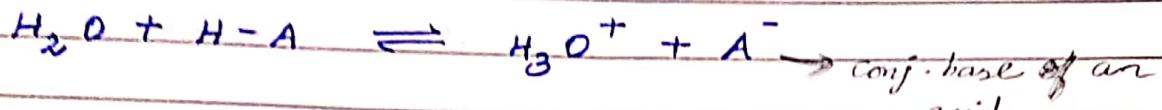
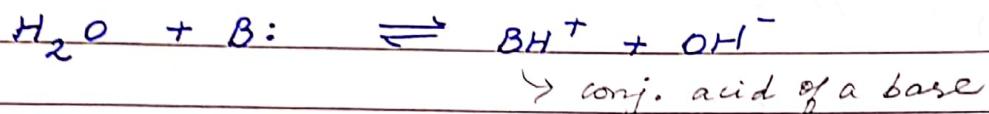


Acid - Base

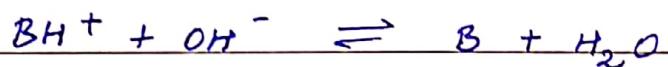


Eq. constant, $k_a = \frac{[H_3O^+][A^-]}{[H-A]}$

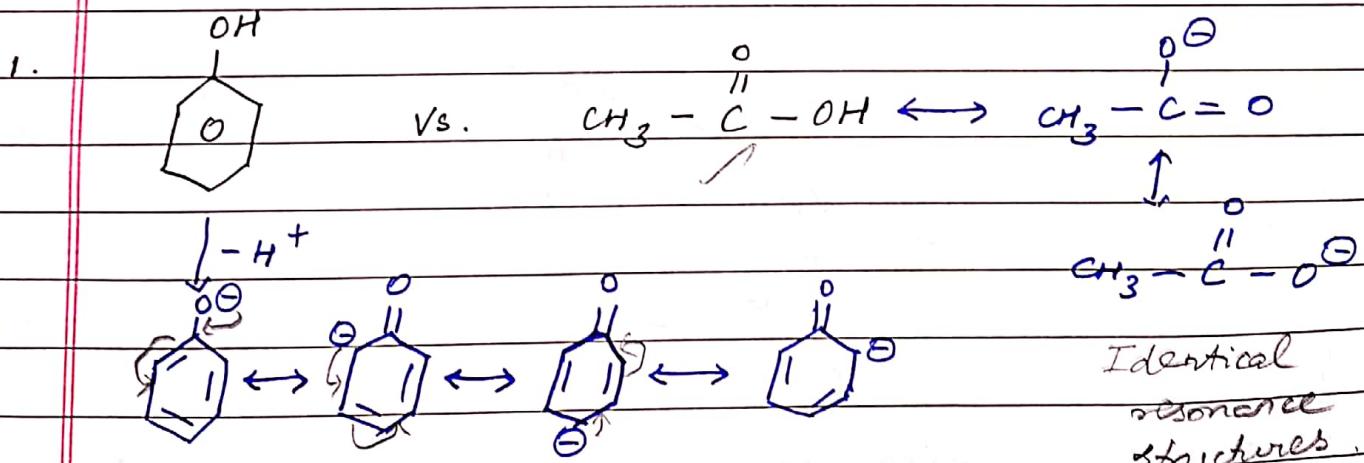
A^- 's stability \propto strength of $H-A$

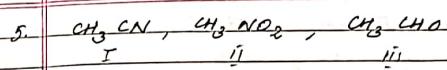
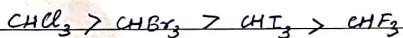
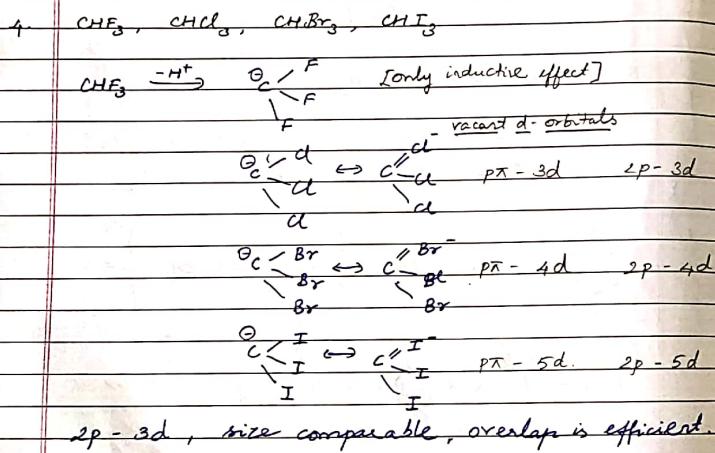
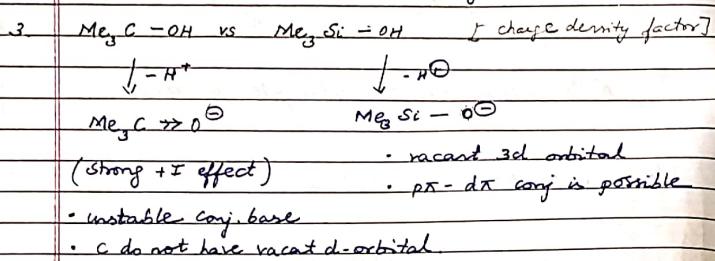
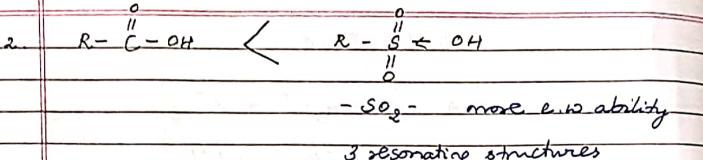


$$k_b = \frac{[BH^+][OH^-]}{[B:]}$$



$$K_a = \frac{[B:]}{[BH^+][OH^-]} \quad [\text{corr. } k_b \rightarrow k_a]$$

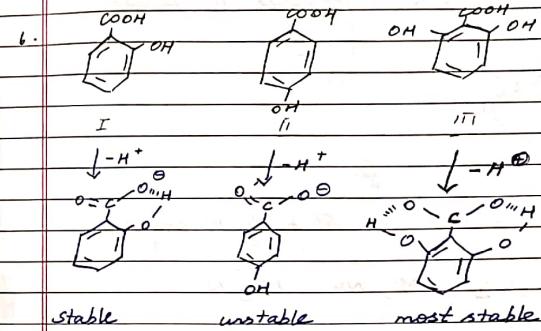




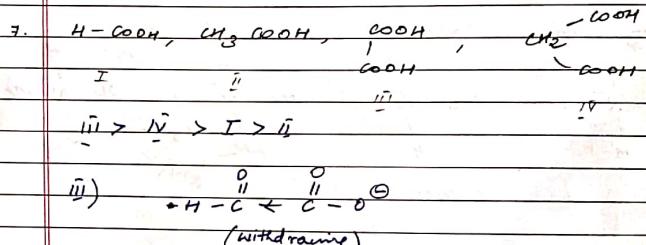
L-E-A ability order:

- NO₂ > - CHO > - CN

II > III > I [Acidic strength]

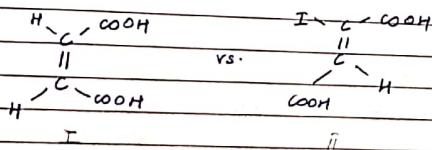


* pKa of CH₃COOH = 4.76

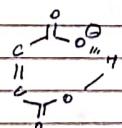


IV) effect is not present due to -CH₃ group.

8. Maleic acid vs. Fumaric acid



I > II Intra-molecular H-bonding.

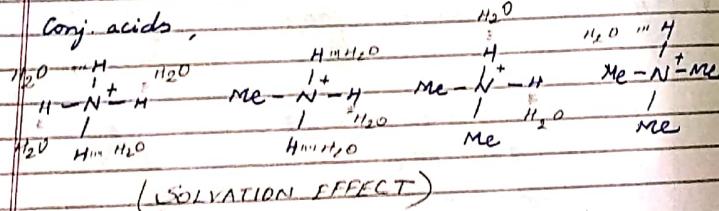


* Basic strength & Stability of conj. acid.

PK_a 9.25 10.64 10.77 9.80
 1. NH₃, MeNH₂, Me₂NH, Me₃N

i) In terms of inductive effect,
 $\text{IV} > \text{III} > \text{II} > \text{I}$

ii) Conj. acids,

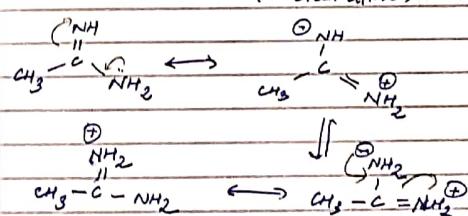
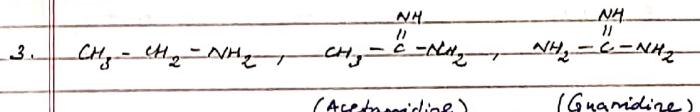
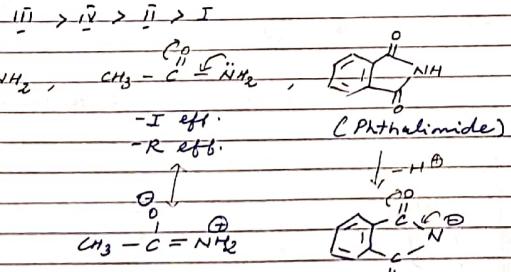


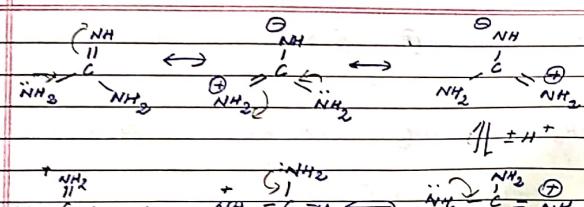
$$I > \bar{I} > II > \bar{II}$$

classmate

Net: $\text{Li} > \text{I}^- > \text{Br}^- > \text{Cl}^-$

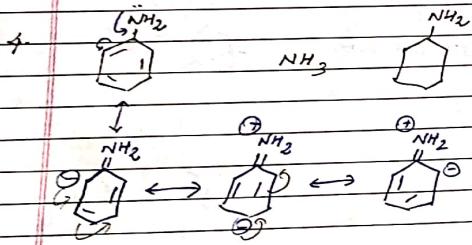
*	NH_3	EtNH_2	Et_2NH	Et_3N
pK_a	9.25	10.67	10.93	10.98





(Identical canonical structures)

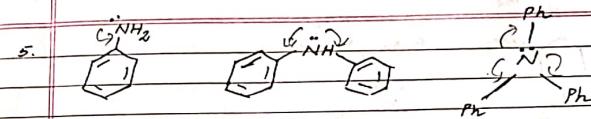
III > II > I



If it takes up a proton, the above sort of stabilization is not possible.

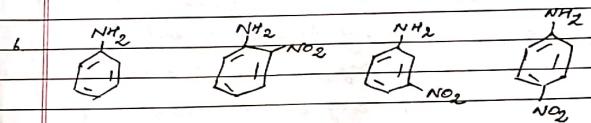
III > II > I

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Stability is more if the lone pair availability N is more

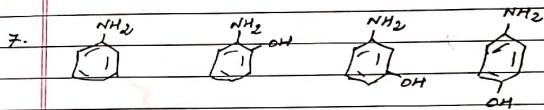
I > II > III



ENg at ortho & para is dominant (ortho & para)

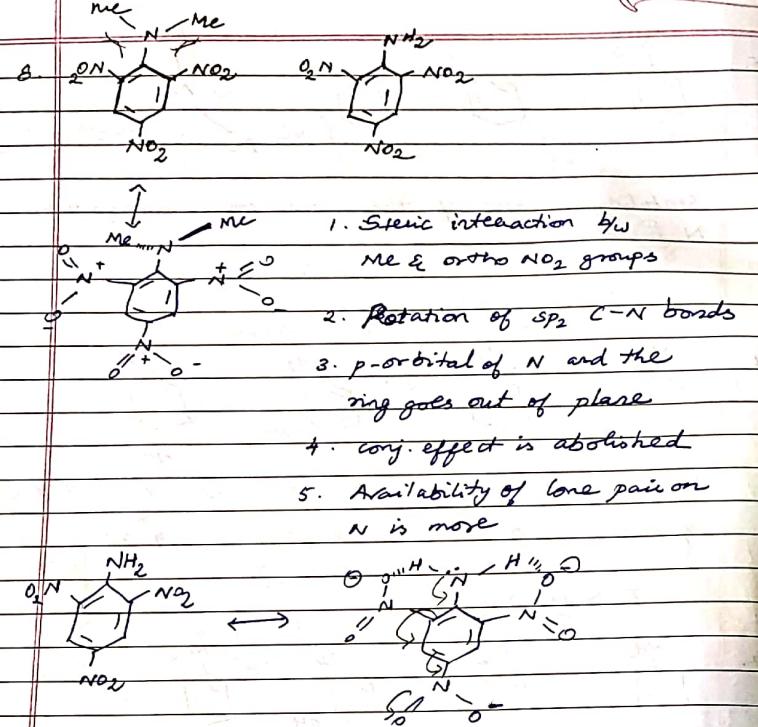
pKa 4.62 -0.28 2.45 0.98

I > II > IV > III



pKa 4.62 4.72 4.17 5.30

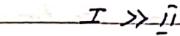
p > o > m (+R eff)



[locked in *cis*-plane config. due to (with the ar. ring)
intermolecular H-bonding]
Conj. effect is enhanced.

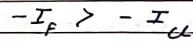
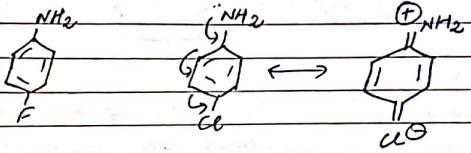
Mesomeric effect is pronounced

Lone pair availability on N is drastically decreased



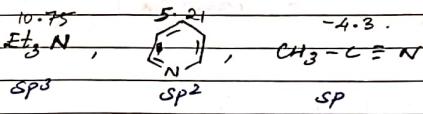
(about 40,000 times more basic)

9.



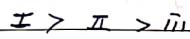
(-R eff.)

10.

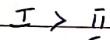
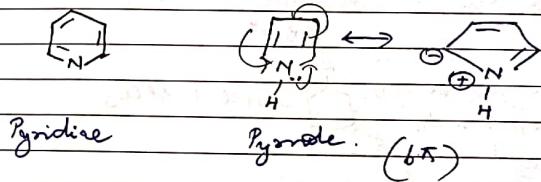


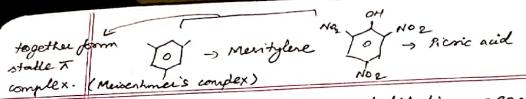
s char inc. - electronegativity inc.

↓
Ele. donating char dec.



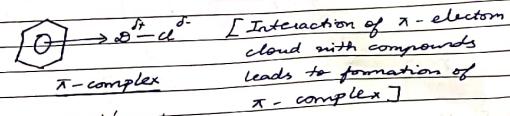
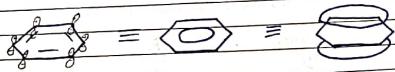
11.



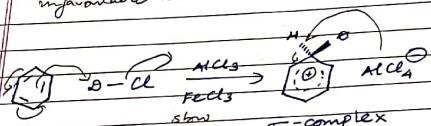


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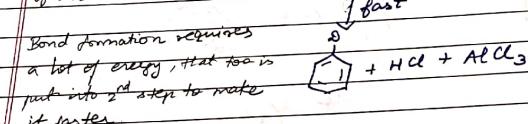
Aromatic Electrophilic substitution reaction



(highly unstable under unfavorable conditions).

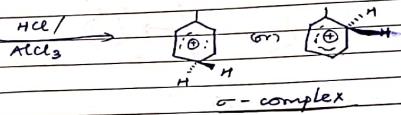


i) Fast due to gaining of aromatic character

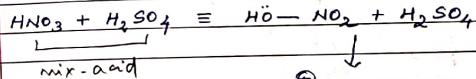
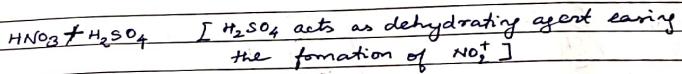


π -complex.

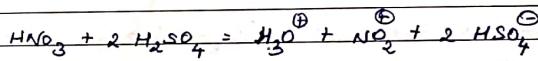
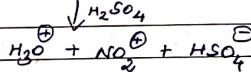
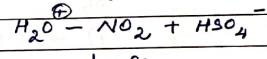
- (i) does not show color change
- (ii) soln. is not electrically conducting
- (iii) UV spectrum does not show significant changes.



Nitration:



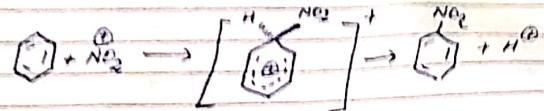
mix-acid



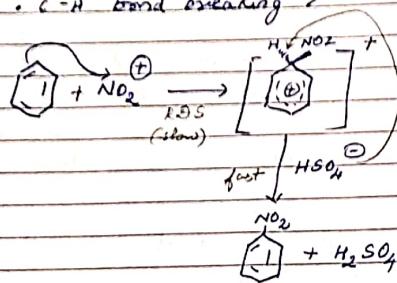
Primary nitrate Nucleophile effect
directly oxidized



Possible mechanisms:



- Single concerted step (i.e.,
- C-NO₂ bond formation > simultaneously.
- C-H bond breaking

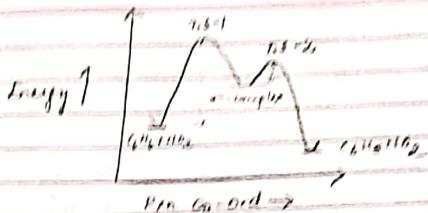


$$\text{Rate} = k [C_6H_5] [NO_2^+] \dots \text{2nd order.}$$

When C_6H_5 was taken at 25°C, $k = 1$

elastomer
water
Pt

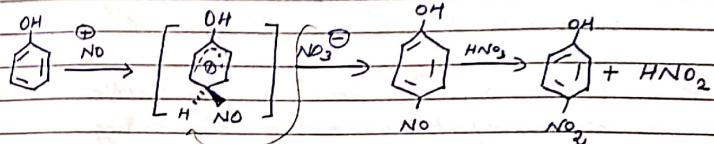
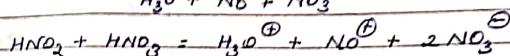
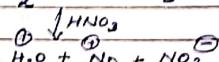
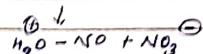
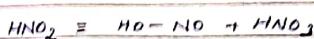
elastomer
water
Pt



$\text{Phenol} \xrightarrow{\text{Conc. } HNO_3} \text{Nitrophenol}$

Q: Phenol can be easily nitrated by dil. HNO_3 but not conc. HNO_3 (or) mix acid. Explain.

(Dil. HNO_3 always contains some amount of HNO_2)

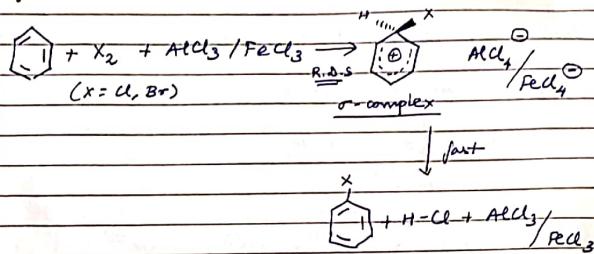


Since conc. HNO_3 and mix acid are strong oxidizing agents, no ring oxidation takes place instead of nitration of phenol. Due to high e^- availability in the phenyl ring by the +R effect of -OH group.

However dil. HNO_3 which contains small amounts of HNO_2 , that produces NO^+ [Nitrosonium ion] as the effective E^⑥ to produce para-nitro-phenol.

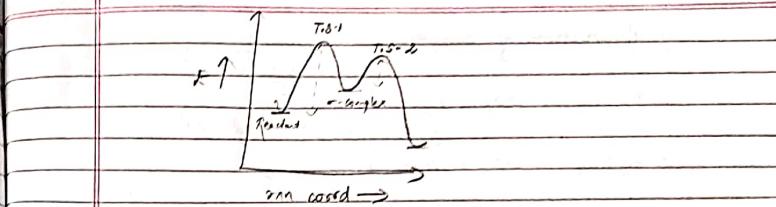
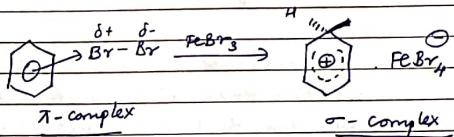
This when oxidized very rapidly by HNO_3 to yield para-nitro phenol and HNO_2 . Thus the process gets speeded up.

Halo-genation rxn:

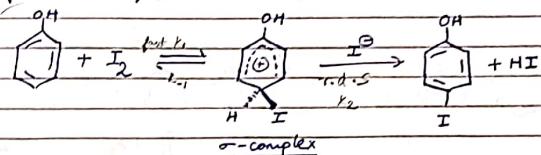


$$\text{Rate} = k [C_6H_6][X_2][AlCl_3 / FeCl_3] \text{ -- 3rd order.}$$

* The rxn does not show primary kinetic isotopic effect as C-H bond breaking does not happen in the R.D.S

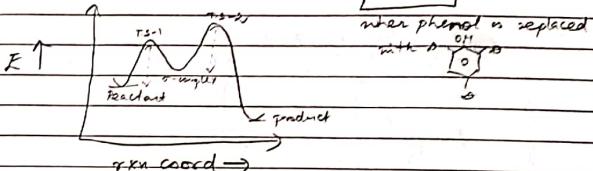


Iodination of phenol:



$$k_{-1} > k_2 \quad (\text{C-I bond can be broken easily})$$

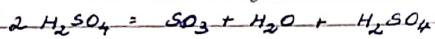
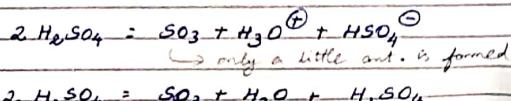
Primary kinetic isotopic effect is observed, $\frac{k_H}{k_D} = 4$ at 25°C



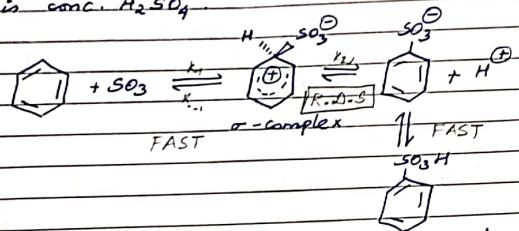
Here the 1st step is reversible where loss of iodine from the σ -complex takes place early than the loss of H. Thus $k_{-1} > k_2$. Hence the overall equilibrium lies on the LHS. The overall equi. can be shifted to the RHS by using either base / oxidising agents which will remove HI from the rxn. medium. Since the 2nd step is the R.D.S, so it exhibits PKIE as R.D.S involves breakage of C-H bond.

Conc. of SO_3 in oleum is more than that of conc. H_2SO_4 , hence making the rxn proceed forward.

Sulphonation of benzene:

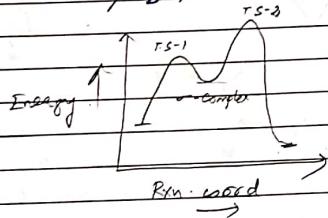


- * Sulphonation rxn is faster in oleum than is conc. H_2SO_4 .



Primary kinetic isotopic effect is observed.

$$k_H / k_D \neq 1$$



S^- is the place of rxn as,

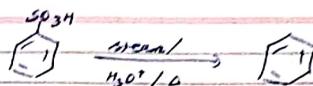
- more electropositive center.
- Electron deficient.

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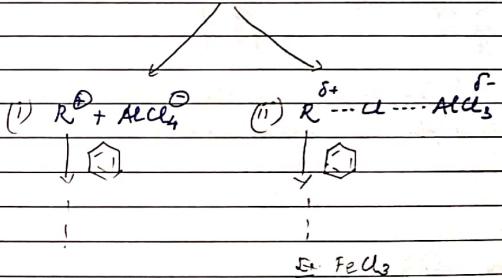
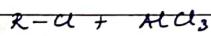
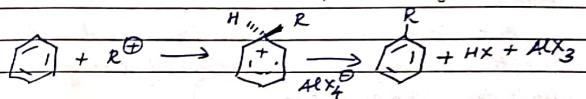
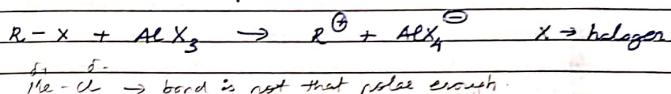


- goes through the same path as that of forward rxn
- involves same σ -complex intermediate

Microscopic reversibility:

The reverse reaction from the product to the reactant must follow the same mechanism as that of the forward rxn. The sulphonation and desulphonation of benzene follow the same mechanism as both of them involves the formation of σ -complex as intermediate.

Friedel-Crafts Alkylation:



- i) depending on R group.
ii) strength of Lewis acid.

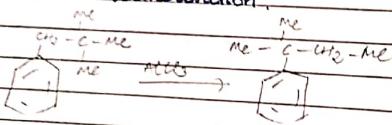
When FeCl₃ is used the rxn goes via (ii) path.

Formation of complex is the R.O.S. in all the cases. [no PKE]

When benzene is treated with Mg(C₂H₅)₂-Cl with acetyl AlCl₃, rearranged product is formed, but with FeCl₃ unarranged product formed.

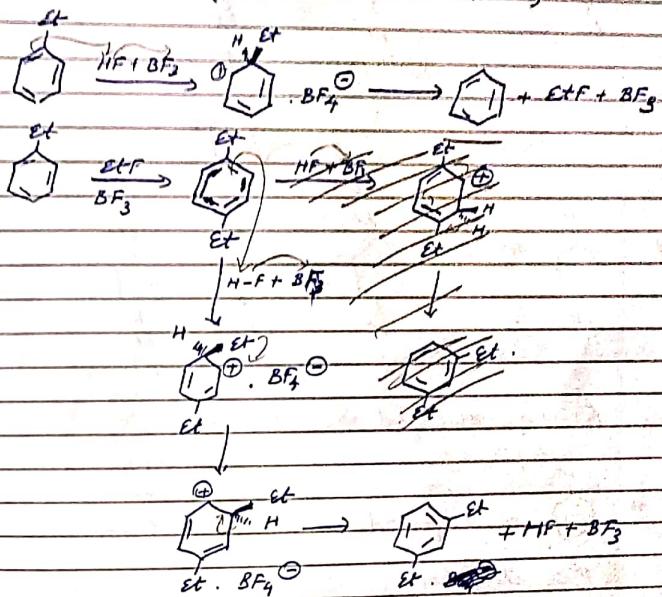
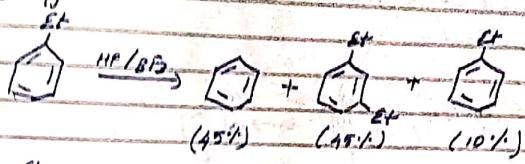
AlCl₃ is a stronger Lewis acid, so the electrophilic complex is polarised enough to allow the rearrangement to a more stable carbocation.

But, FeCl₃ is a weaker Lewis acid and hence the complex is not polarised enough to allow the isomerisation.

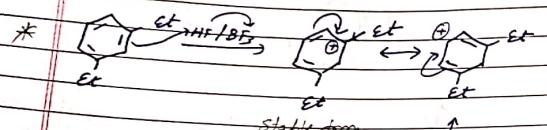


AlCl₃ is so strong such that the above can take place to some extent.

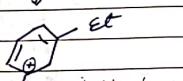
Dealkylation:



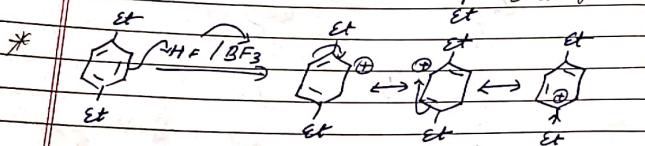
Meta product is more stable than the para product.



Stable form

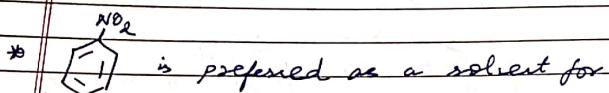


Stable form



Stable form.

(+) charge stabilized \rightarrow more stable

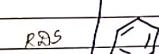
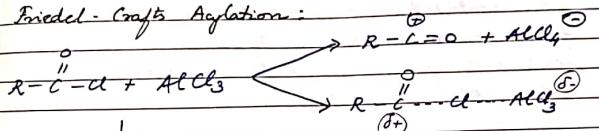


F.C. alkylation.

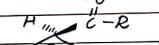
(i) Benzene is more reactive than nitrobenzene

ii) AlCl_3 is more soluble in nitrobenzene

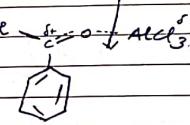
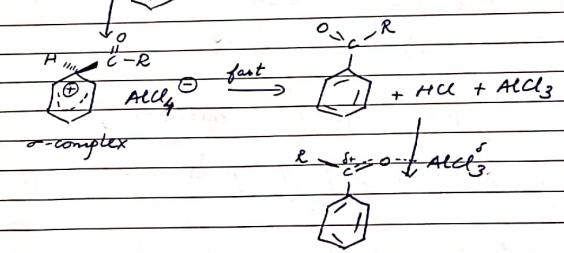
Friedel-Crafts Acylation:



α -complex



α -complex



Q. Why more than 1 eq of Lewis acid catalyst is needed for acylation rxn.

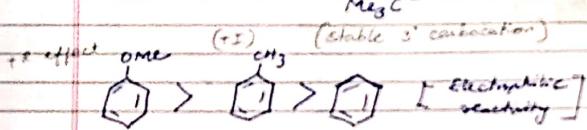
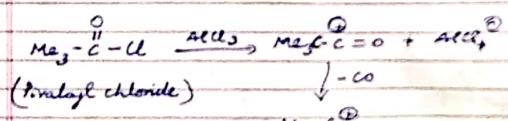
The acylated product further reacts with AlCl_3 to give a stable complex. So further acylation rxn takes place if further AlCl_3 is added.

Q. Why is acylation rxn, poly acylation doesn't take place?

The ring is deactivated in presence of acyl group (EWG) thus not leading to poly acylation.

Therefore, further acylation takes place only in benzene ring and not acyl benzene.

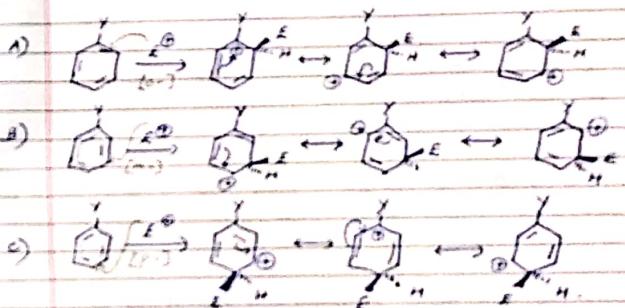
Q. The contribution of parent CO gas increases from anisole to toluene to benzene when reacts with phenyl chloride in presence of anhyd. AlCl₃. Explain.



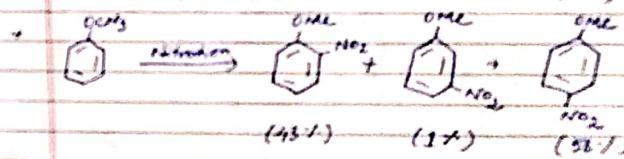
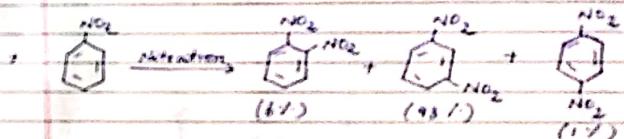
The reactivity of phenyl ring decreases from left to right. Hence, the contribution of CO gas increases from LHS to RHS. Thus the contribution of alkylated Product inc from left to right and the contribution of acylated product decreases.

Benzene react slowly, hence giving more time for Me₃C=O to release the CO.

ES / attack on mono-nitro benzene: [CsH₅N₃]



* γ-EWG o-, p- directing
* γ-ENIG m- directing



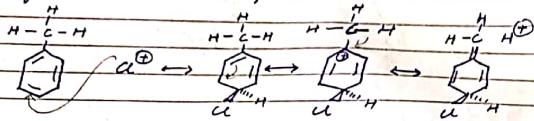
iii. γ-EWG: NR_3 , CCl_3 , NO_2 , CHO , COCH_3 , C_6F_5 , CN , COR etc.

Stronger the EWG, the rate of the rxn decreases but the selectivity (or) the amount of meta product is higher. [due to steric effect on C_6H_5^+ (rate is enough for C_6H_5^+ attack.)]

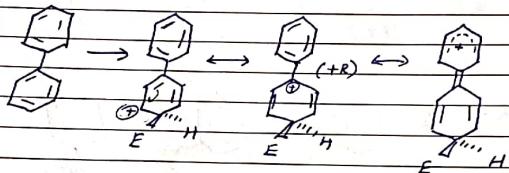
NO_2^+ - polar out of mech. \rightarrow kinetically controlled
 Cl^\ominus - non-polar \rightarrow transition state decides

2. $\gamma = E\text{Og}$ - Acyl, phenyl.

3. Nitration of $\text{C}_6\text{H}_5\text{CH}_3$ is faster than $\text{C}_6\text{H}_5\text{CH}_2$ but chlorination is faster for the latter. Explain.

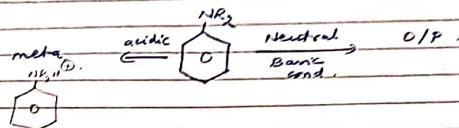


For $\text{C}_6\text{H}_5\text{CH}_3$, greater $+I$ effect is operational than the latter which stabilises the $-$ -complex. But for chlorination which is a less polar rxn, the e^- donation through hyperconjugation is much greater for $\text{C}_6\text{H}_5\text{CH}_3$

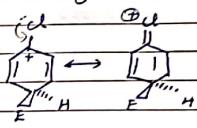


3. $\gamma = (-I, +R) - \overset{\overset{\text{O}}{\parallel}}{\text{C}}-\text{R}, \text{NH}-\overset{\overset{\text{O}}{\parallel}}{\text{C}}-\text{R}, \text{OR}, \text{OH}, \text{NH}_2, \text{NR}_2$

R - the selectivity of the attack
 I - the kinetics of the attack

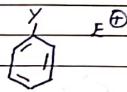


4. $\gamma = \text{Halogens } \text{Cl}, \text{Br}, \text{I } (-I, +R)$



The lone pair of e^- is used in stabilising the $+\text{I}$ charge here whereas in aryls it is used to stabilise the ring. (ring activation)

* O/P - product ratio :

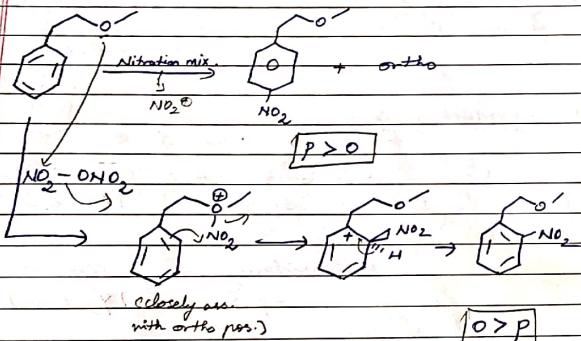


* Considering steric factor of Y
 $-p > -o$. [E is const.]

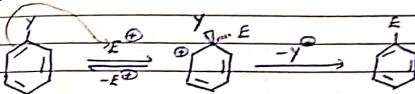
* Considering inc. in size of E+
 $-p > -o$. [Y is const.]

* When $\gamma = F, Cl, Br, I$ and E^\ominus remains constant, here the e^- availability at ortho position increases from LHS to RHS as the E.N. of the halogen atom decreases from LHS to RHS. That is the reason for the contribution of ortho product increases and consequently the contribution of para product dec. from LHS to RHS although the size of the halogen atoms dec. from RHS to LHS.

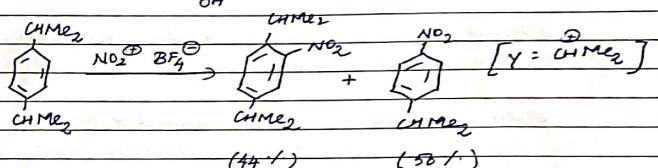
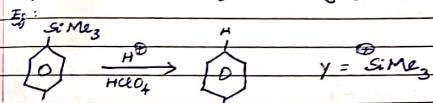
Q. Nitration of 1-methoxy-2-phenyl ethene leads to 32% ortho & 59% para isomers when treated with nitrating mixture, but 69% ortho 28% para isomers when treated with N_2O_5 in $MeCl$



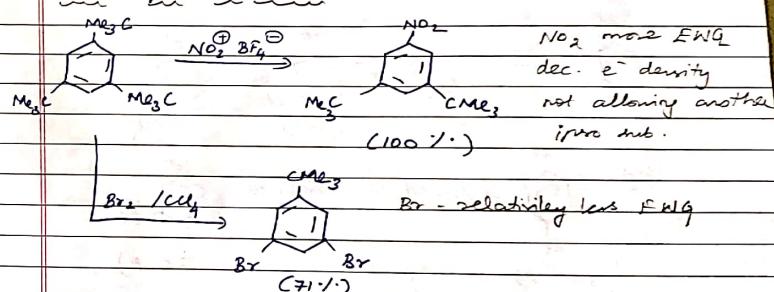
• I_{so}-substitution



γ^\ominus is stable \rightarrow good leaving group.

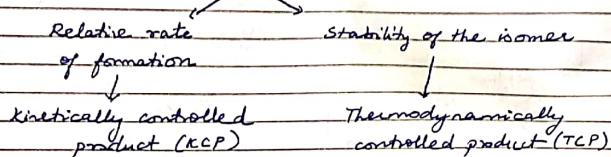


• Forced - ipso substitution:



* Kinetic vs. Thermodynamic control:

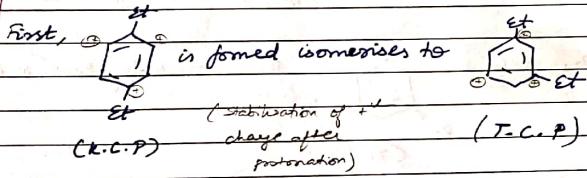
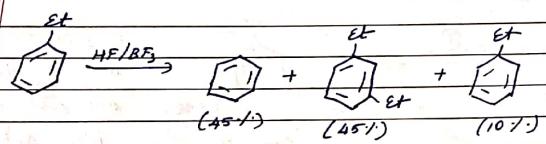
Proportion of alternate product formation



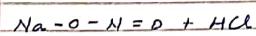
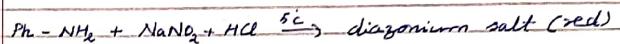
Alternative products are mutually interconvertible under the rxn conditions.

Direct isomerization

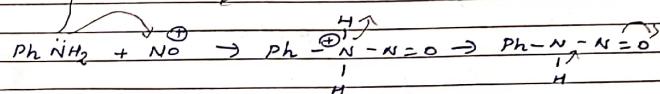
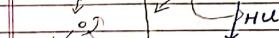
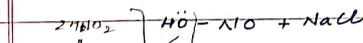
Reversal of the rxn
to form the starting material
followed by new attack
to the stable isomer



I.C. rxn of phenol:-



Acetate



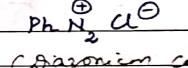
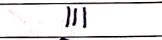
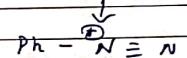
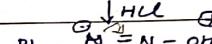
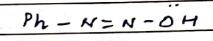
amide

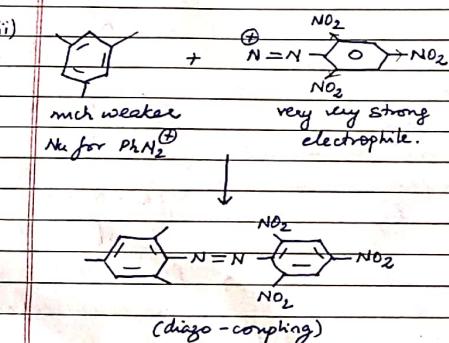
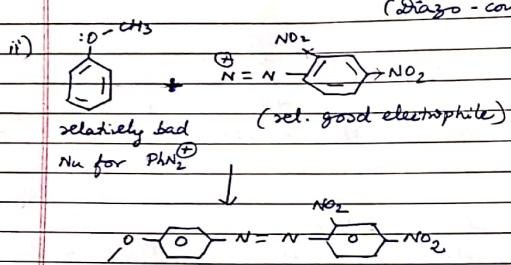
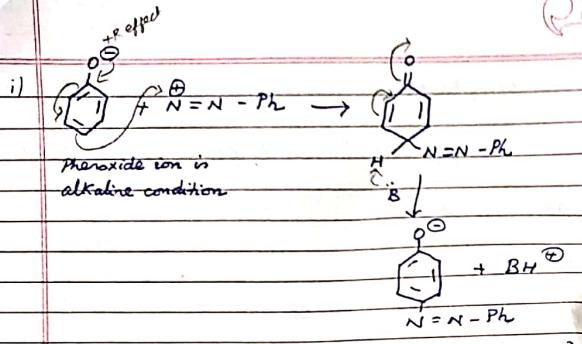
Q. Unlike phenol, doesn't give diazoethane reaction when treated with benzene diazonium salt but gives the above rxn when treated with

2,4-dinitrobenzene diazonium cation.

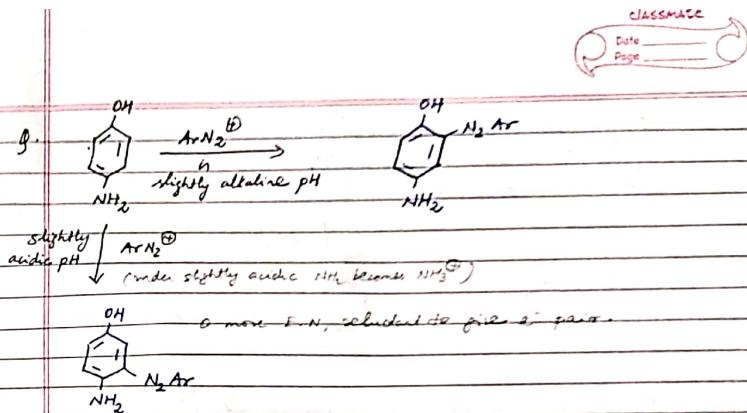
Mesmerites

gives the above rxn when treated with 2,4,6-trinitrobenzene diazonium cation. Explain

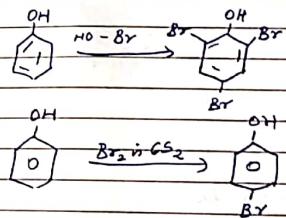
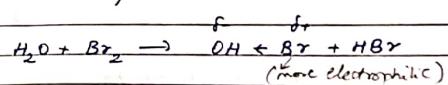




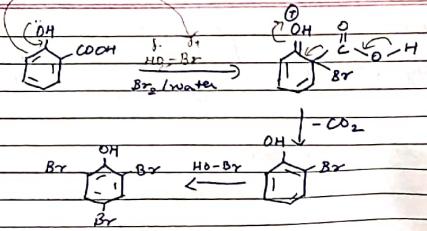
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g) Phenol on treatment with Br_2 water gives 2,4,6-tribromo phenol. On treatment with Br_2 in CS_2 gives para bromo phenol. Explain.

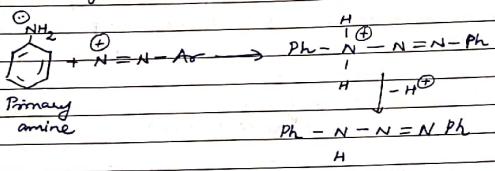


In case of the former, more
electrophilic HO-Br is generated,
w.r.t. Br atom is a Br_2 molecule,
but for the later case Br_2 is
less associated with the
solvent CS_2 . Therefore the
electrophilic character of Br_2 is
very less.

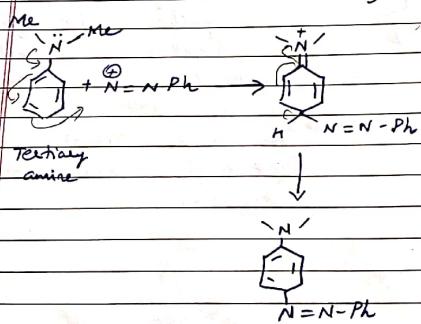


ES rxn of aromatic amine compounds:

ED ability of NH_2 is less than O^-



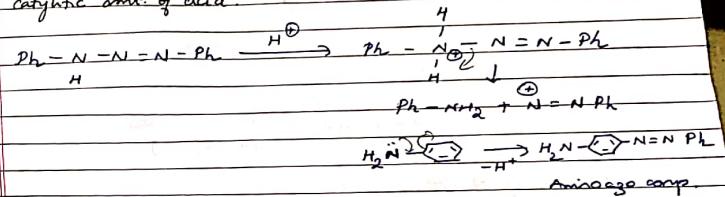
diazo-amino compounds.



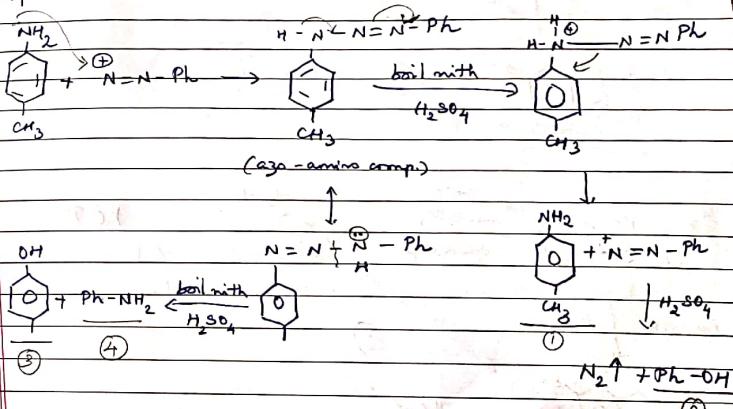
diazo coupling
(amino azo compound)

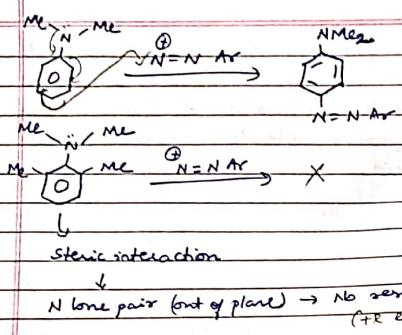
* Secondary amine gives a mixture of both products.

Q. What happens when the diazo amino compound of aniline with benzene diazonium chloride is warmed with catalytic amt. of acid.

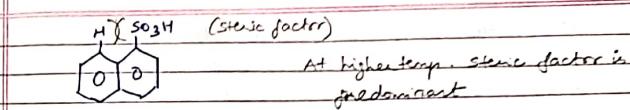
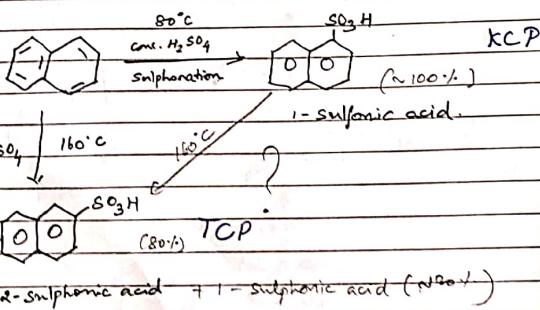
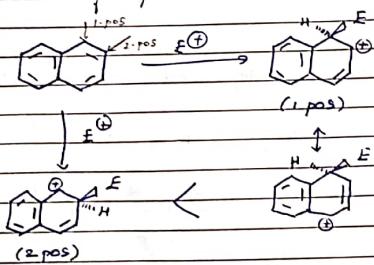


Q. Para-toluidine reacts with $\text{Ph}-\text{N}_2^+$ to give a compound which on boiling with dil. H_2SO_4 produces 4 products. Explain.

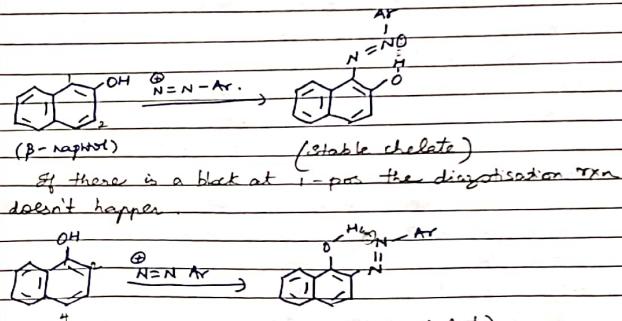




ES rxn of Naphthalene:

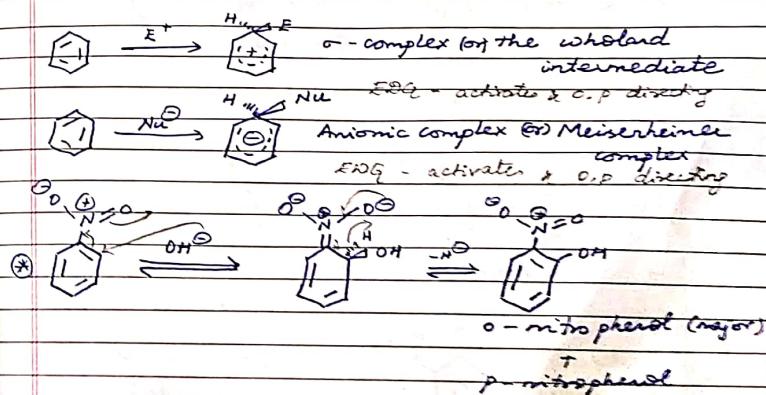


At higher temp., steric factor is predominant



When 2 pos is blocked the rxn occurs at 4-position.

Aromatic Nu^- sub. rxn :

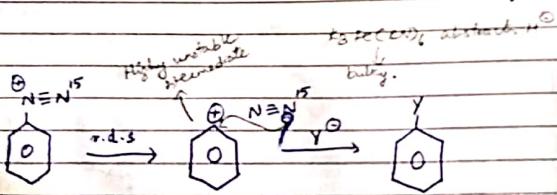
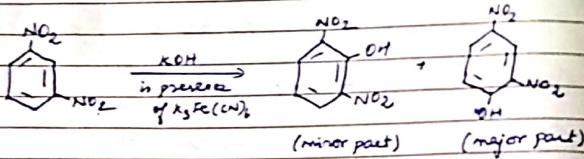


When $\text{NO}_2 - \text{C}_6\text{H}_5$ is fused with KOH in presence of air, α -nitrophenol is formed as major product.

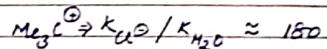
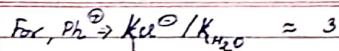
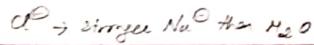
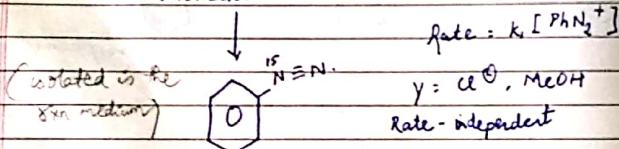
But in absence of air, the yield of final product is very very less.

In rxn ② H^\ominus is a path \perp to the OH^\ominus , hence the overall equilibrium lies to the left but in presence of air (oxidizing agent), elimination of H^\ominus is preferable as the H^\ominus gets destroyed by the oxidizing agent.

In absence of air (or) other oxidizing agents (KNO_3 or $\text{K}_3\text{Fe}(\text{CN})_6$) some extent of conversion takes place because $\text{NO}_2 - \text{C}_6\text{H}_5$ can act as the oxidizing agent on its own, but the yield of nitrophenol is very very poor.

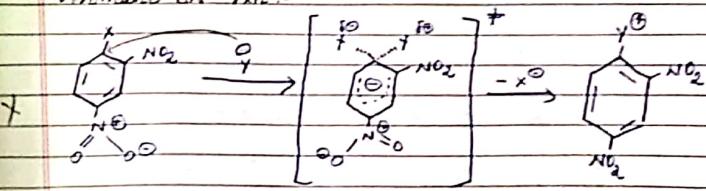


Aromatic SN' Rxn.

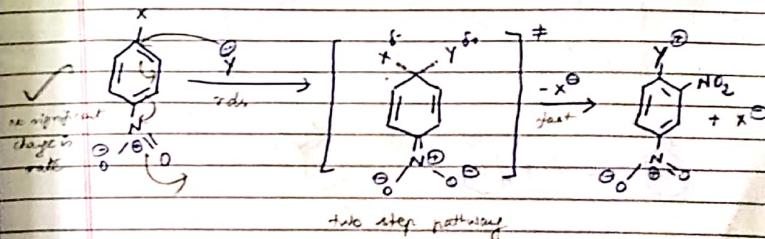


$\text{Ph}^\oplus \rightarrow$ highly reactive \Rightarrow less selective
 $\text{Me}_3\text{C}^\oplus \rightarrow$ less reactive \Rightarrow highly selective

Aromatic Ar^2 rxn:-



Concerted (one step) path



Rate: $k_2 [\text{Ar}-x][y]$ (2nd order)

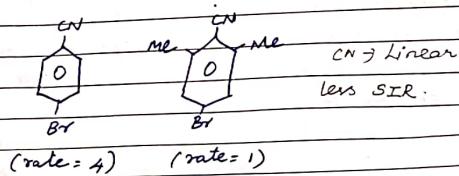
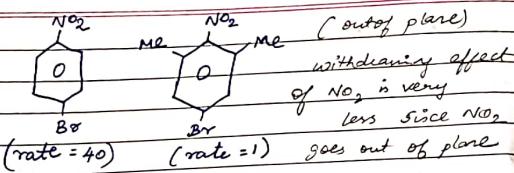
When, $y = \text{Piperidine}$, $x = \text{Cl}^\ominus, \text{Br}^\ominus, \text{I}^\ominus$

(*) For F^\ominus , it is exceptionally high as it makes the C centre highly electropositive.

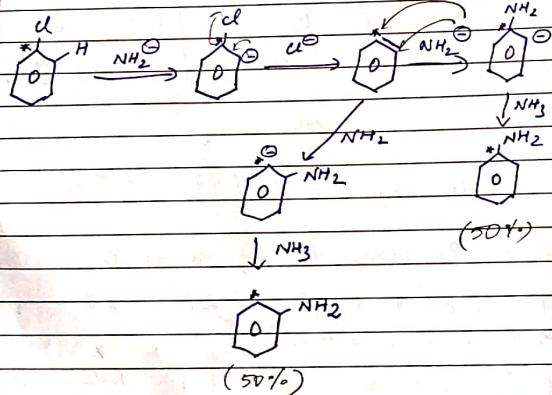
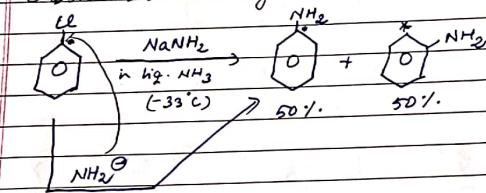
Rate = 4.3×10^{-3}

$x = \text{F}^\ominus$

Rate = 3300



Substitution via Aryne intermediate:



Benzyne confirmation:

