Nishant Jindal

Aromatic Compound

Few Aromatic Compounds:

(1) Benzene

(2) Chloro Benzene

(3) Toluene

(4) Cumene

(5) Nitro Benzene

(6) Aniline

(7) Benzaldehyde

(8) Benzoic Acid (white crystelline)

(9) Benzene Sulphonic Acid

(10) Phenol (Carbolic Acid)

(11) Benzene diazonium chloride

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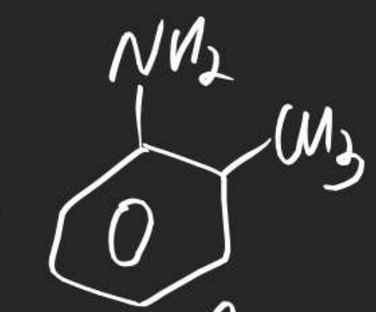
(12) Benzonitrile

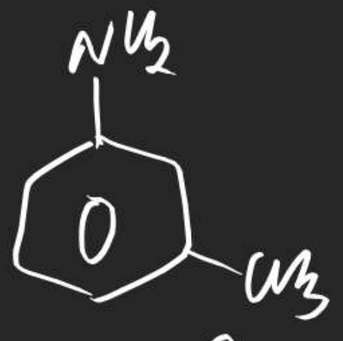
(13) Acetophenone

(14) Benzophenone

(15) Toluidine (o, m, p)



o-Toluidine



m-Toluidine

p-Toluidine

(16) Acetinlide

(17) Cresol (o, m, p)

(18) Catechlol

(19) Resorcinol

(20) Quinol

(21) pthalic Acid

(22) Tep pthalic Acid

(23) Xylene (o, m, p)

(24) Styrene

(25) Anisole

(26) Furan

(27) Pyrole

(28) Thiophene

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(29) pyridine

(30) Napthlene

(31) Anthracene

(32) phenthrene

(33) Azulene

(34) α-Napthol

(35) β-napthol

(36) DDT (Insectiside)

(37) picric Acid

(38) TNT (Explosive)

(39) phenolphthelire

(40) methyl orange

(41) Aspirin (Analgesic)

(42) paracetamol

(43) oil of wintergreen

(44) Chloramine-T

(45) Benzene sulphonyl chloride

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(46) Inorganic Benzene / Borazine / Borazole

(47) Indole

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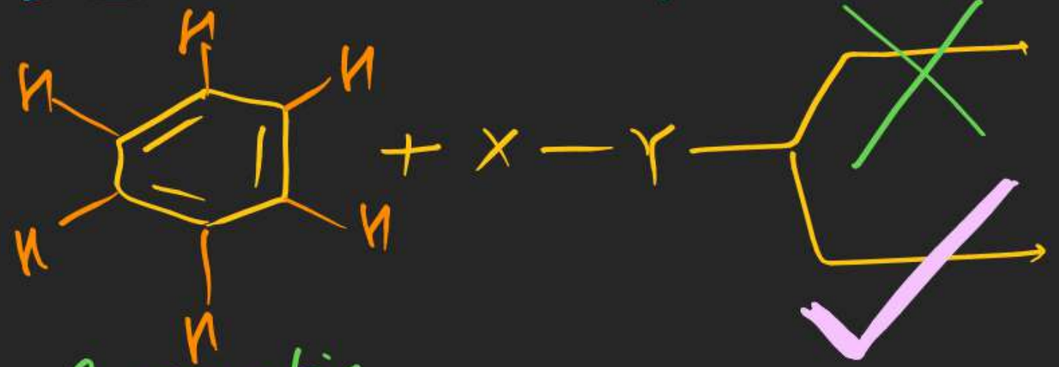
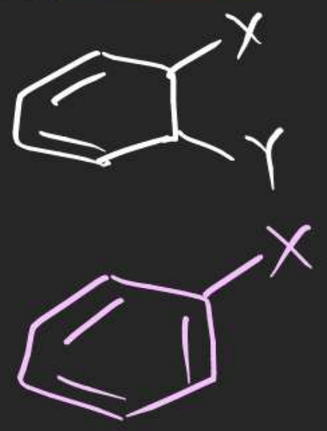
(#) Reactions shown By Aromatic Compound :-

(i) 

Aromatic
(Nucleophilic)



Addⁿ Rxⁿ

Substitution Rxⁿ

Note (i) Aromatic Compound doesn't undergo addⁿ Reaction usually.

(ii) Aromatic Compounds usually show Substitution Reaction.

(a) Nucleophilic Aromatic Substitution (SN_{Ar})

(b) Electrophilic Aromatic Substitution (EAS)

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Nucleophilic Aromatic Substitution :

(SN-Ar)

⟹ when a Nucleophile substitutes another NU attached on Aromatic Ring, it is known as SN-Ar Reaction.

possible mechanism

(i) Ipso / SN^2-Ar / SN_{AE} mechanism

(ii) SN^1-Ar / Aryl Cation mechanism

(iii) SN_{EA} / Cine / Benzyne mechanism

SN^2-Ar mechanism

(1) 

+ NaOH ⟶ No Rx^n

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(2) 

Where

Z (EWG)	lg	Nu^-
−F	−F	$^{\ominus}OH$
−Cl	−Cl	$^{\ominus}OR$
−Br	−Br	$^{\ominus}CN$
−I	−I	NH_2-NH_2
$-NO_2$		OH_2
−CN		
−CHO		
−COR		
⋮	⋮	⋮

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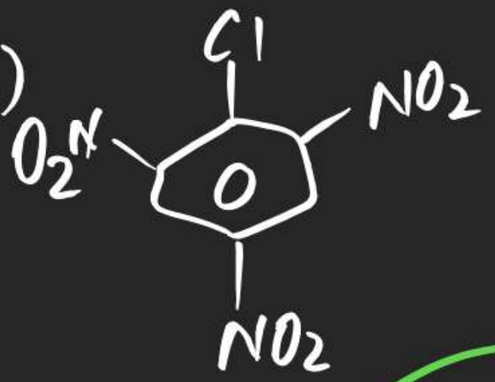
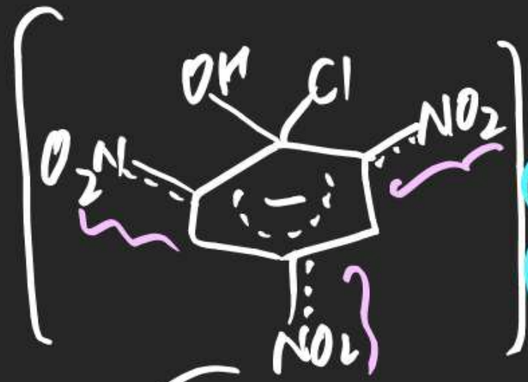
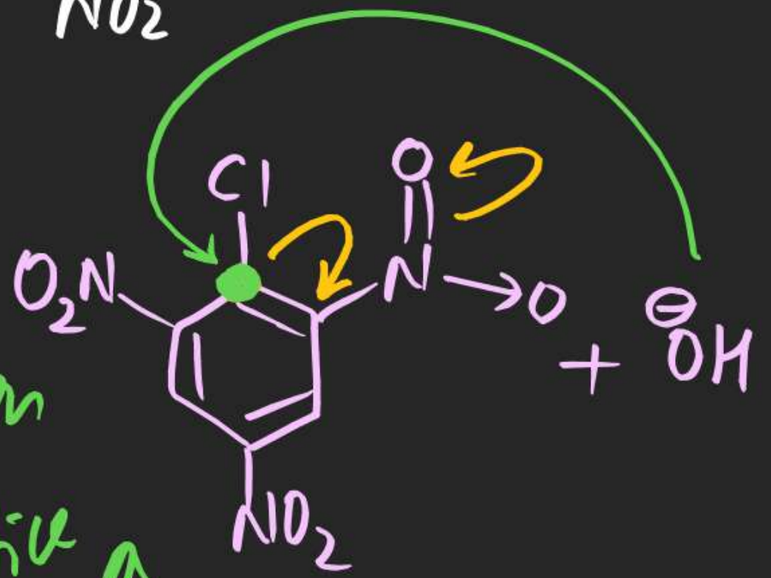
(3) 

+ NaOH ⟶



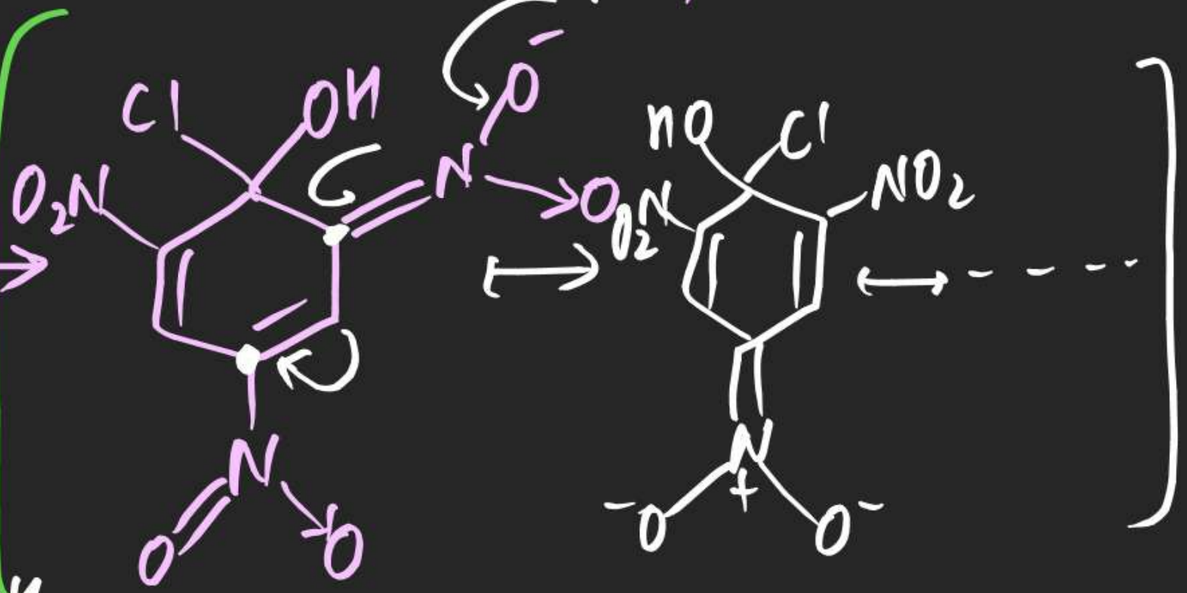
(*) Carbanion
(*) M-Complex

Mechⁿ:

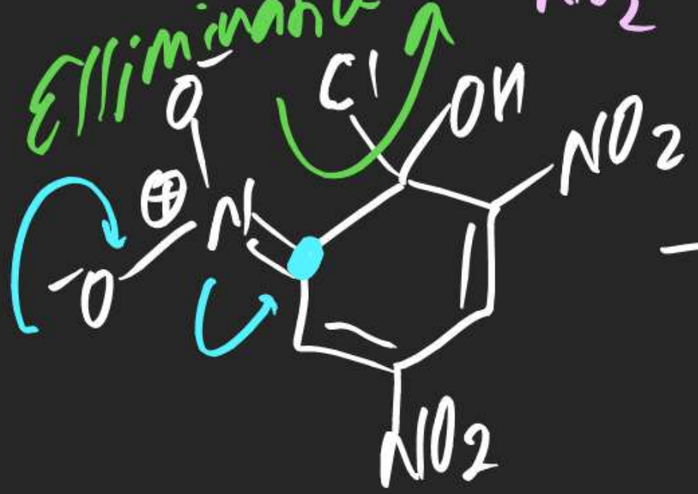


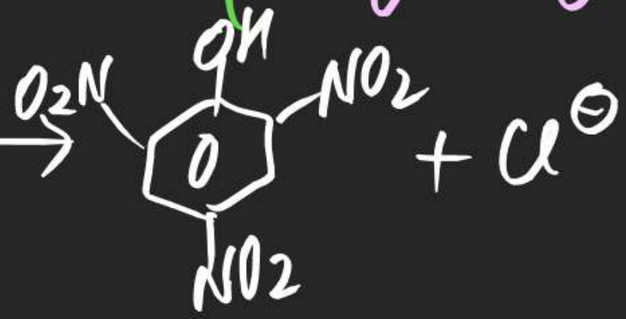
Addition

γ-dis



Elimination





Note (i) Carbanion (M-complex) intermidiate

(ii) Formation of M complex / addn of Nu^- / loss in Aromaticity is R.D.S

(iii) Rate of Reaction SN-Ar $\propto$ Stability of M-complex
$\propto$ (EWG)

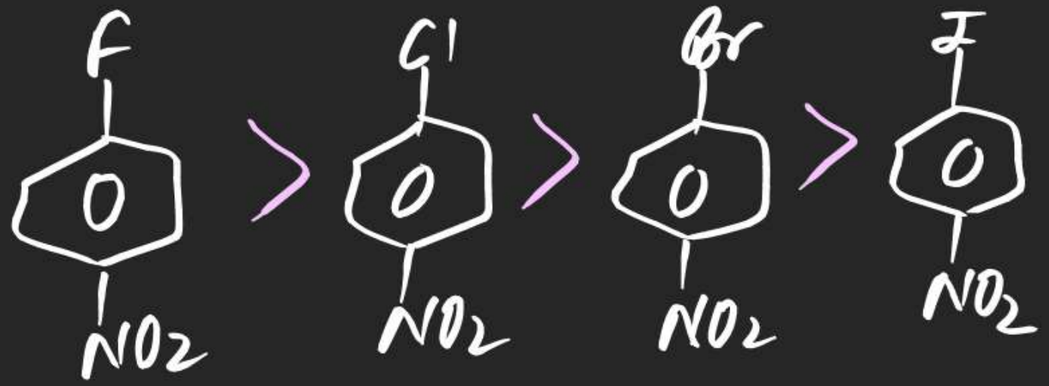
M.Imp

(iv) M-complex can be stablised By

(a) EWG present at ortho & para site

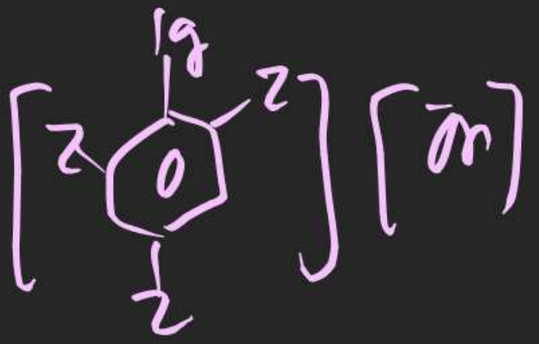
(b) -I effect of lg

(v) order of rate of SN^2-Ar mechn for Ar–X



(vi) Breaking of C–X Bond is not involved in r.d.s

(vii) rate exp $r = K[\text{Ar–X}][\text{OH}^-]$



(viii) II-order

(ix) Bimolecular

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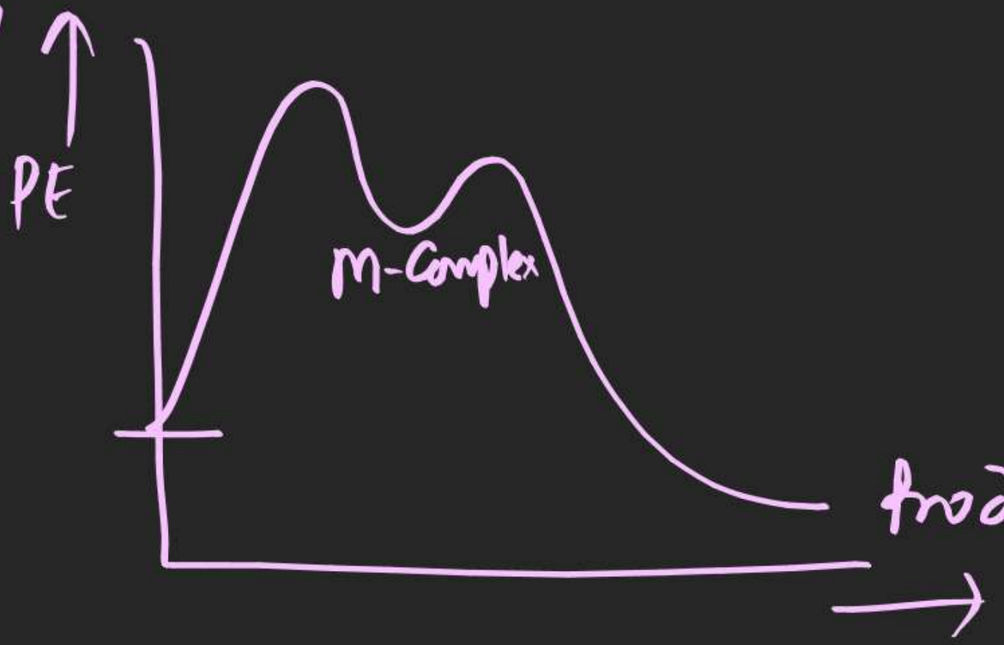
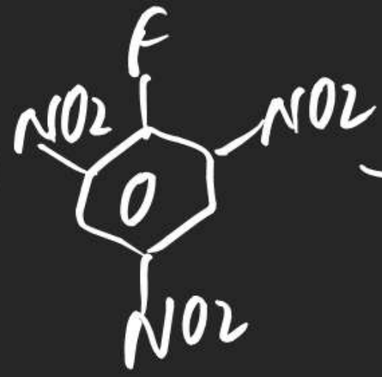
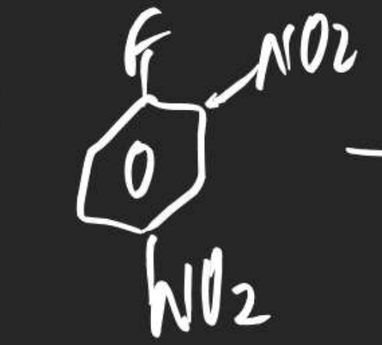
(x) P.E Diagram



(xi) Two step mechⁿ

(4)  $\xrightarrow{NaOH}$

(5)  $\xrightarrow{\quad ll \quad}$

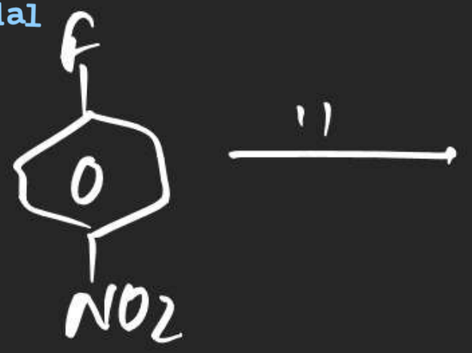
(xii) Rxⁿ is used in POC To distinguish $-NO_2$ group.

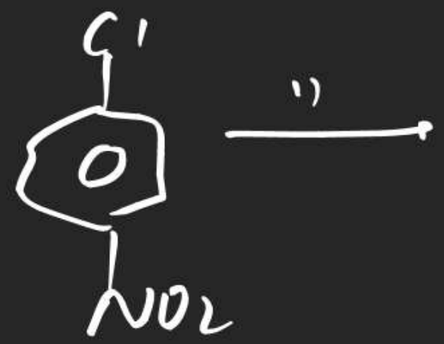
M-Complex

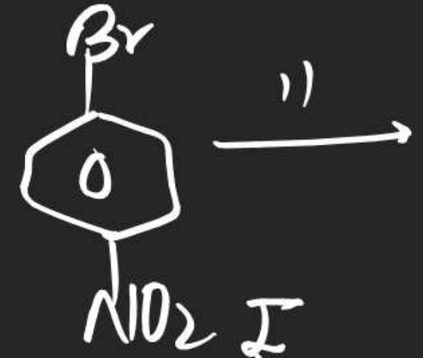
Red when $3\,NO_2$

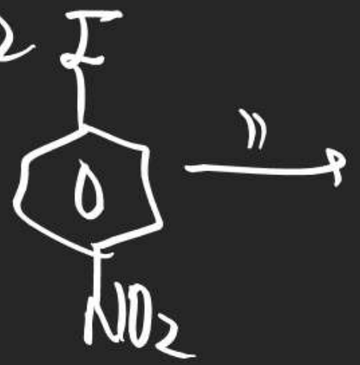
purple — $2\,NO_2$

yellow — $1\,NO_2$

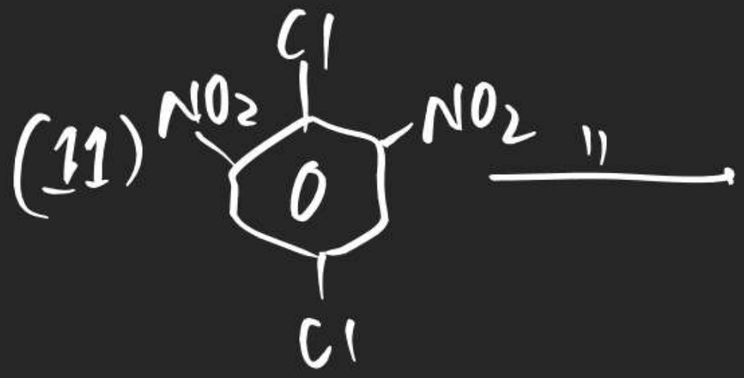
(6) 

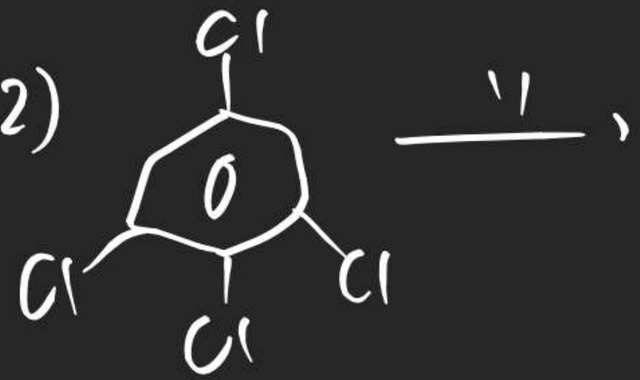
(7) 

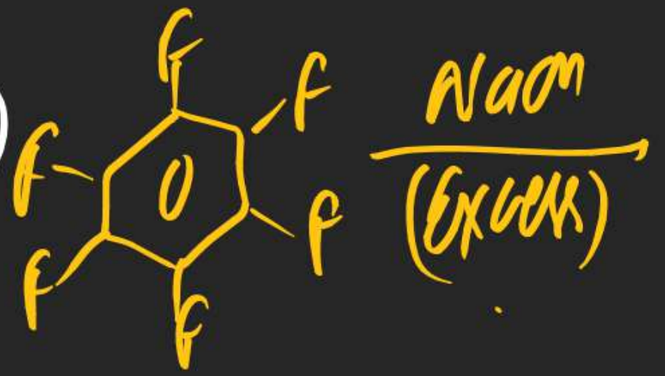
(8) 

(4) 

(10) 

(11) 

(12) 

(13) 

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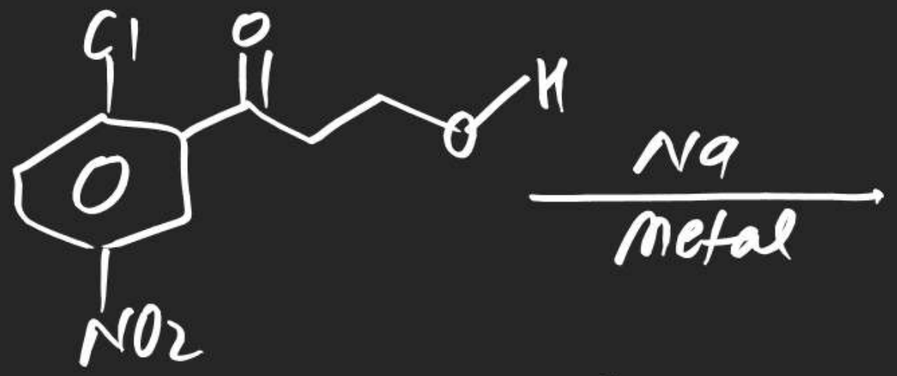
(14)



Na
Metal

(15)

NaOH
(Excess)

NaCN
(Excess)

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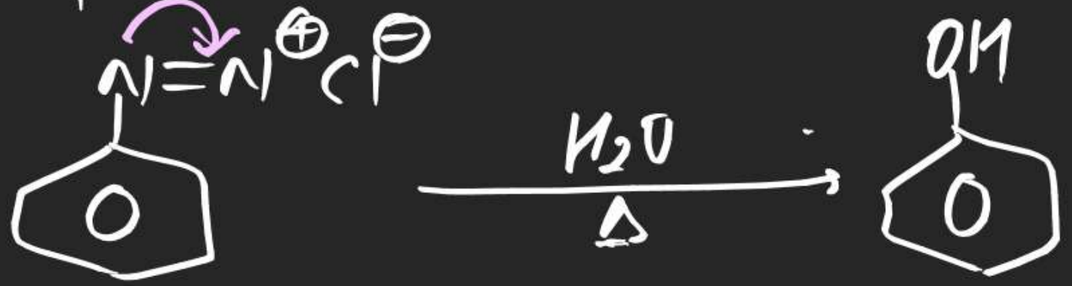
(#) SN^1-Ar mechⁿ :-

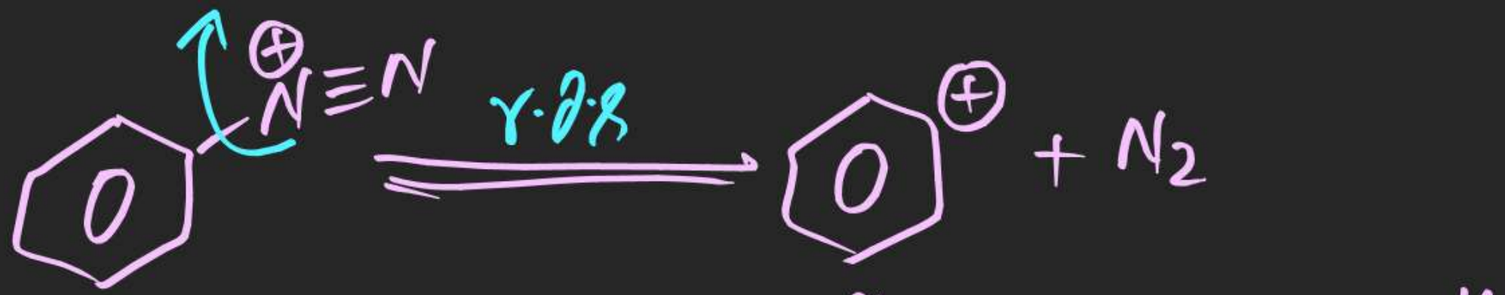
⇒ whenever Benzene diazonium chloride is treated with steam, it gives phenol as a product.

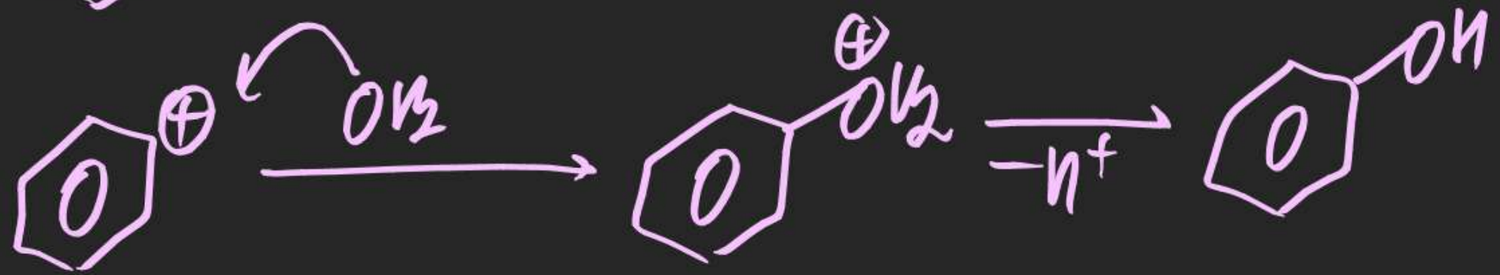
M.I.Imp

(1)



mechⁿ :-





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Note (i) Aryl cation intermidiate

(ii) Formation of Aryl cation is r.d.s

(iii) Nu is not involved in r.d.s

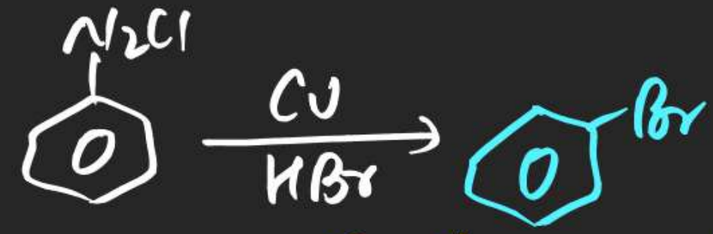
(iv) rate exp $r = K[\text{Ar}N_2^{\oplus}]$

(v) unimolecular Rxn

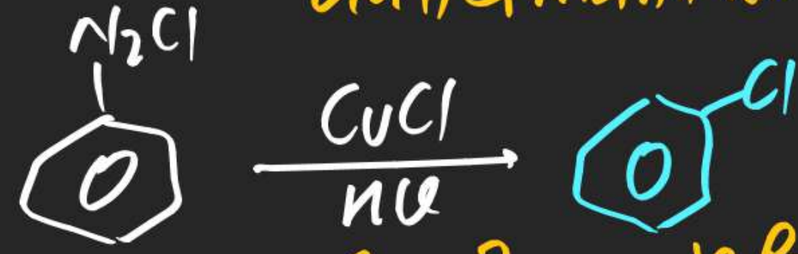
(vi) SN^1 Ar.

(2) 

Gattermann Rxn

(3) 

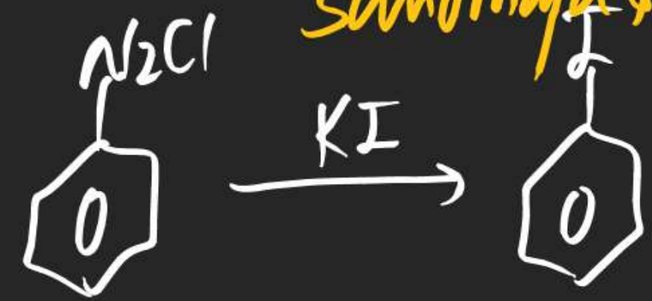
Gattermann Rxn

(4) 

Sandmeyer's Rxn

(5) 

Sandmeyer's Rxn.

(6) 

(7) 

(Baltz-Schiemann Rxn)

(8) 

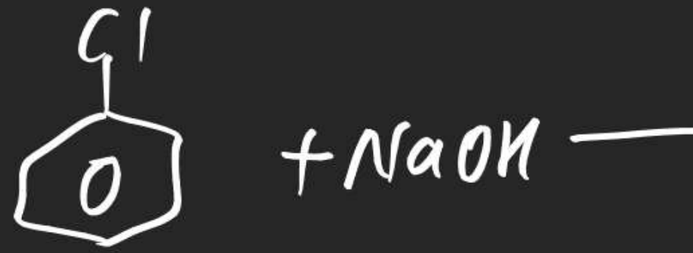
M. Imp
(9) 

M. Imp
(10) 

M. Imp
(11) 

(12) 

(13) 

(14) 

Imp. (15) 

(Dow's Process)

(16)

(a)  NaOH → X

(b)  NaOH →

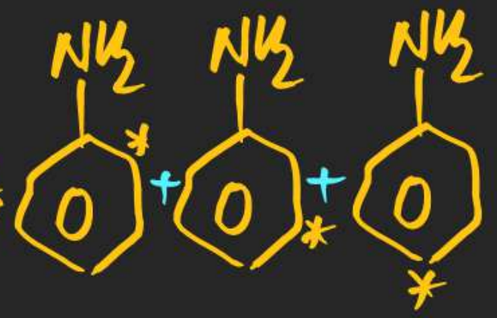
Jump (c)

 NaOH →

* SNEA Mech

(17)

 (Stry Base) + NaNH$_2$ $\xrightarrow[NH_3]{in}$ 

(18)  $\xrightarrow[NH_3]{NaNH_2}$ 

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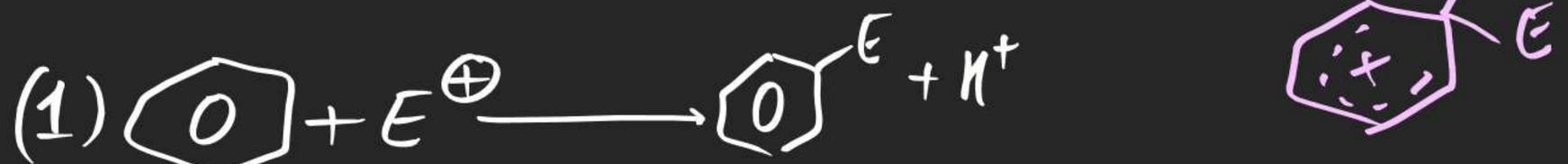
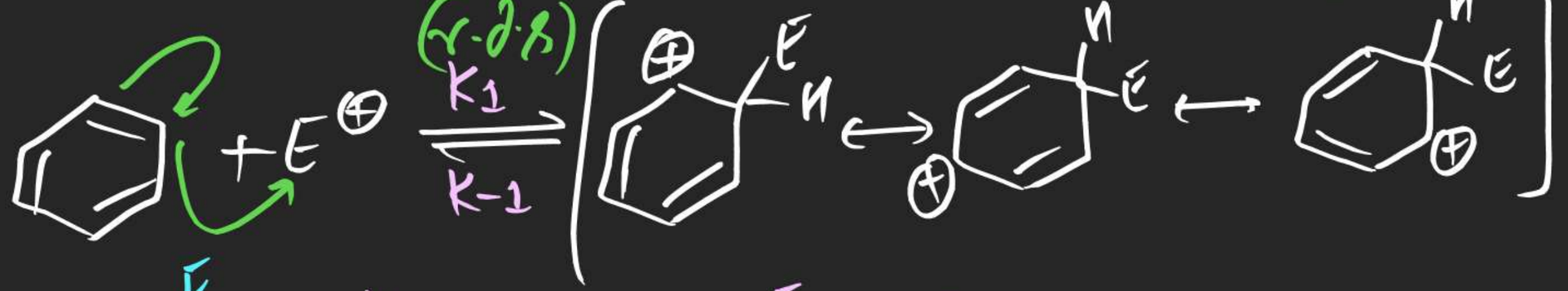
Electrophilic Aromatic Substitution

⇒ Aromatic Compounds usually prefer to show Electrophilic Aromatic Substitution C_6H_6, C_6D_6, C_6T_6



* Arenium Ion
* σ-Complex
* Wheland In
* Carbocation

mechⁿ:



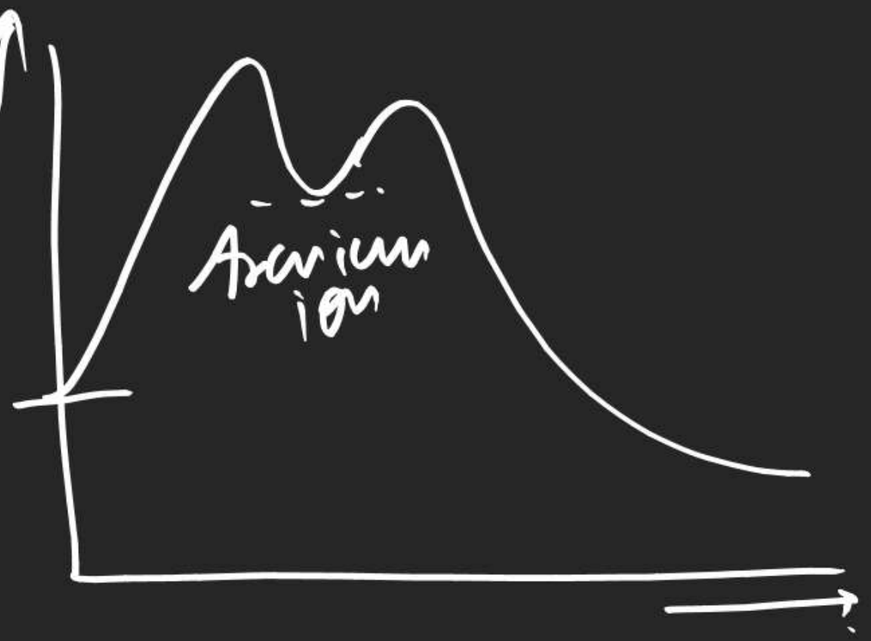
Note (i) Step-I is r.d.s

(ii) Arenium ion intermidiate

(iii) Rate of Electrophilic Aromatic substitution $\propto$ Stability of Arenium ion $\propto$ EDG.

(iv) rate exp $r = k[\text{C}_6\text{H}_6][E^{\oplus}]$

(v) P.E. diagram



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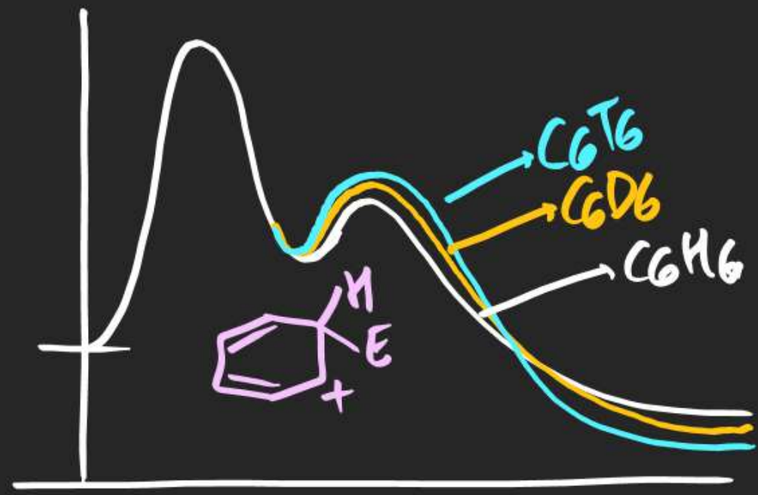
(vi) if $K_2 \ggg K_{-1}$

$\Rightarrow$ Rxn is irreversible

$\Rightarrow$ No kinetic isotopic effect observed.

$$\gamma_{C_6H_6} \simeq \gamma_{C_6D_6} \simeq \gamma_{C_6T_6}$$



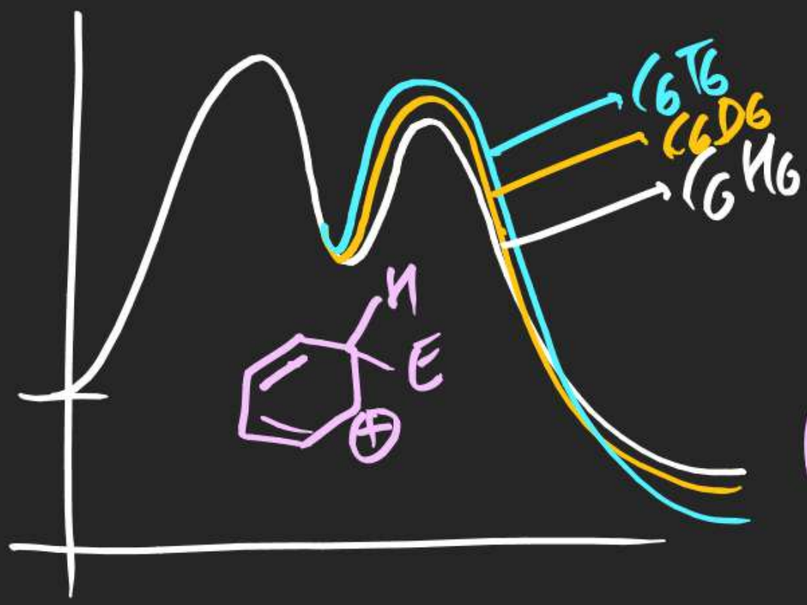
Ex: (i) Nitration
(ii) Chlorination of Benzene
(iii) Bromination of Benzene.

(vii) If $K_2 > K_{-1}$

$\Rightarrow$ Rxn is Reversible

$\Rightarrow$ Kinetic isotopic effect observed.

$$\gamma_{C_6H_6} > \gamma_{C_6D_6} > \gamma_{C_6T_6}$$



Ex: (i) Sulphonation
(ii) Iodination of Benzene
(iii) Alkylation

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(#) Application of EAS:

(i) Nitration of Benzene

(ii) Sulphonation of Benzene

(iii) Halogenation of Benzene

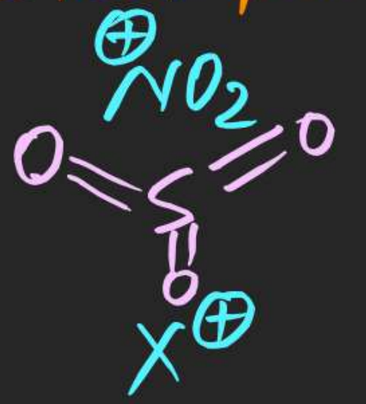
(iv) Alkylation of Benzene

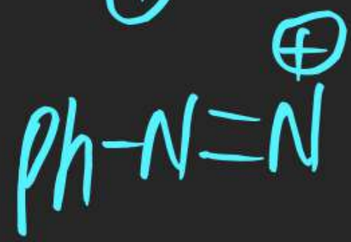
(v) Acylation of Benzene

(vi) Formylation of Benzene

(vii) Coupling Rxn

Electrophile ($E^{\oplus}$)





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Nitration of Benzene

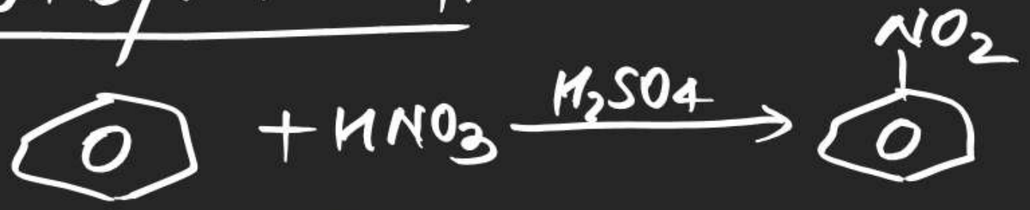
$\Rightarrow$ On nitration of Benzene, nitro Benzene is obtained as a Product.

(1) 

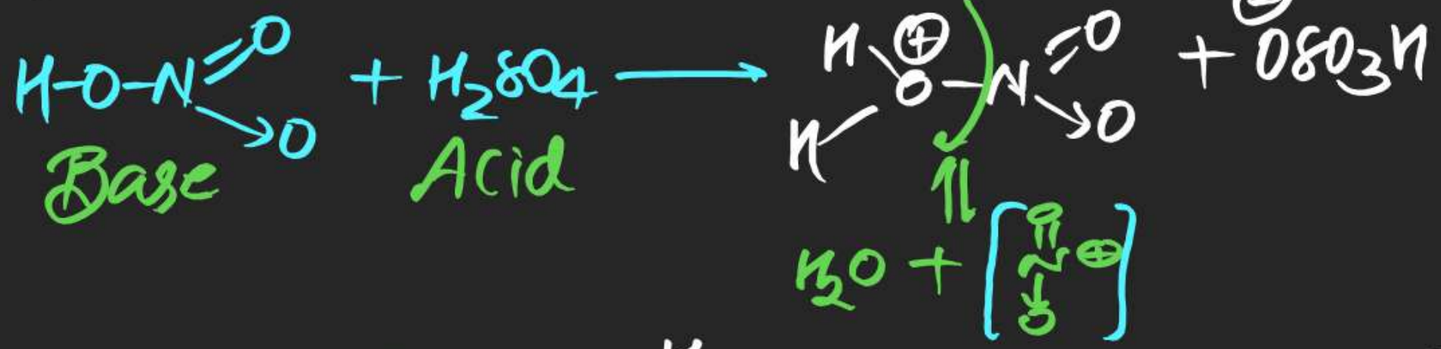
P may be

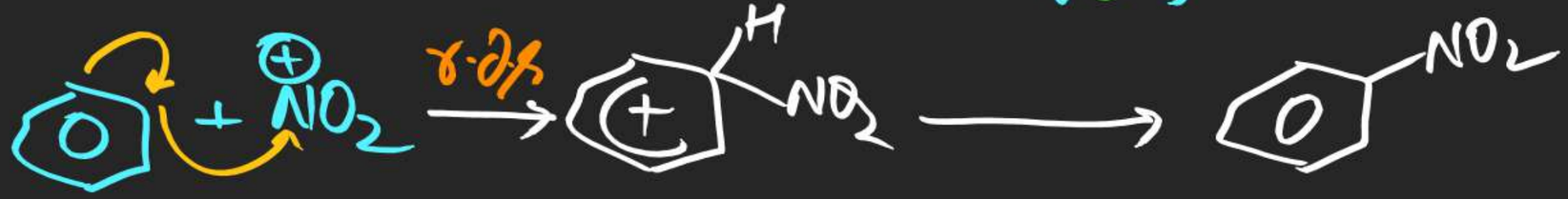
(i) Mixed Acid / Nitrating mixture / $HNO_3 + H_2SO_4$
(ii) Conc. HNO_3
(iii) Dil HNO_3
(iv) N_2O_5 / $AcONO_2$
(v) NO_2BF_4 / NO_2ClO_4

Nitration By Mix Acid:-

(2)  $+ HNO_3 \xrightarrow{H_2SO_4}$

mechⁿ:





Nitration By Conc. HNO_3:

(3)  $+ HNO_3$ (Conc.) ⟶

mechⁿ:

$HNO_3 + HNO_3 \rightleftharpoons H_2O^{\oplus}-NO_2 + NO_3^{\ominus}$

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(#) Nitration By Dil HNO_3/N_2O_5/$AcONO_2$

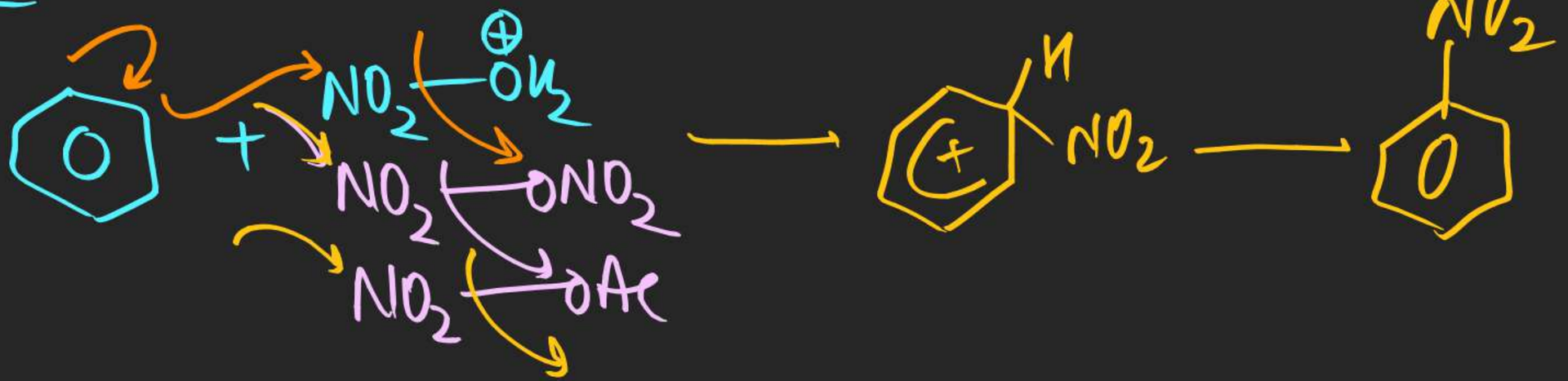
(A)  + Dil HNO_3 ⟶

+ N_2O_5 ⟶

+ $AcO-NO_2$ ⟶

mech?

$$2HNO_3 \rightleftharpoons H_2\overset{\oplus}{O}-NO_2 + \overset{\ominus}{NO_3}$$



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