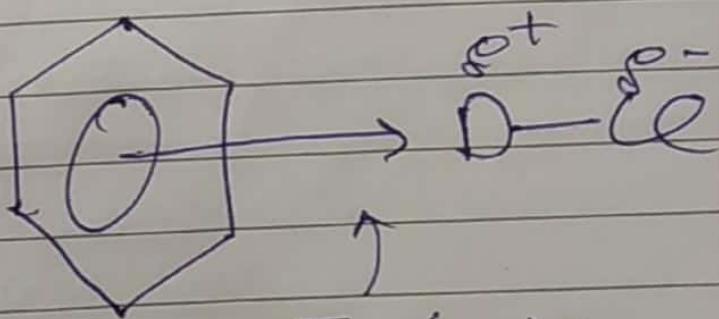
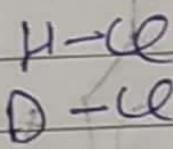
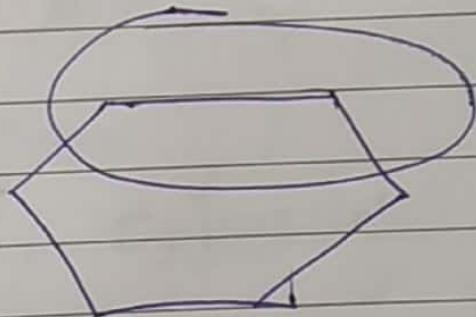
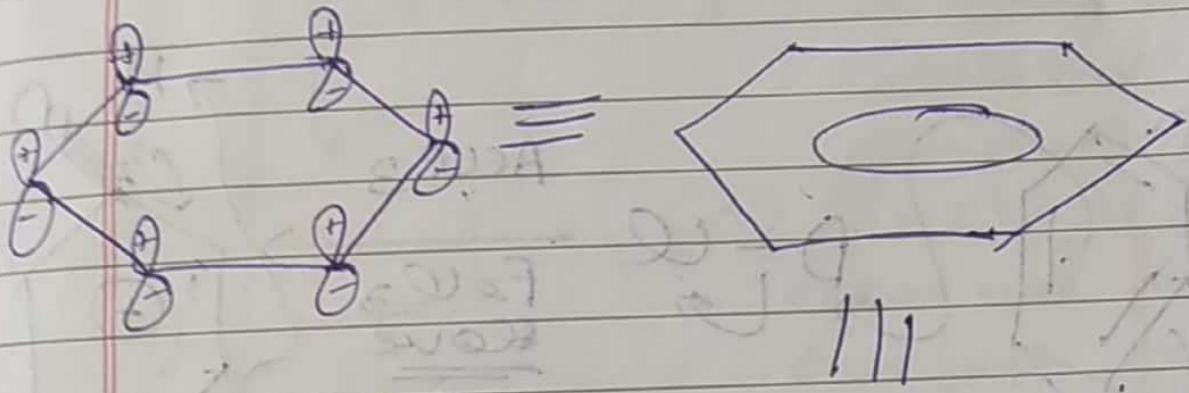


Electrophilic Aromatic Substitution

Pxn

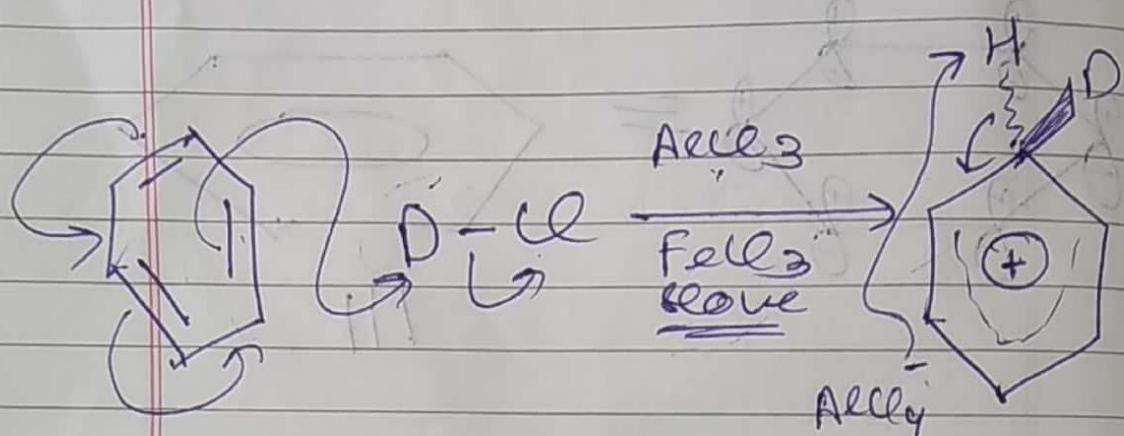
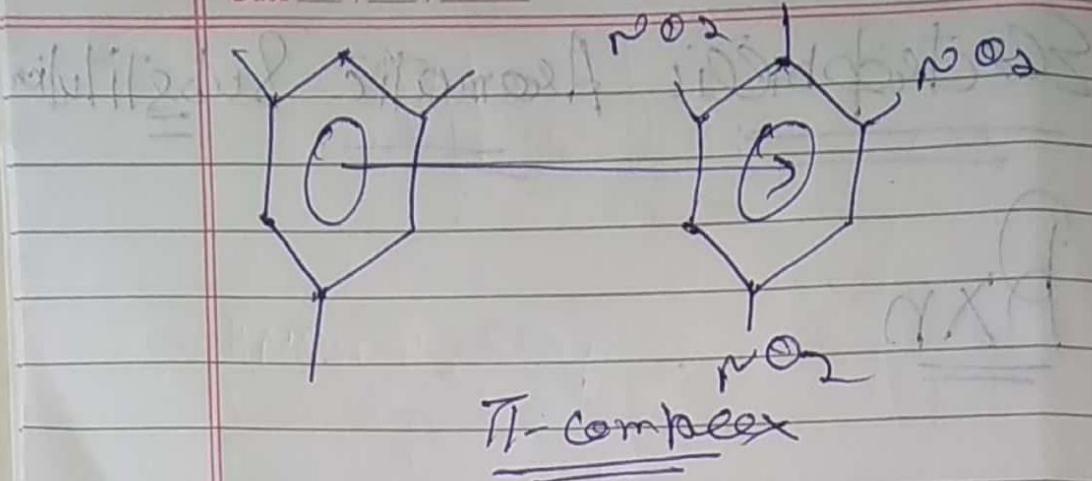


π -Complex
When πe^- is donated to
electrophile through co-ordination

Date _____

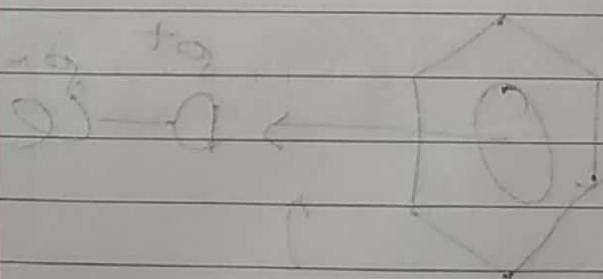
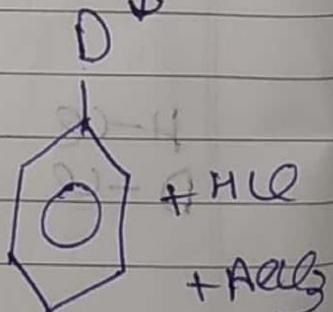
Saathi

04



complexe

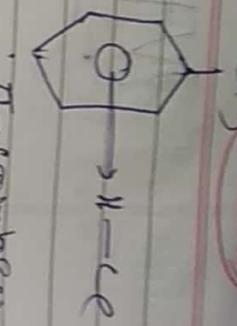
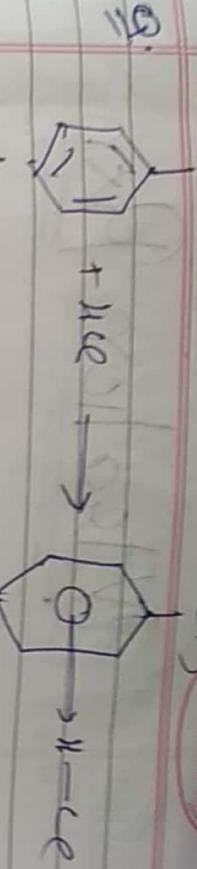
part



ox (no) - II

OT column of II
different with what
broad

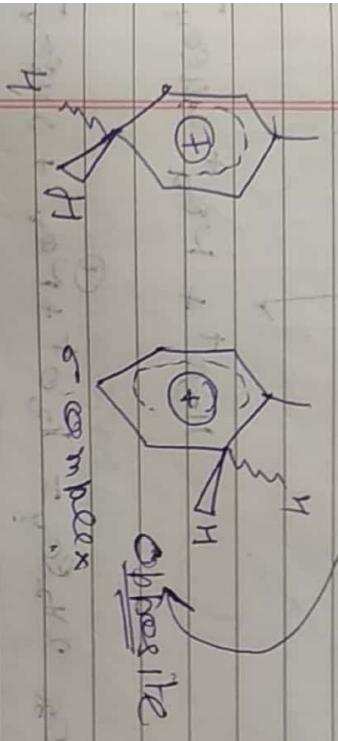
Page No. _____



(i) does not change
metres

(ii) colour, charge
(iii) solution is not
electrically
conducting

(iv) UV spectrum
does not show
surrounding charges



Cyclohexadienyl
anion

H-C=C-H → H-C=C-H

→ H-C=C-H → H-C=C-H

α-hydrogen

β-hydrogen

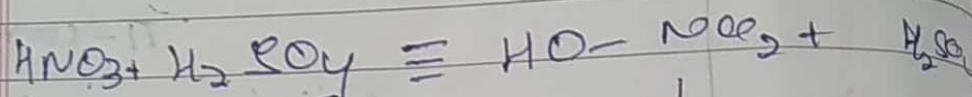
γ-hydrogen

δ-hydrogen

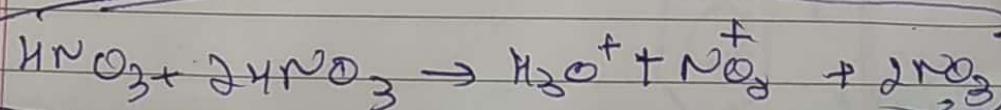
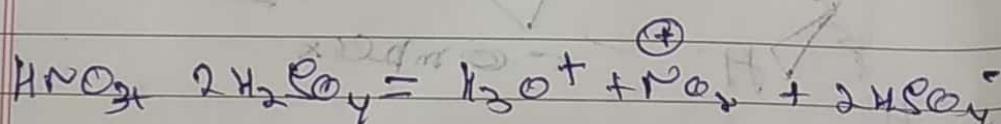
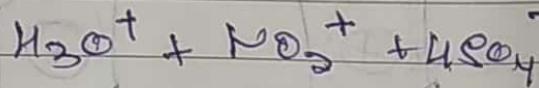
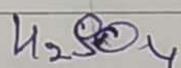
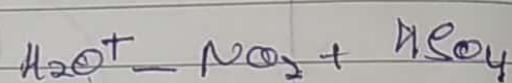
ε-hydrogen

η-hydrogen

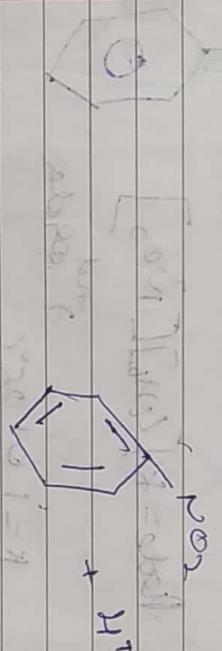
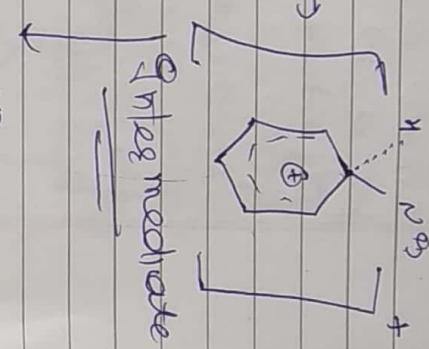
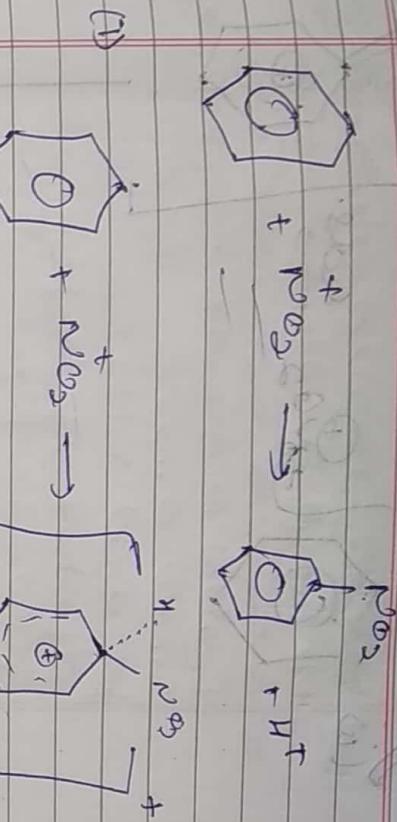
Date 24/2/21

Mitigation Rxn

\curvearrowleft
mix acid



\curvearrowleft very slow so does not happen.

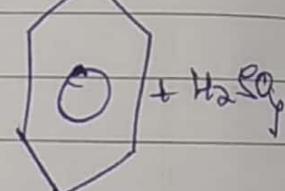
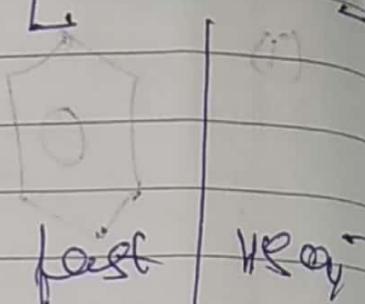
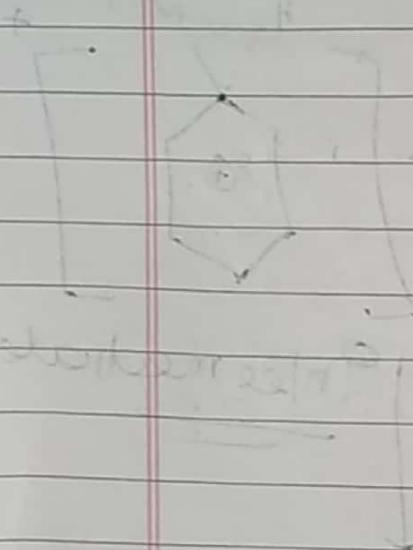
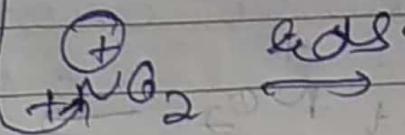
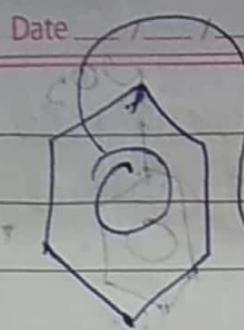


Single concerted step C-NO₂ bond formation + C-H bond

Decarboxylation in single step

D/
H
Haar

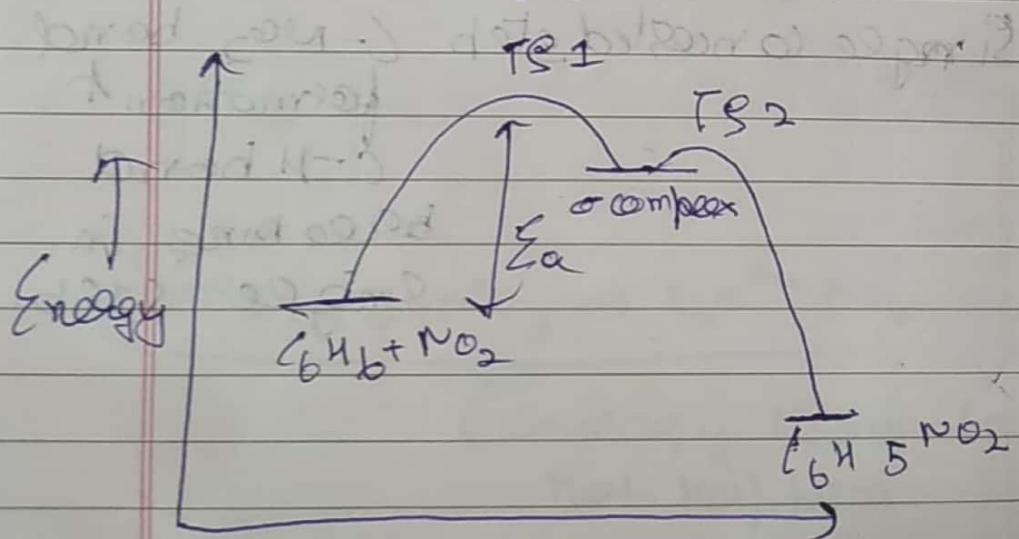
✓ (iv)



$$\text{Rate} = k [C_6H_6][NO_2]$$

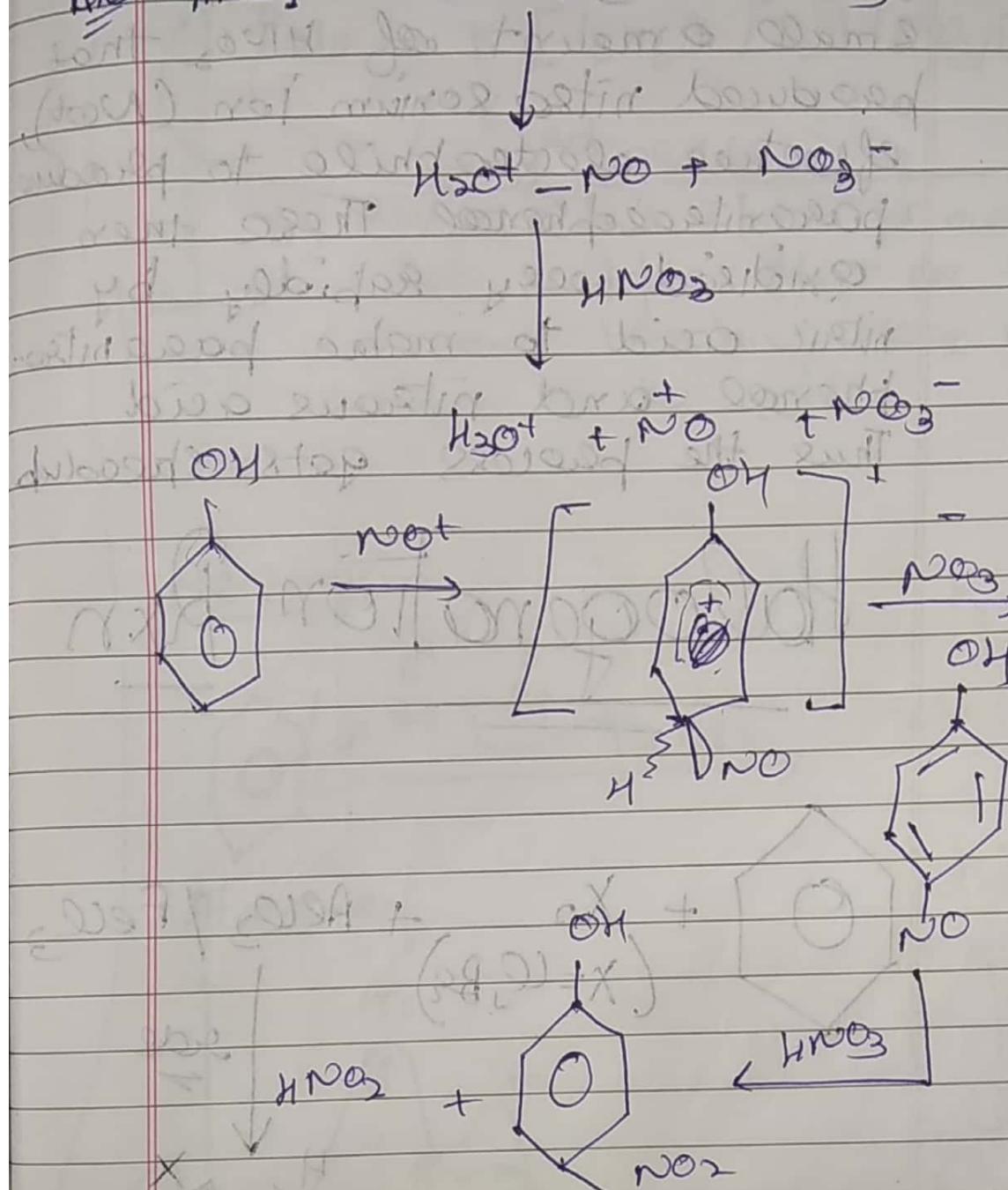
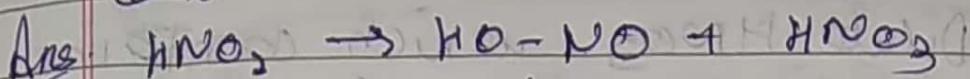
2nd order

$$k = 1 \text{ at } 25^\circ\text{C}$$



reaction coordinate

Q. Phenol can be easily nitrated by dilute nitric acid but not by conc. Nitric acid or mixed acid.

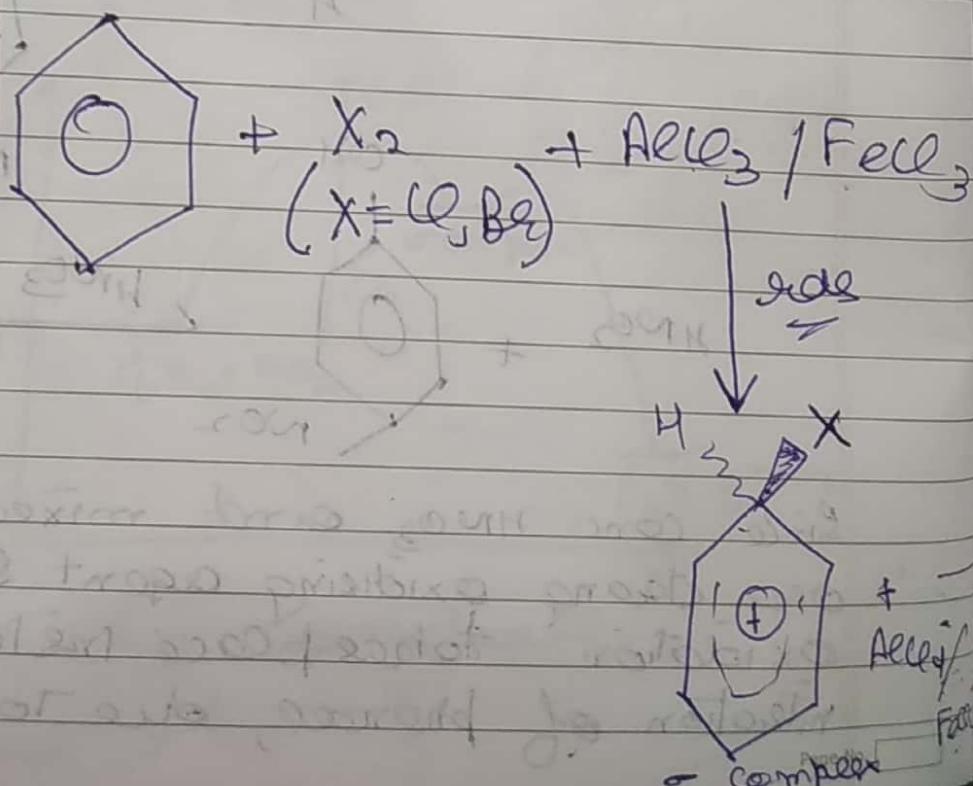


Since conc. HNO_3 and mixed acid are strong oxidising agent so, ring oxidation takes place instead of nitration of phenol, due to high reactivity.

electron availability by which
is the effect of OH group.

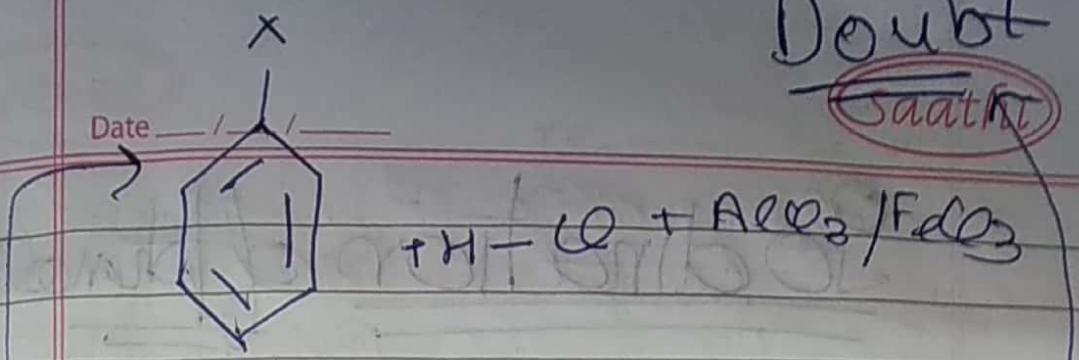
Dilute HNO_3 which contains small amount of HNO_2 that produced nitrosonium ion (NO_2^+) effective electrophile to produce p-nitrophenol. These then oxidised very rapidly by nitric acid to make p-nitrophenol and nitrous acid. Thus the process gets speedup.

Haloogenation Rxn



Doubt
Saath

Date / /

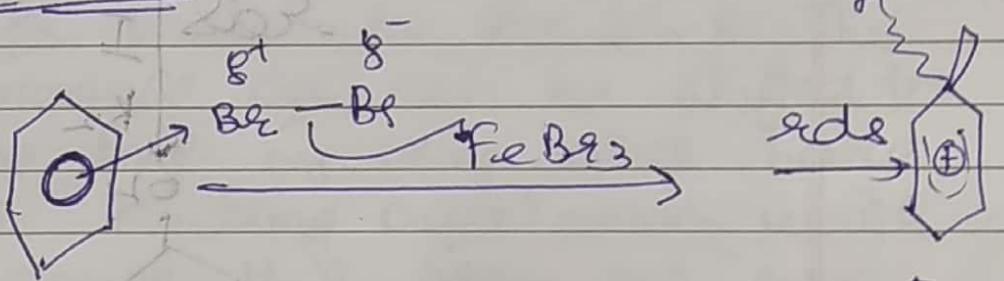


$$\text{Rate} = k [(\text{H}_2)] [\text{X}_2] [\text{FeBr}_3]$$

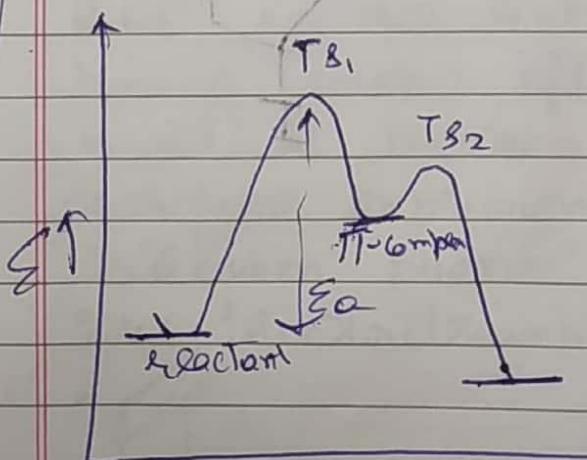
3rd order

* Rxn doesn't show primary loss of kinetic isotope effect or the (-H bond breaking does not happen in the rate).

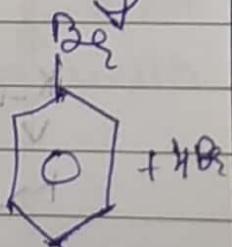
Mechanism



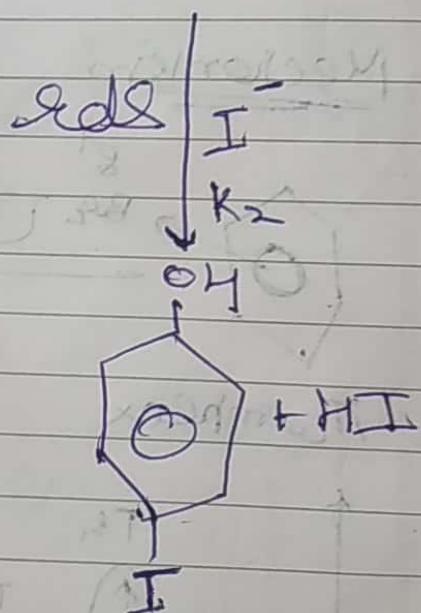
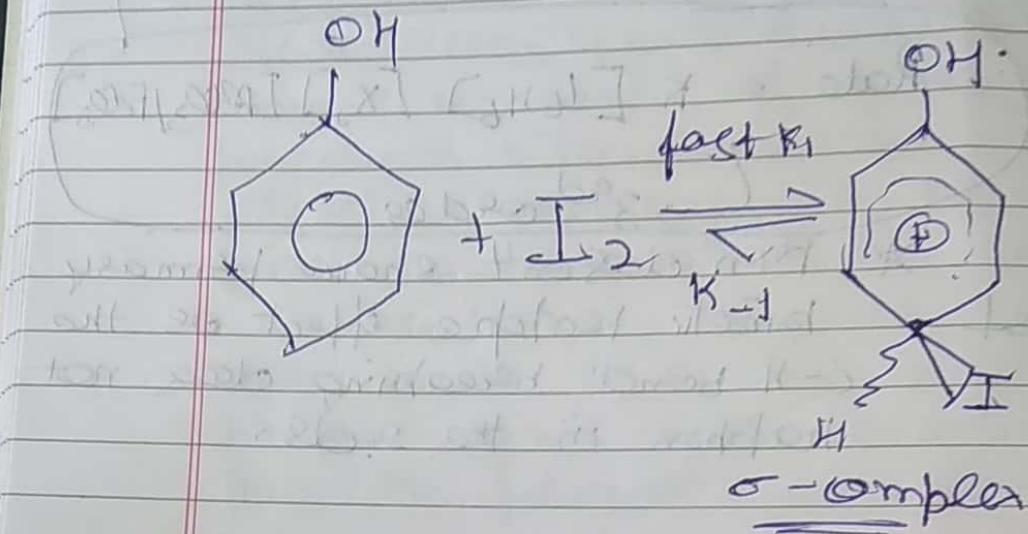
Tricarbonyl



Exn coordinate



Iodination of phenol

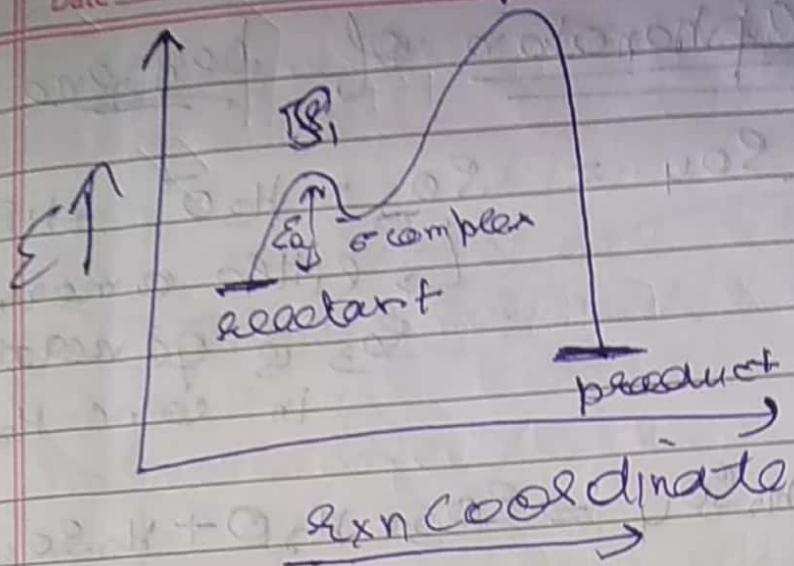


$$K_H \neq 1 = H$$

 K_D

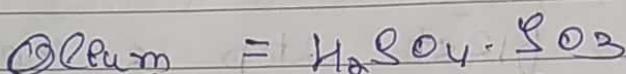
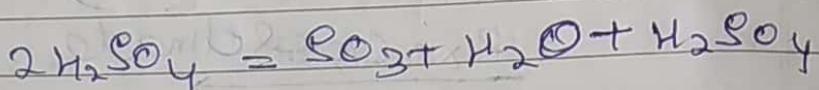
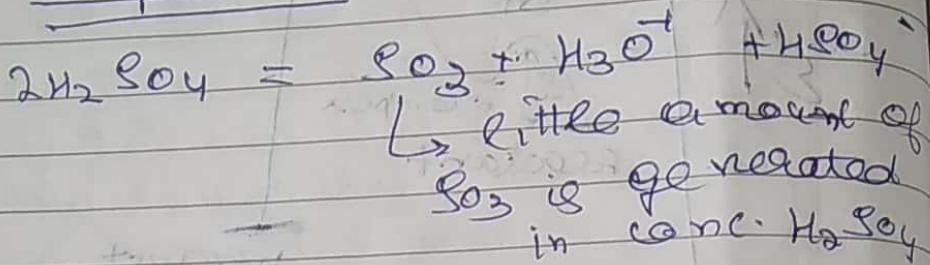
$$K_{-1} > K_1$$

$$\sqrt{K_2}$$

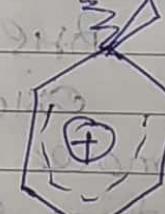
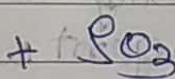
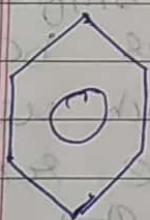


Here the first step is reversible where loss of H_β from the sigma-complex takes place easily then the loss of H_α , thus $K_{\alpha_1} > K_{\alpha_2}$. Hence the overall eqb lies on the L.H.S.: The overall eqb can be shifted to the R.H.S. by using either base or oxidising agent which will remove $\text{H}-\beta$ from the rxn medium since the 2nd step is the A.D.S. So this rxn executes a primary kinetic isotope effect as the C-H bond is broken in the A.D.S and therefore experimentally $\text{K}_{\text{H}_2\text{KO}-\text{D}_2\text{O}} > 1$ at 25°C when phenol is reacted with 2,4,6-tri-deuteriumphenoxide.

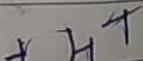
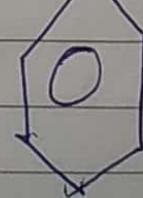
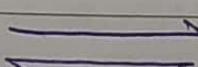
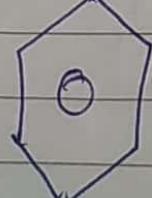
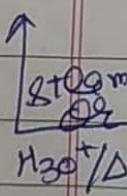
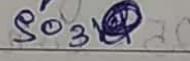
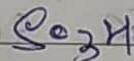
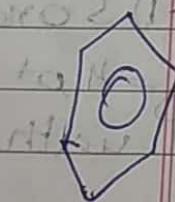
Date / /

Sulphonation of benzene

* Sulphonation rxn is faster in H₂SO₄ than in C₂H₅SO₄.



σ complex



Doubt

Date / /

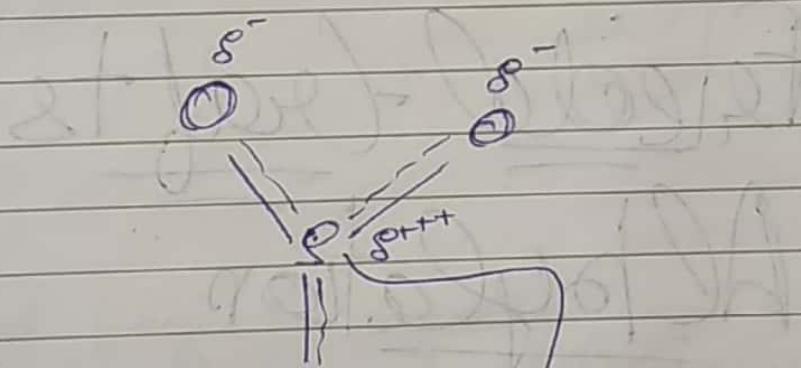
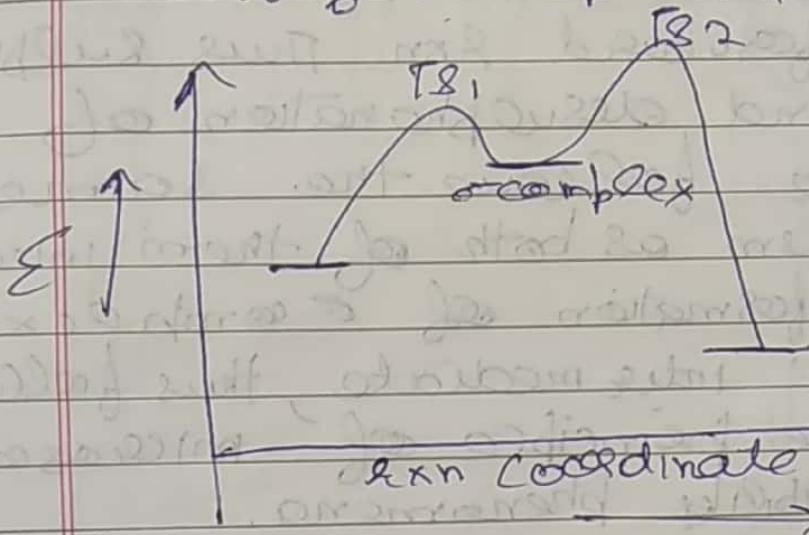
Saathi

★ primary kinetic isotope effect.

Number of moles $k_H \neq k_D$

so $k_H \neq k_D$

$^{16}\text{H}_2$ is replaced with $^{16}\text{D}_2$



is more electropositive
center

(\Rightarrow Electron deficient)

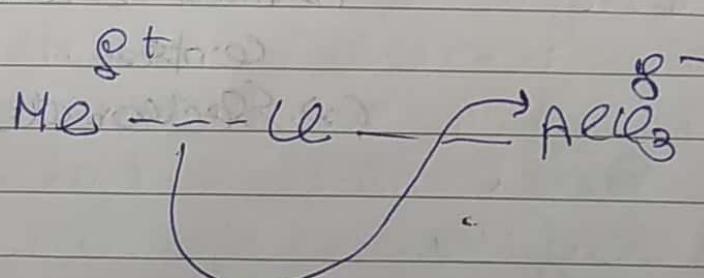
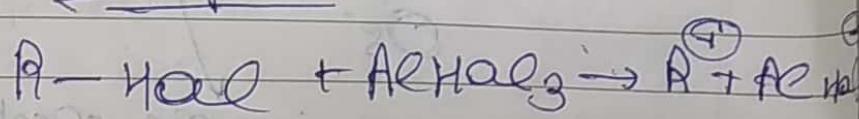
Date / /

* Microscopic Reversibility

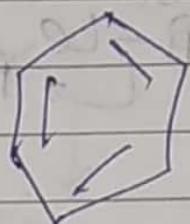
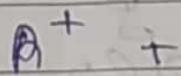
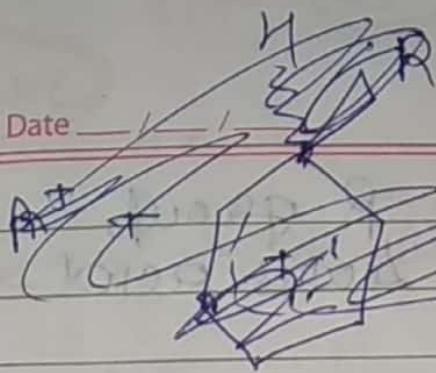
The reverse rxn from product to the reactant must follow the same rxn mechanism as the forward rxn. Thus sulphonation and desulphonation of benzene follows the same mechanism as both of them involve the formation of σ complex as the intermediate, thus following the principle of microscopic reversibility phenomena.

Friedl-Crafts

Alkylation

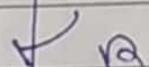


Date



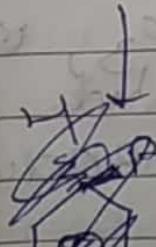
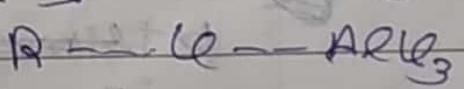
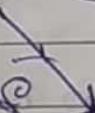
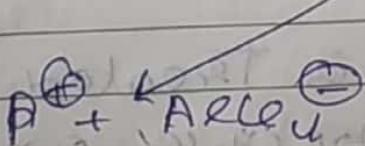
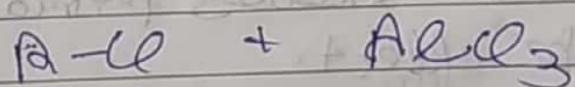
(σ -complex)

$\cdot \text{ArH}_2\text{C}_6\text{H}_4^-$

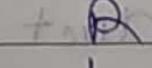


+ H-Hal

+ ArHal_2



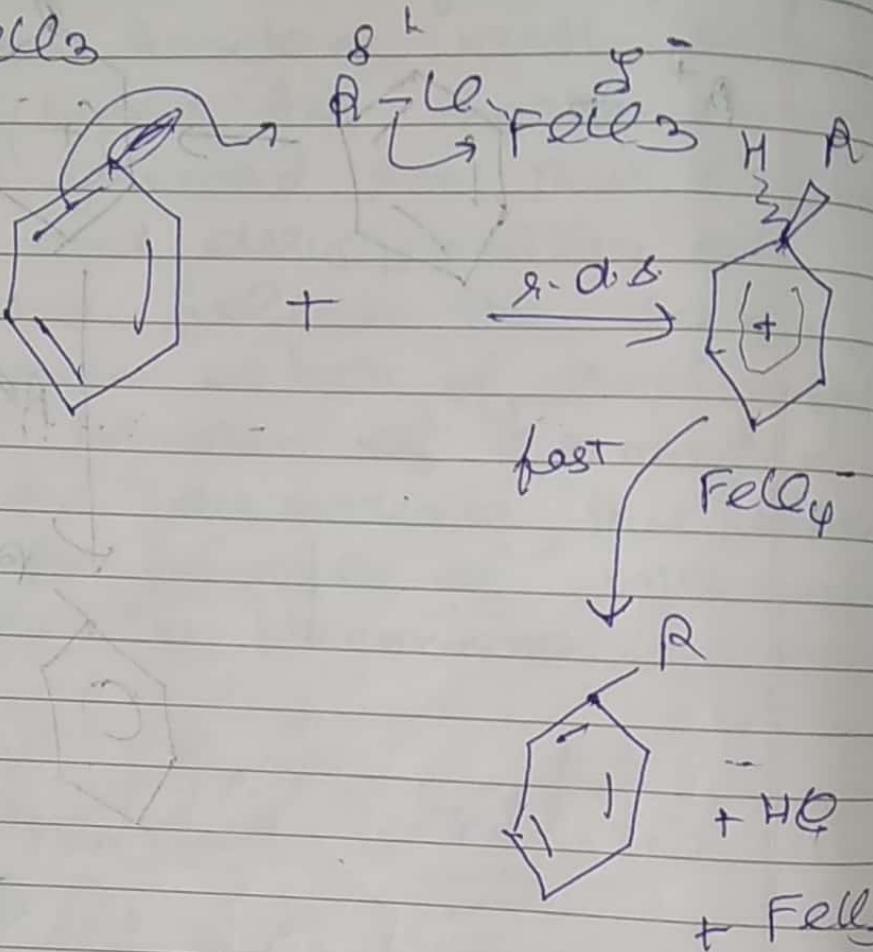
(σ -complex) + AlCl_4^-



+ H-Cl

+ AlCl_3

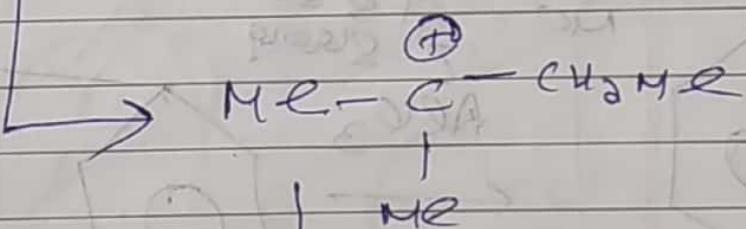
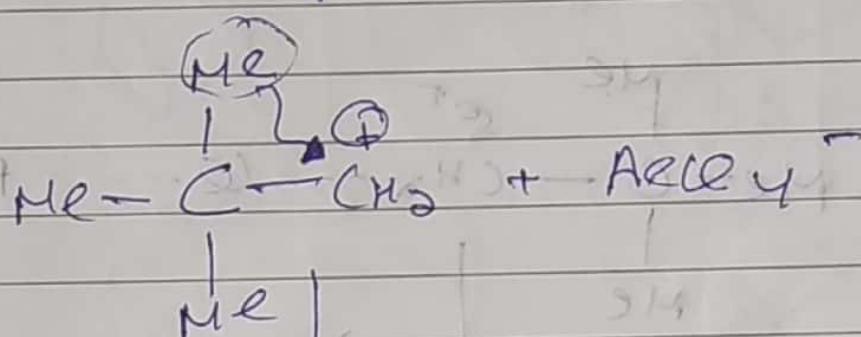
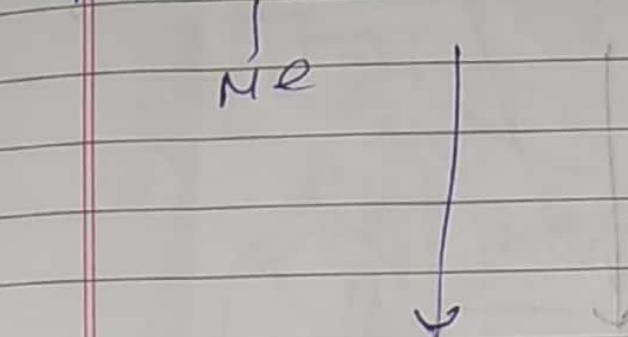
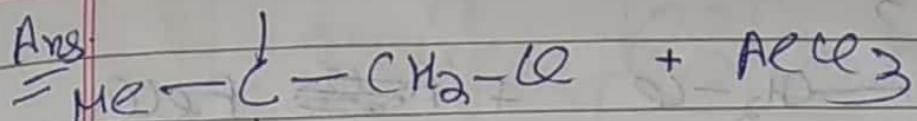
- (i) depending on R group
 (ii) Strength of Lewis acid

FeCl₃

* Does not shows primary kinetic isotope effect.

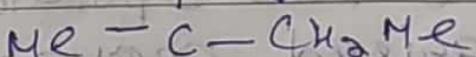
* When benzene is treated with ~~tri-n-butyl~~ (CH₃)₂C₆H₅Cl and ~~with~~ with anhydrous AlCl₃, ~~rearranged~~ rearranged product is formed, but with FeCl₃ unarranged product is formed.

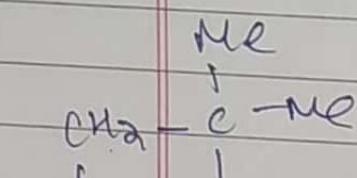
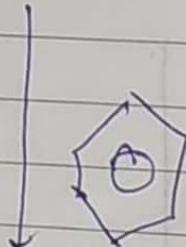
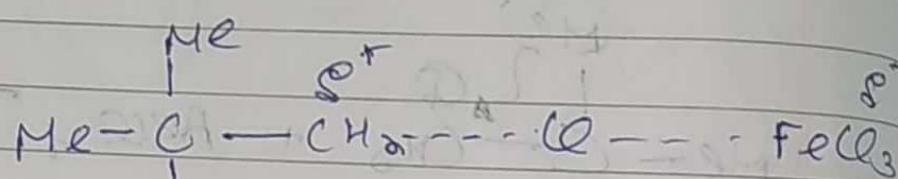
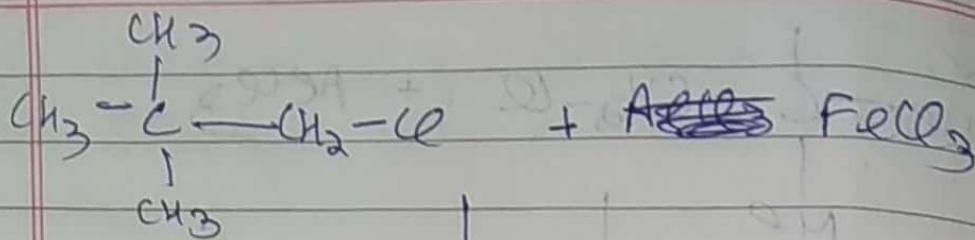
Date — He —



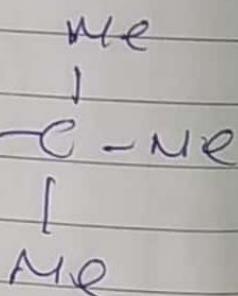
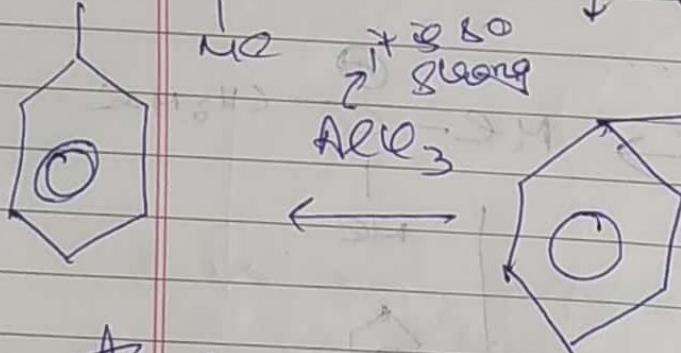
Me

↓





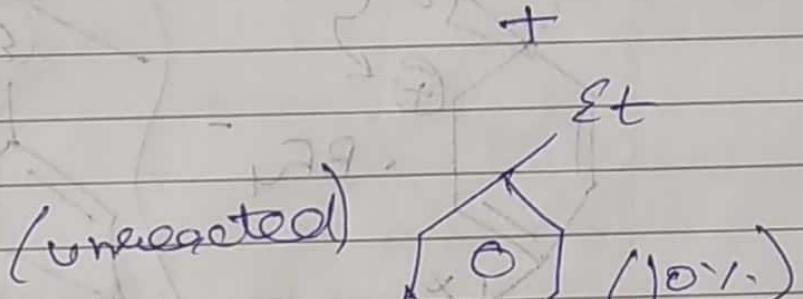
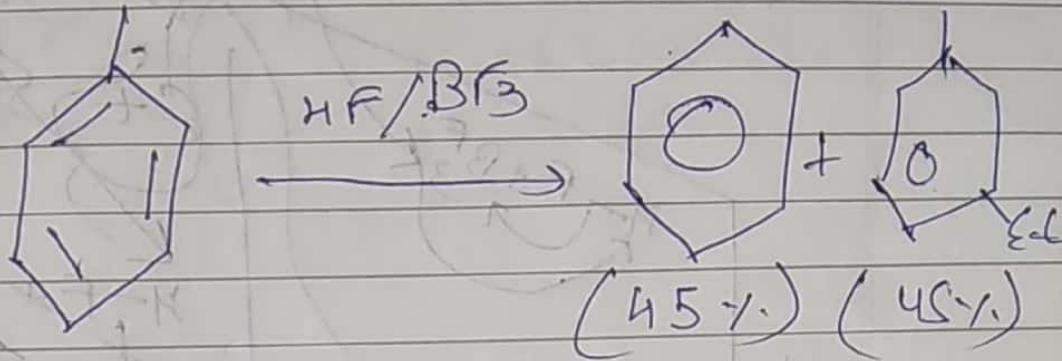
AlCl_3 is strong



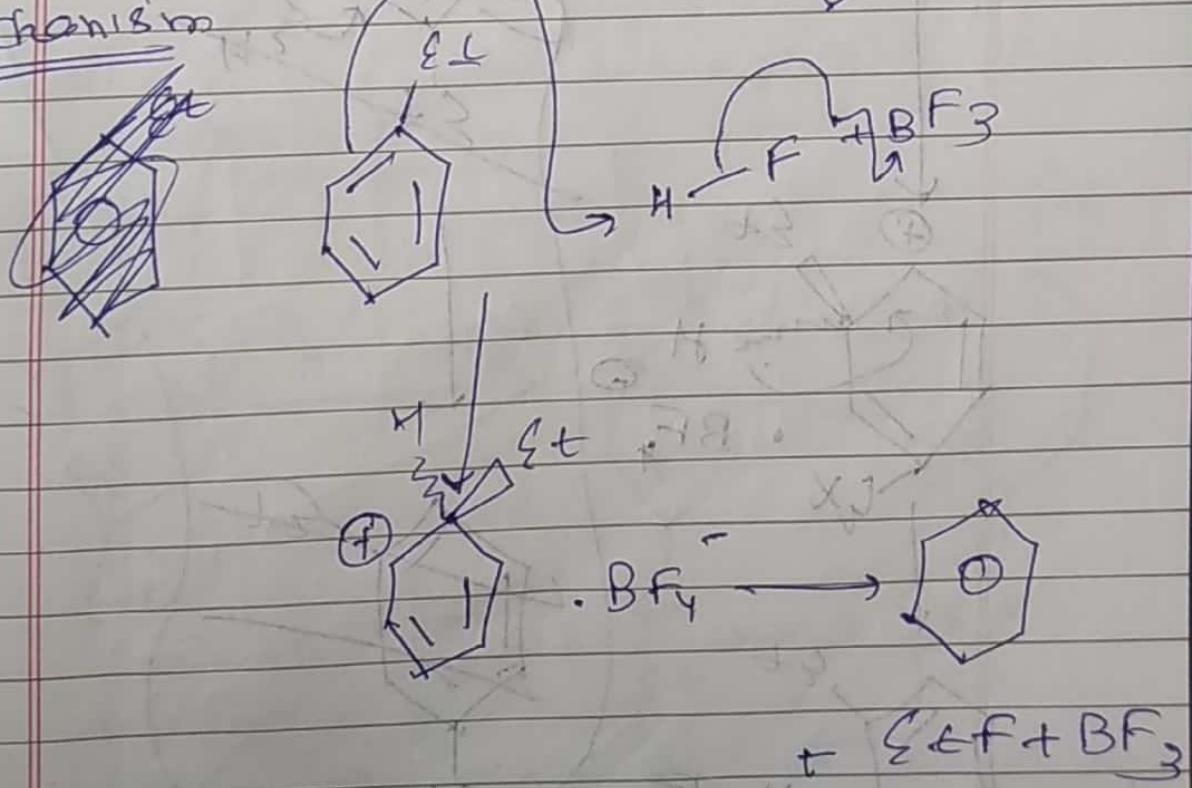
much

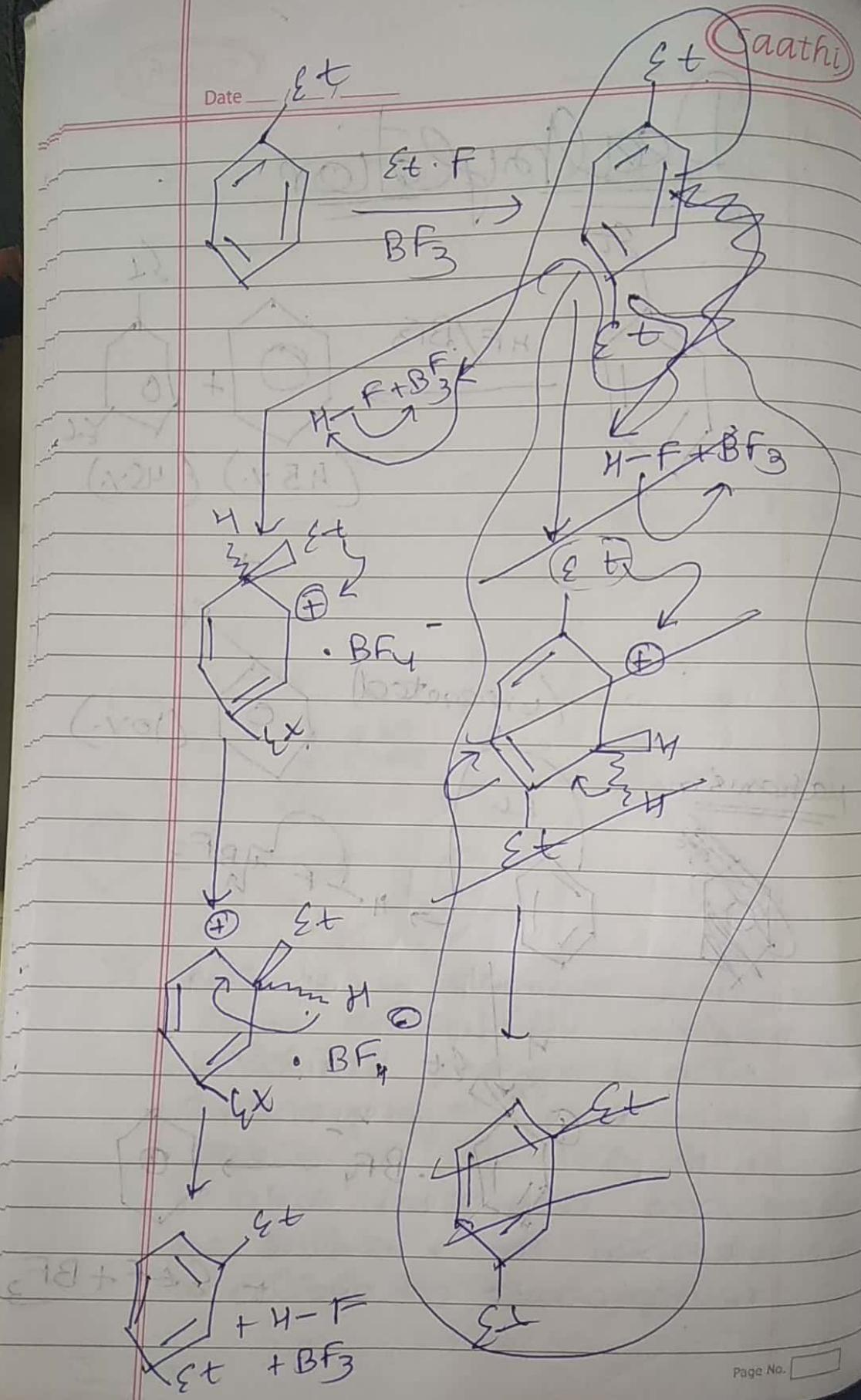
★ AlCl_3 is a stronger Lewis acid, so the electrophilic complex is polarised enough to allow the rearrangement to a more stable C^+ . But FeCl_3 is a weaker Lewis acid and therefore the complex is not polarised enough to allow the rearrangement.

Dealkylation



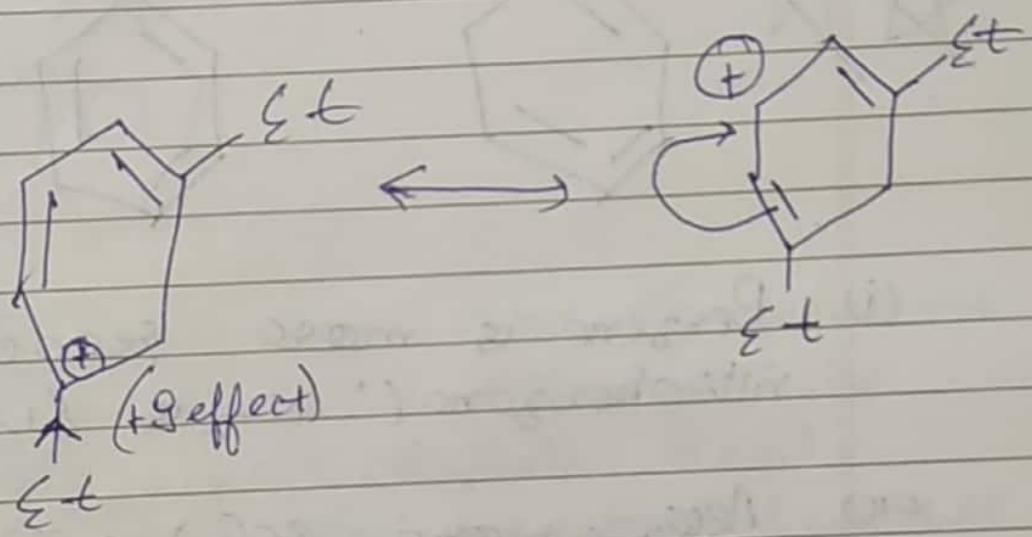
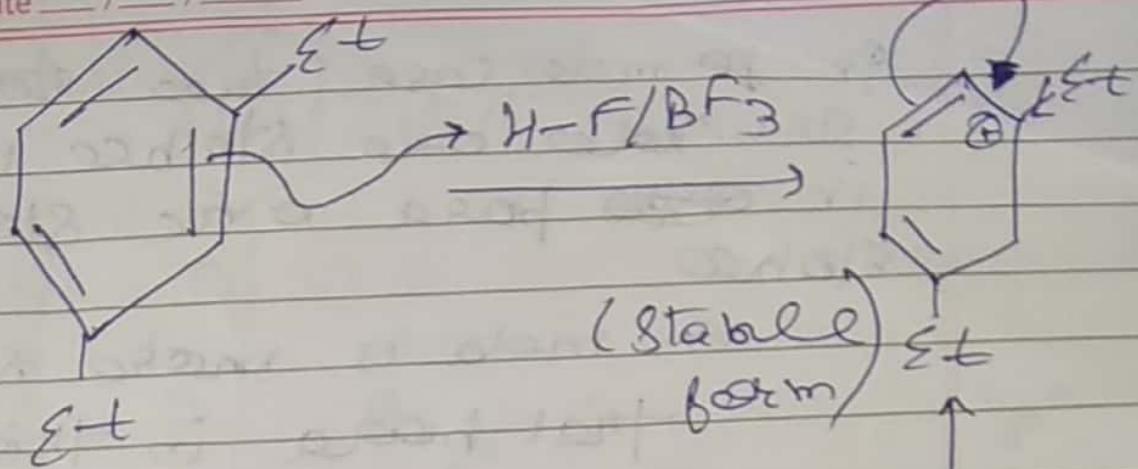
Mechanism



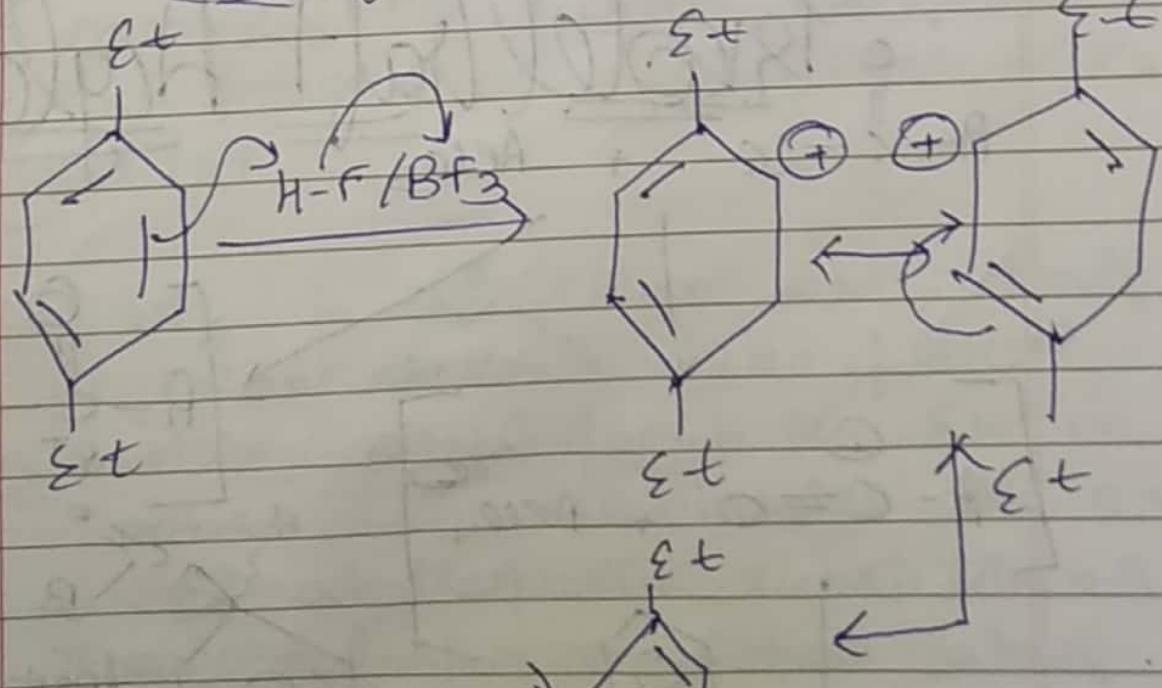


Scatti
(+g effect)

Date / /

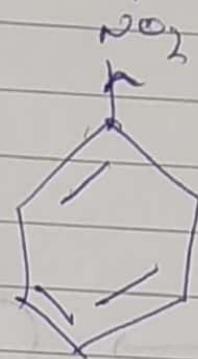
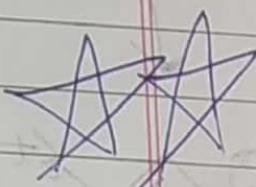


Stable form



In ~~the~~ meta case two resonating structures are stable while in ~~the~~ para one struc is stable

\Rightarrow meta is more stable than para in this case

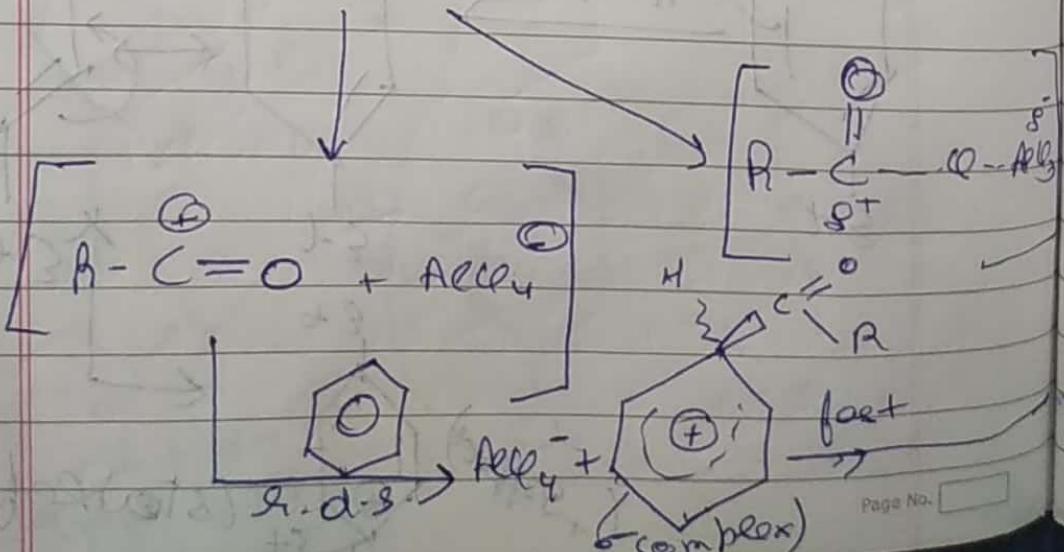


(Always asked in exams)

(iv) Benzene is more reactive than nitrobenzene (\because NO₂ is EWG)

(v) Acetone is more soluble in nitrobenzene.

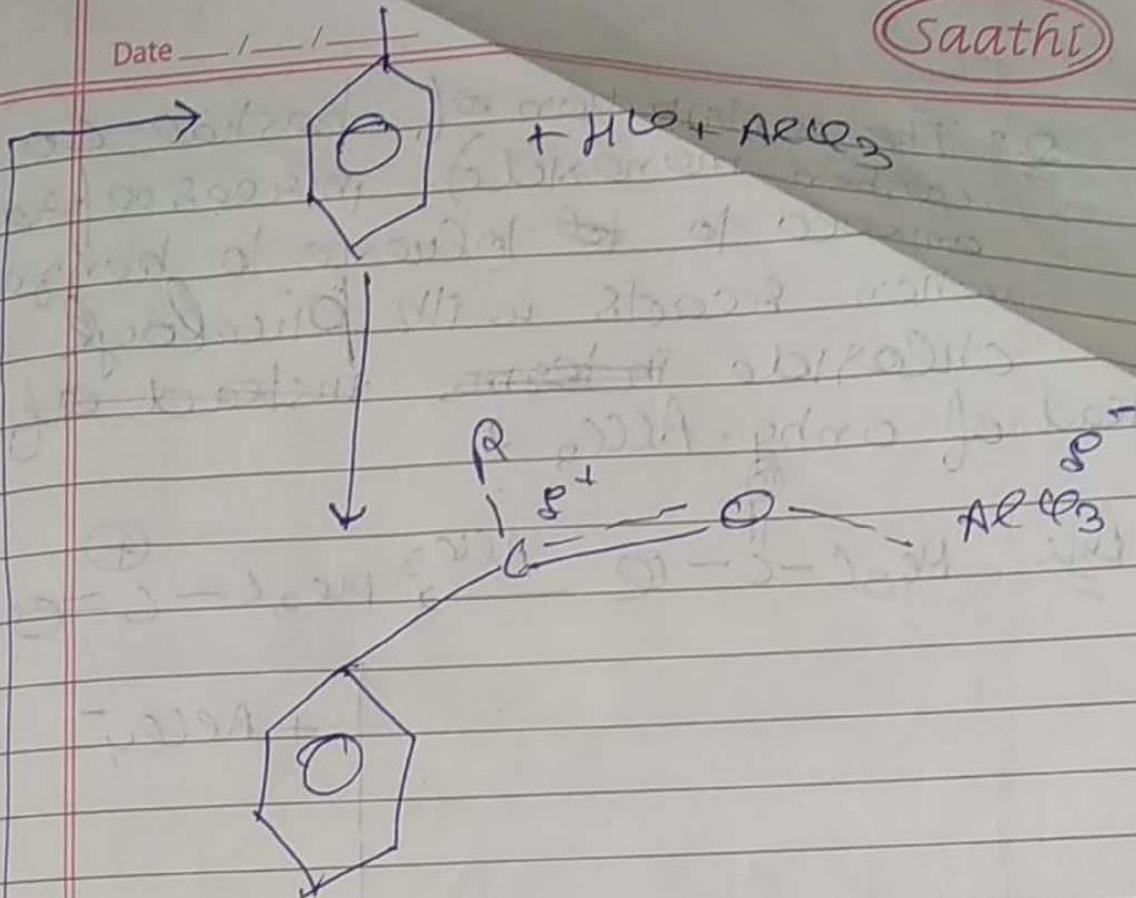
Friedel-Crafts Alkylation





Date _____

Saathi



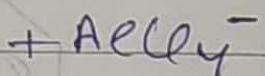
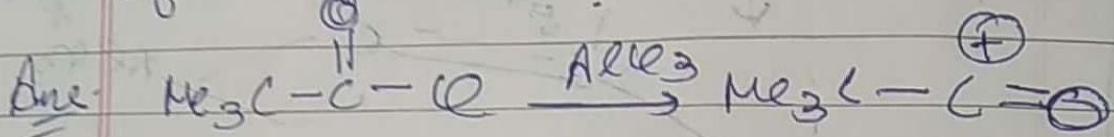
Q1. Why more than one equivalent of Lewis acid catalyst is needed for acylation rxn?

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

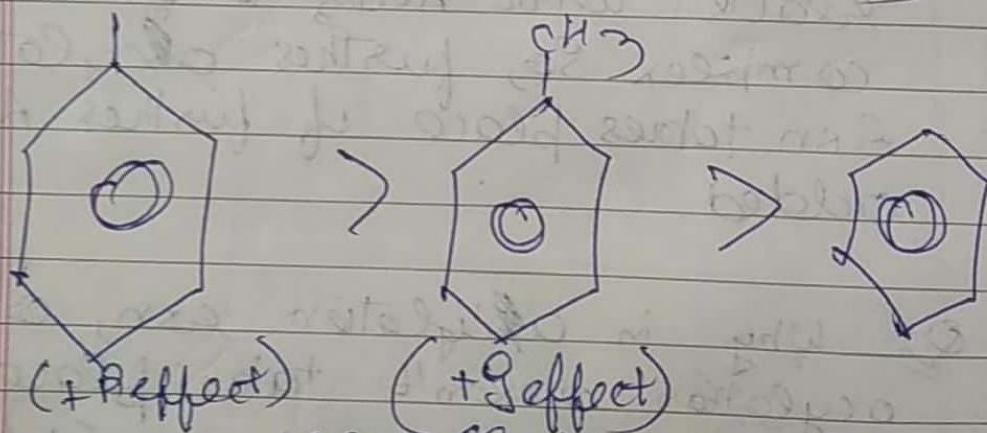
Q2. Why in acylation rxn, only acylation doesn't take place?

Ans. Here, acyl group is EW in nature which deactivates the ring to S_{E} electrophilic substitution rxn. Therefore further acylation takes place in benzene ring instead of acylation benzene.

Q.3. The contribution of partial CO (carbon monoxide) increases from anisole to toluene to benzene when reacts with ~~pivaloyl~~ instead of ~~anhy.~~ AlCl_3 ?

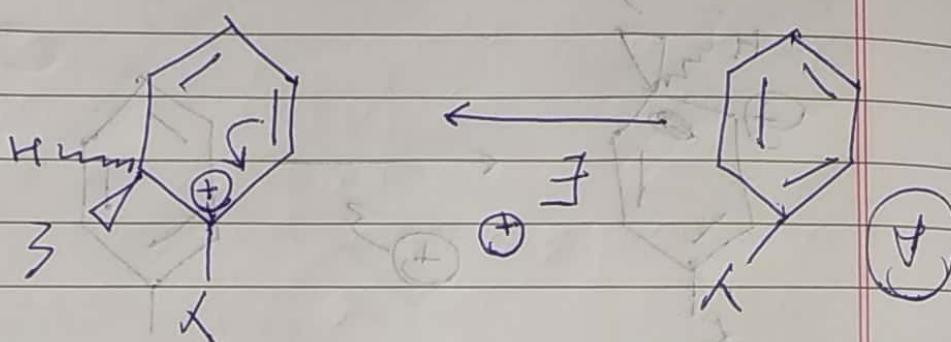
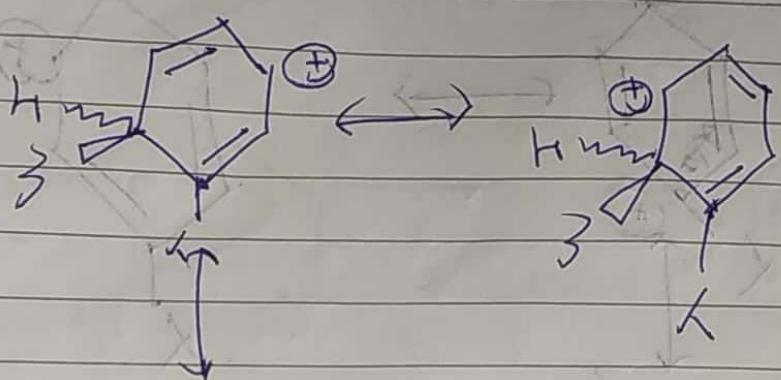


OMe (stable 3° C^\oplus)



(~~Electrophilic Reactivity~~)

The reactivity of phenyl ring increases from I-H-S to R-H-S . Therefore the contributions of 'CO' goes increases from I-H-S to R-H-S .



Benzene Ring: (6H₂)

Molecular Substitution on

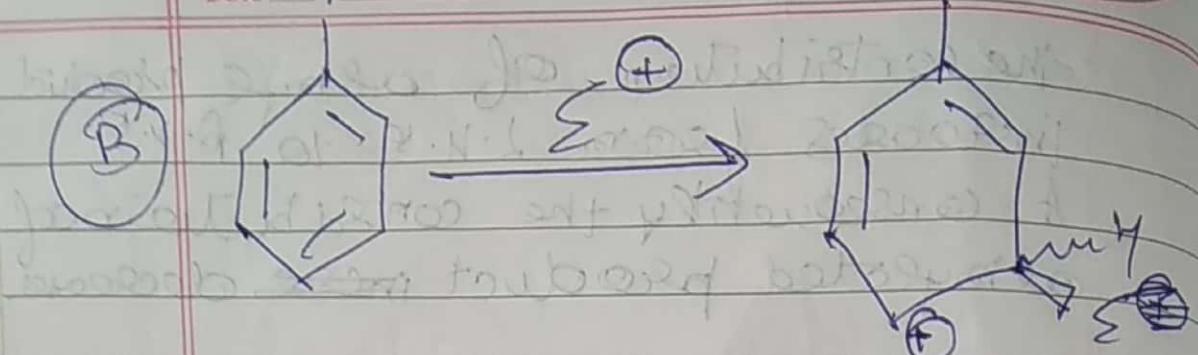
Electrophilic Attack

The central theme of aromatic substitution
is the formation of an intermediate product
in which the C-H bond is partially broken.
As a consequence, the C-H bond is partially
broken, leading to the formation of a quinonoid
intermediate product.

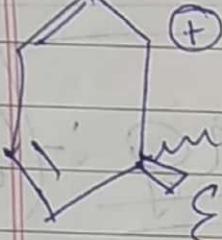
Satish

Date

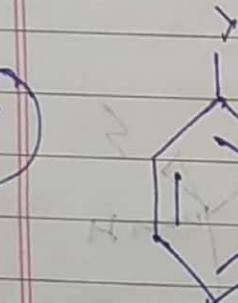
(B)



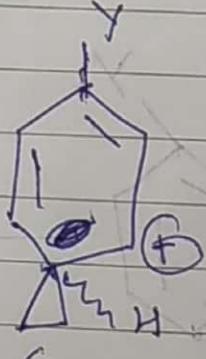
Y



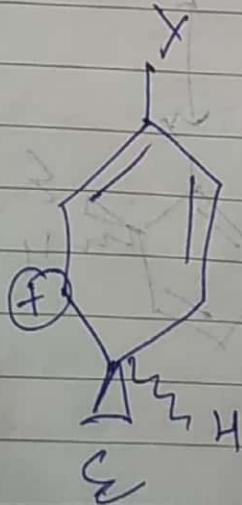
+



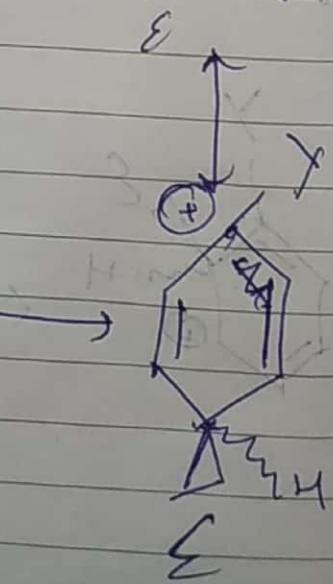
(C)



E



+

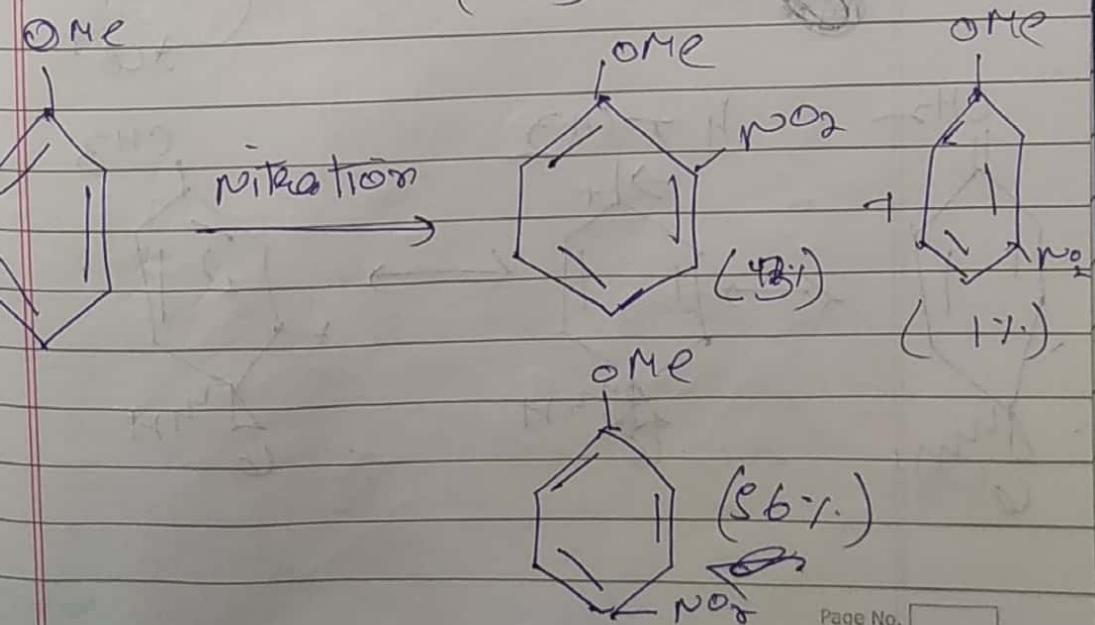
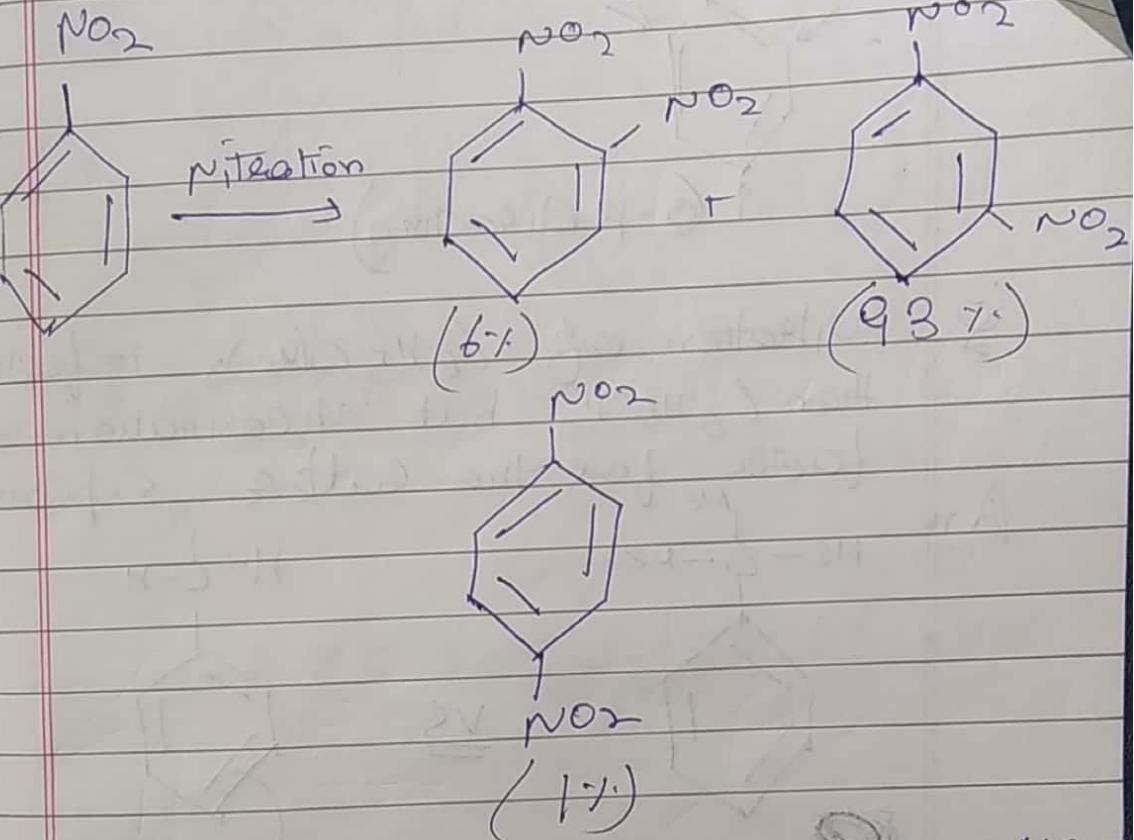


→ (i) When X is EOG.

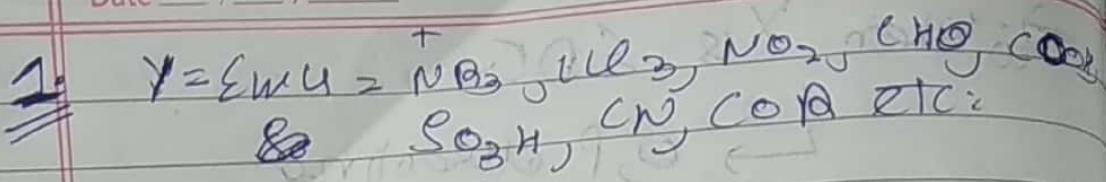
↳ O, P directing

• (ii) When Y is EMIG

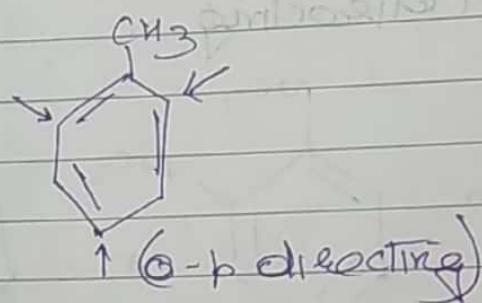
↳ M directing



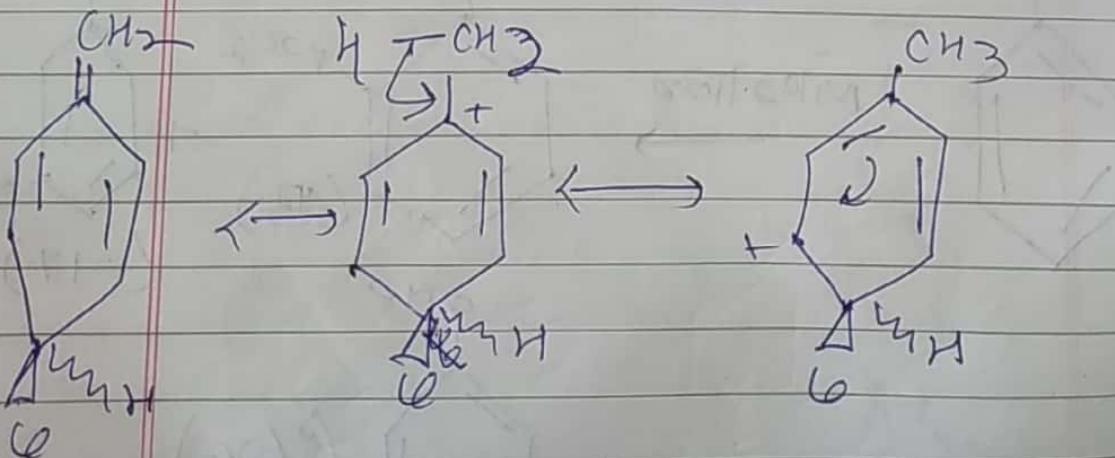
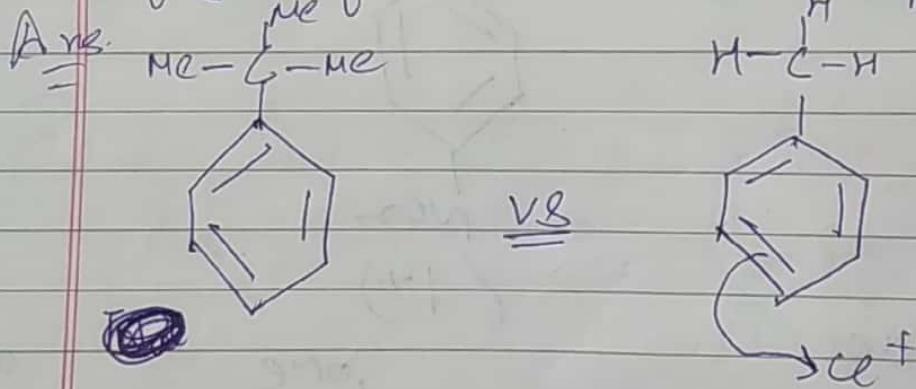
Date _____



2. $\text{Y} = \text{EDG} = \text{Alkyl, phenyl}$



Q. Nitration of $C_6H_5C(Me)_3$ is faster than $C_6H_5CH_3$ but chlorination is faster for the latter. Explain?

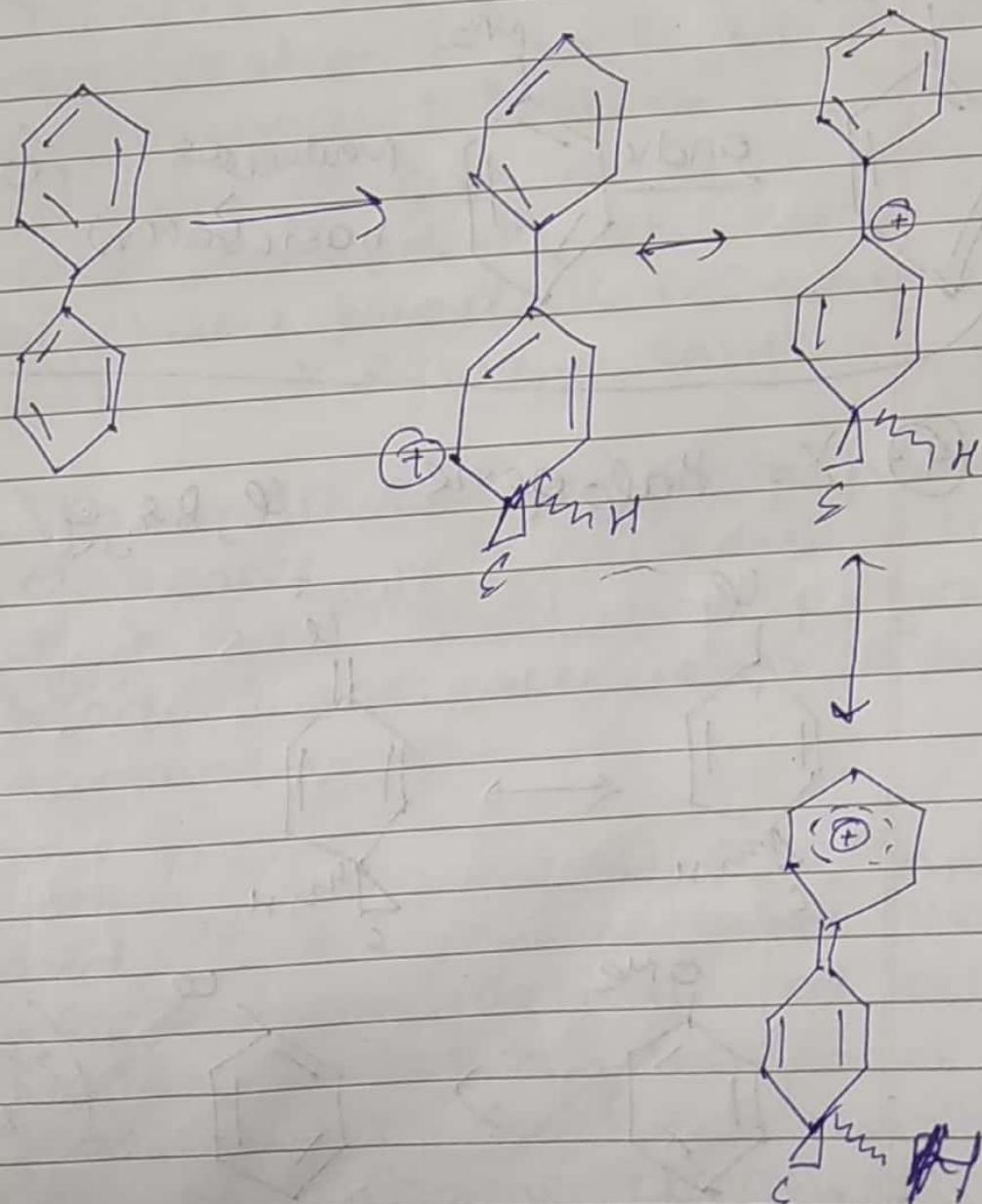


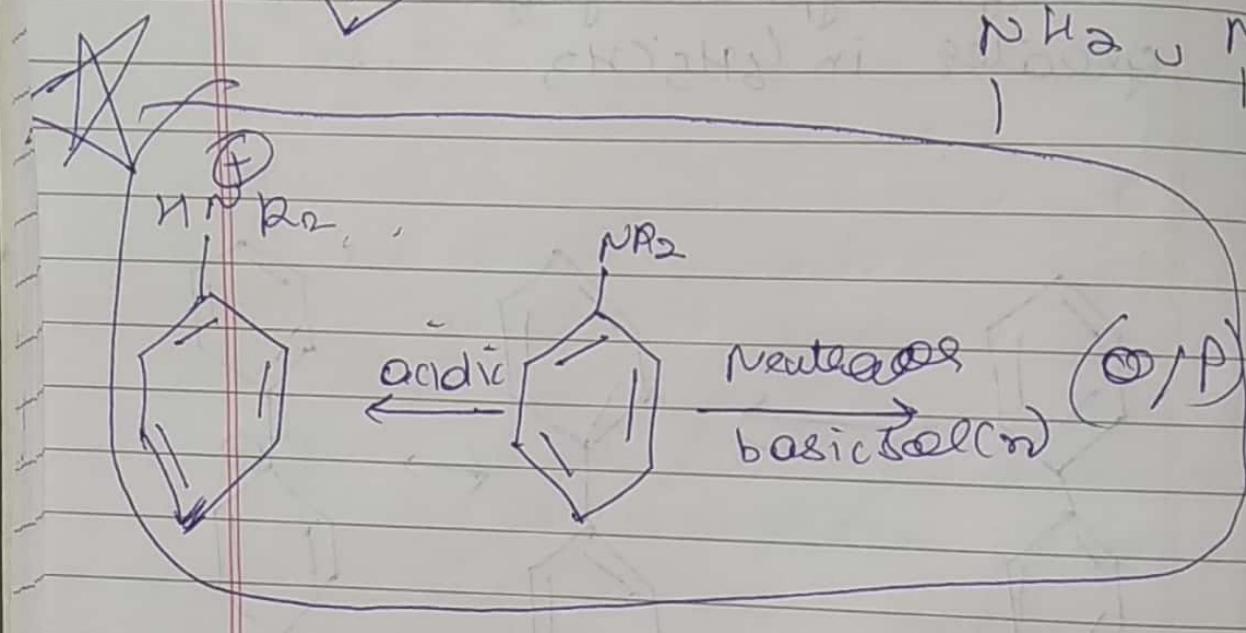
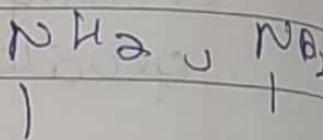
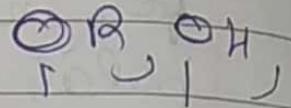
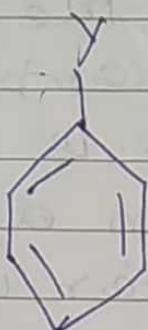
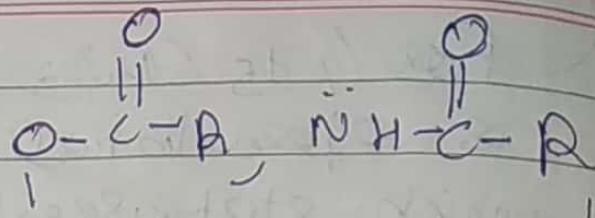
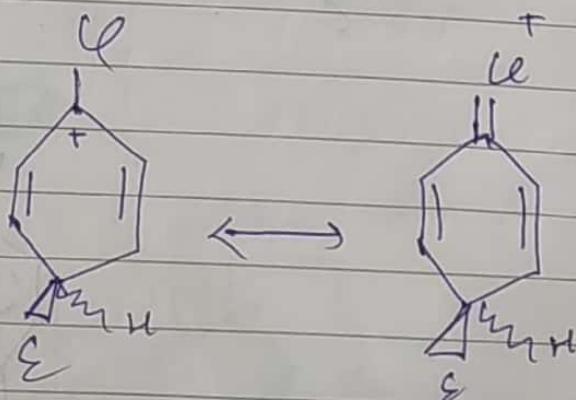
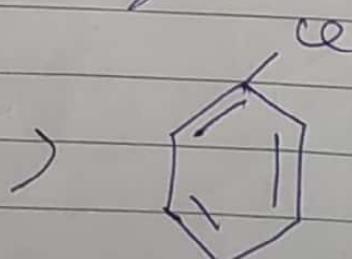
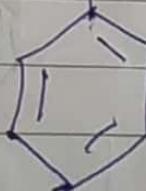
Doubt

Date / /

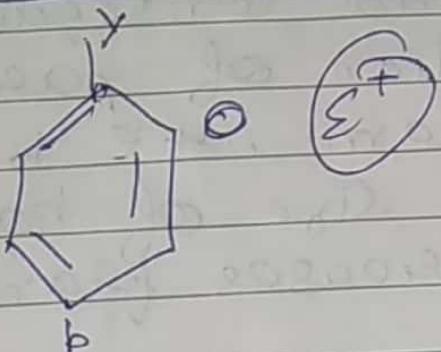
in ~~add~~ nitration also
Hyperconjugation can
occur so reactivities
decrease

For $C_6H_5CH_2$ greater + effect
is operational than the latter
which stabilizes the σ complex. But
for ionization which is a loss
polar rxn, the electron donation
through hyperconjugation is much
greater in $C_6H_5CH_3$



3- $Y = (-\text{O}, +\text{P})$ ④ $Y = \text{Halogenes}$ (Cl, Br, I / $-\text{O}, +\text{P}$) OMe 

Electrophilic
Substitution

O/b - product ratio

steric factor

$$-b > -O \quad (E \text{ is const.})$$

$$E = \text{steric factor}$$

$$b > O \quad [Y \text{ is const.}]$$

① ~~as~~ ~~to~~ ~~base~~ The contribution of other ~~other~~ product ~~decreases~~ decreases with increase in size of electrophile and consequently the contribution of para product increases when Y remains const.

② The contribution of ortho product decreases with increase in size of Y and consequently para product increases when ~~E~~ ~~remains~~ remains const.

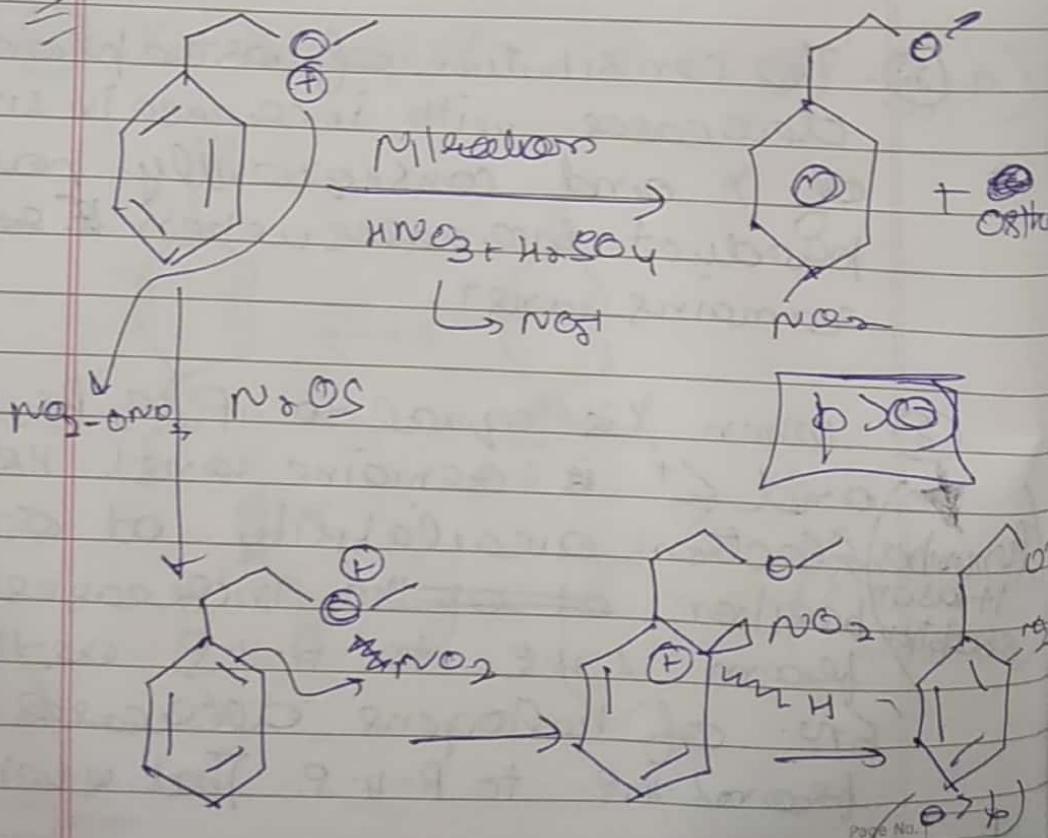
③ when Y is equal to F, Cl, Br, I
 and E^+ is remains const. Here
 (remember) electron availability at ortho
 position ~~at~~ increases
 from L-H-P to P-H-P at the
 sn. of halogens decreases
 from L-H-P to P-H-P. That's why

Date _____

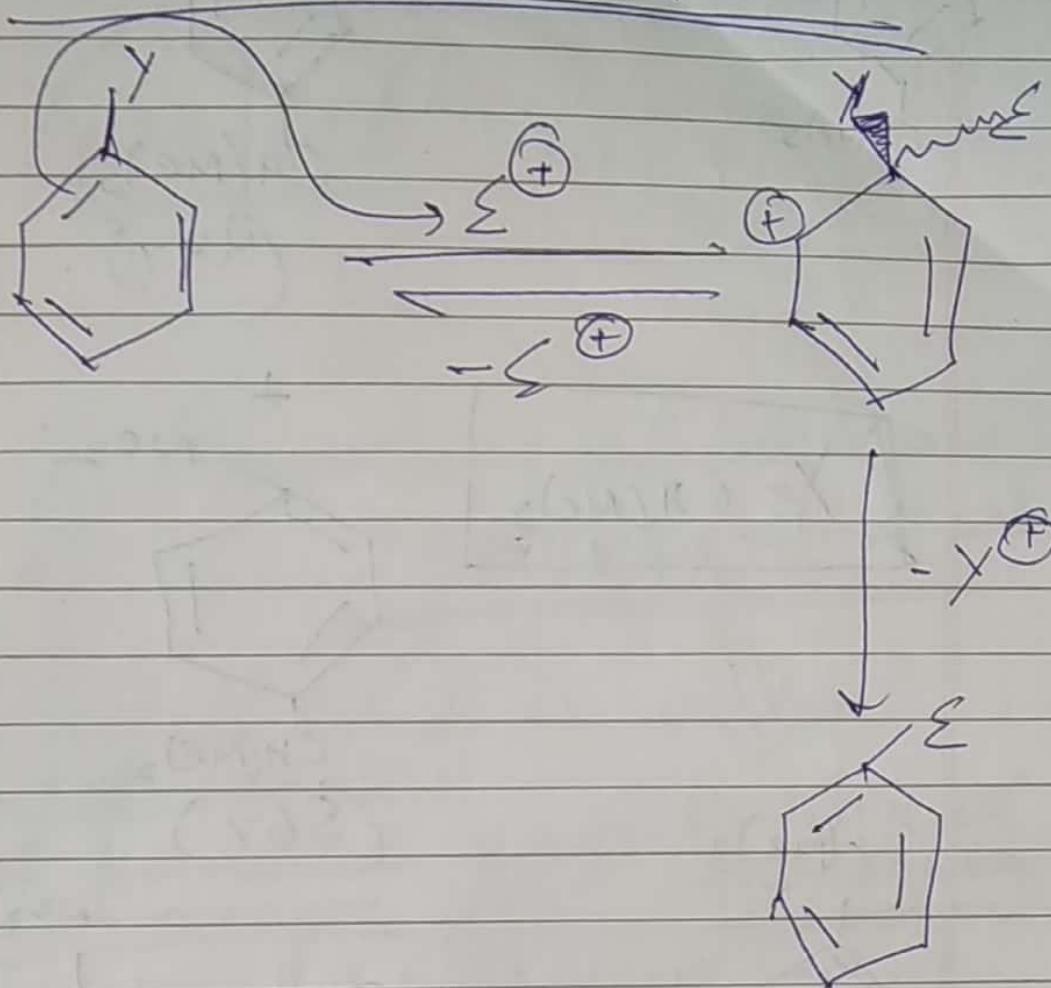
the contribution of ortho position increases and consequently the contribution of para position decreases from 1-H-S to 0-H-S. Although the size of halogen atoms decreases from 0-H-S to 0-H-S.

Q. Nitration of 1-methoxy-2-phenyl ether leads to 32% ortho and 69% para products when treated with nitrating mixture. But 69% ortho and 28% para isomers when treated with $\text{NO}_2\text{H}_2\text{SO}_4$.

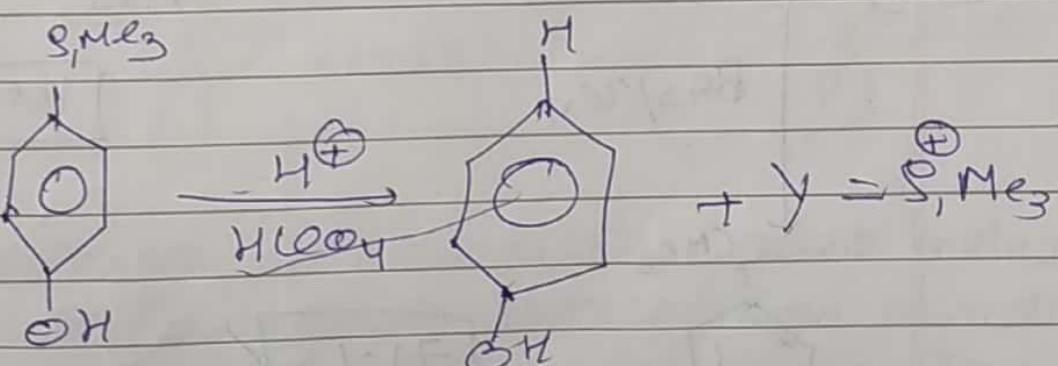
Ans.



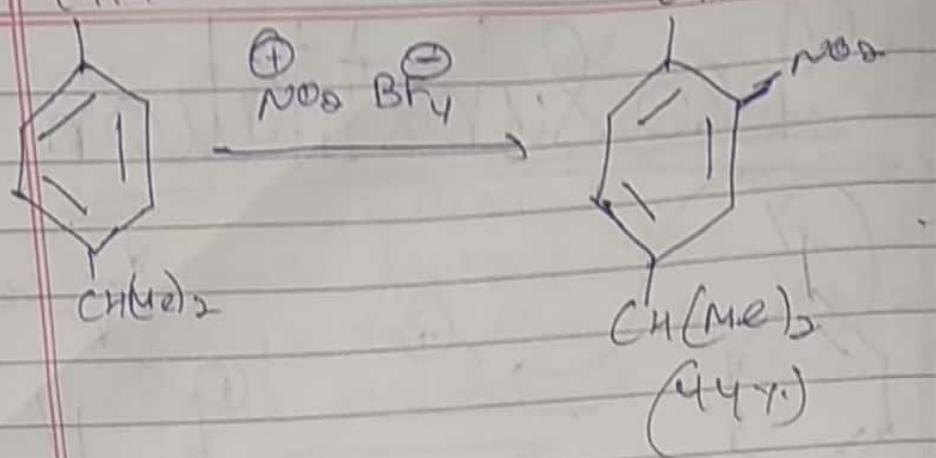
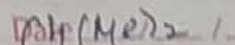
91% Substitution



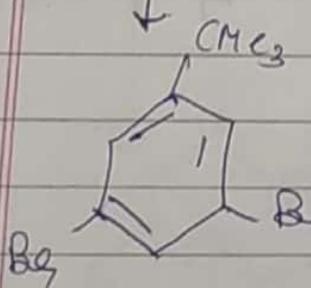
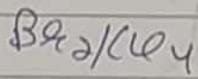
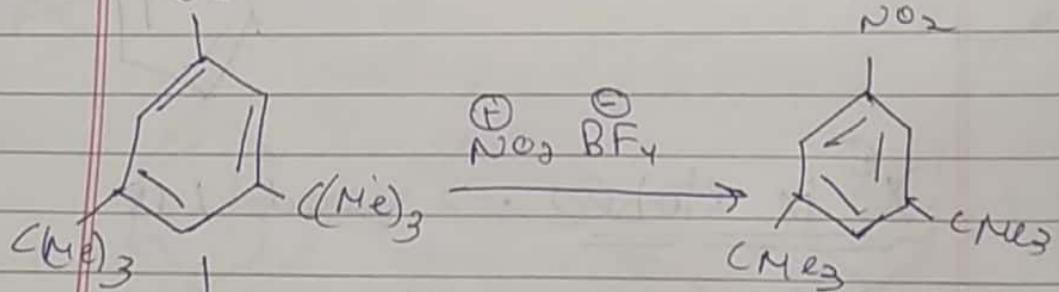
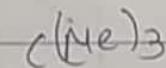
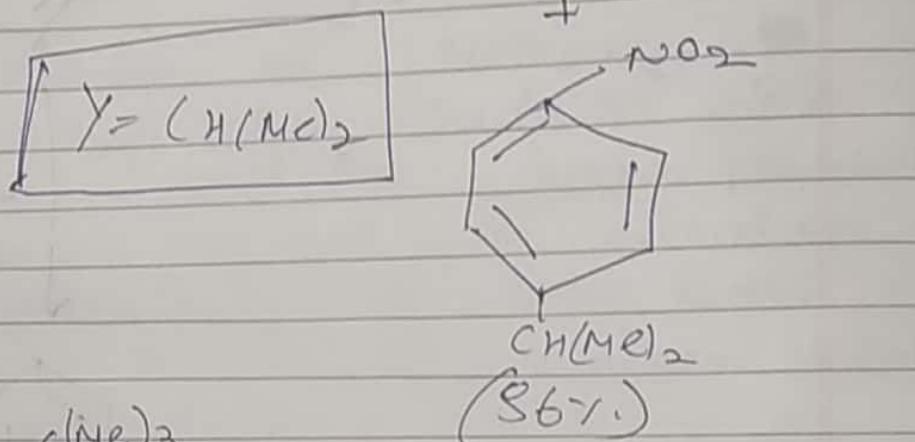
X^+ is stable \rightarrow good I.U.



Saathi



4



Kinetic vs Thermodynamic Control



Proportions of alternate
product formation

relative rate
of formation



Kinetic control
part

(K.C.P)

stability of
the isomers

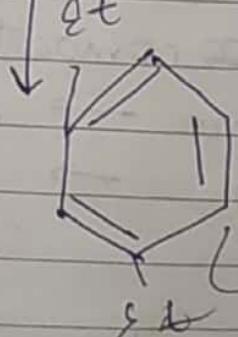
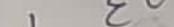
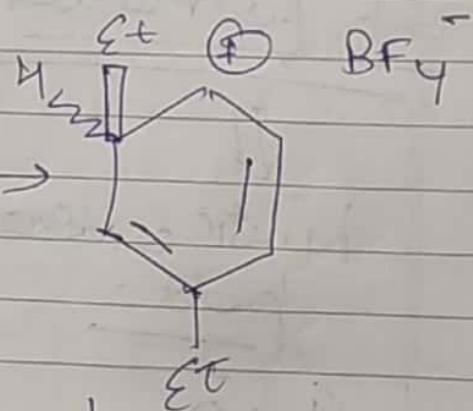
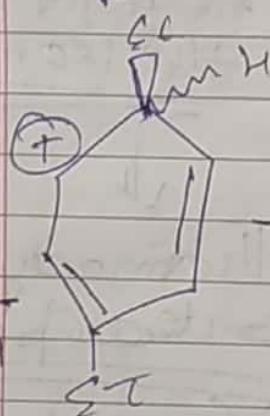
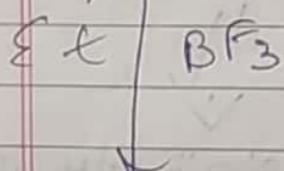
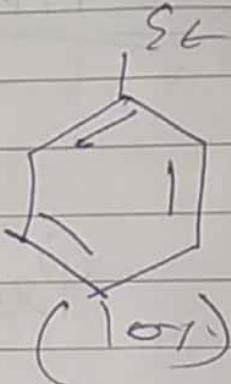
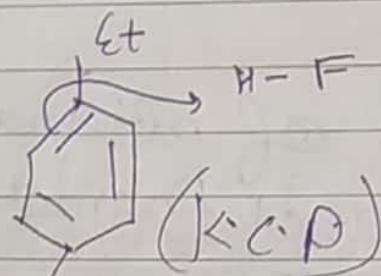
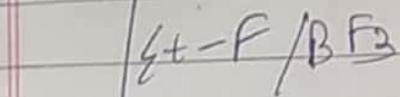
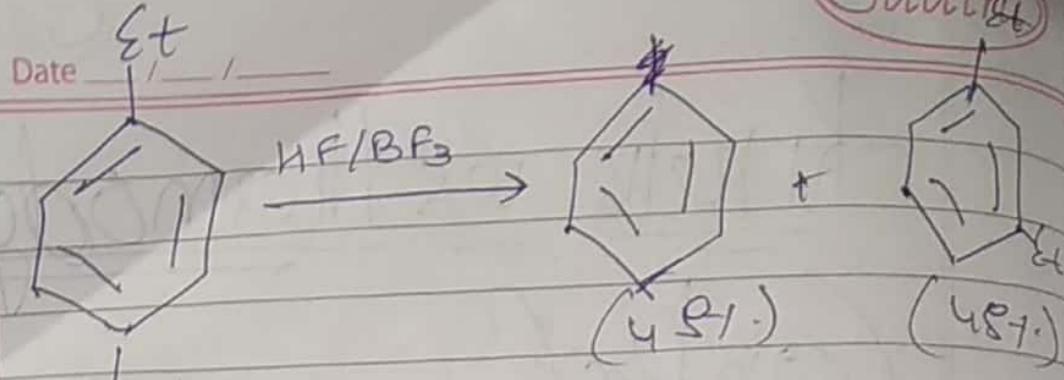


Thermodynamic
control part

(T.C.P)

Alternative products are mutually
interconvertible under favourable condi-
tions → direct polymerization
→ reversal of the rxn
to form the starting
material followed by
new attack to the stable
isomer.

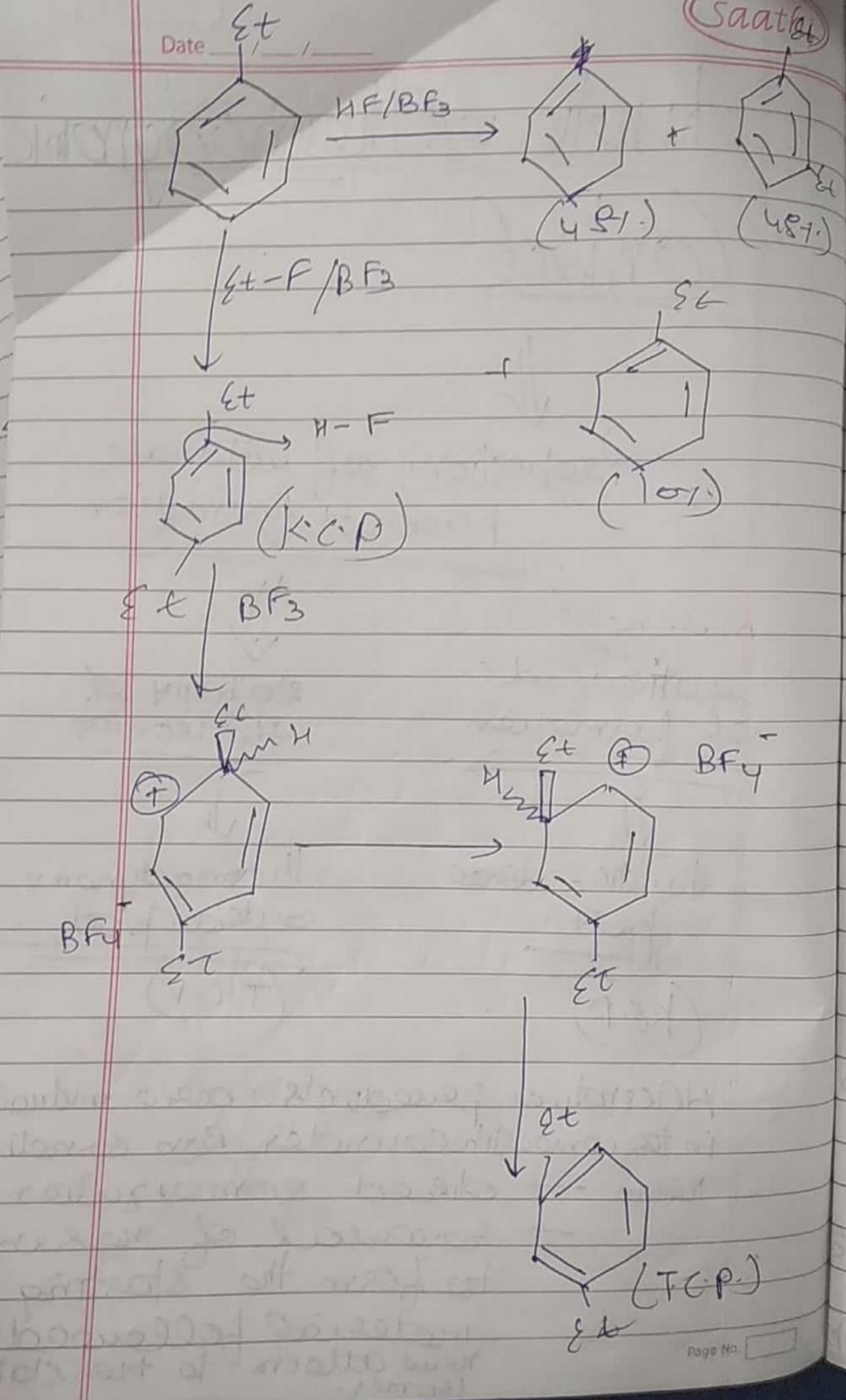
Saatgut

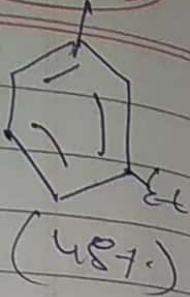


Ph - n

Saat

Date _____

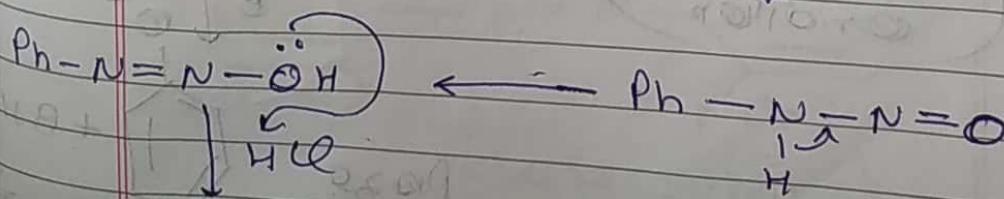
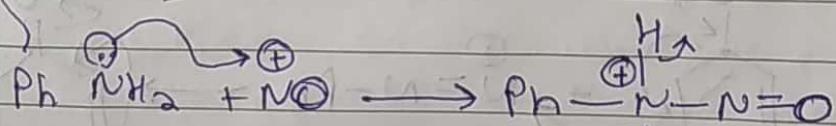
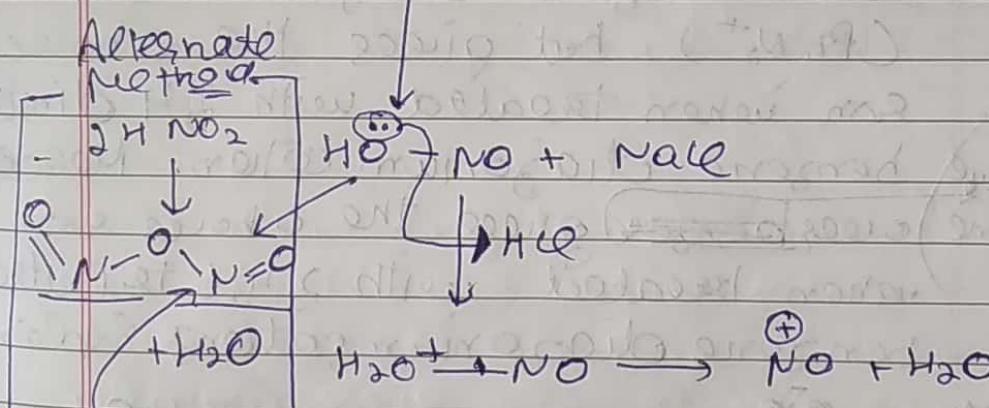
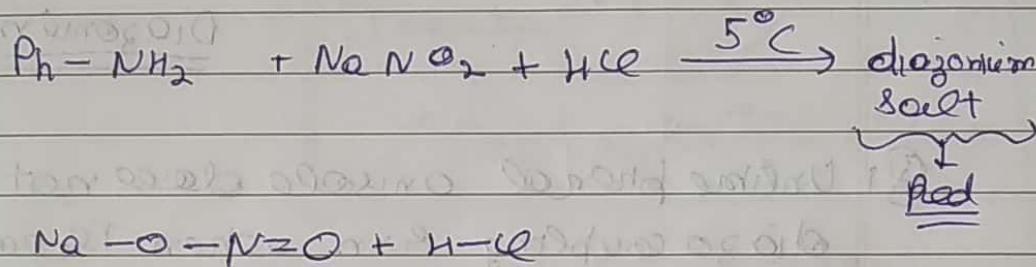




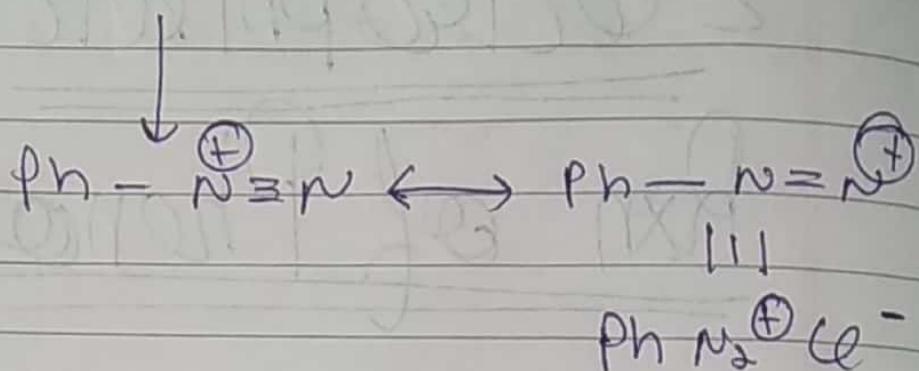
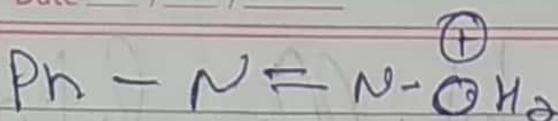
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Electrophilic Substitution

Rxn of Phenol :-



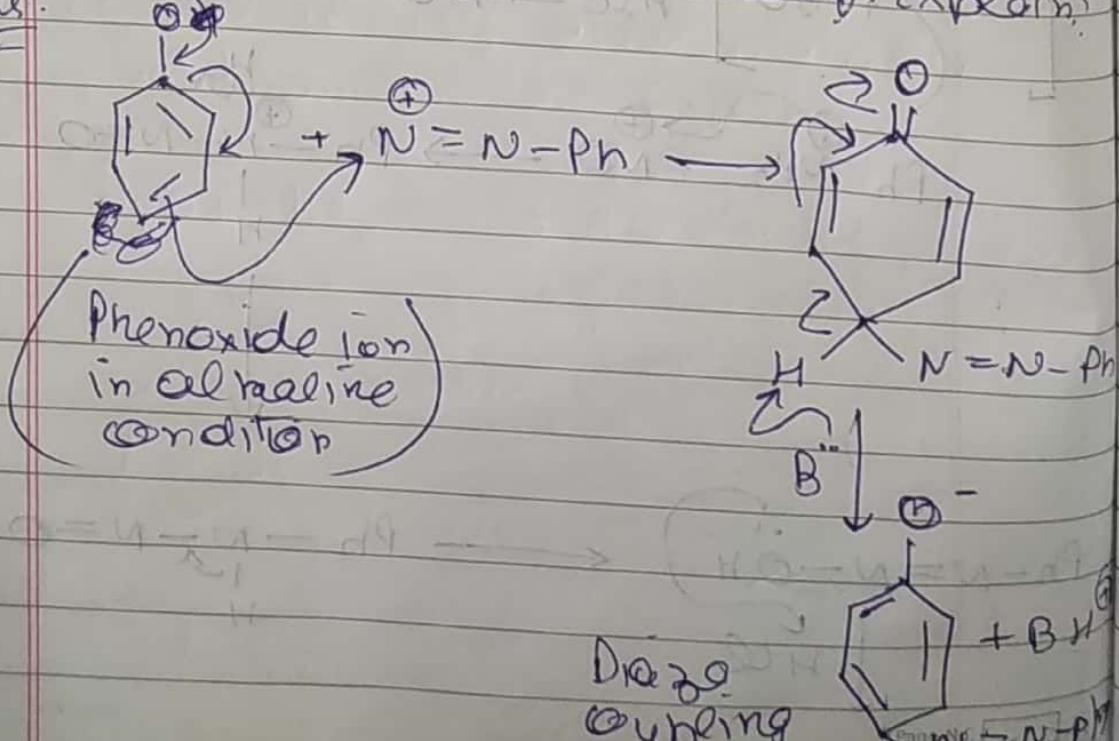
Date / /



Diazonium cation

- Q1. Unlike phenol anisole does not give diazo coupling rxn when treated with benzene diazonium salt (Ph N_2^+) but gives the above rxn when treated with 2,4 dinitro benzene diazonium cation. More over ~~benzene~~ gives the above rxn when treated with 2,4,6 trinitro benzene diazonium cation. Explain?

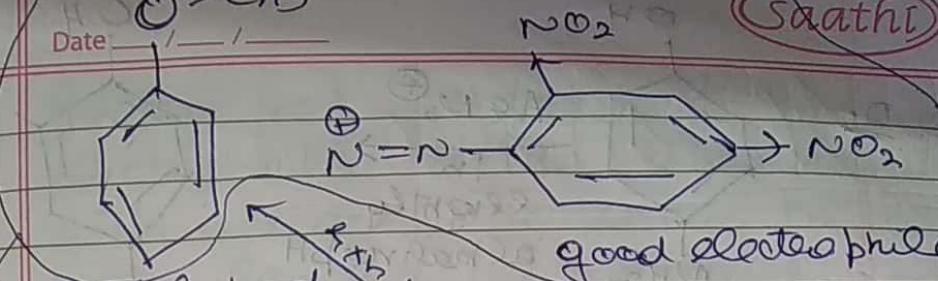
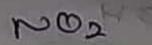
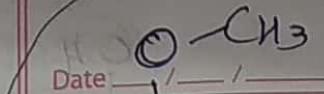
Ans.



Saathi

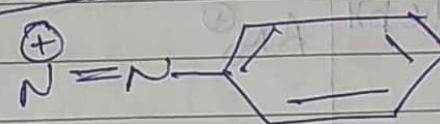
Date

Saathi

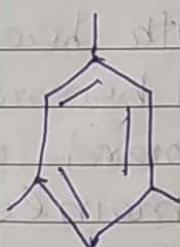
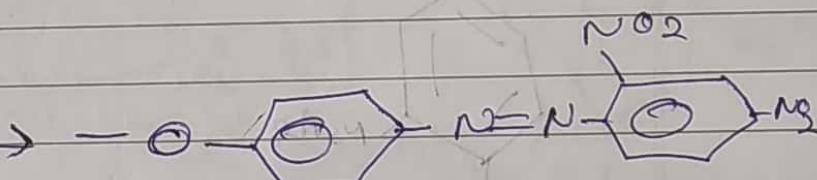


relatively bad
Nu for PhN₂

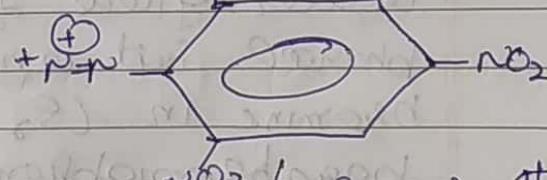
good electrophile



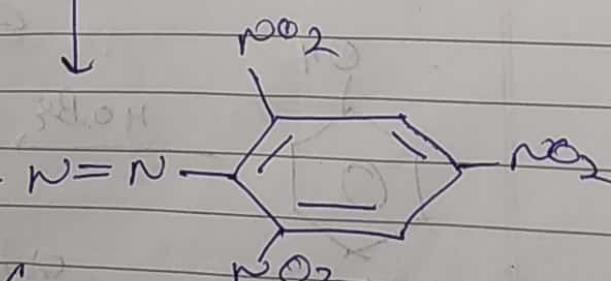
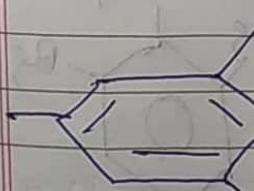
(Bad electrophile)



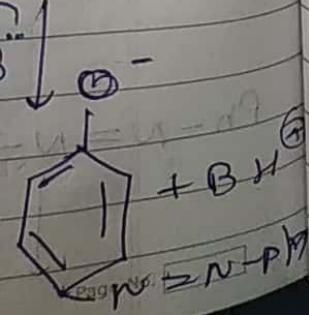
Much weaker
Nu for PhN₂



(Very \rightarrow strong
electrophile)



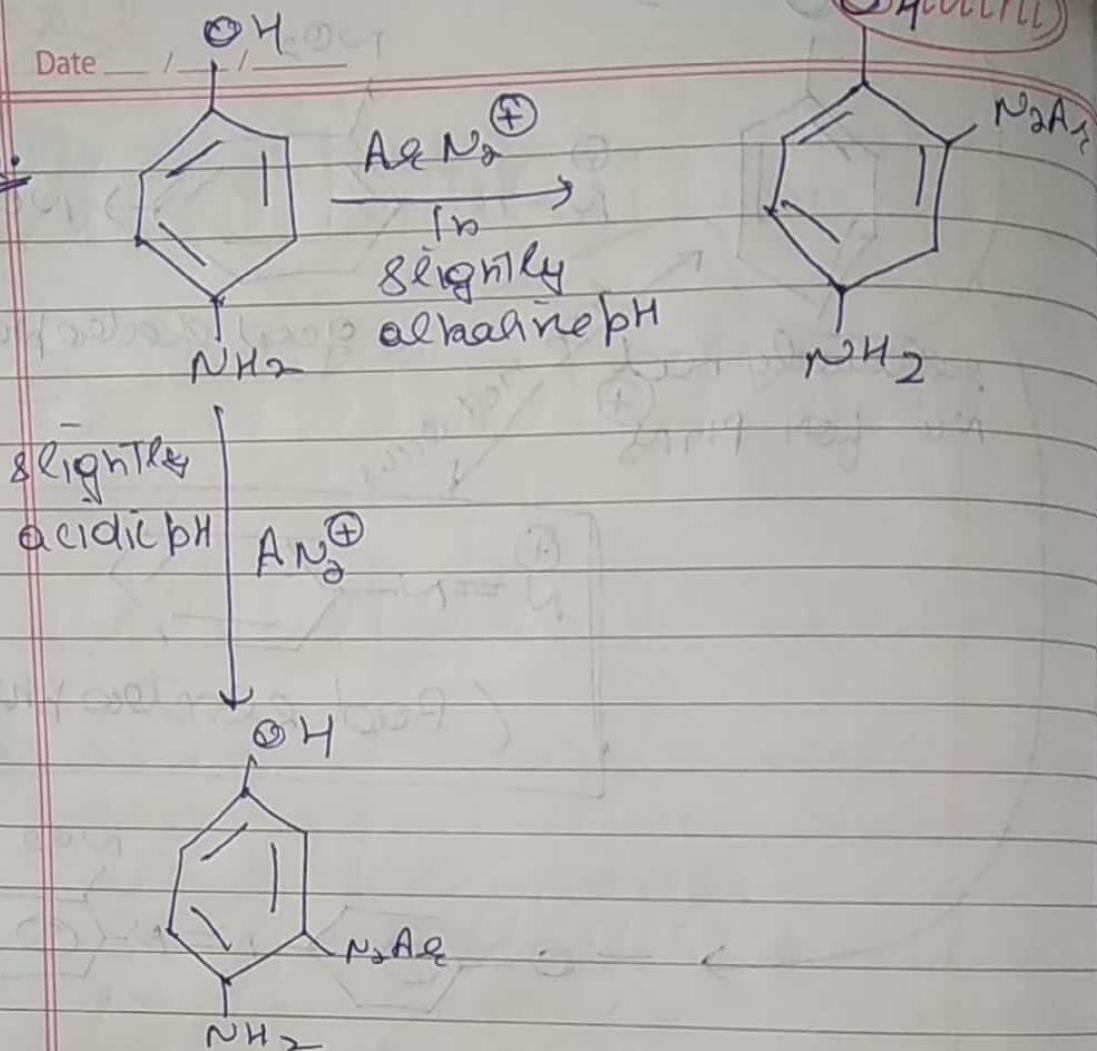
(diazo coupling)



Osathhi

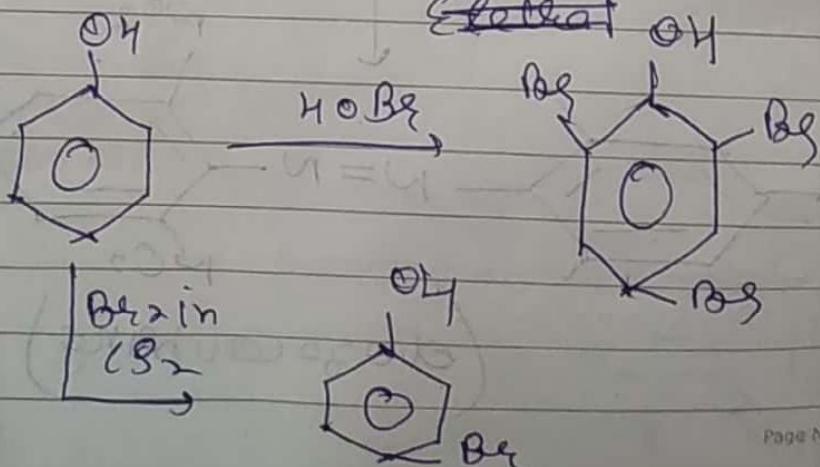
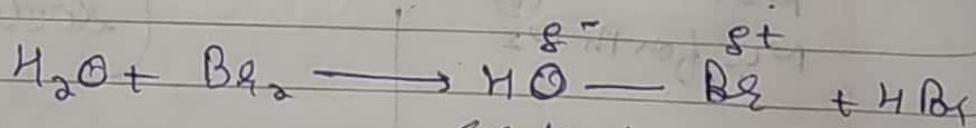
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Q 2:

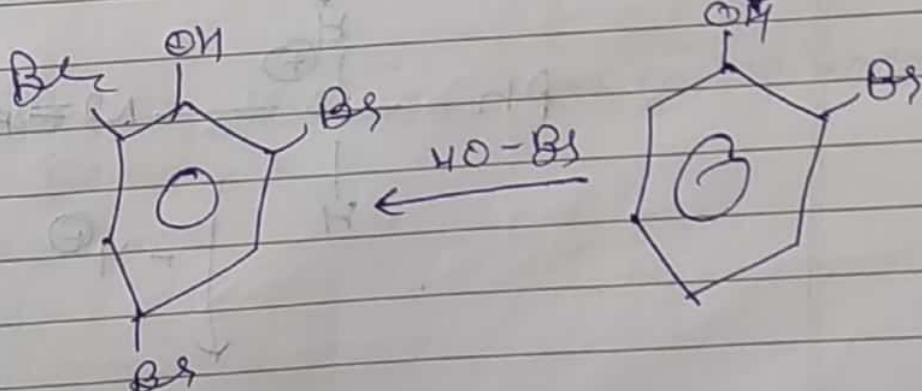
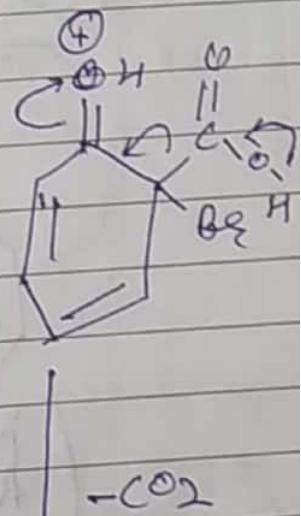
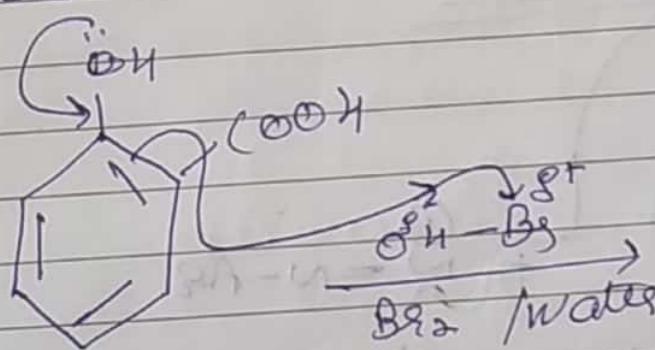


Q 3. Phenol on treatment with bromine in water gives 2,4,6 tri bromo phenol but on treatment with bromine in CS_2 gives mainly para bromophenol. Explain

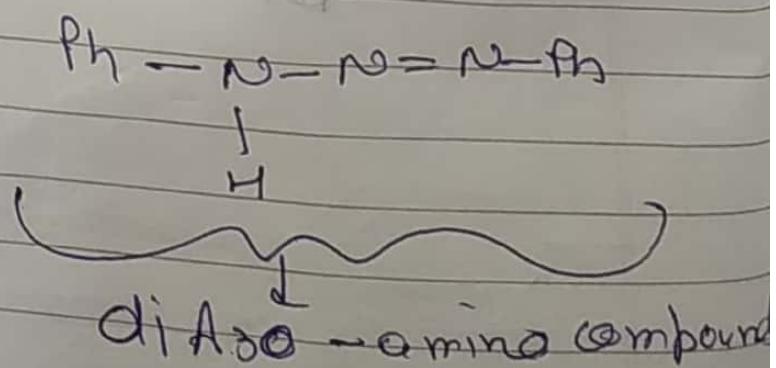
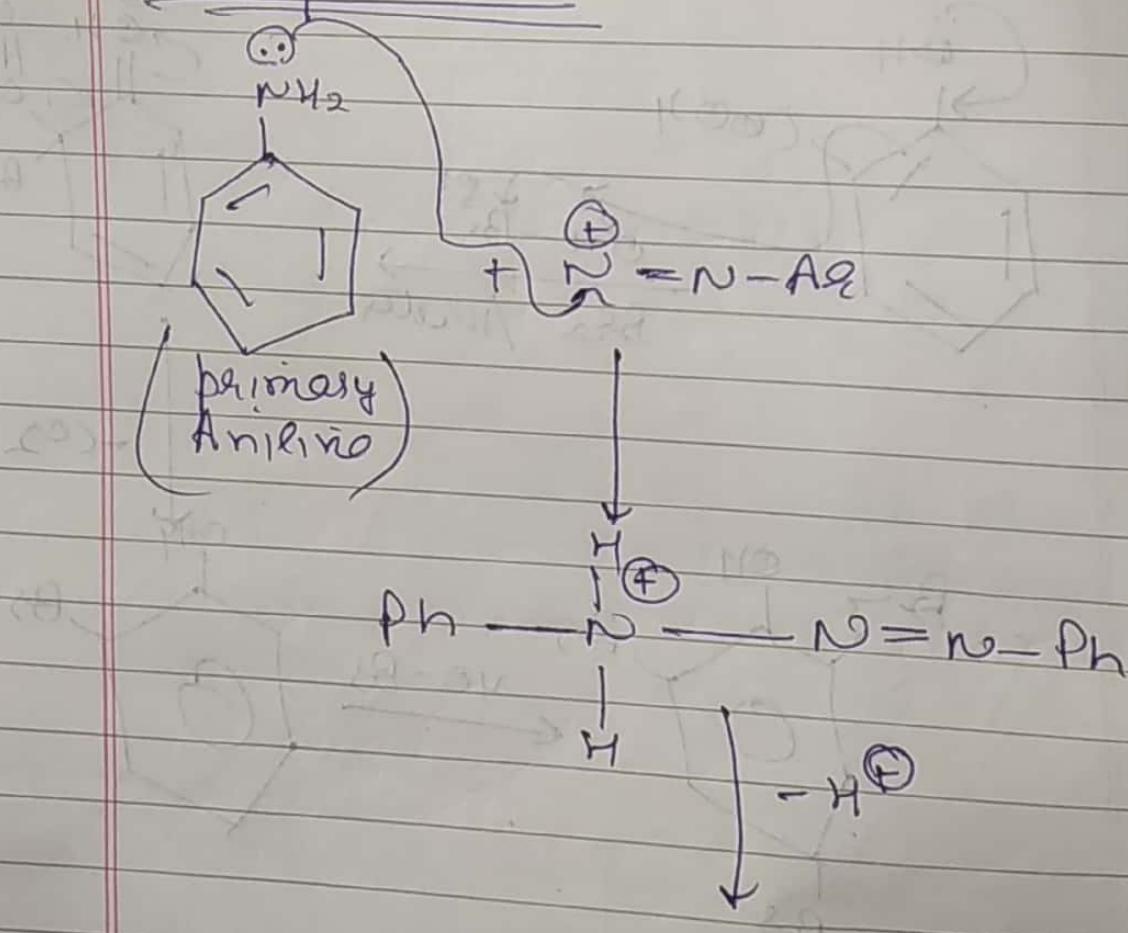
Ans.

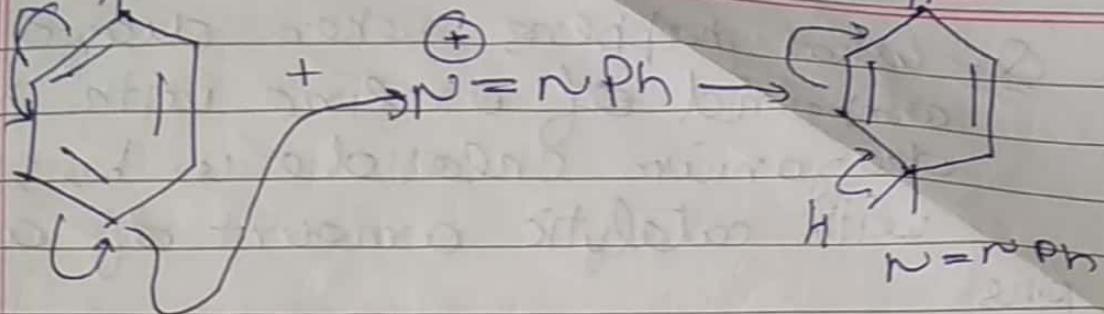
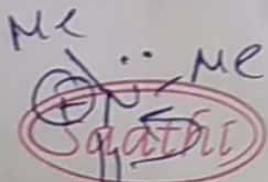
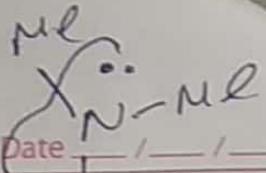


In case of the former more electrophilic HOB_2 is generated with respect to Be atom in Be_2 molecule. But for the latter case, Be_2 is less associated with the solvent (S_2) therefore the electrophilic character of Be is easily lost.



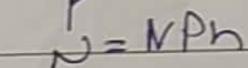
Electrophilic Substitution of Aromatic Amino Compounds





(Tertiary amine)

Here +ve charge
can't stabilize so it
occurs this way.

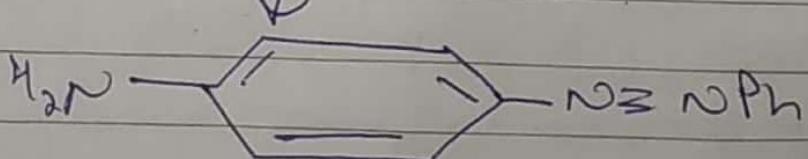
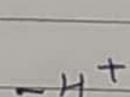
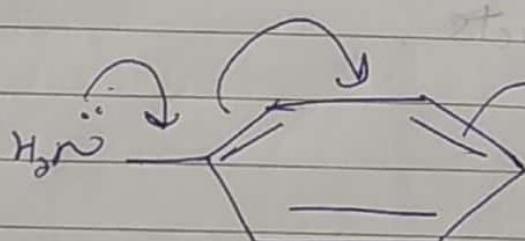
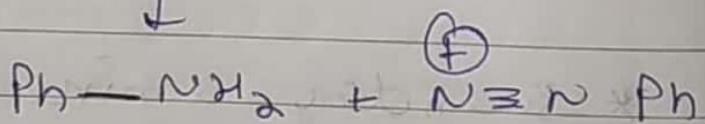
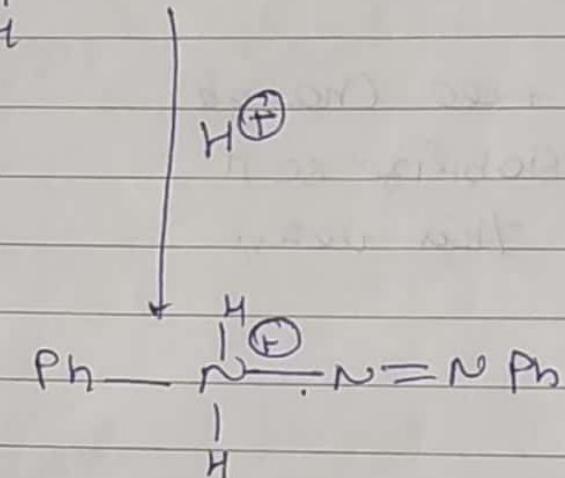
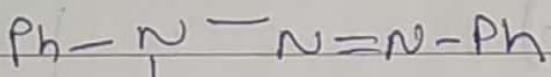


diazo coupling
(amine - azo
compound)

* Secondary amine ~~gives both~~ gives both
the products.

Q.1 What happens when diazoamine compound of aniline with benzene diazonium chloride is burnt with catalytic amount of acid?

Ans.

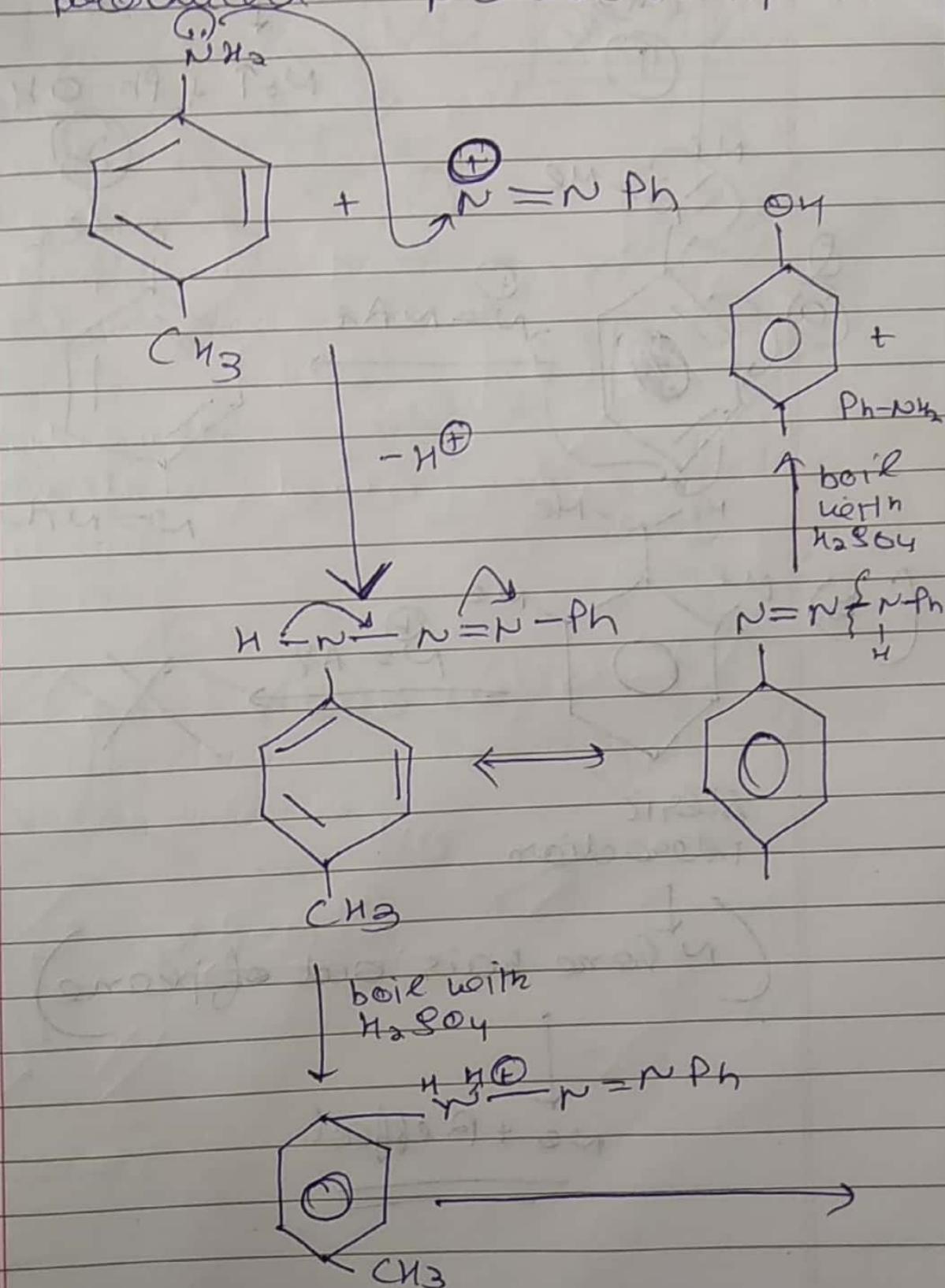


amino-Q_{zo} compound

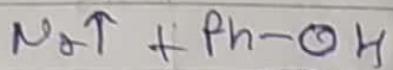
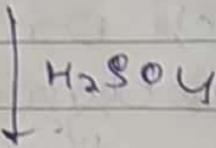
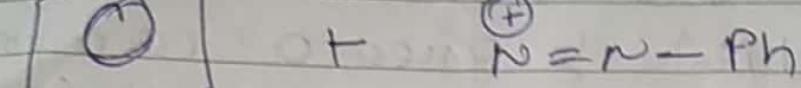
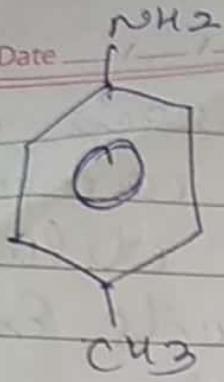
Q.2

Ans.

Q.2 ~~para~~ Toluidine reacts with PhNO_2^+ to give a compound which on dilute acid produces 4 products. Explain.

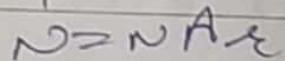
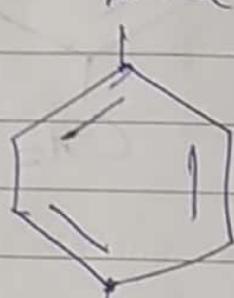
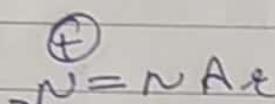
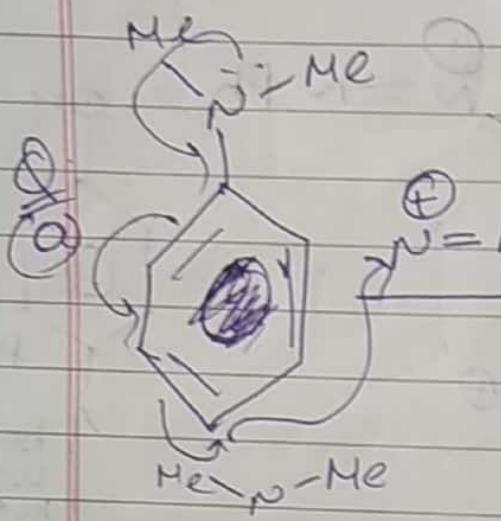
Ans

Date _____

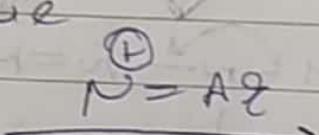
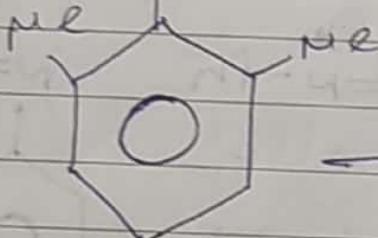


(1)

(2)



(b)

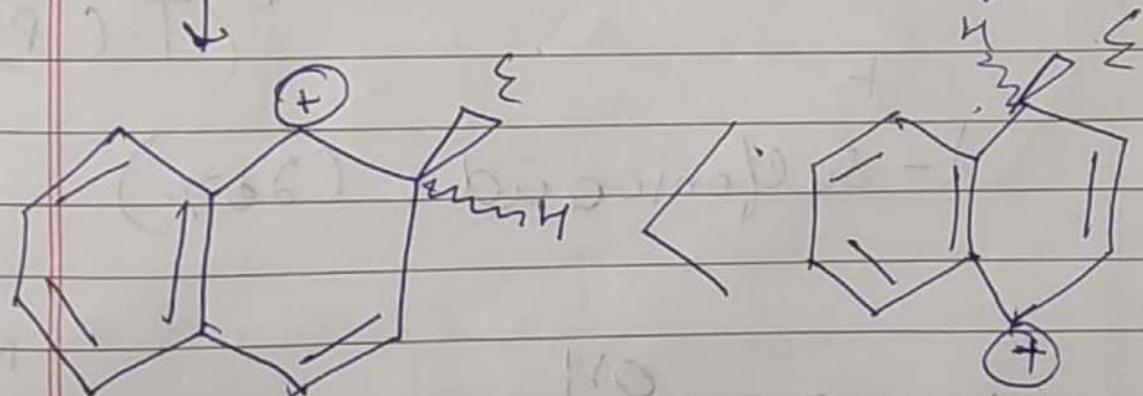
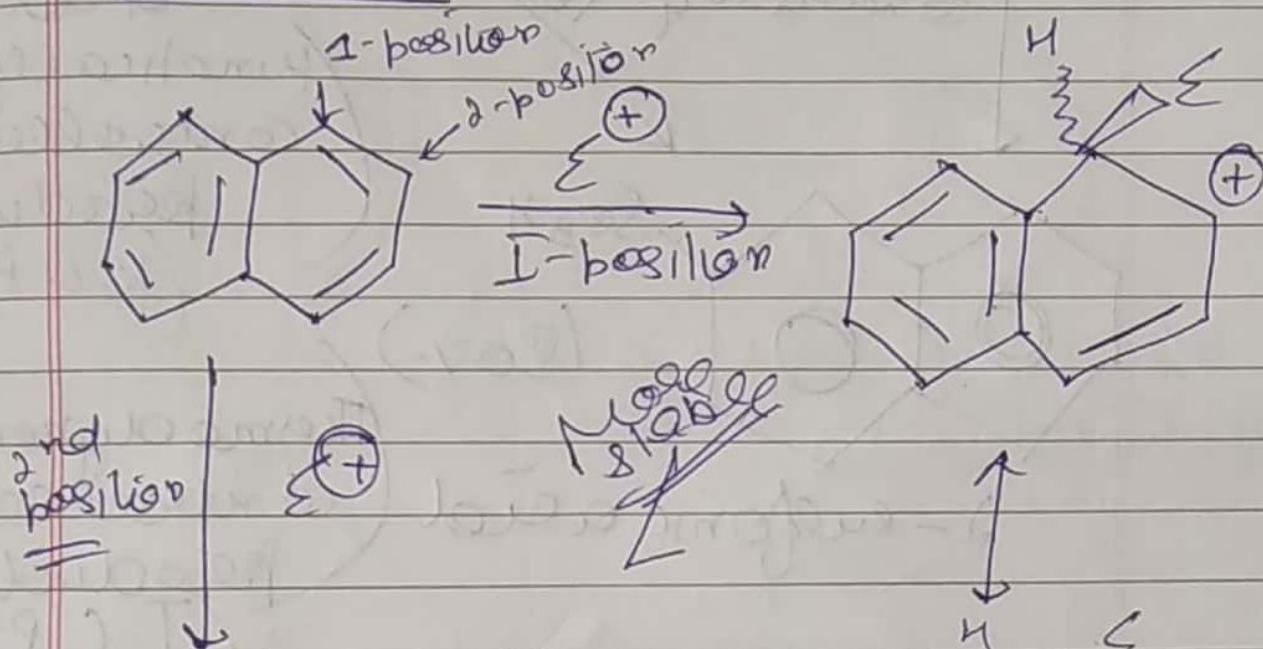
STERIC
interaction

(N lone pair out of plane)

$\text{no} + \text{P effect}$

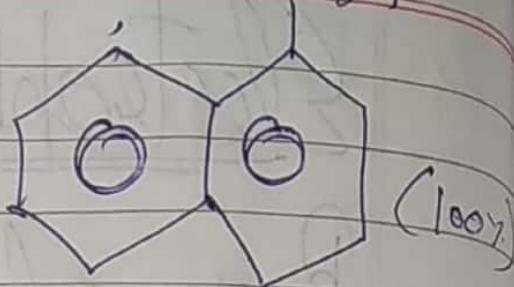
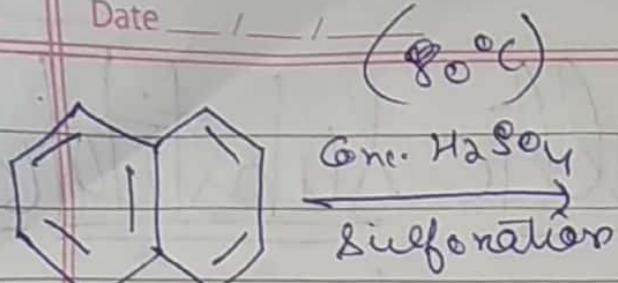
Electrophilic Substitution

Rxn of Naphthalene



Date / /

Saathi
 SO_3H



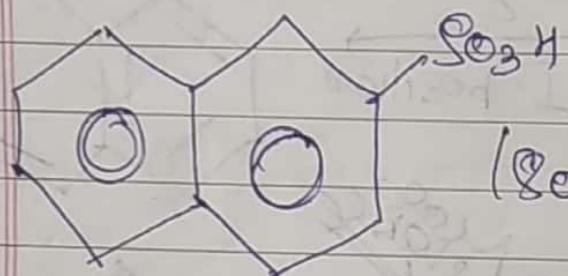
160°C

Cone. H_2SO_4

160

1-sulfonic acid

Kinetically controlled product
(K.C.P)

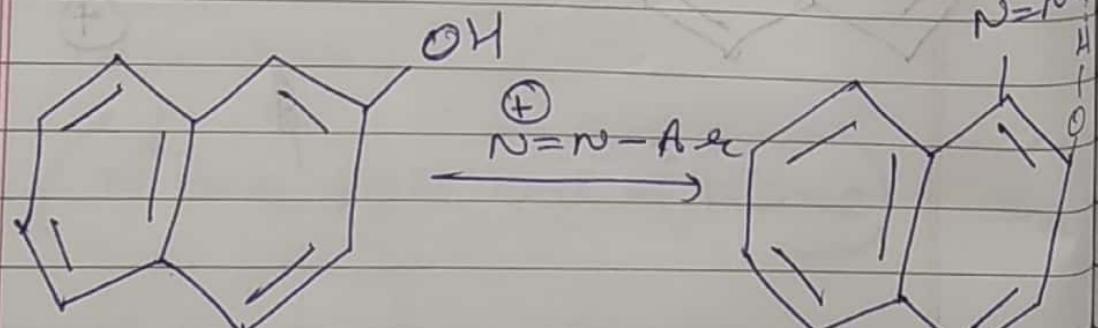


2-sulfonic acid

Thermodynamically controlled product
(T.C.P)

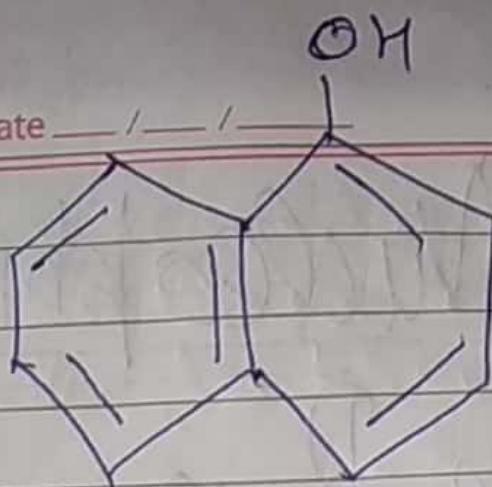
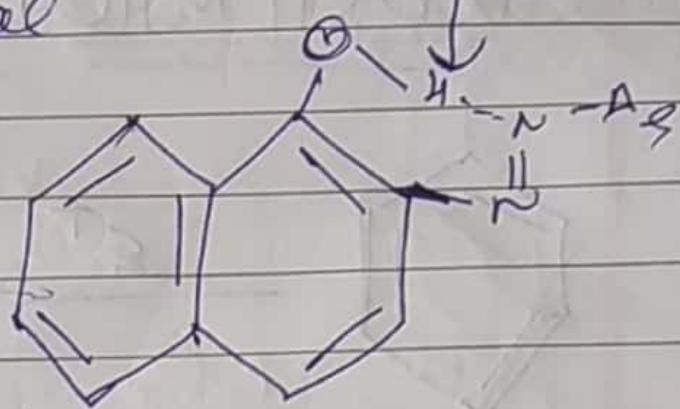
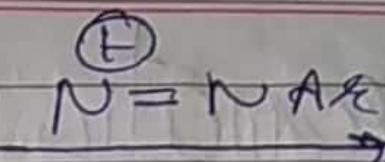
+

1-sulfonic acid (20%)

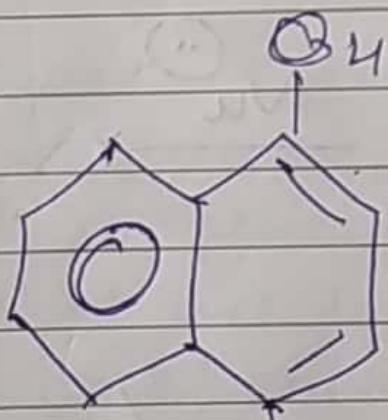


stabilo cation

Date / /

 α -Naphthalen-2-ol

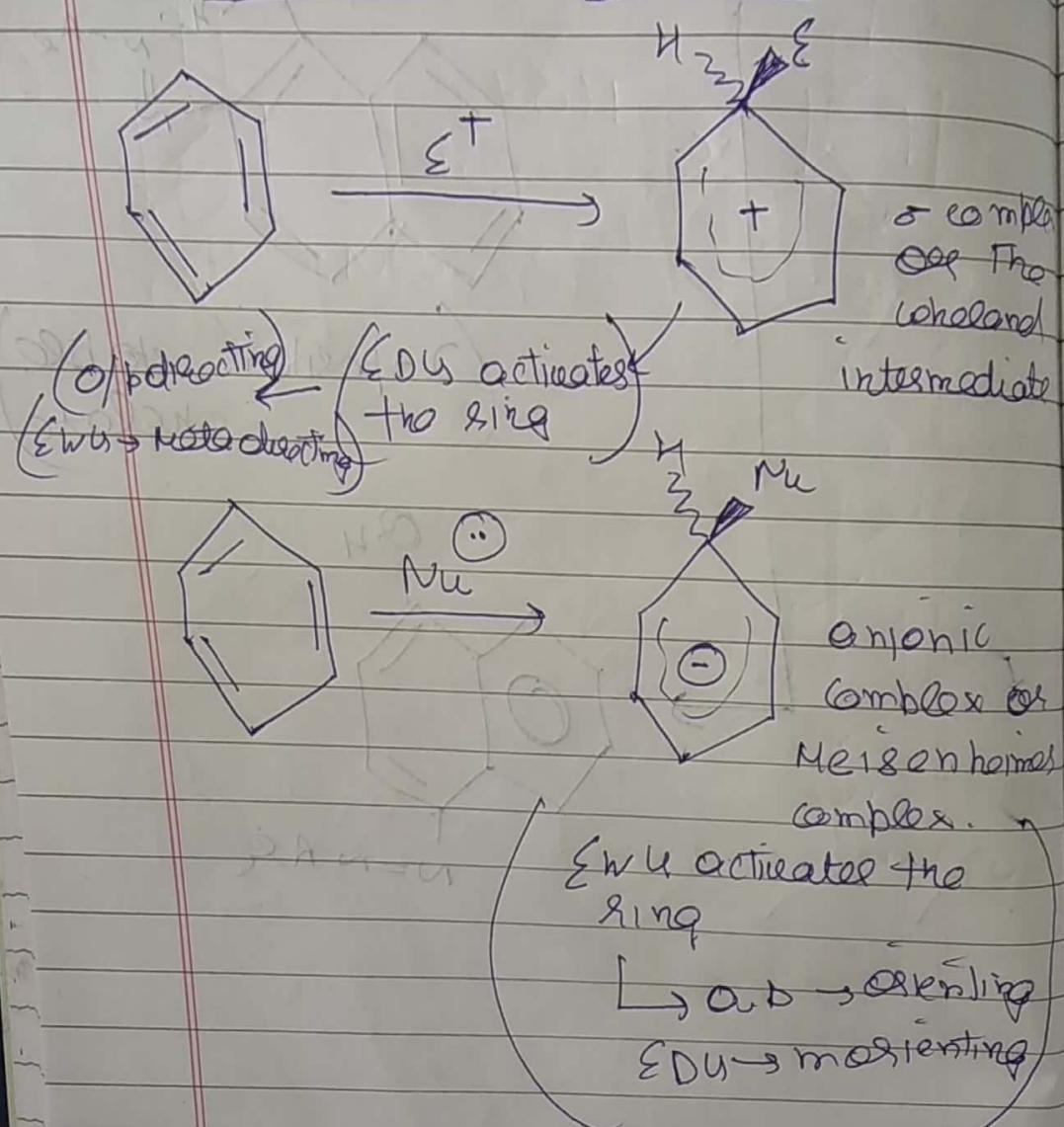
(2-position stable chelate)

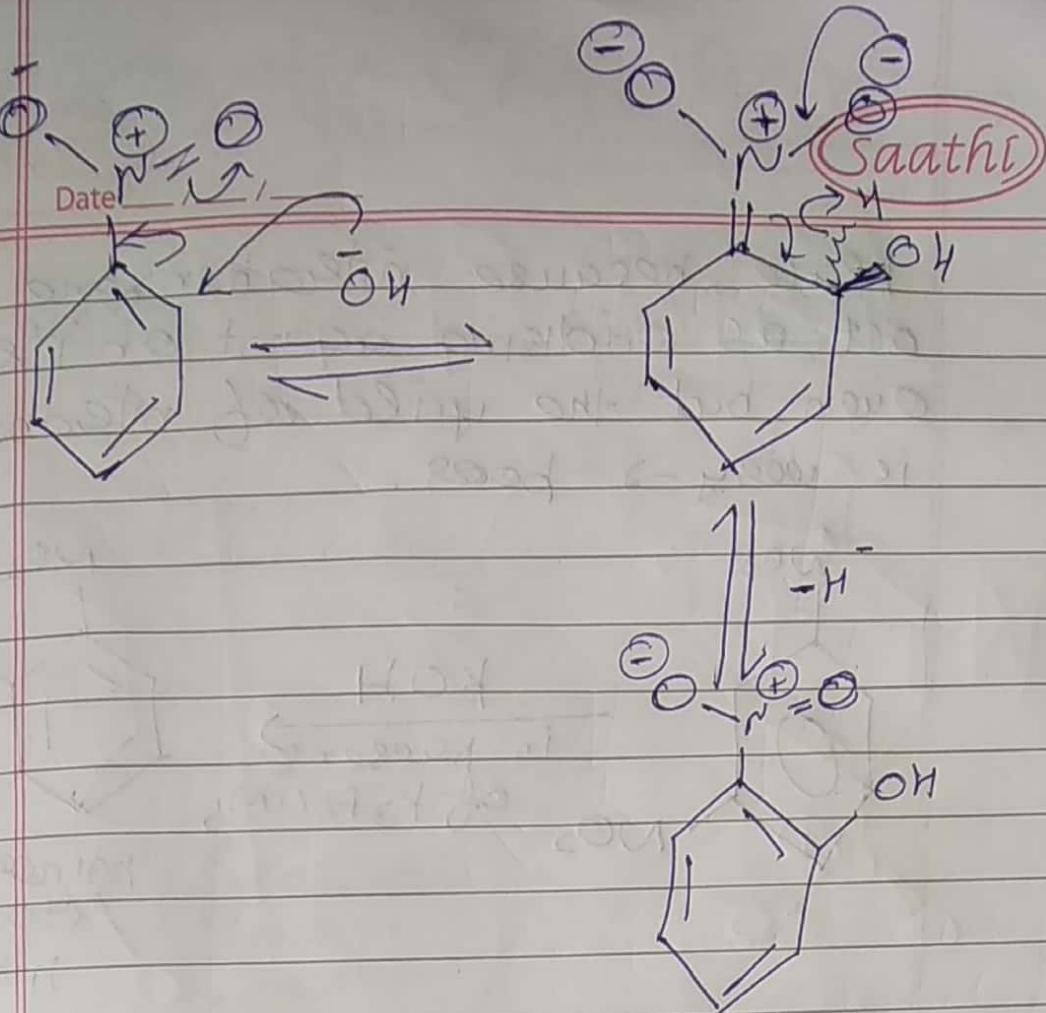


$\text{H}^+ \text{---} \text{N}=\text{n---Ar}$

Aromatic Nucleophilic Substitution Rxn :-

Substitution Rxn :-



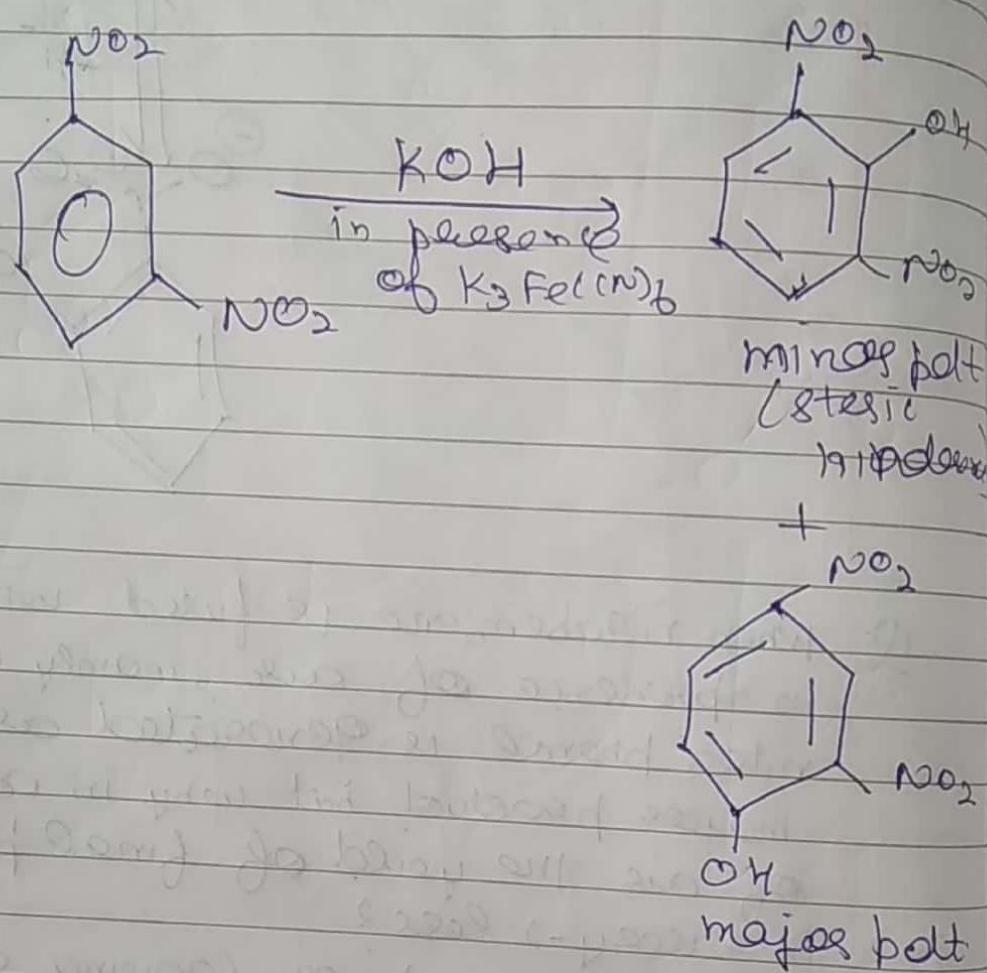


Q: When nitrobenzene is fused with KOH in presence of air, mainly ortho-nitro phenol is generated as the major product but why in absence of air the yield of final product is very less?

Ans. Here H^- is a poor leaving group than OH^-, so the overall equilib. lies over the left. But in presence of air (oxidising agent) ~~also~~ elimination of H^- is preferable as H^- is oxidised by O_2 (oxidising agent).

In absence of air or ~~or~~ K_3Fe(CN)_6 oxidising agent (KNO_3 or ~~K_3Fe(CN)_6~~) some extent of conversion takes

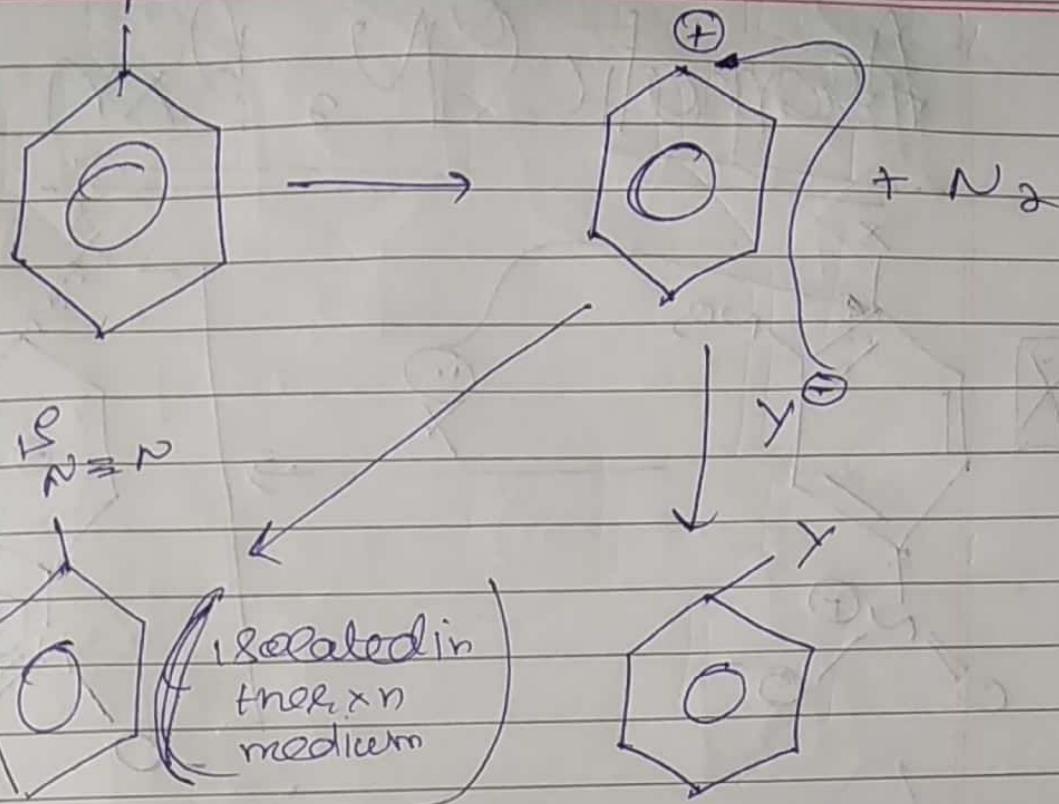
place because nitrobenzene can act as oxidising agent on its own but the yield of nitrobenzen is very \rightarrow poor.



Aromatic SN₁

Date: $\text{N}_3^+ \text{N}^{18}$

Rx No: Saathi



$$\text{Rate} = k_1 [\text{PhN}_3^+]$$

$$Y = \text{O}^- \text{ MeOH}$$

Rate = independent / does not change
on changing Y

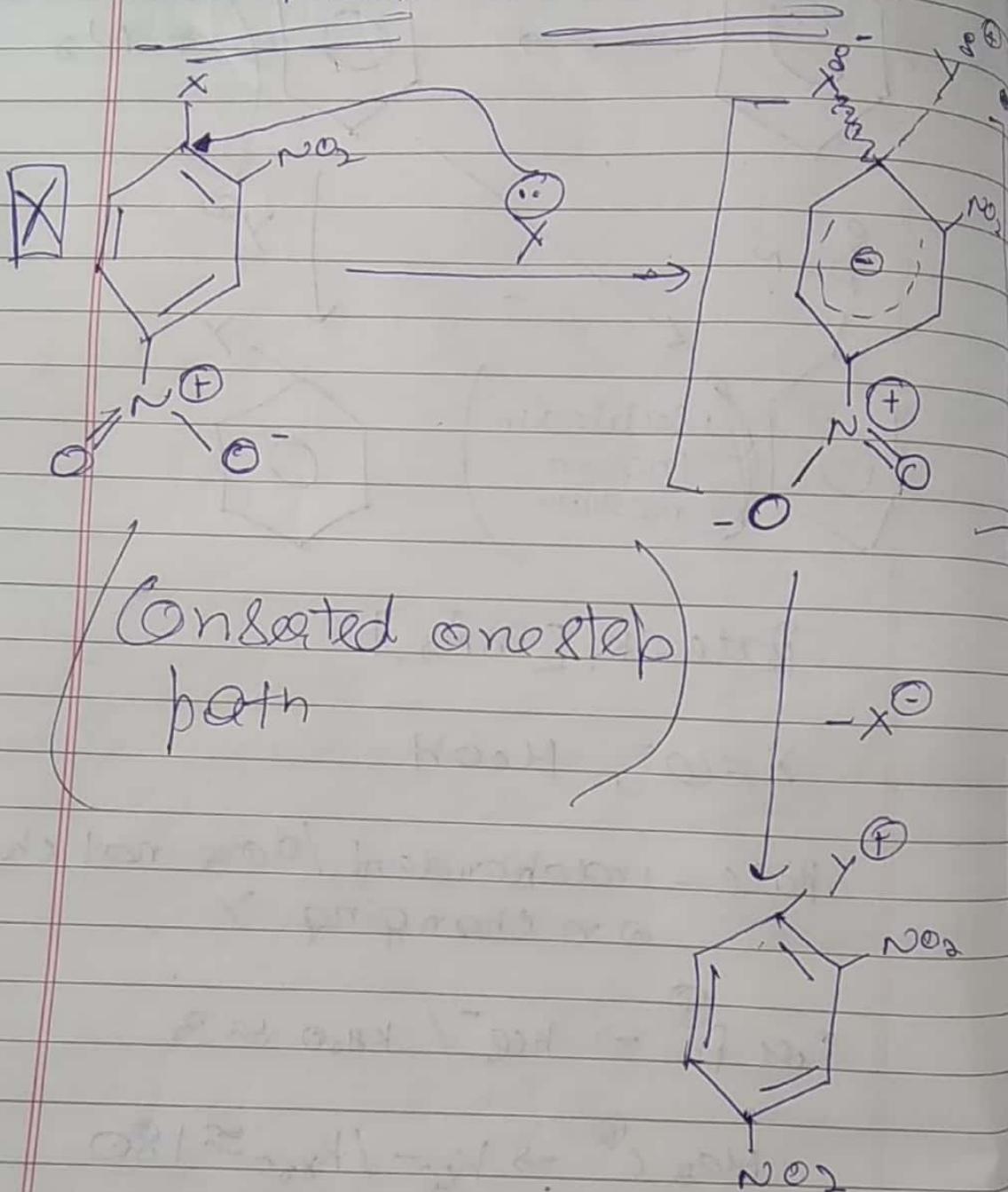
For Ph^+ $\rightarrow \text{KCl}^- / \text{K}_2\text{SO}_4 \approx 3$

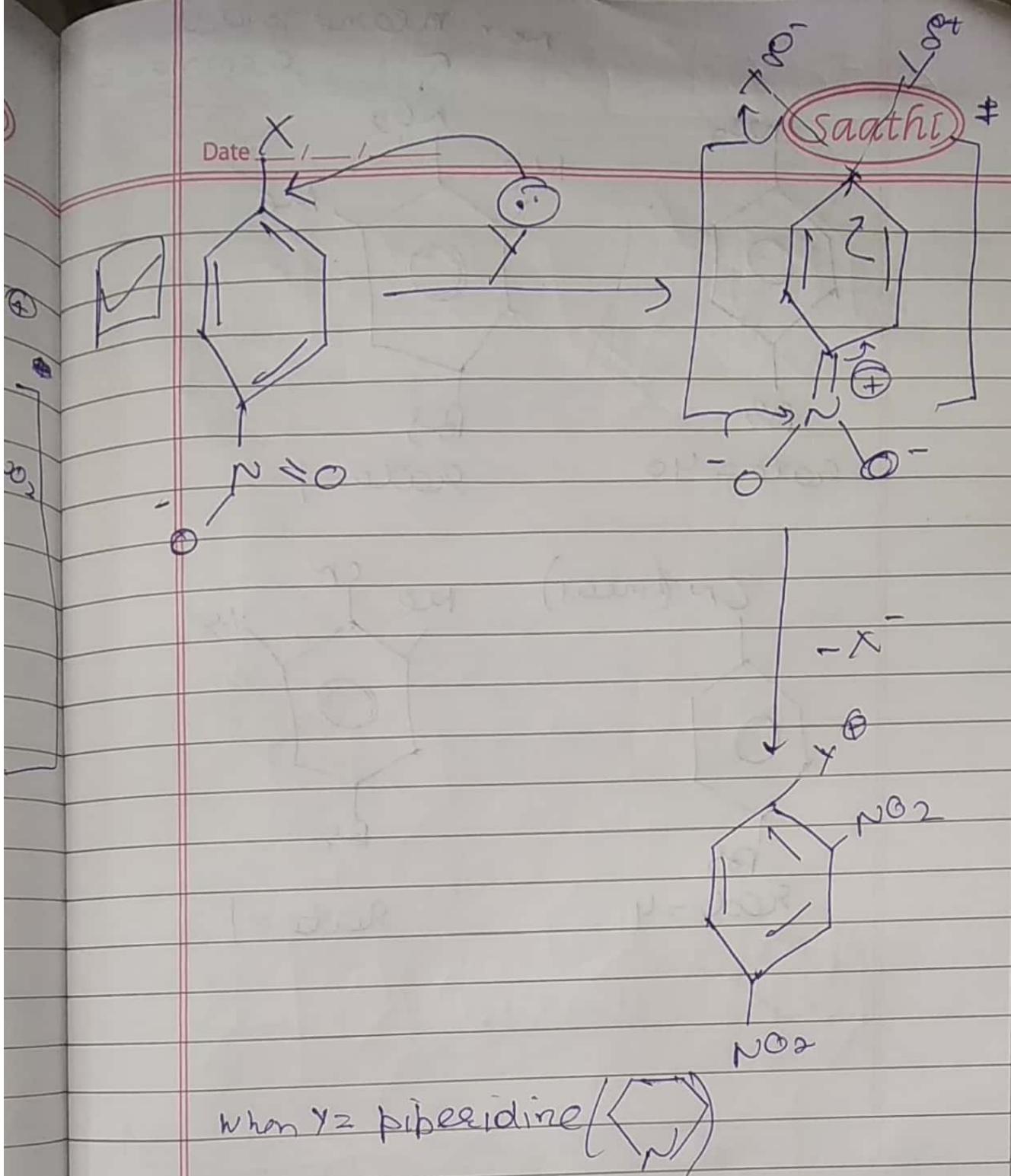
$\text{Me}_3\text{C}^+ \rightarrow \text{KCl}^- / \text{K}_2\text{SO}_4 \approx 180$

\therefore For Ph^+ \rightarrow highly reactive \Rightarrow less
selectivity \Rightarrow pdt ratio is less

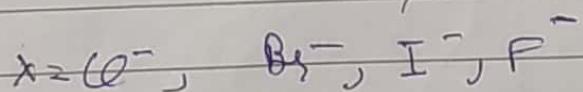
For $\text{Me}_3\text{C}^+ \rightarrow$ less reactive \Rightarrow highly
selective
 \Rightarrow pdt. ratio is more

Aromatic $\text{P}_\text{N}_2 \text{Rxn}$





When $\gamma = \text{piperidine}$



Rate = $4.3, 4.3, 1.0, 3300$

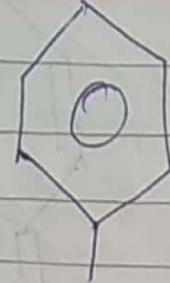
$(-\text{I}^-) > (-\text{Br}^-) > (-\text{O}^-)$

$$\boxed{\text{Rate} = k_2 [A_2 - X] [\gamma]} \\ \underline{\text{2nd order}}$$

non polar to do
lepton and
Saathi

Date

NO_2

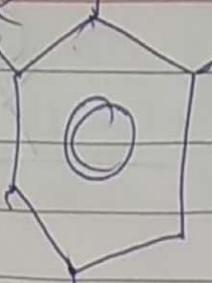


Br

rate = 40

NO_2

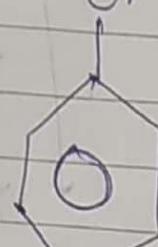
Me



Br

rate = 1

Cr (linear)

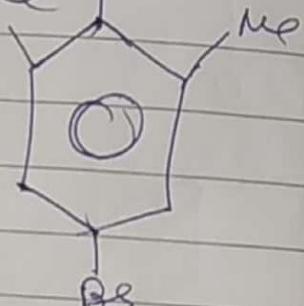


Br

rate = 4

Me

Cr

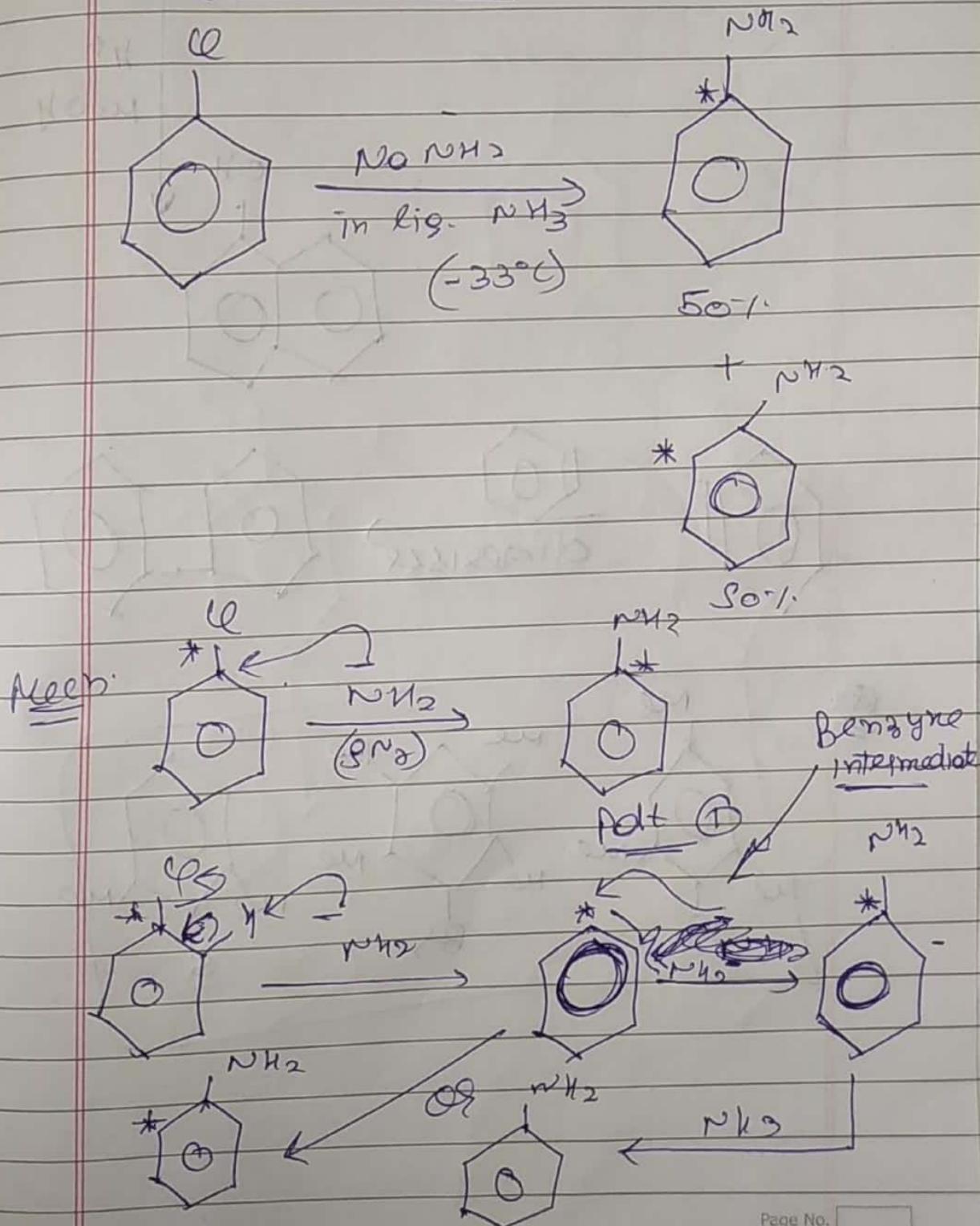


Br

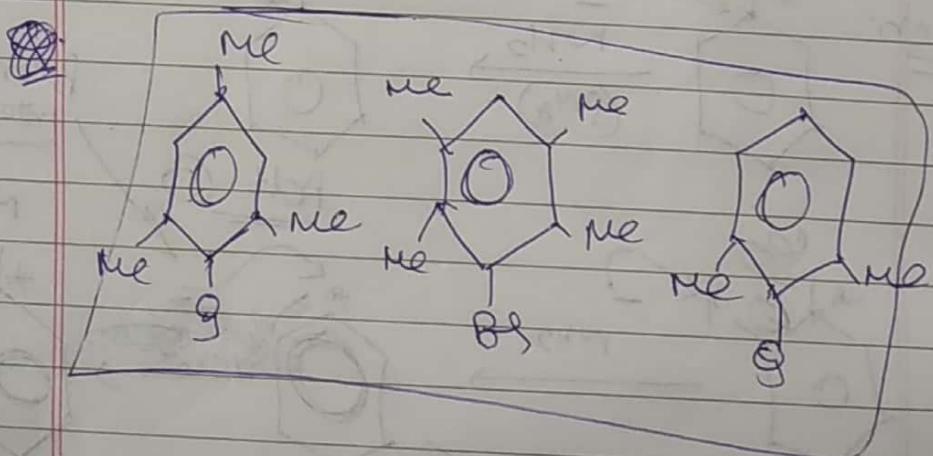
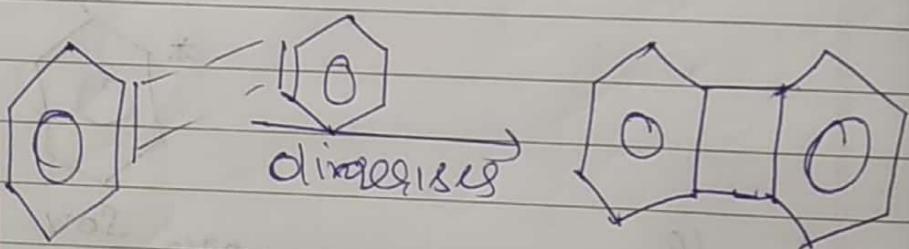
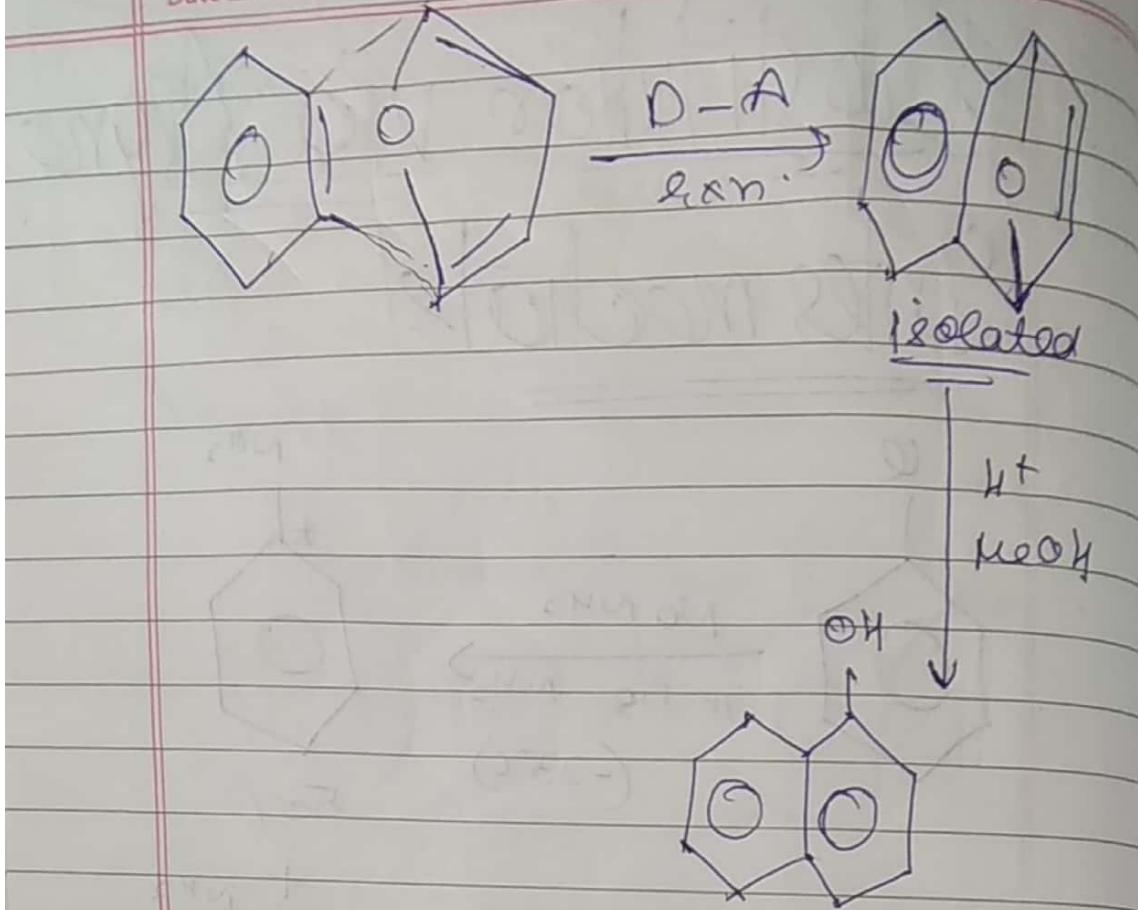
rate = 1

Substitution via Alyne

Intermediate



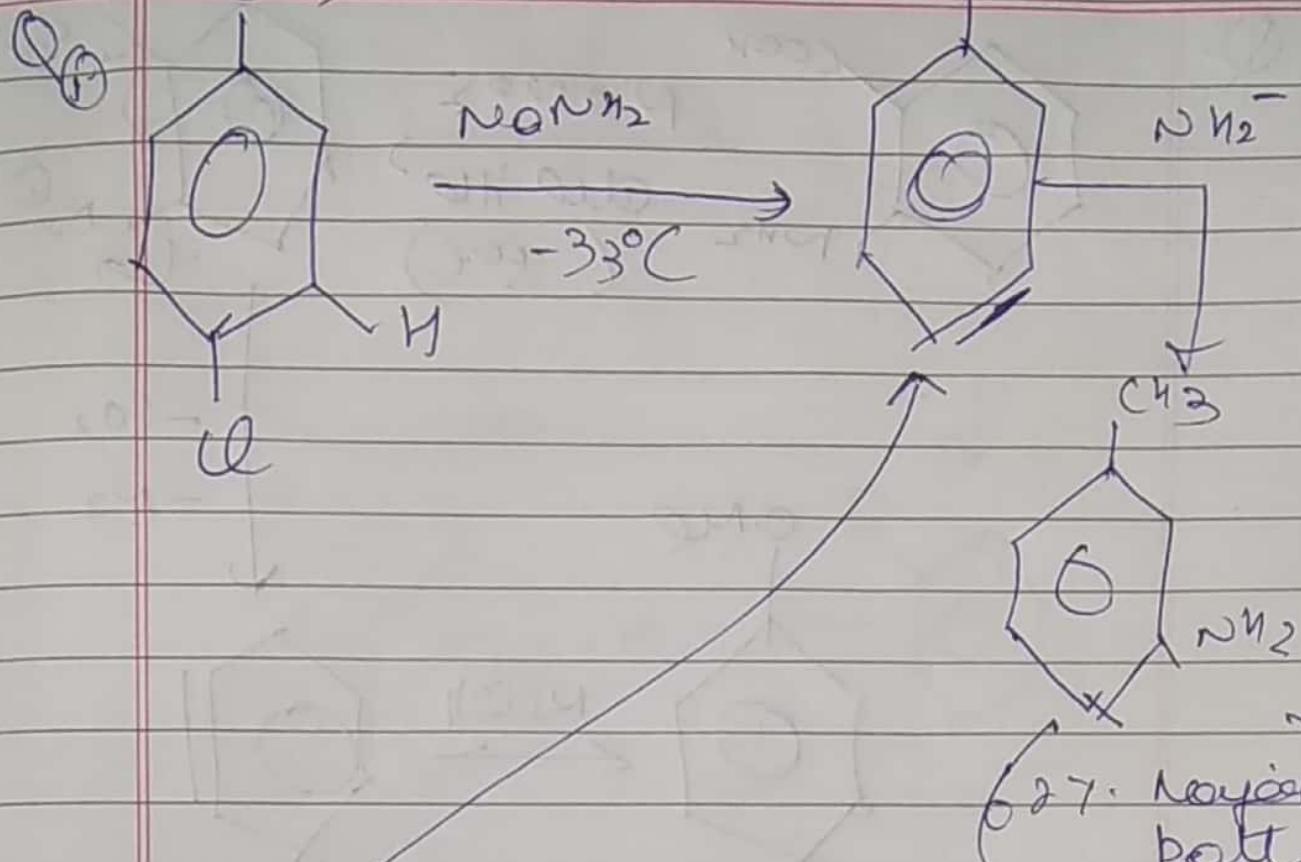
Date 1/1/1



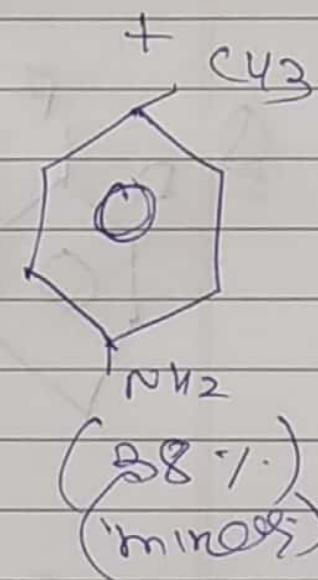
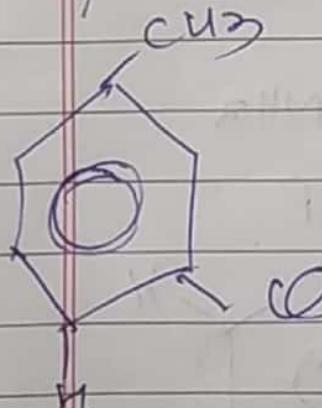
Date

Cu3

Cu Saathi



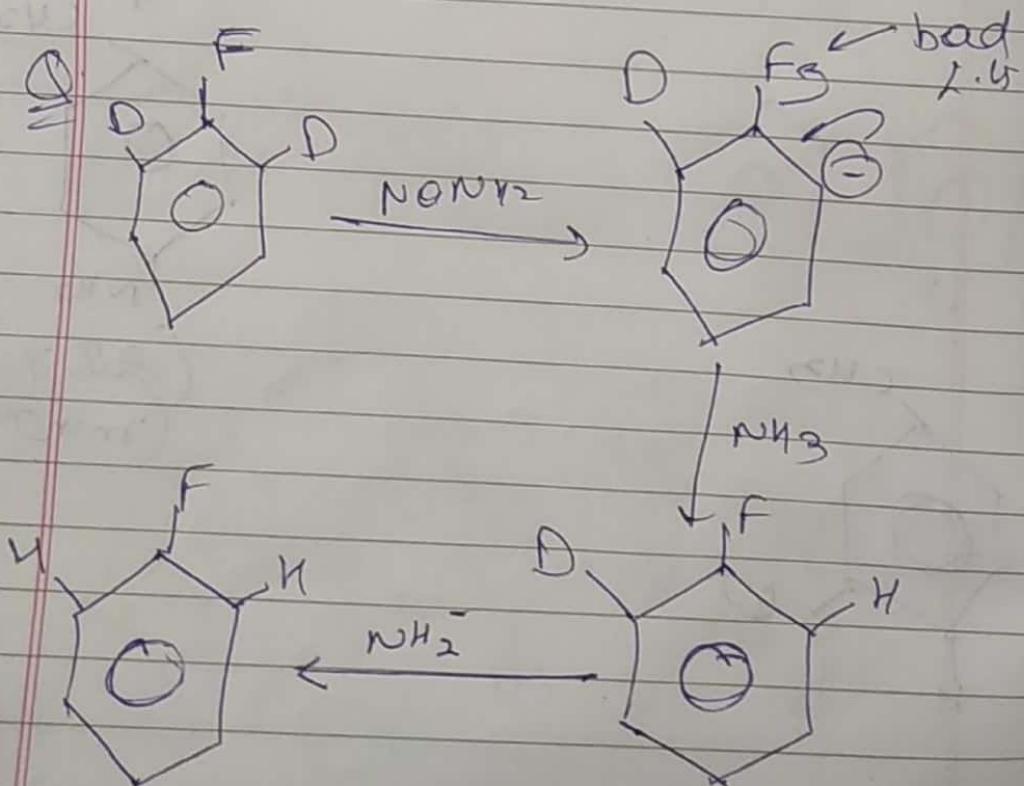
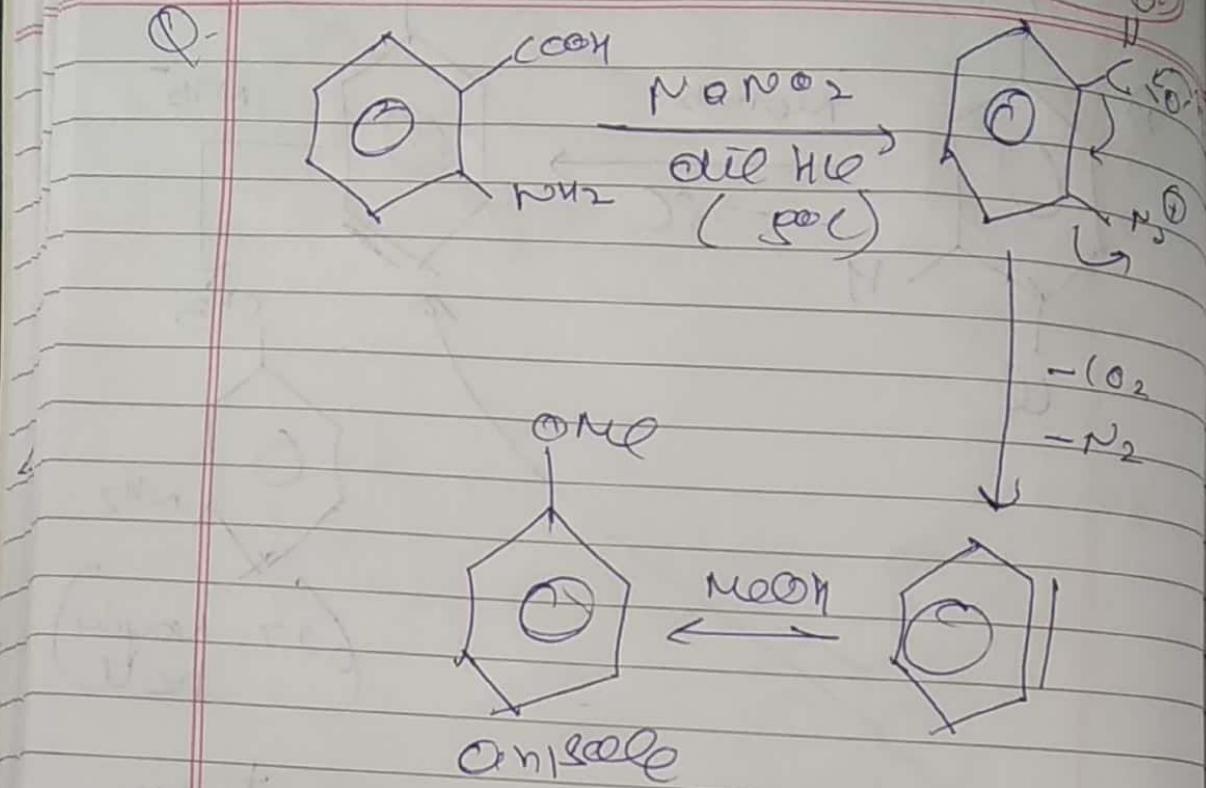
Q2



NH_2^- MeOH CH_3OH

Date _____

Saath



Date _____ / _____ / _____

Saath

