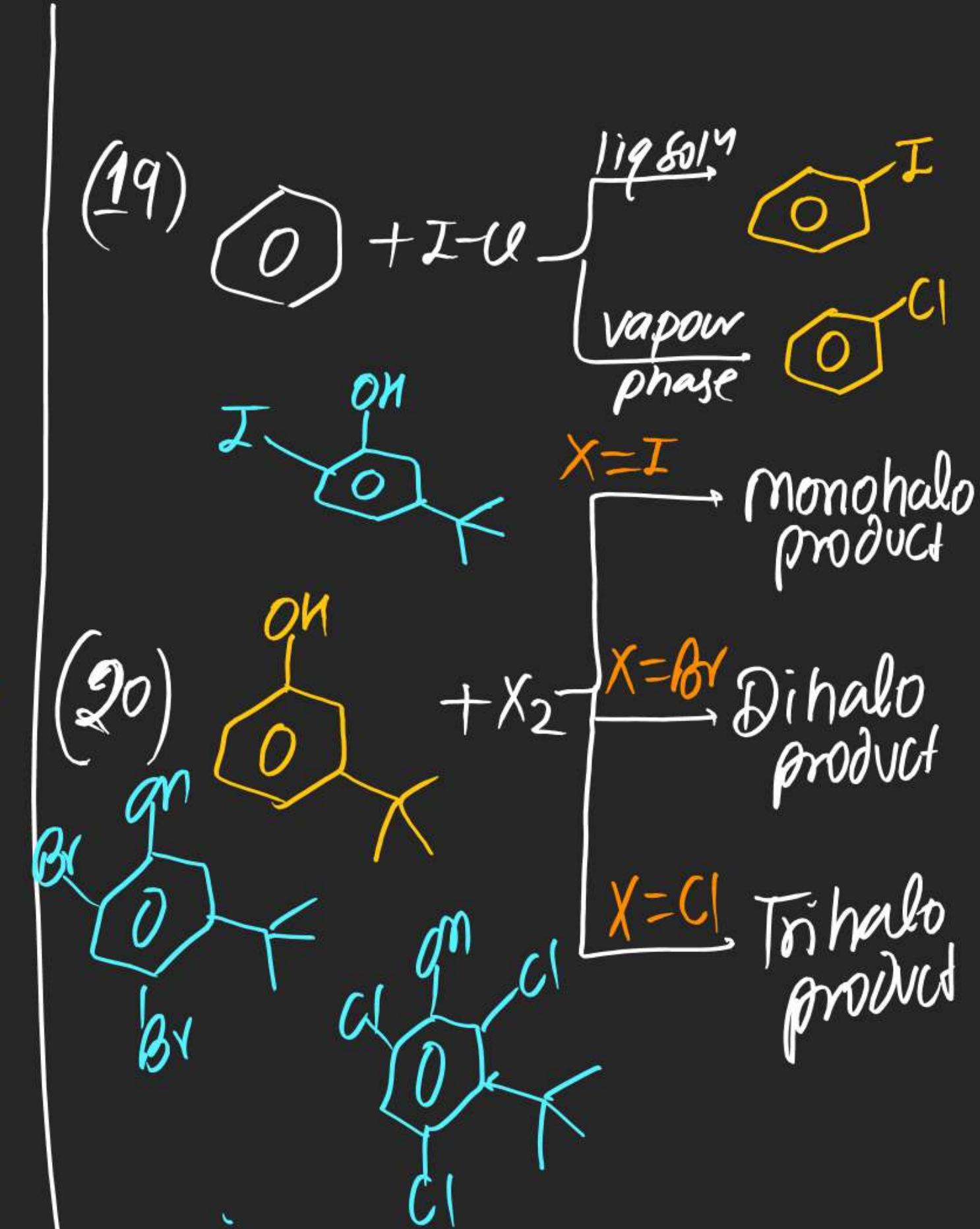
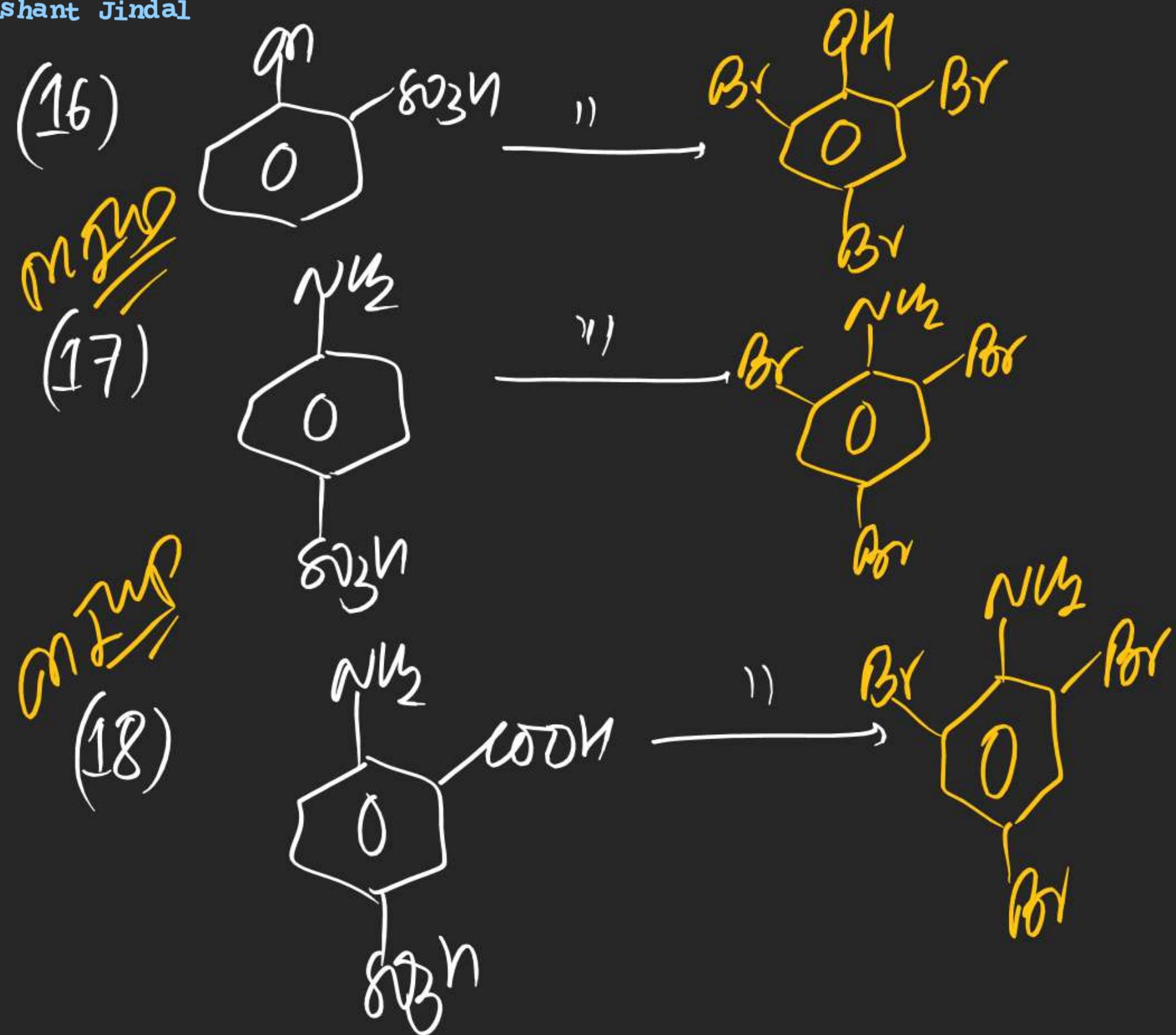
Note Rxn of Ph-OH & Br₂/H₂O is used in POC as a Test of phenol.

~~Expt~~
(13)



(14)

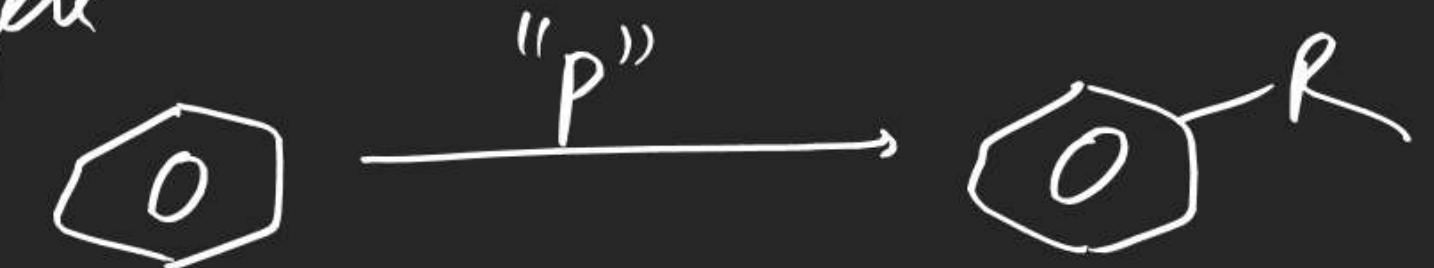






Alkylation of Benzene [F-Craft Rxn]

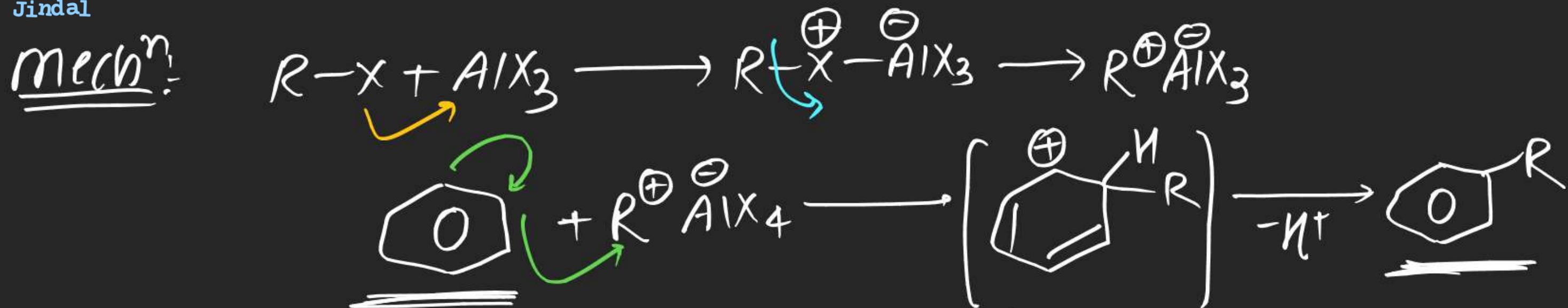
⇒ Formation of alkyl Benzene from Benzene is known as alkylation of Benzene



P may be

- (i) R-X / Lewis Acid
- (ii) R-ONa / Acid
- (iii) alkene / H^+ or Lewis Acid





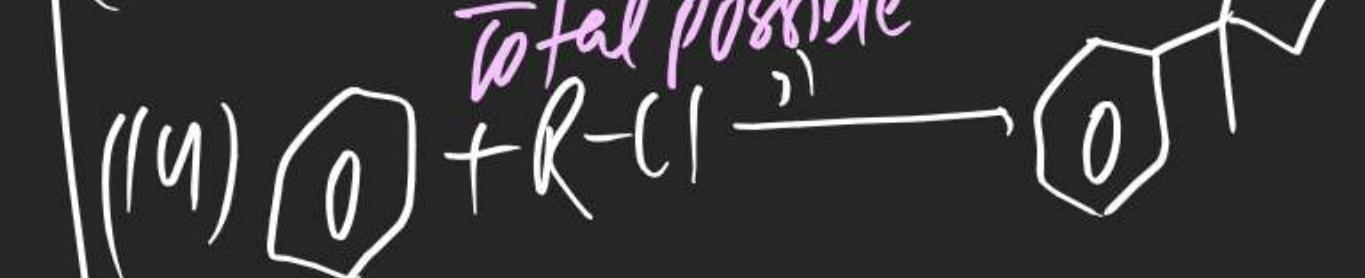
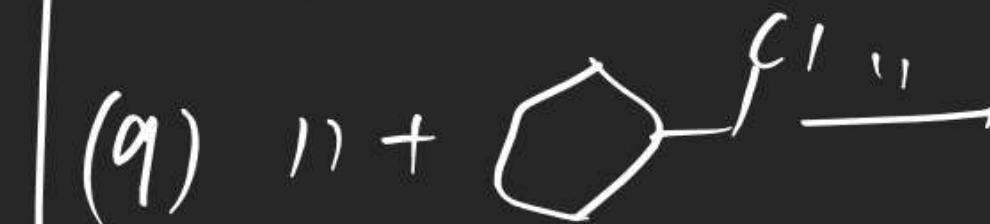
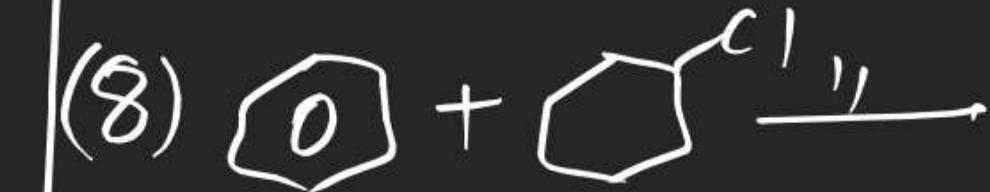
Note (i) Attacking electrophile is R^+ Areonium ion

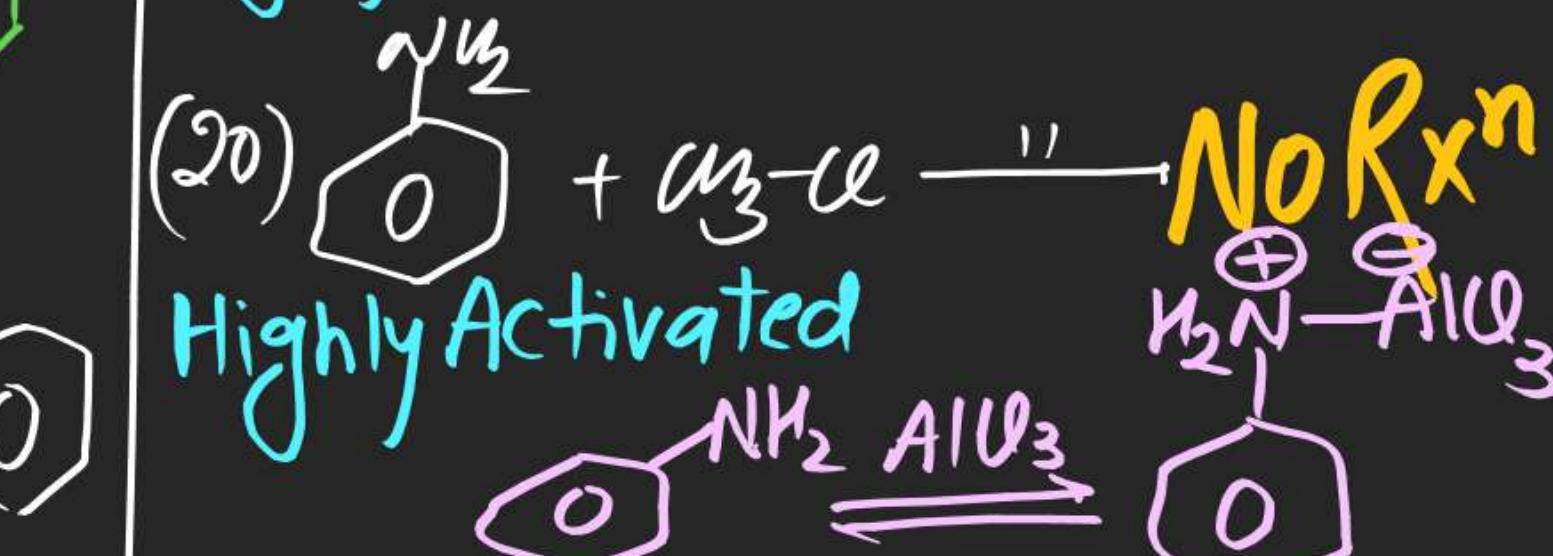
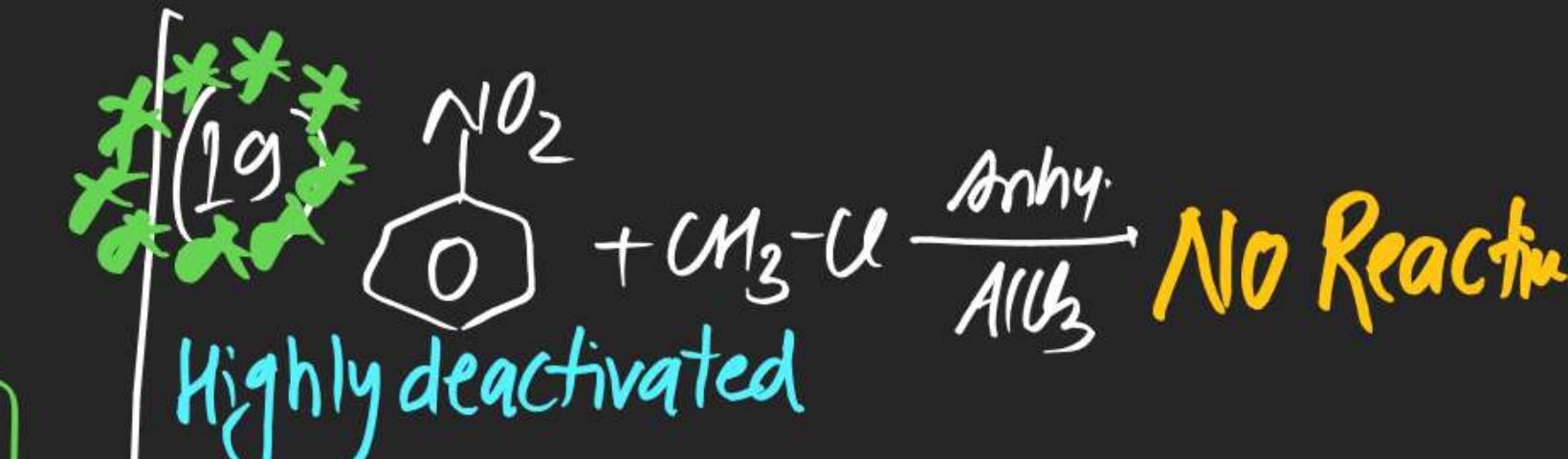
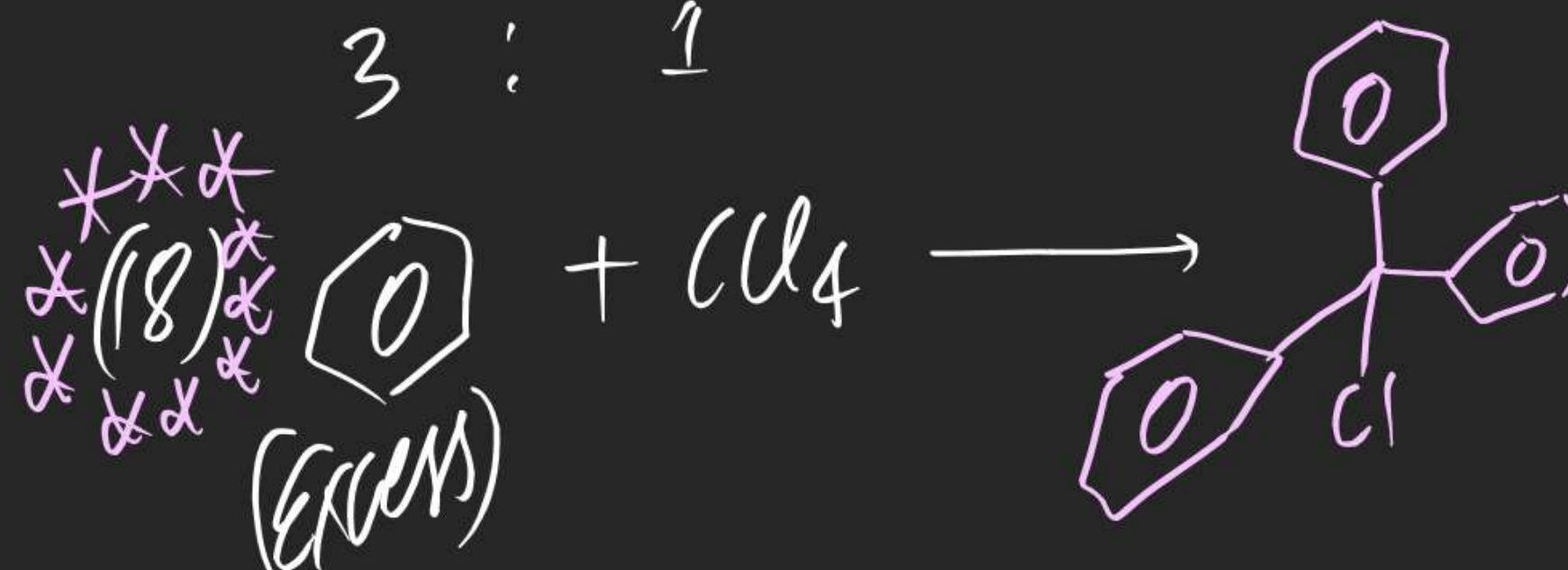
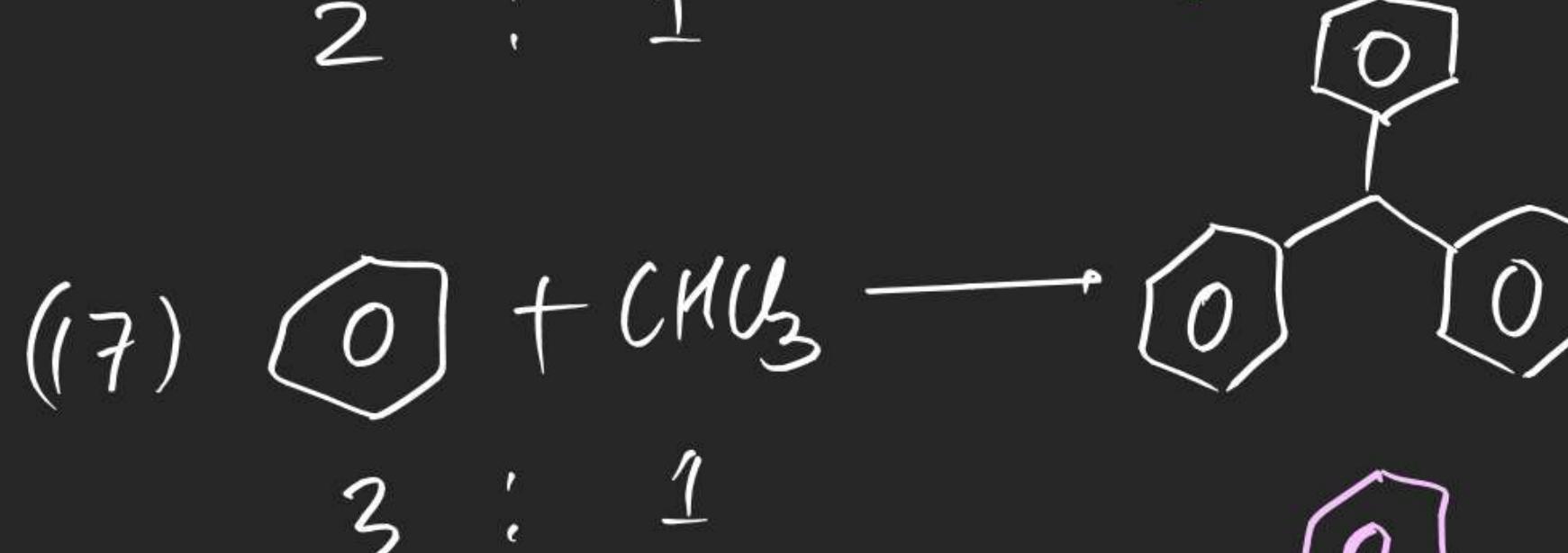
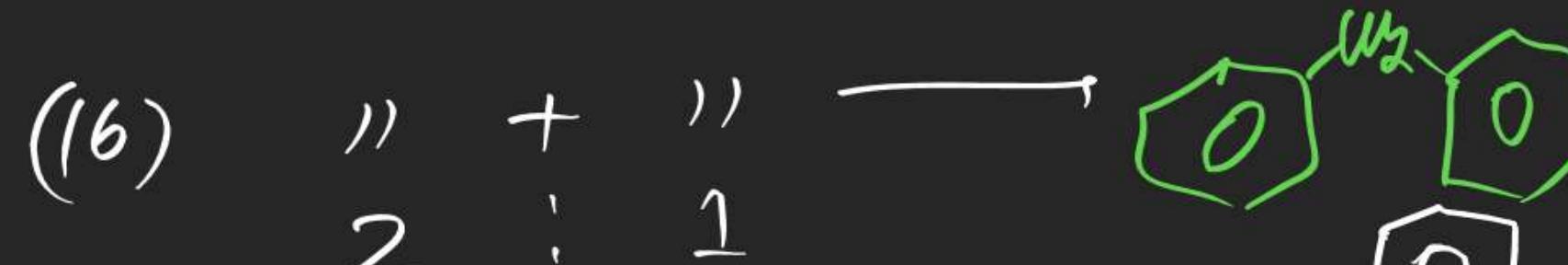
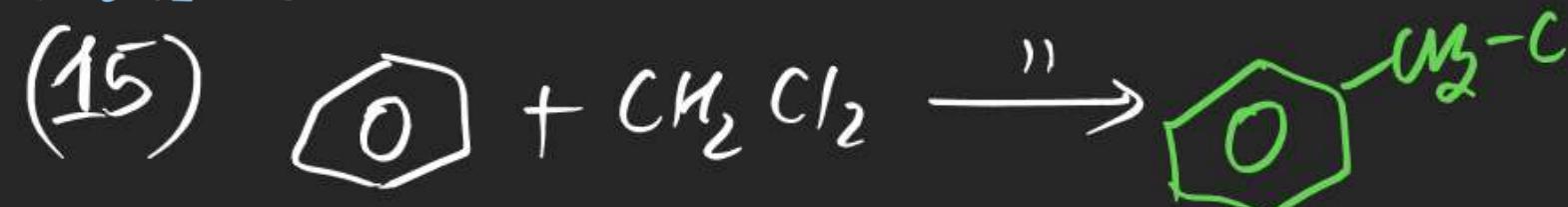
(ii) Corbocation may show Regenert ($AlC_6F_5, BF_3\cdots$)

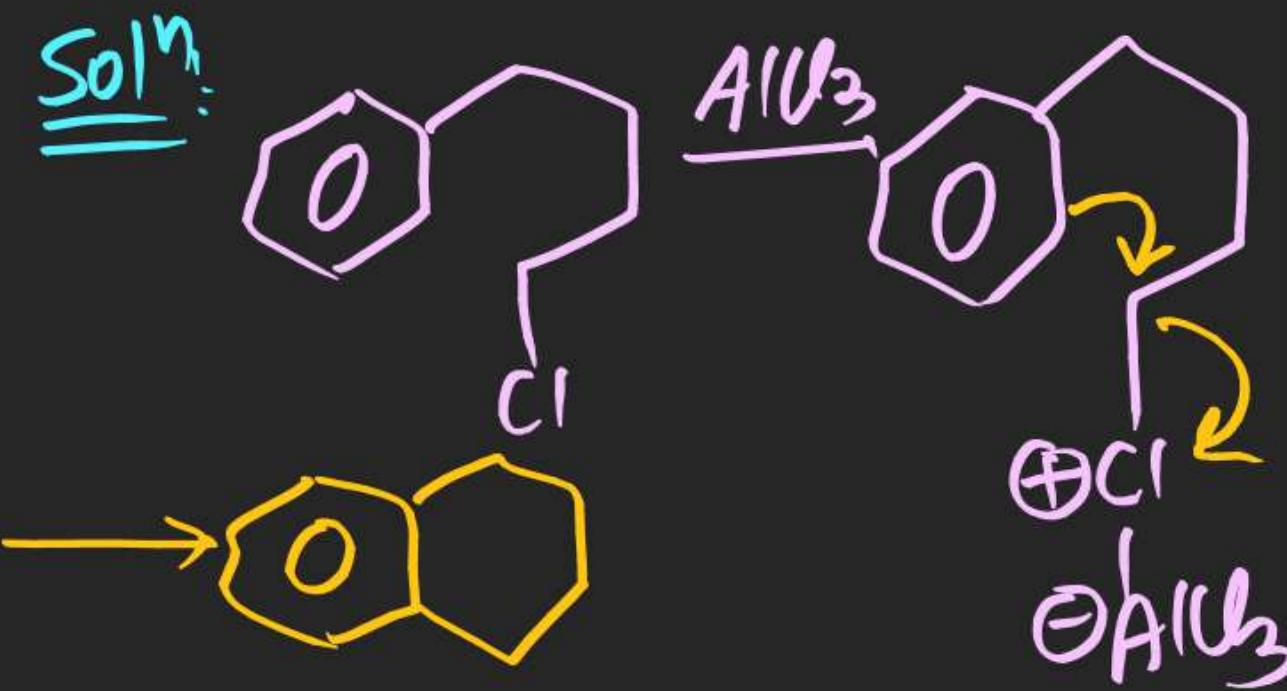
(iii) Polyalkylation is always possible due to having higher electron density than Reactant

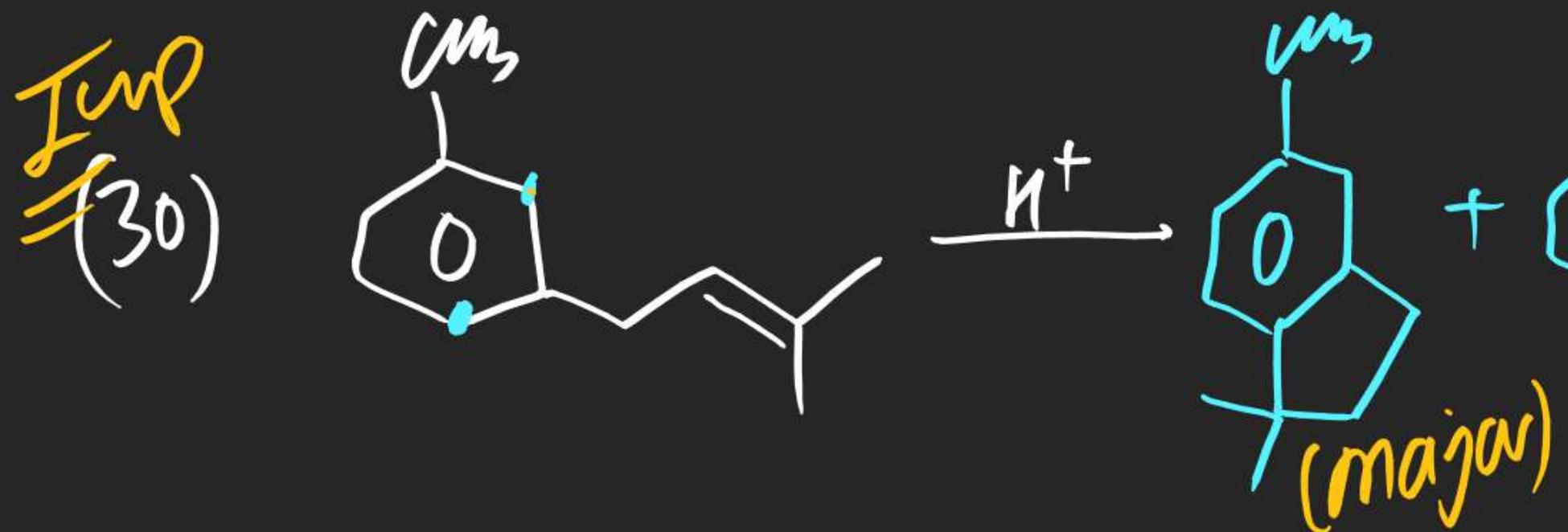
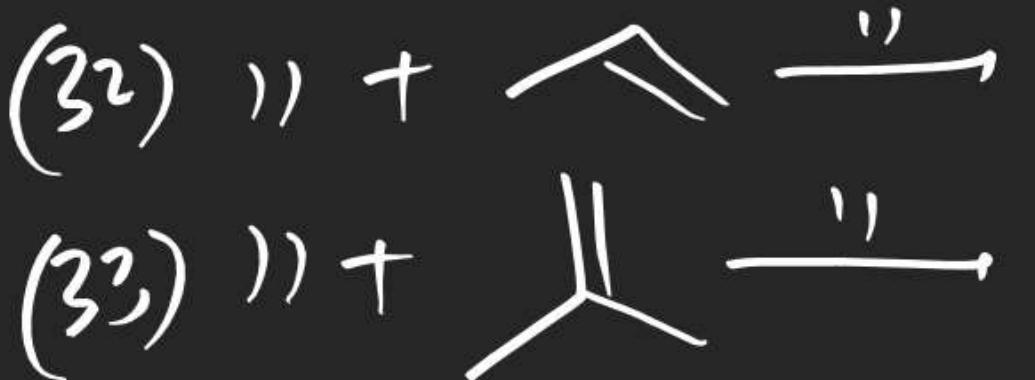
~~(iv)~~ Highly Activated & Highly dechlorinated Aromatic Compounds don't Show Friedel-Crafts RX^n .

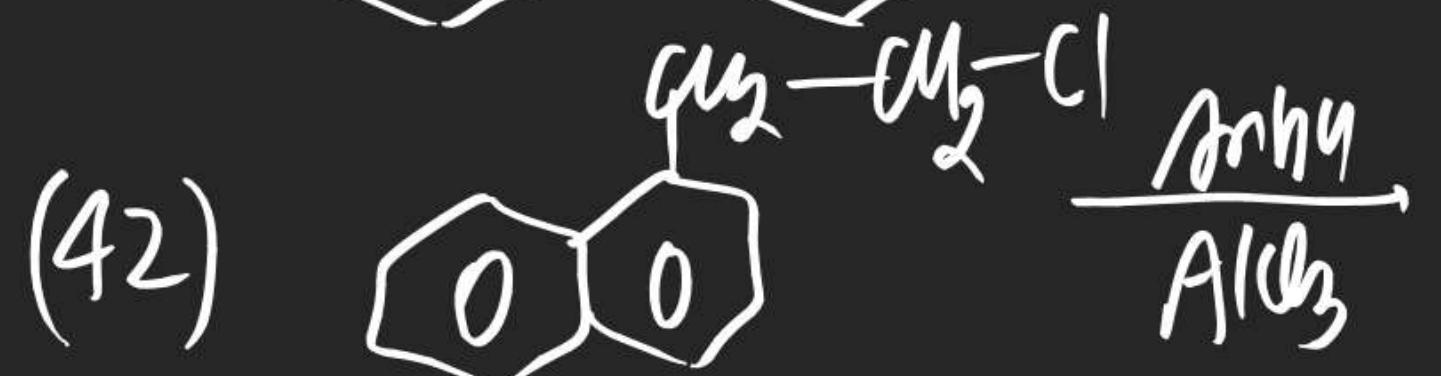
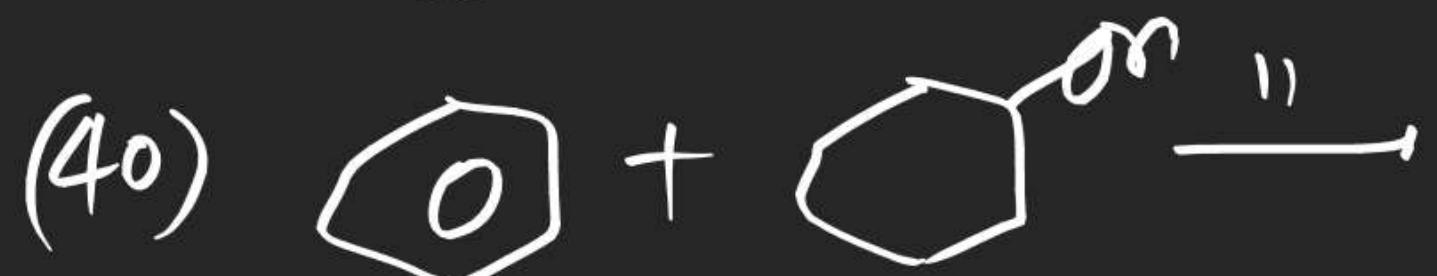
(V) Nitro Benzene  is used as a Solvent during Friedel-Crafts Rxn.





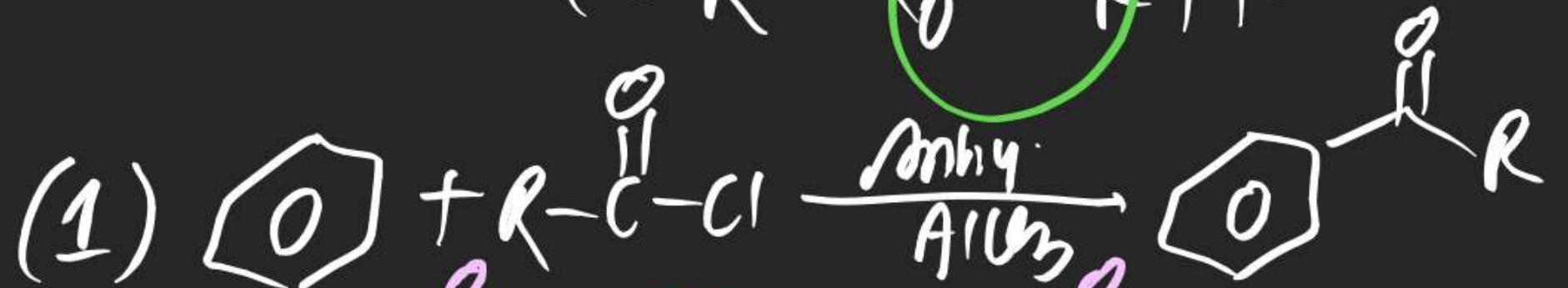


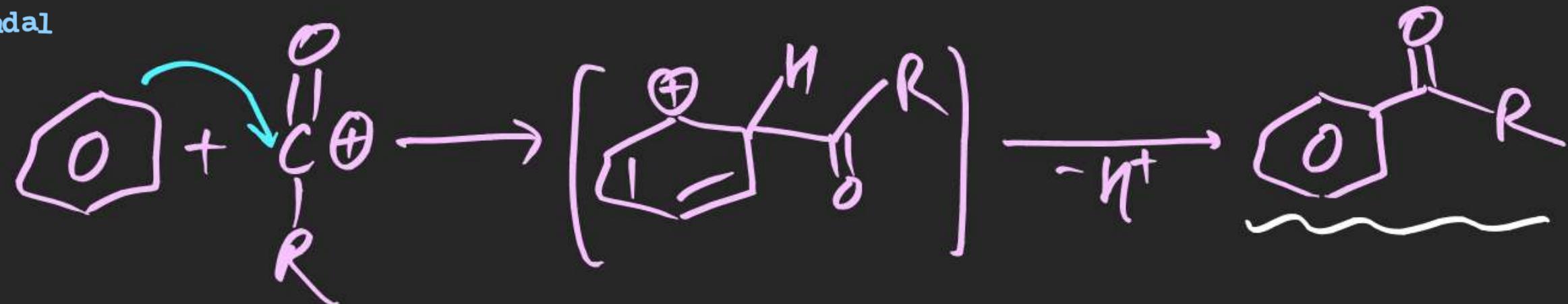




(F) Friedel-Crafts Acylation:

\Rightarrow On Acylation, Acyl Benzene is obtained as a product.



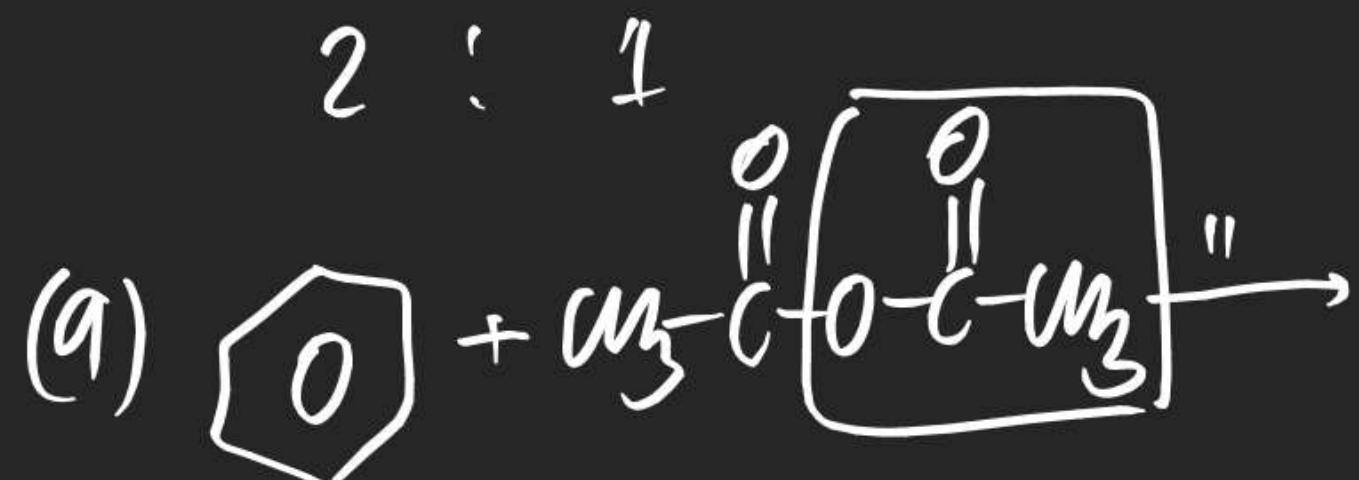
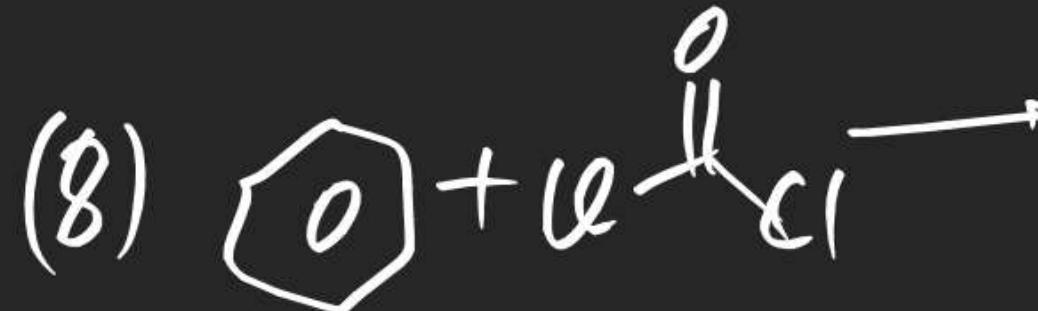
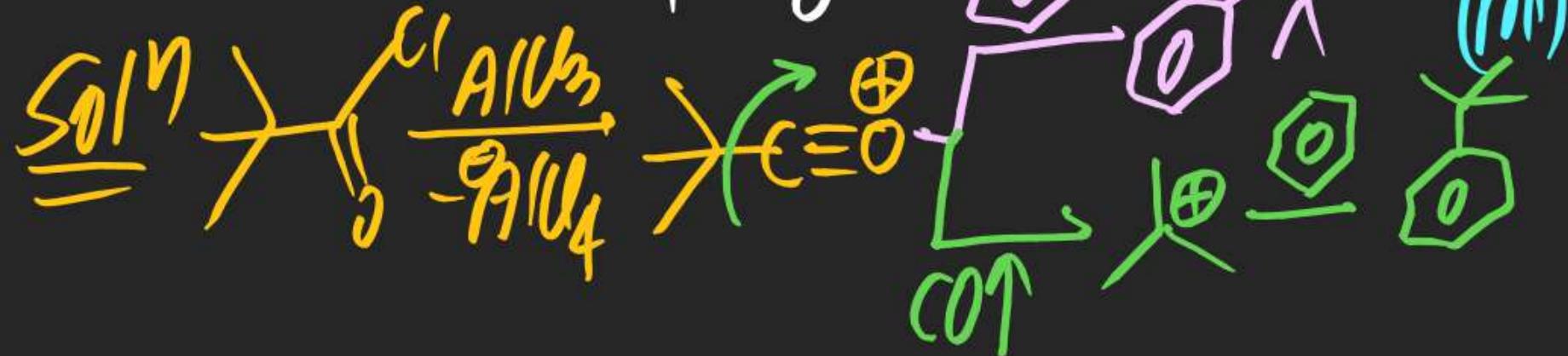
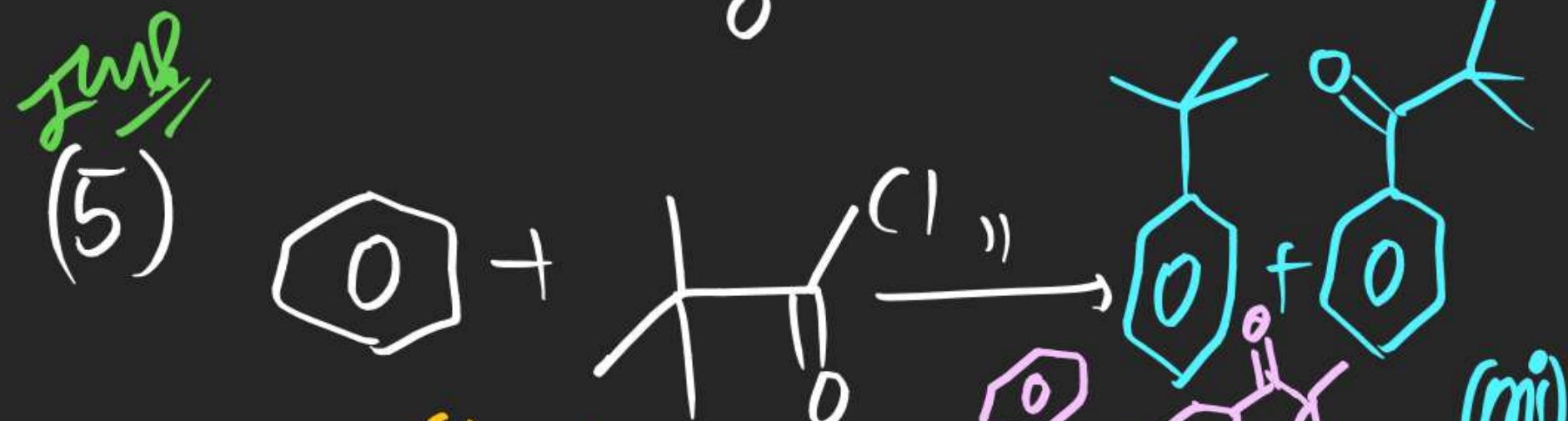
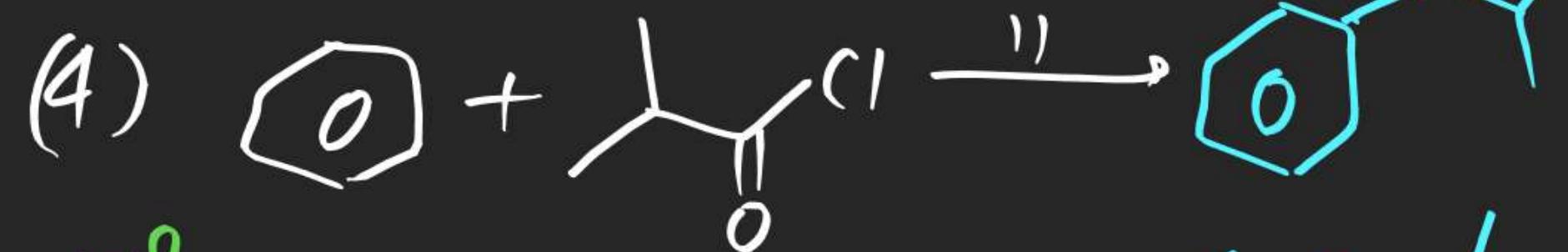
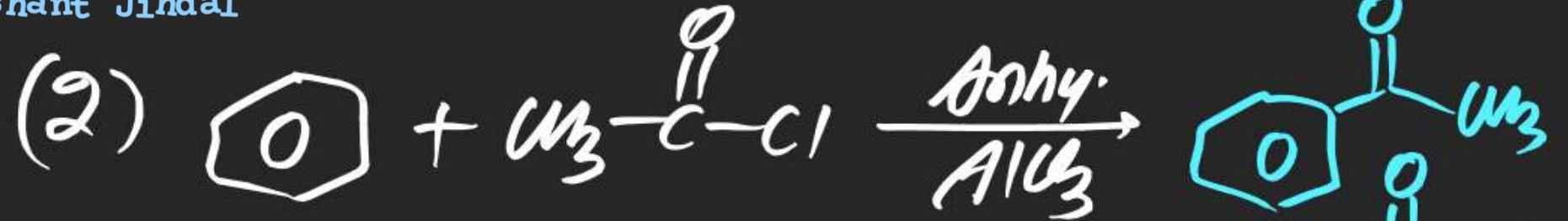


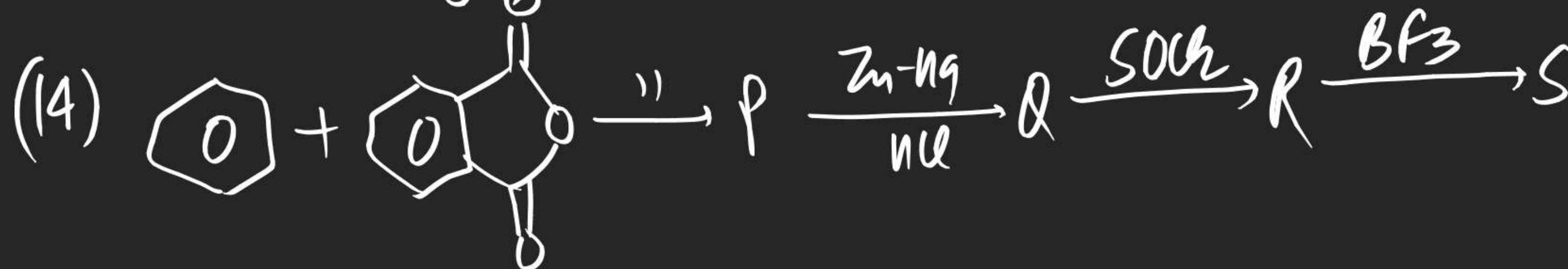
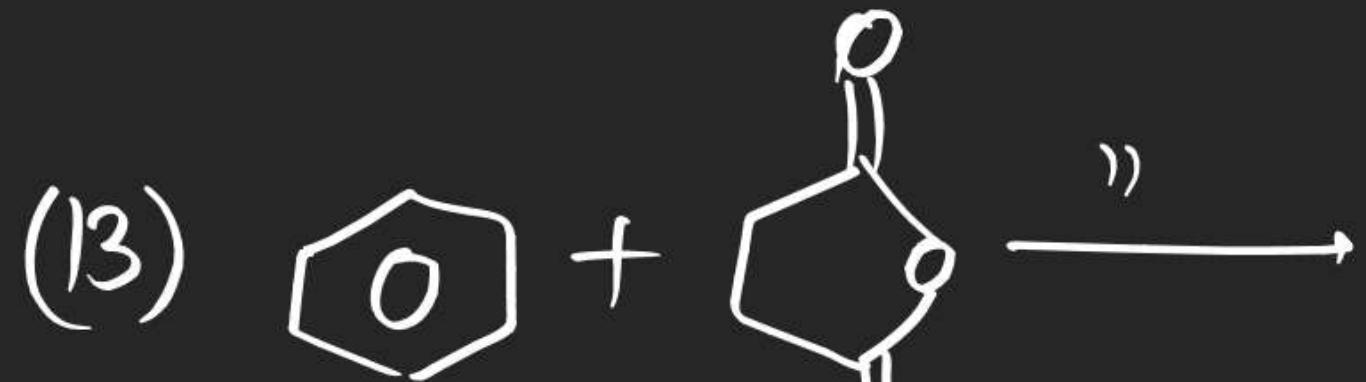
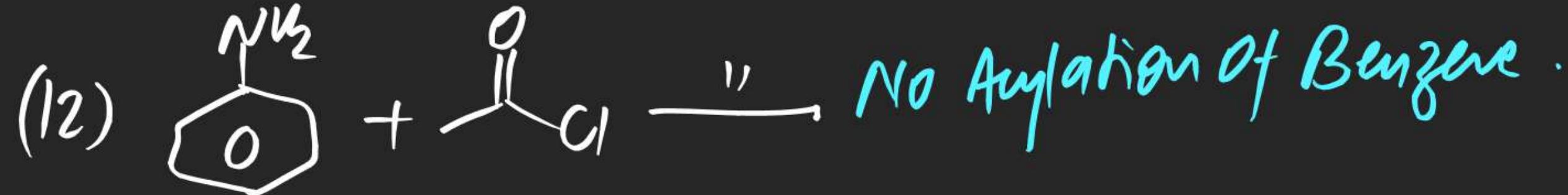
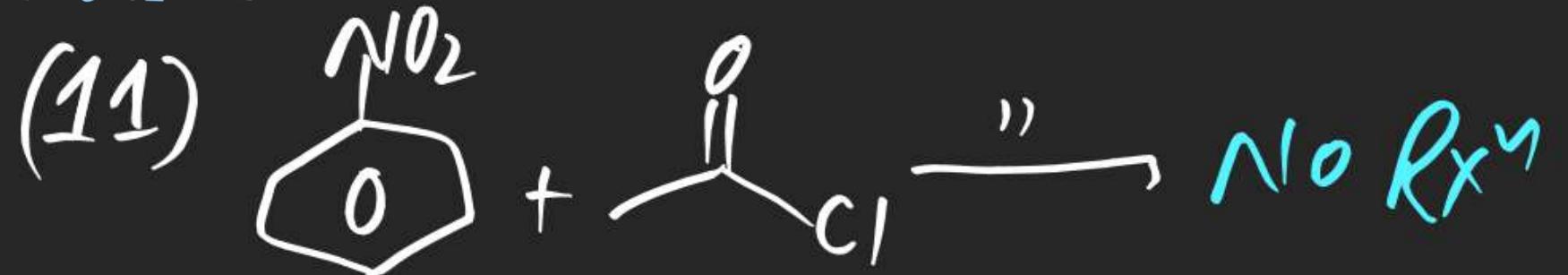
Note (i) $R-C(=O)^+$ is attacking Electrophile (Carbocation)

(ii) No Rearrangement possible

(iii) No chance of Polyacetylation

(iv) In case of Sterically crowded Acid halide, alkylation takes place

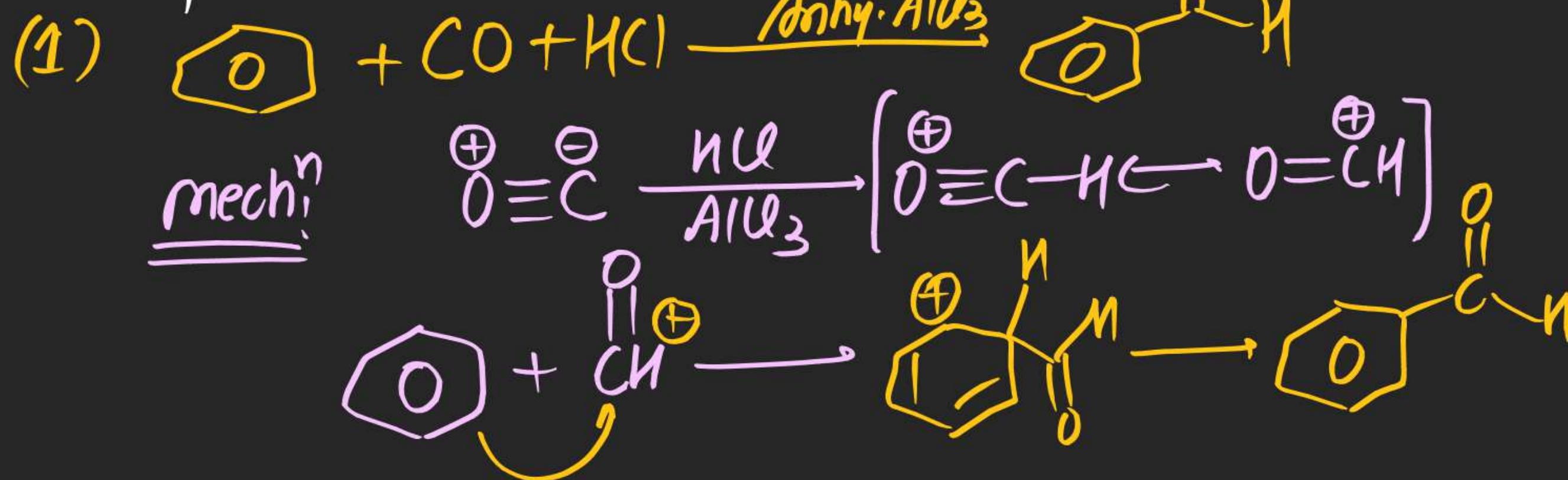


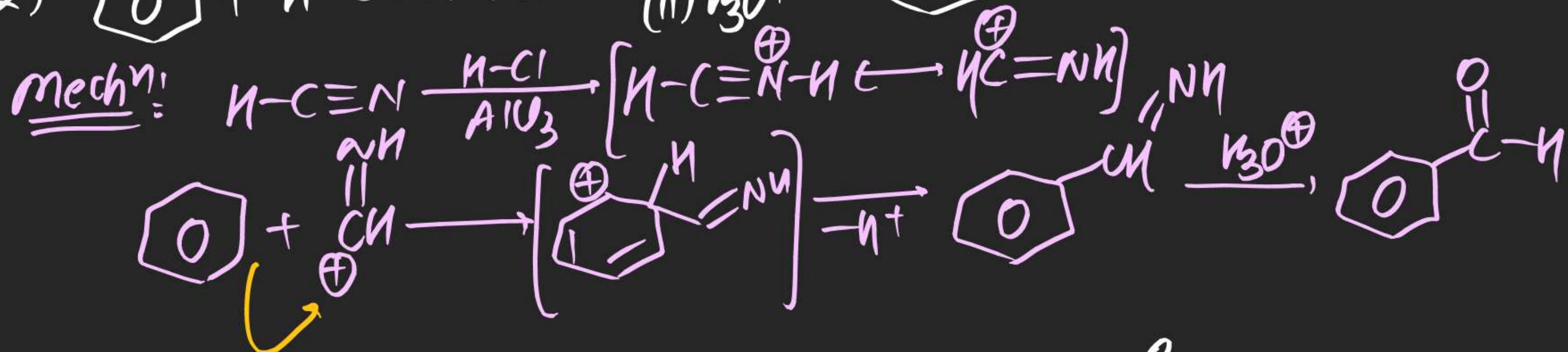
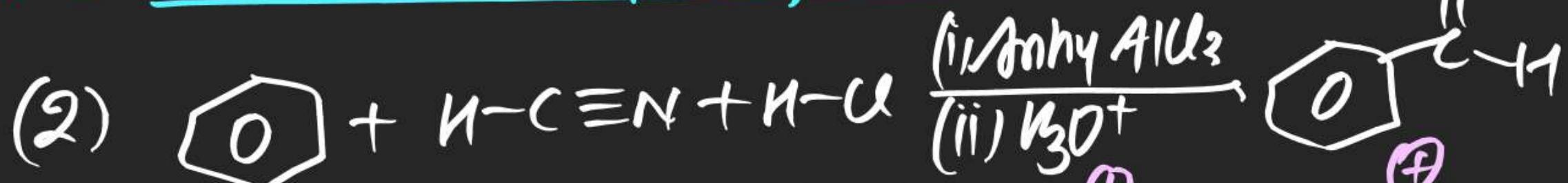
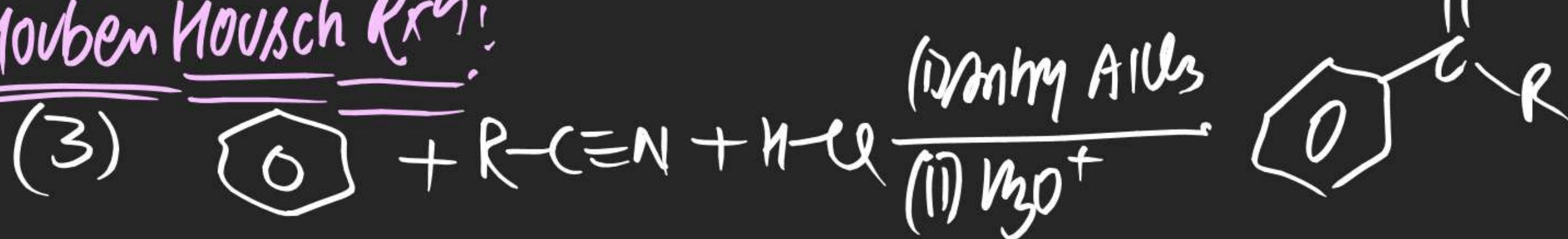




(#) Gattermann Coch Synthesis:

⇒ In this Rxⁿ Aromatic compound gets formylated by Rxⁿ of CO+HCl
in Pr. of AlU₃



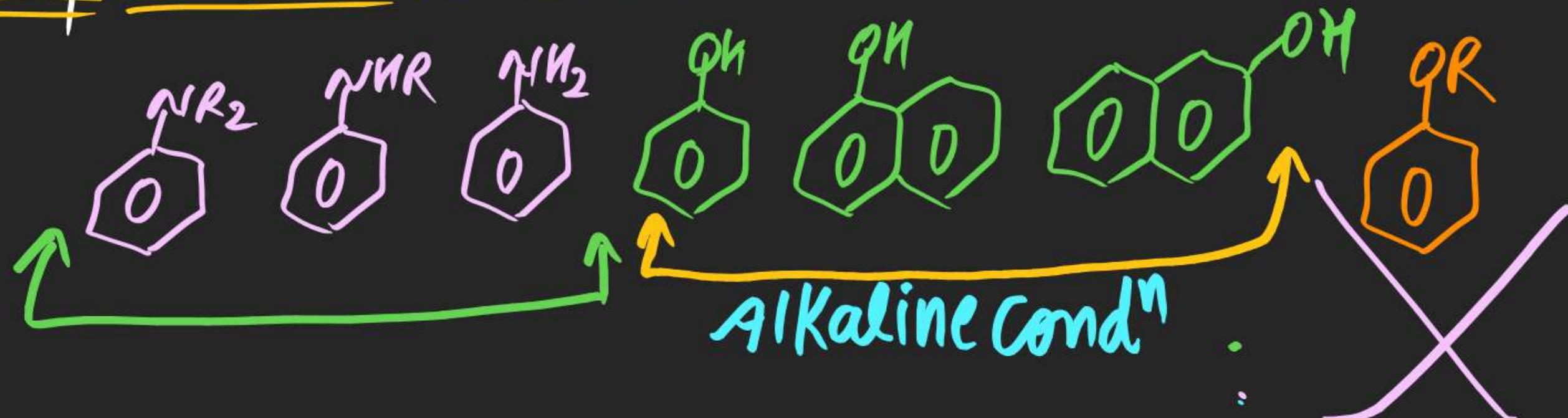
(H) Gattermann Aldehyde Synthesis:Houben Housch Rxn:

(#) Coupling Reaction!

- ⇒ In this Reaction Coloured product, dyes, Indicators are formed
- ⇒ Benzene diazonium is attacking electrophile.



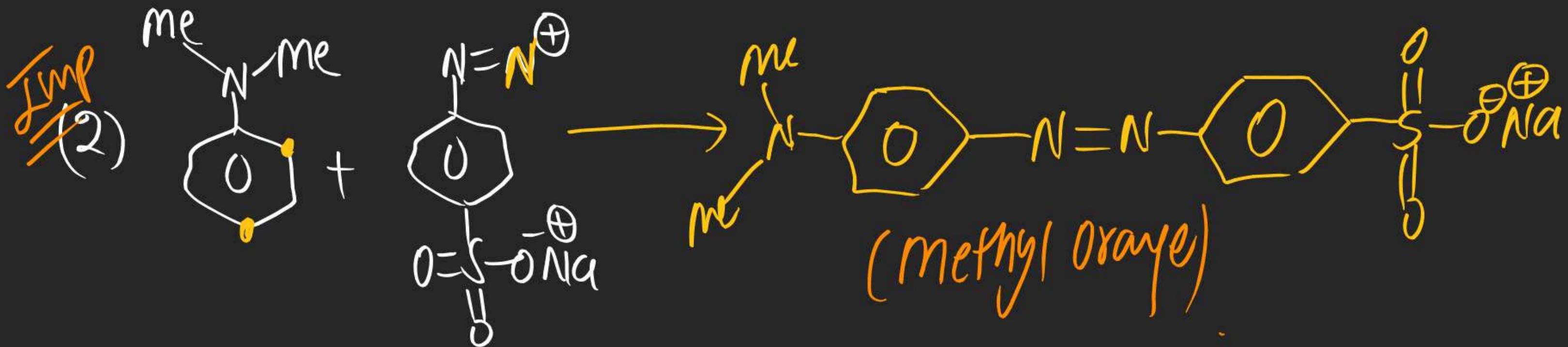
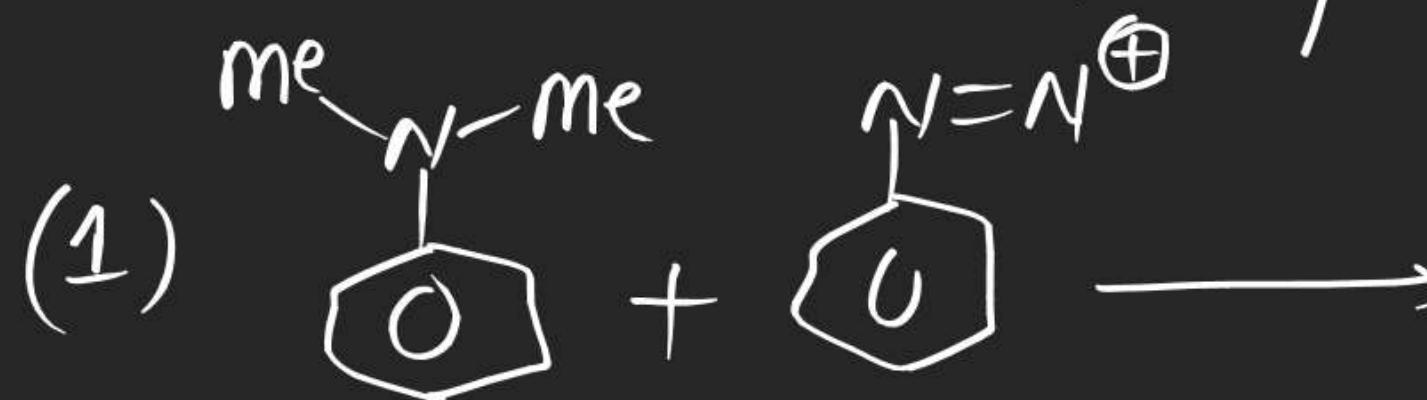
⇒ $\text{Ph}-\text{N}_2^+$ is a weak Electrophile hence it couples only with highly activated Aromatic Compounds.

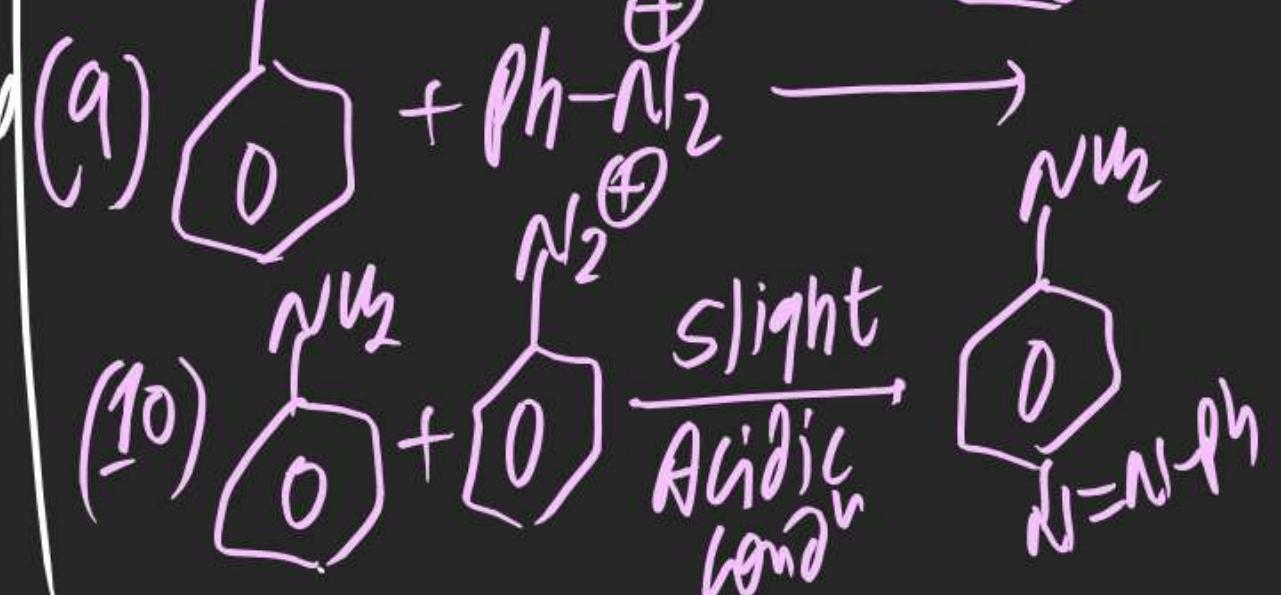
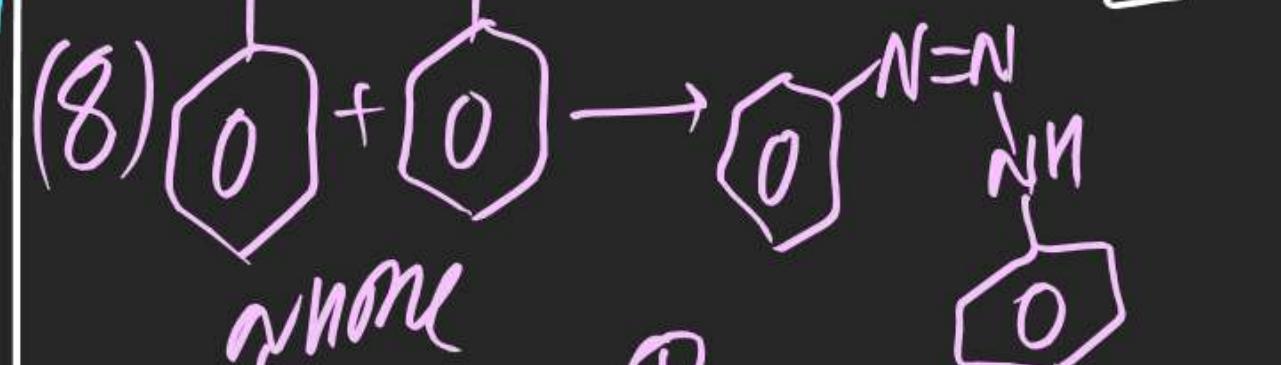
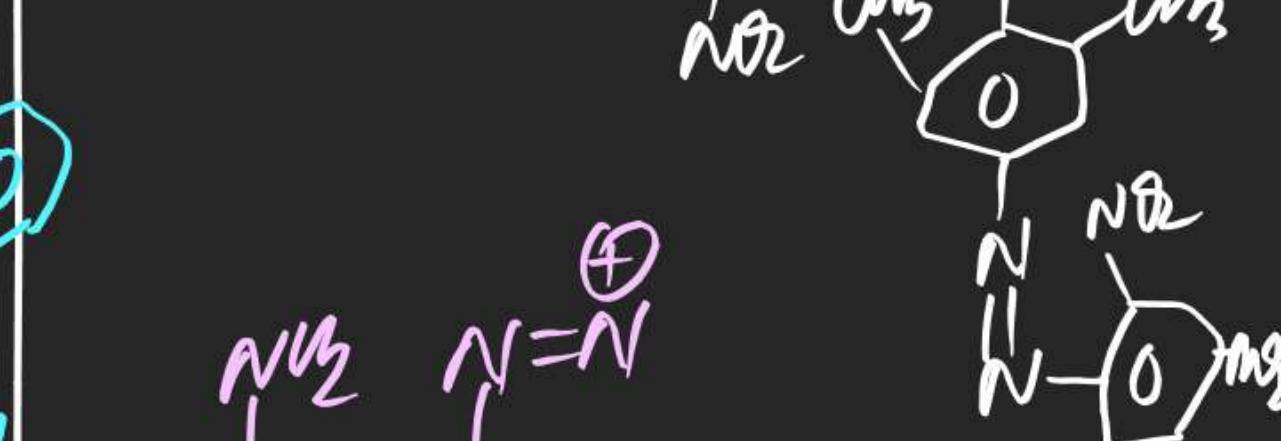
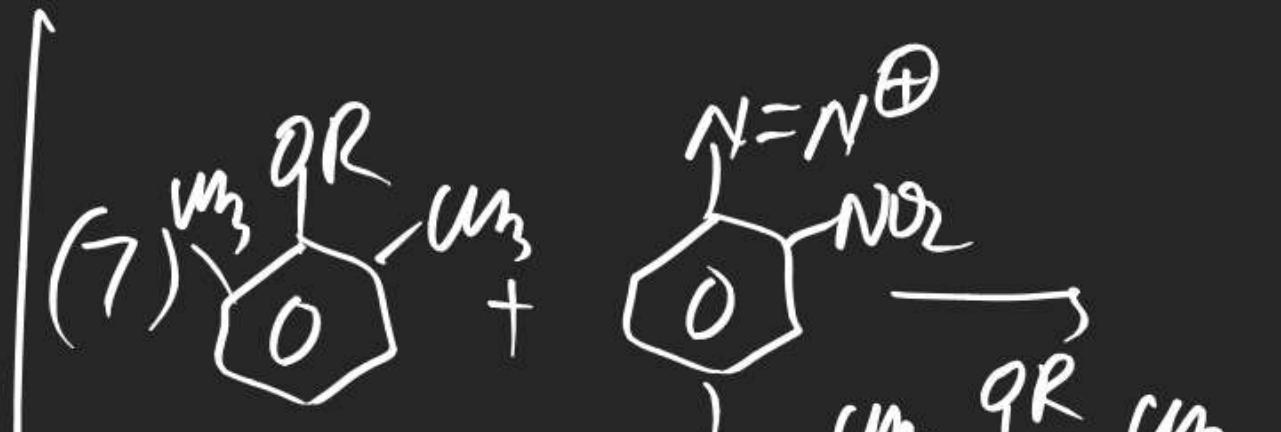
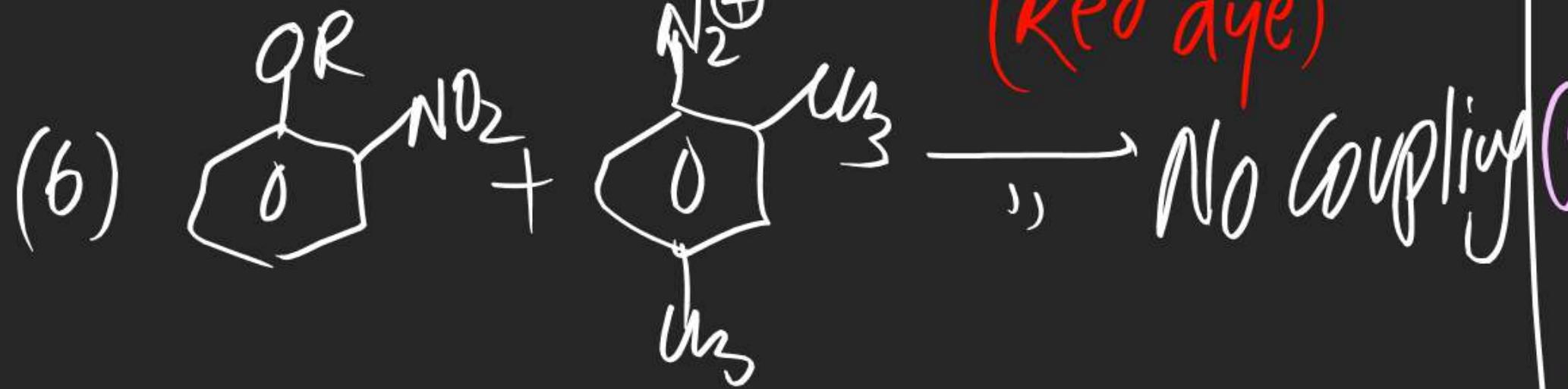
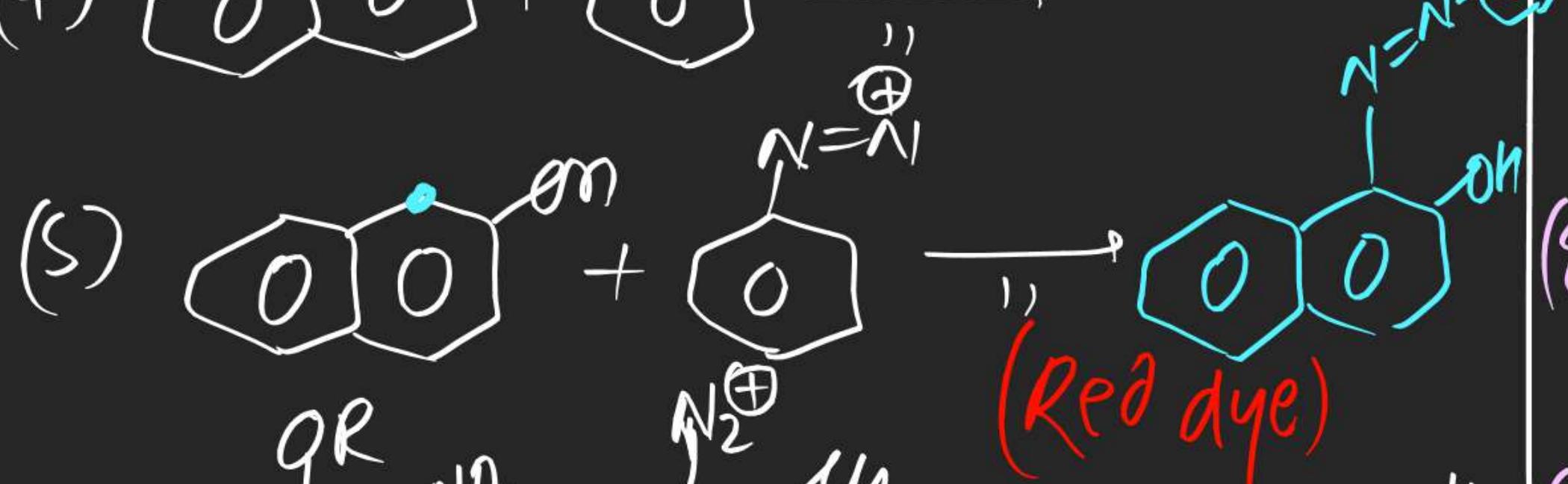
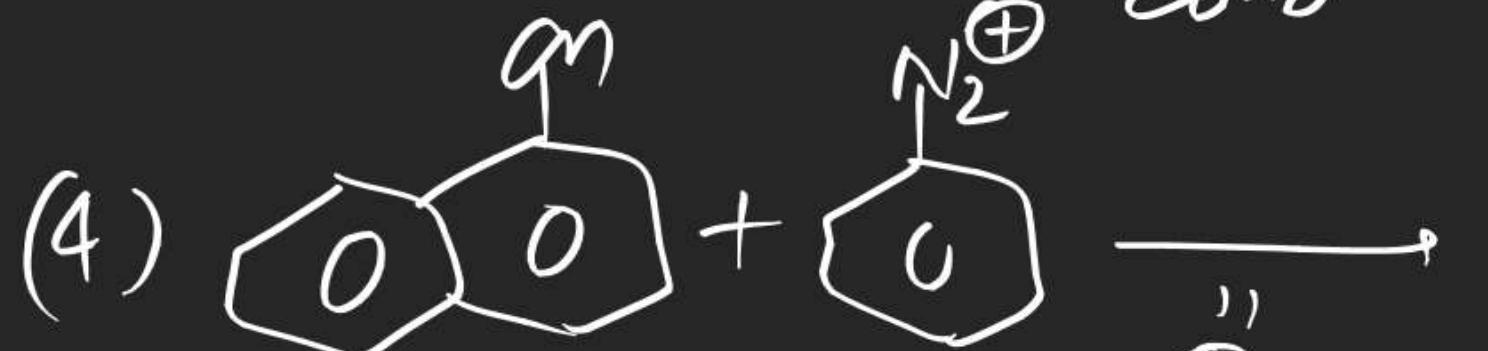
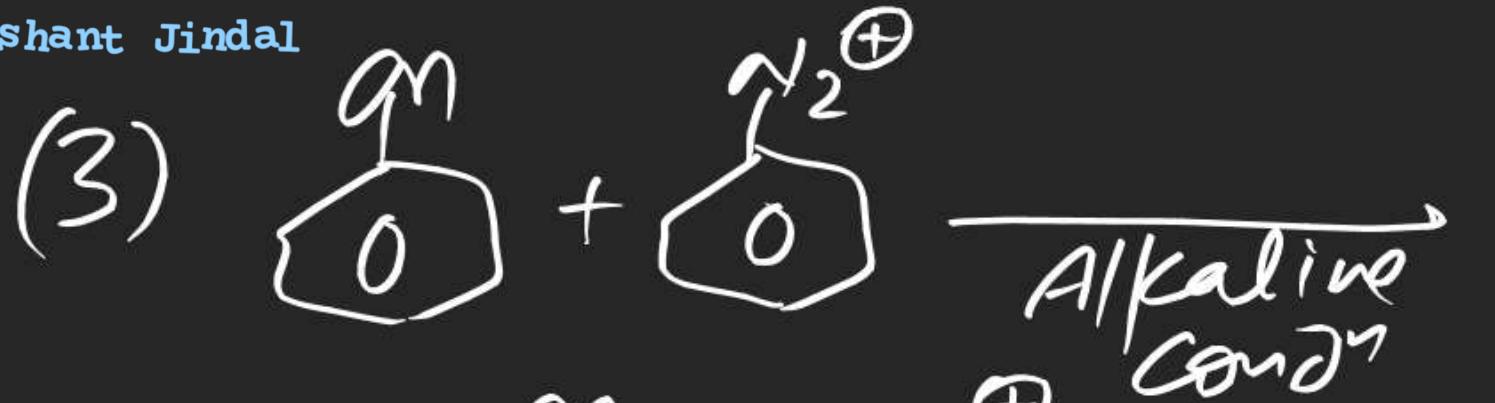


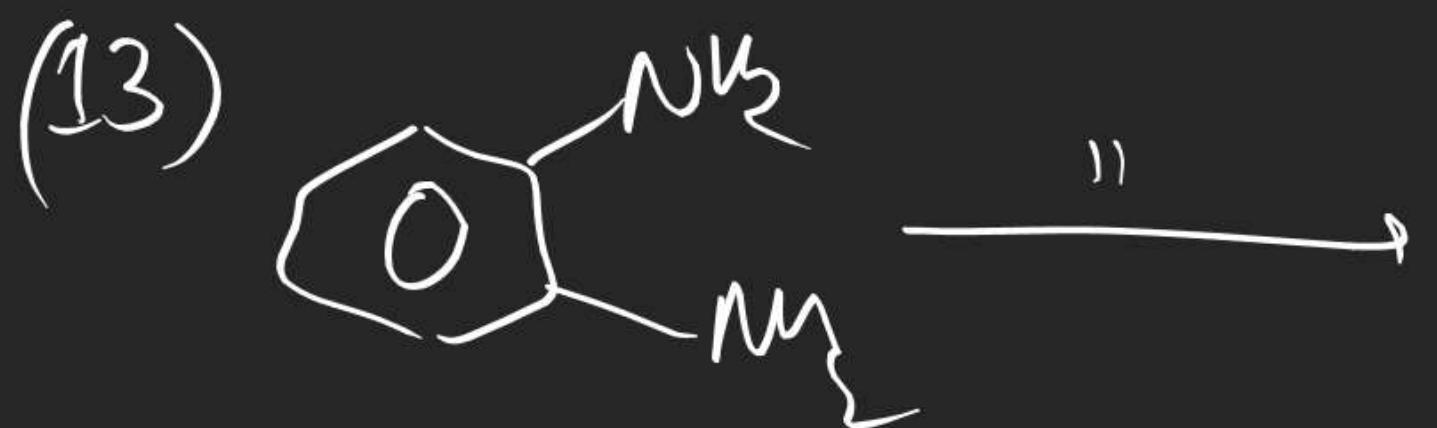
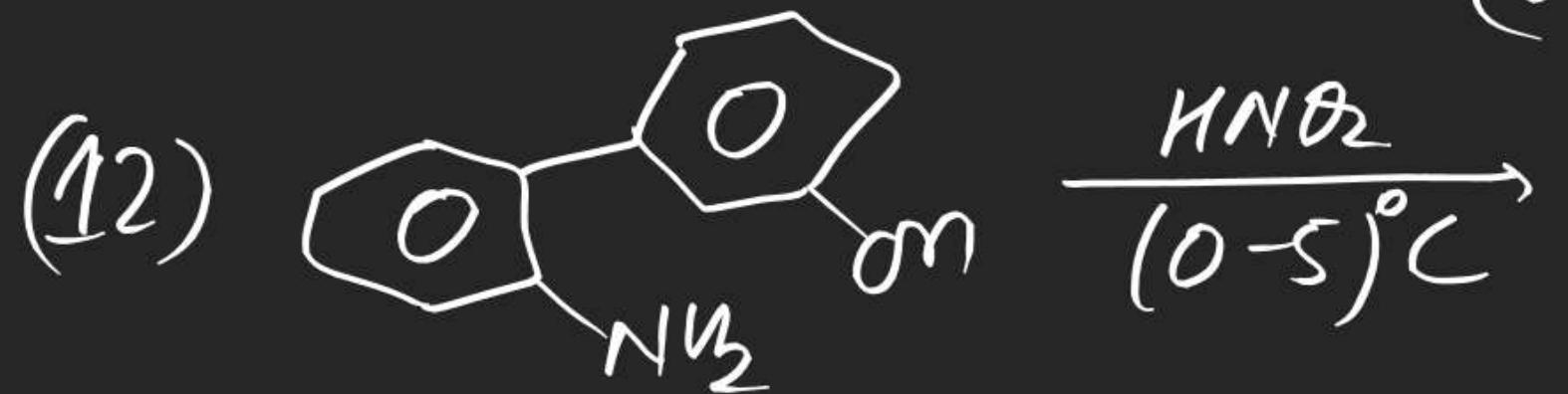
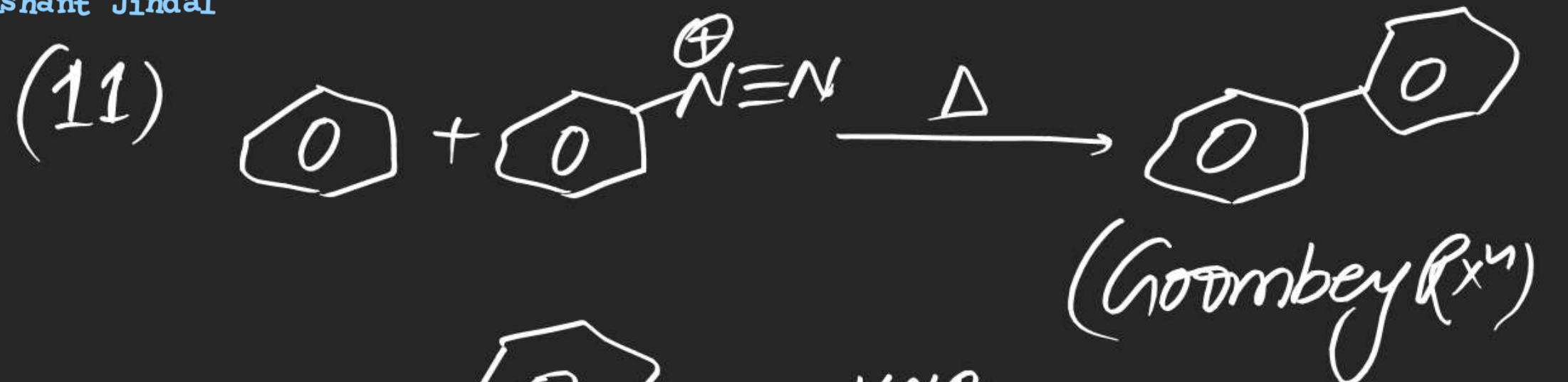
⇒ There are two type of coupling

(i) C-Coupling:- when $\text{Ph}-\text{N}=\text{N}^+$ attacks at Carbon of aromatic Ring

(ii) N-Coupling:- when _____ Nitrogen of Aromatic
primary & sec. Amine

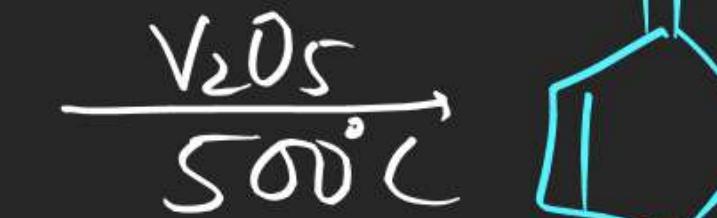
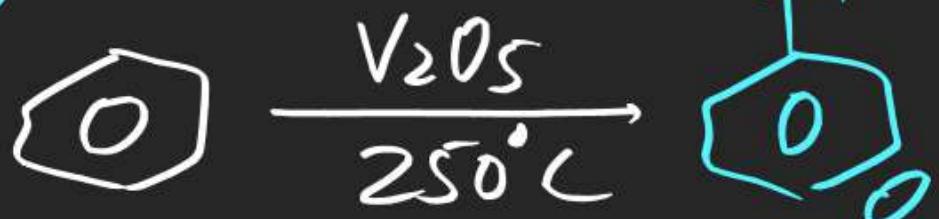






(#) Oxidation of Aromatic Compound

(#) By V_2O_5 :



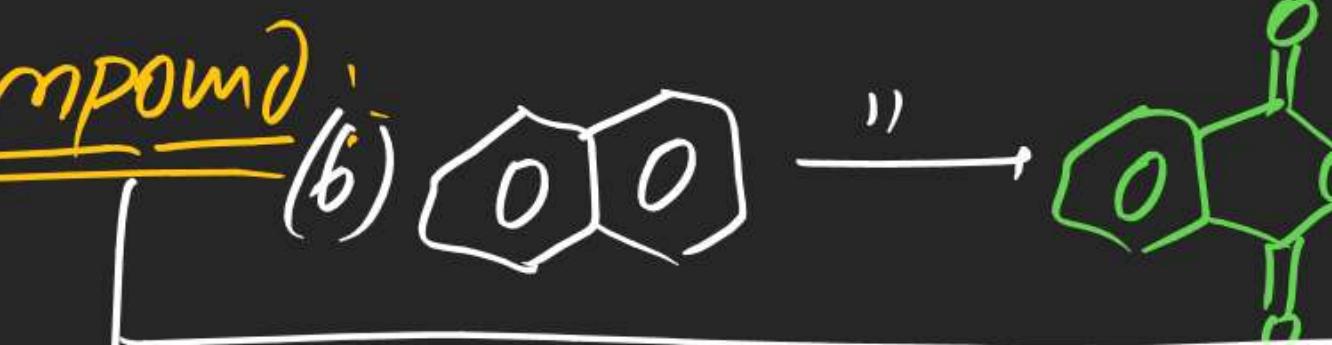
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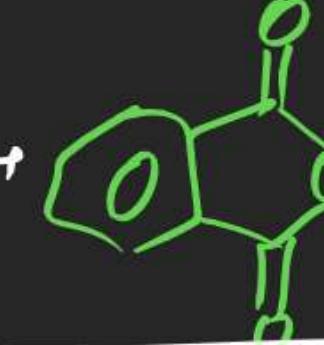
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(#) By $K_2Cr_2O_7$:



X



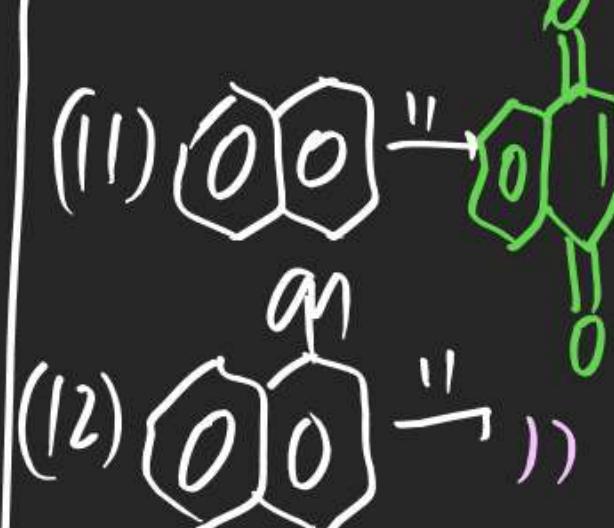
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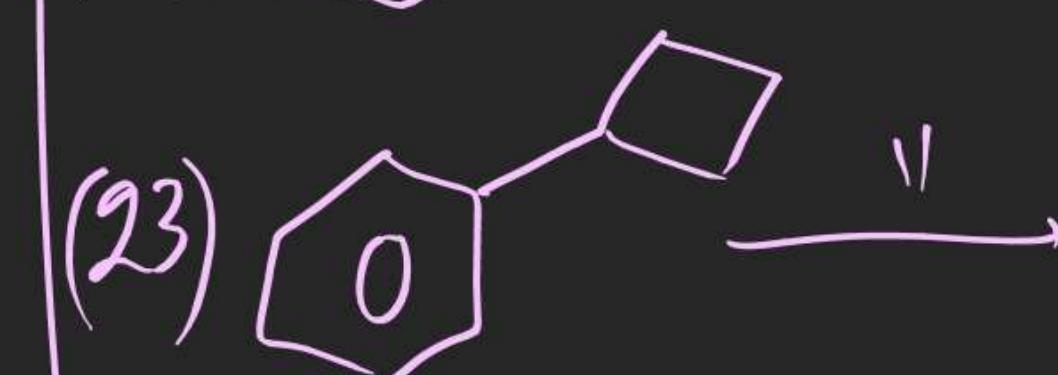
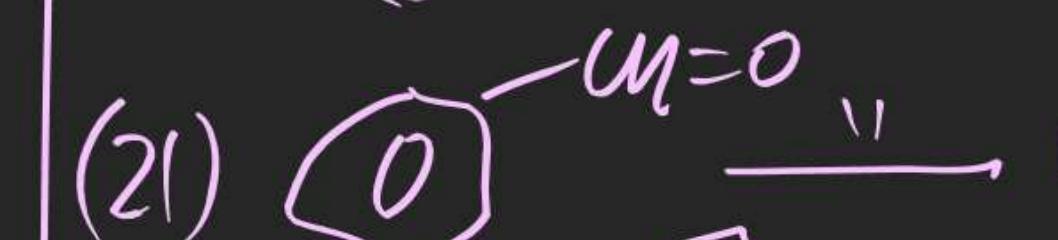
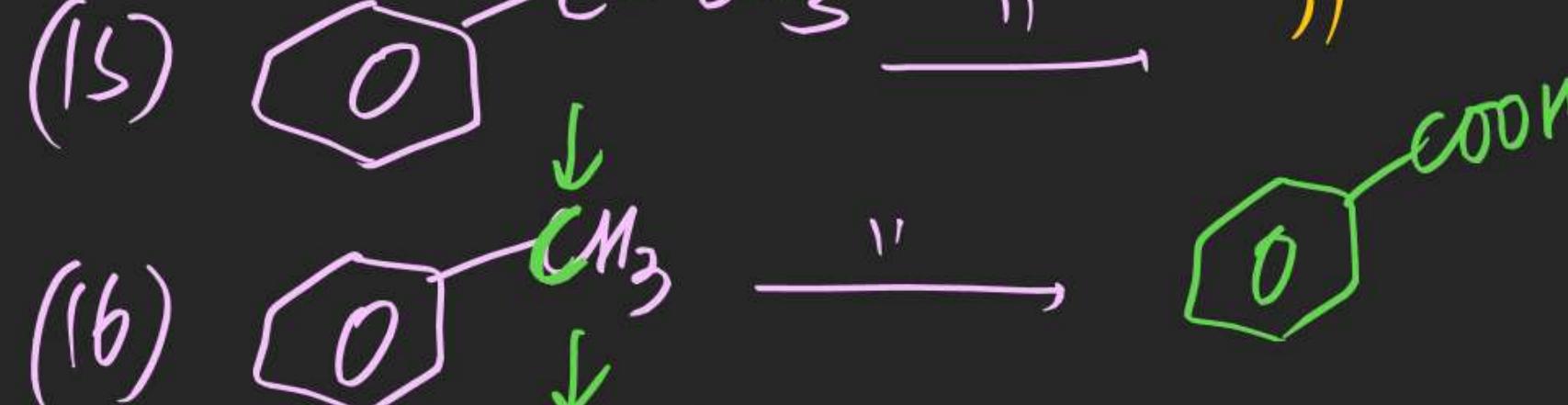
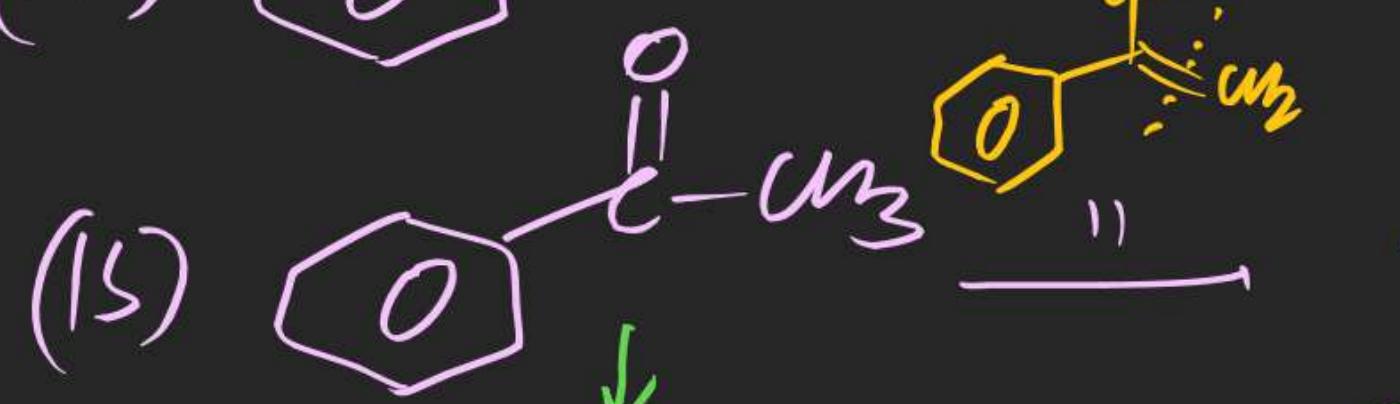
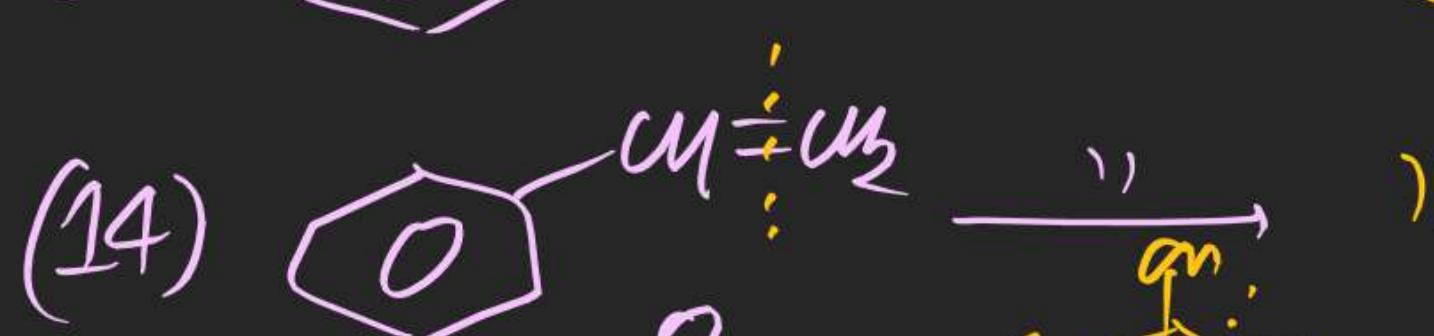
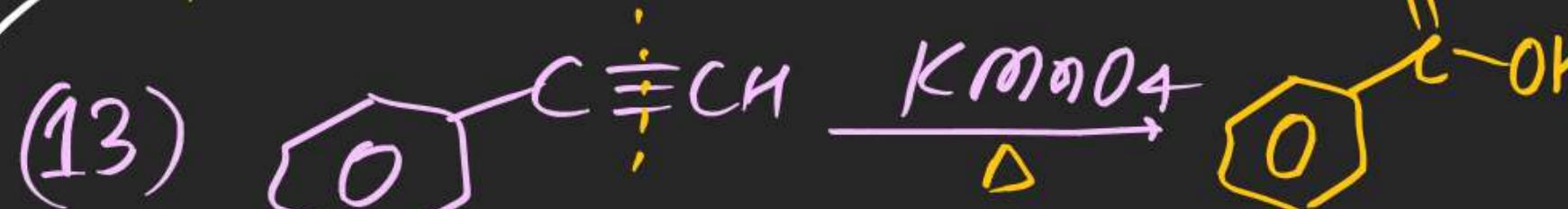


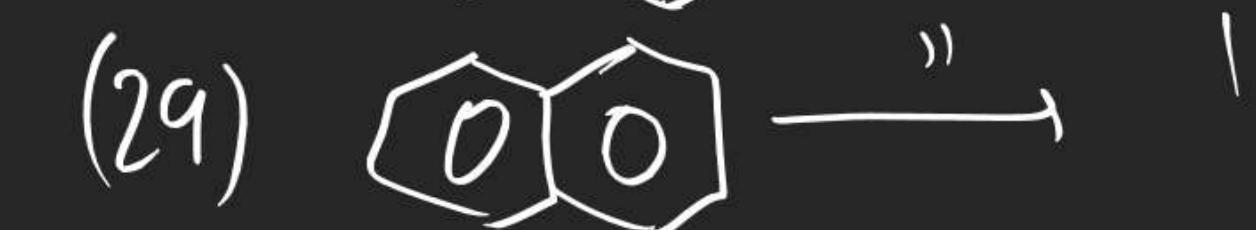
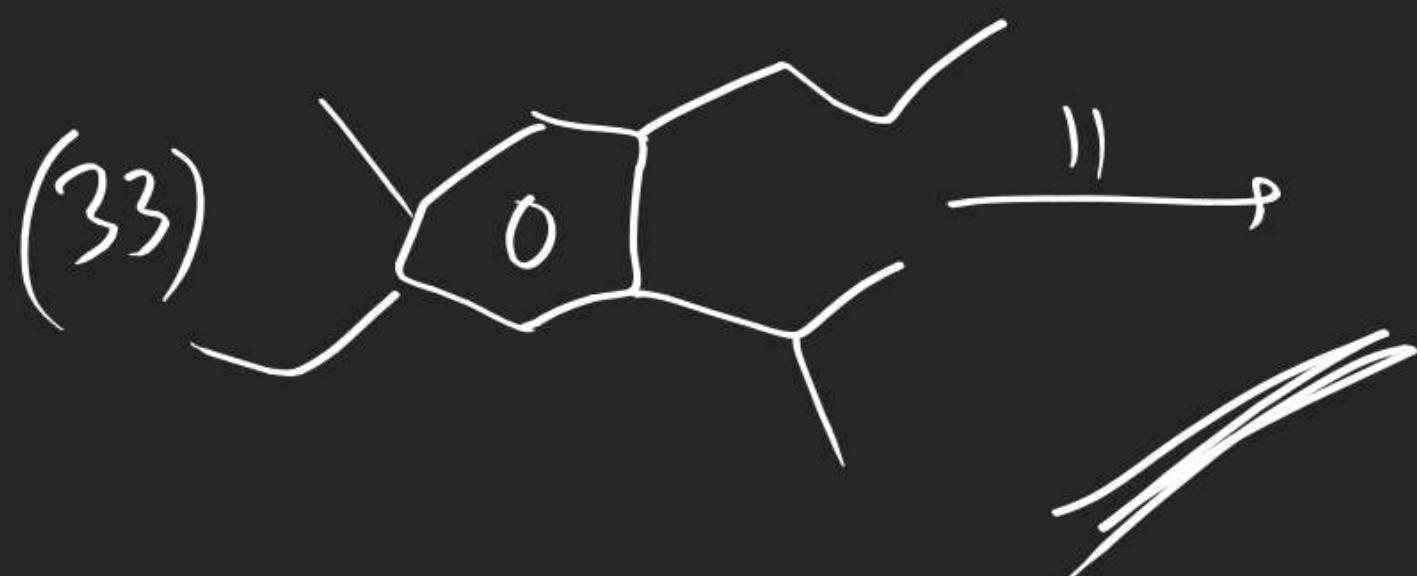
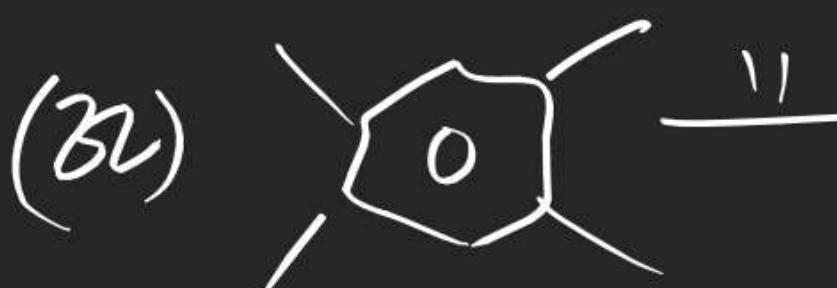
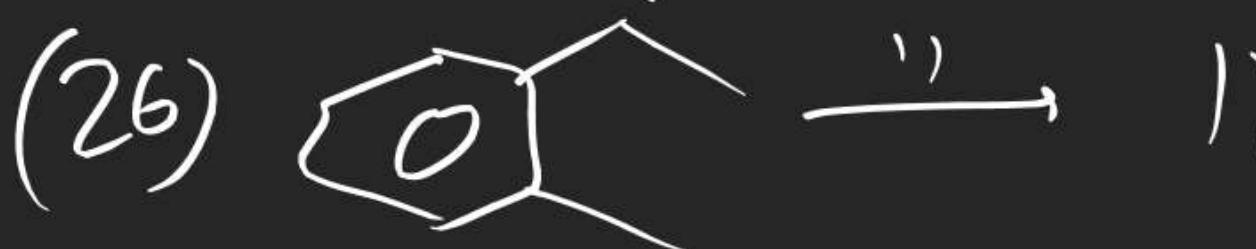
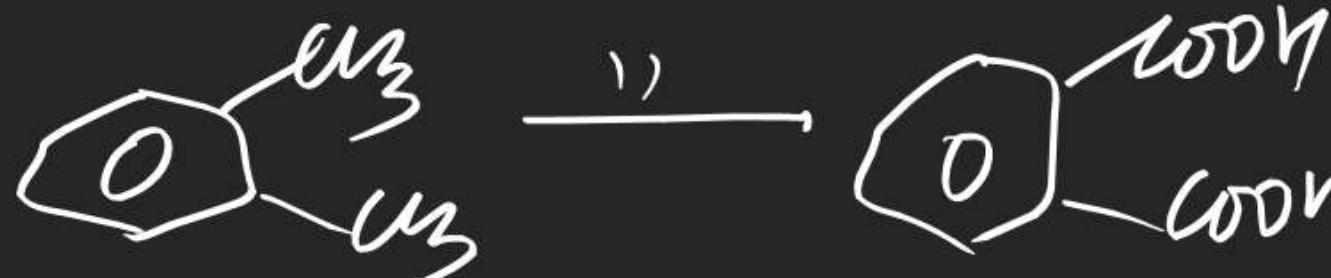
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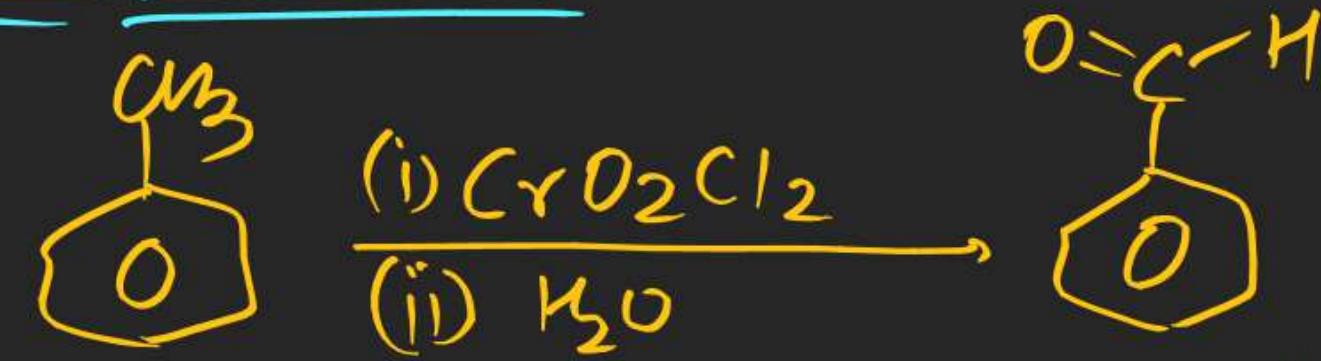






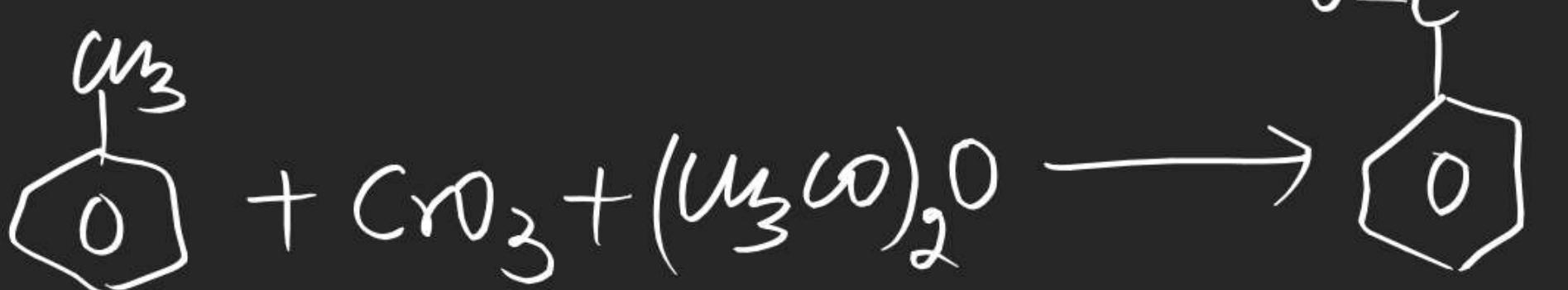
(#) M. Jindal Ether Oxidation :

(34)



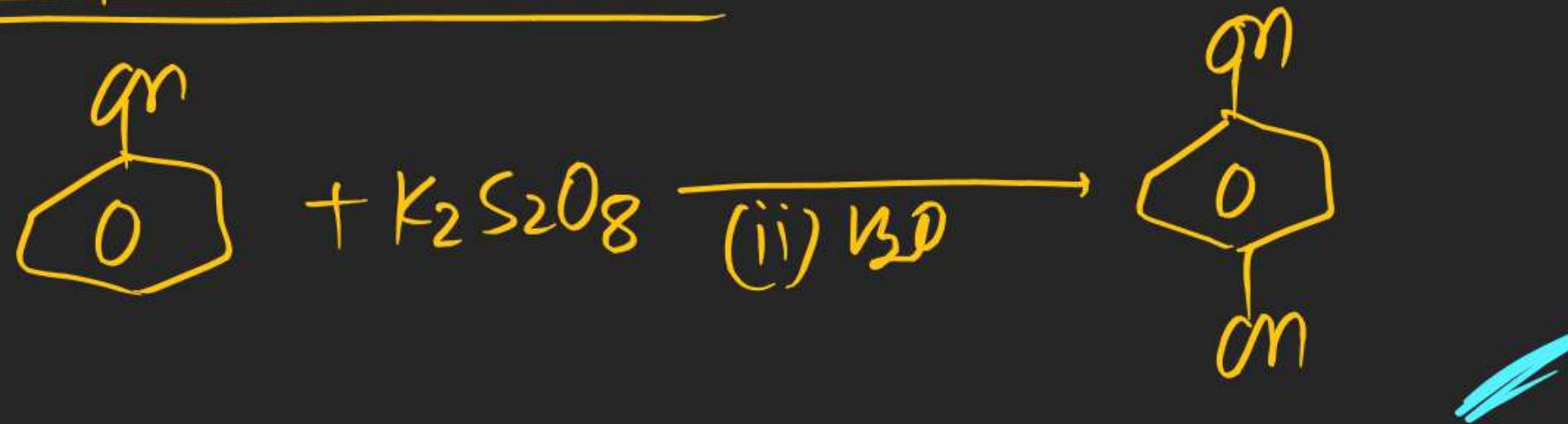
M. Jindal

(35)



(H) Ethyl persulphate oxidation:

(36)



#) Orientation: