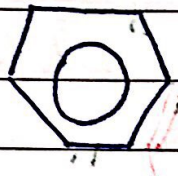
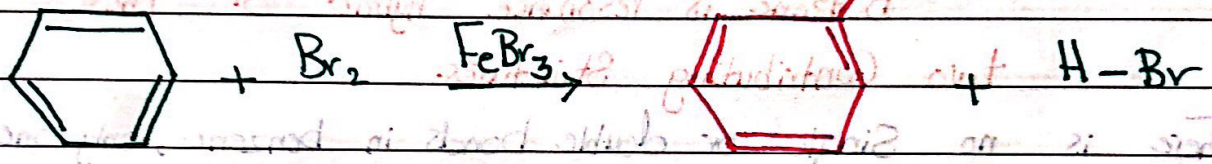
"Chapter 4"
"Aromatic Compounds"

Benzene is highly unsaturated Structure. C_6H_6



* Benzene reacts mainly by Substitution.



Bromobenzene

$C_6H_6 + Cl_2 \xrightarrow{FeCl_3} C_6H_5Cl + H-Cl$

Clorobenzene

* It doesn't decolorize bromine solutions the way alkenes and alkynes do.

---

* only one monobromo/monoChloro Benzene are isolated, NO isomers are obtained in either of the reactions.

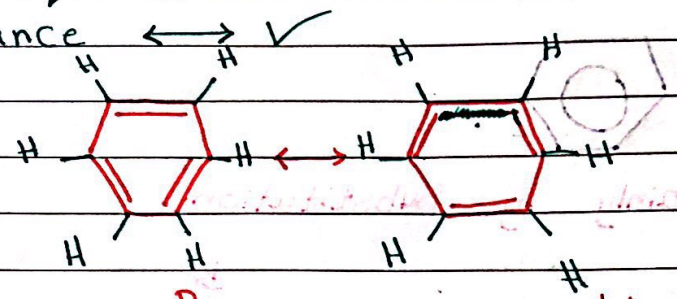
All Six hydrogens in benzene are Chemically equivalent. no matter which hydrogen is replaced by Br/Cl The same result is obtained.

* Benzene is not oxidized by ~~KHO~~ ($KMnO_4$).

* Benzene doesn't oscillate between two Structures it has a hybrid resonance :-

no equilibrium. ⇌ ✗

resonance ⟷ ✓

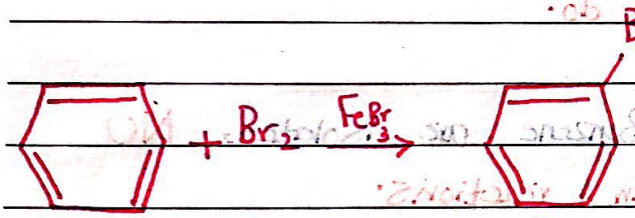


Benzene is resonance hybrid of these two Contributing Structures.

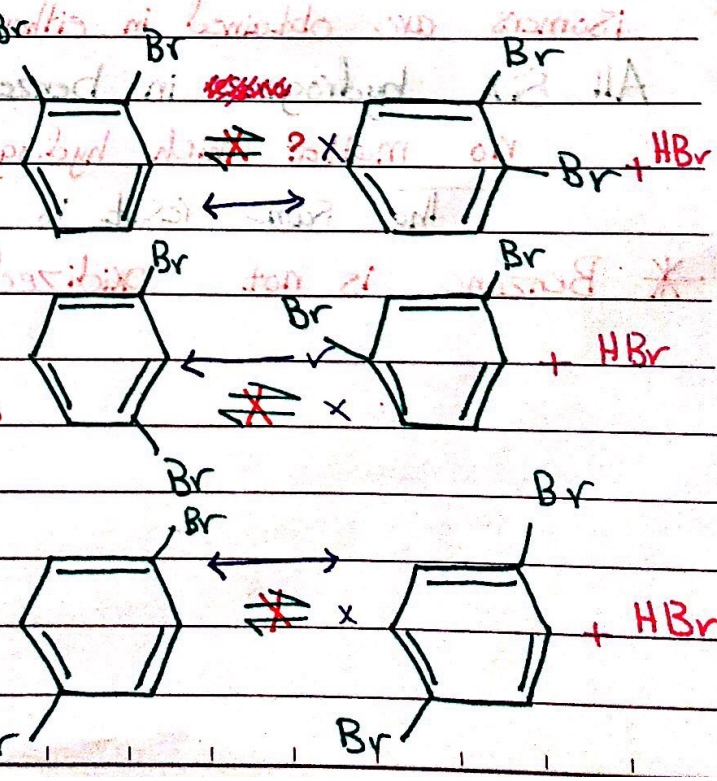
* There is no Single or double bonds in benzene, only one type of C-C bnd, which is some of intermediate between Single and double bonds.

That's why Benzene doesn't react like alkenes.

Bond lengths 1.39 Å



mono Bromobenzene (no isomers).



Three isomers are obtained.

⟷ resonance

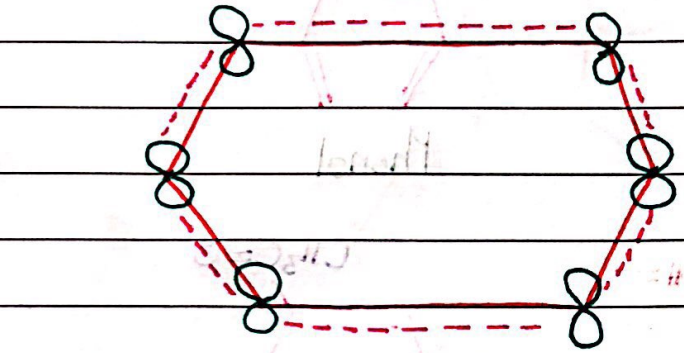
each isomer has a resonance Structure.

4.4 :- Orbital model for Benzene :-

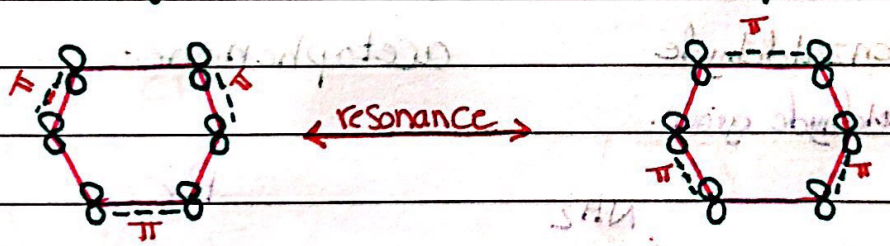
1. Overlaping p orbitals (planar).

C → Sp2 hybridized

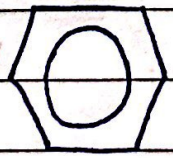
each carbon has a free p orbital.



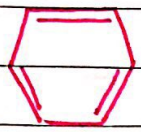
Side by side overlapping:



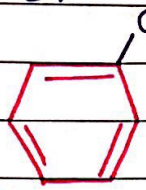
* Decalized pi cloud symbol for Benzene :-



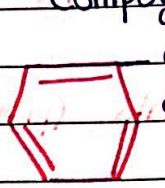
Nomenclature of Aromatic Compounds:-



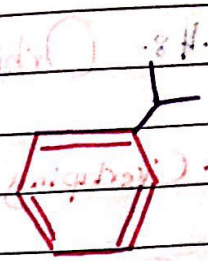
Benzene



Toluene

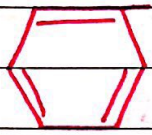


or

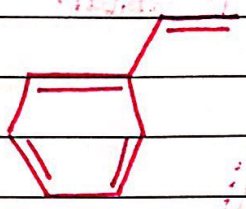


Cumene

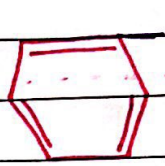
Substitution: isopropyl



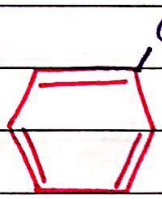
or



Substitution: Vinyl

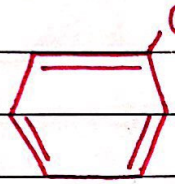


Phenol



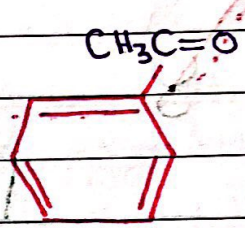
anisole

methoxy group.

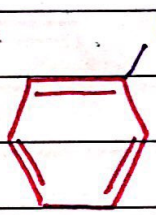


Benzaldehyde

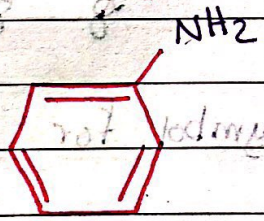
aldhyde group.



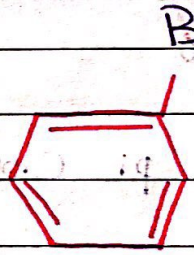
acetophenone.



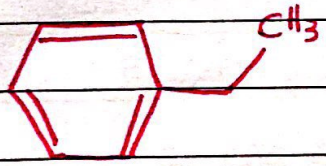
Benzoic acid



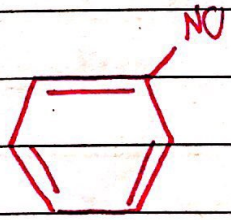
aniline.



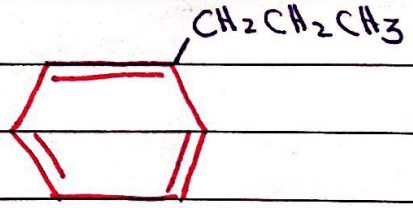
Bromo Benzene.



ethyl Benzene.



nitrobenzene



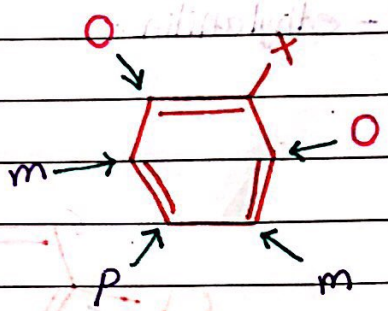
Propylbenzene.

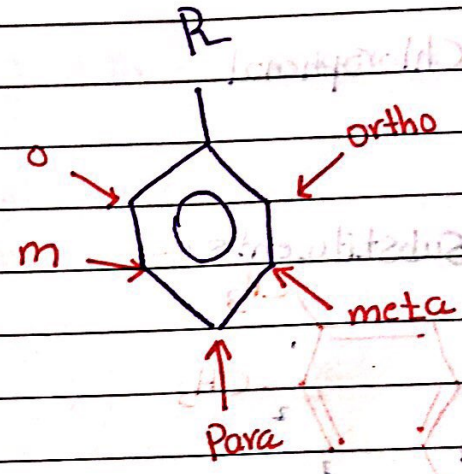
(propyl)! ✓

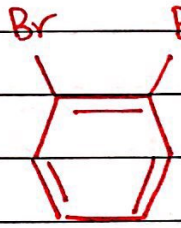
isopropyl → Cumene ✗

* Two Substituents :-

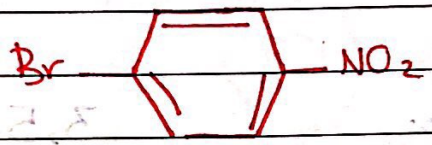
Prefixes :- Ortho → o-
meta → m-
Para → p-



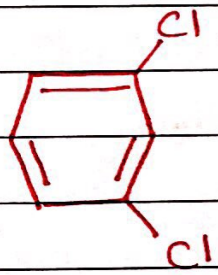




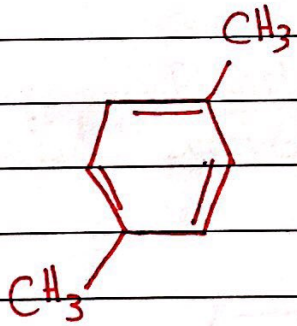
O-diBromobenzene



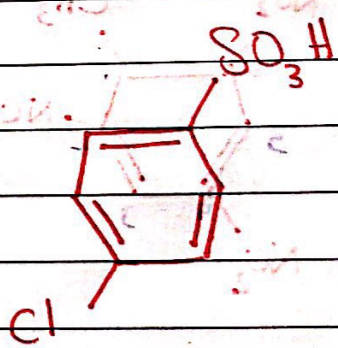
P- Bromonitrobenzene.



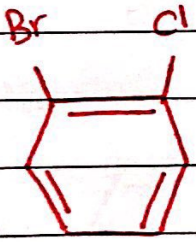
m-di Chlorobenzene.



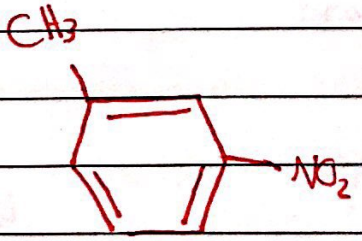
Para - Xylene



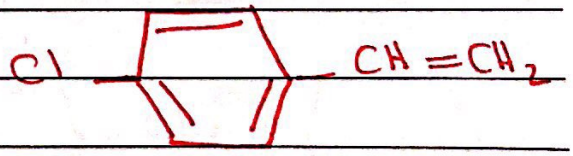
Para - Chlorobenzene - Sulfonic acid.



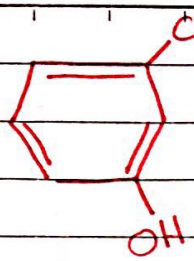
O-Bromochlorobenzene



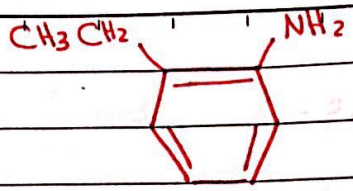
m-nitro toluene.



P-Chlorostyrene.

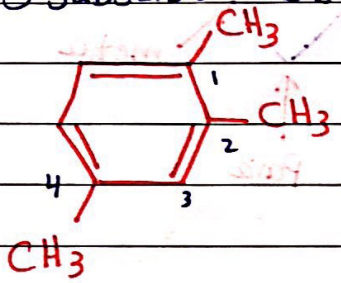


m-Chlorophenol

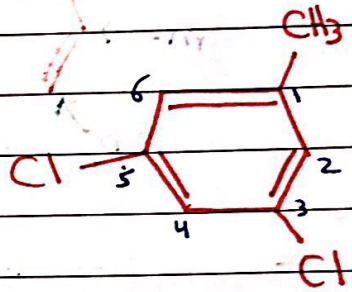


~~O-ethylnitrite~~
O-ethylaniline.

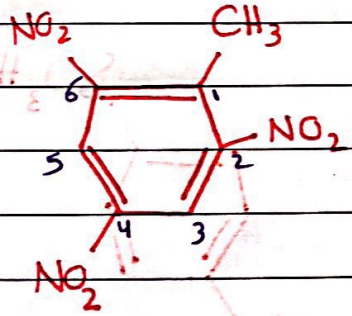
3 substituents:-



1,2,4-trimethyl Benzene.



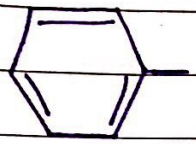
3,5-dichlorotoluene



2,4,6-trinitrotoluene.

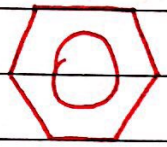
Ar → aryl group → aromatic Substituent.

C_6H_5-

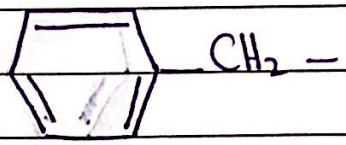


Phenyl group

or

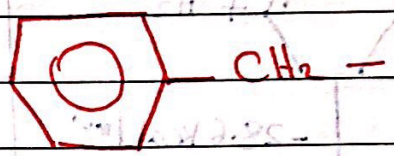


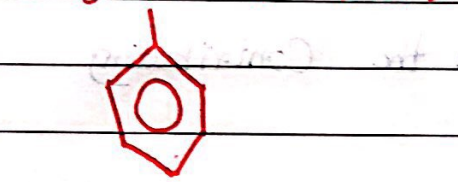
$C_6H_5CH_2-$



Benzyl group

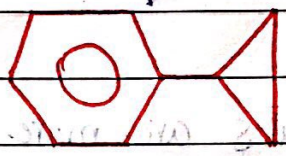
or





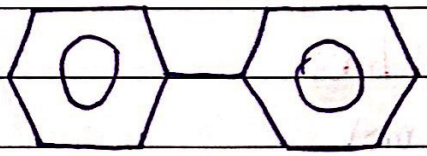
2-Phenylpentane

or 2-pentylbenzene.

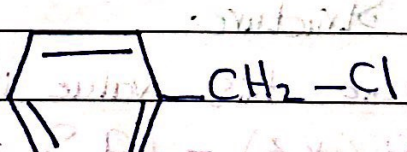


Phynelcyclopropane.

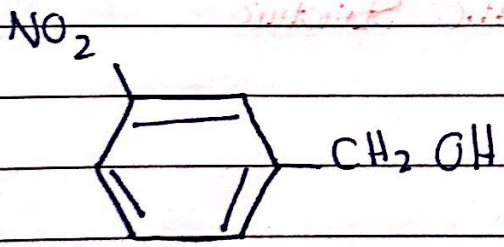
(or) Cyclopropylbenzene.



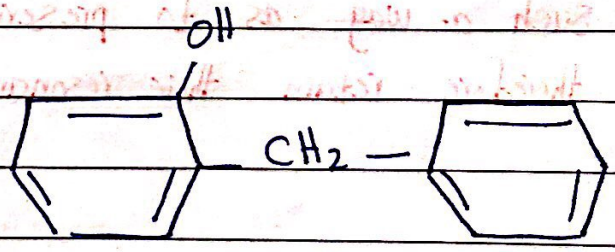
Biphenyl.



Benzyl Chloride.

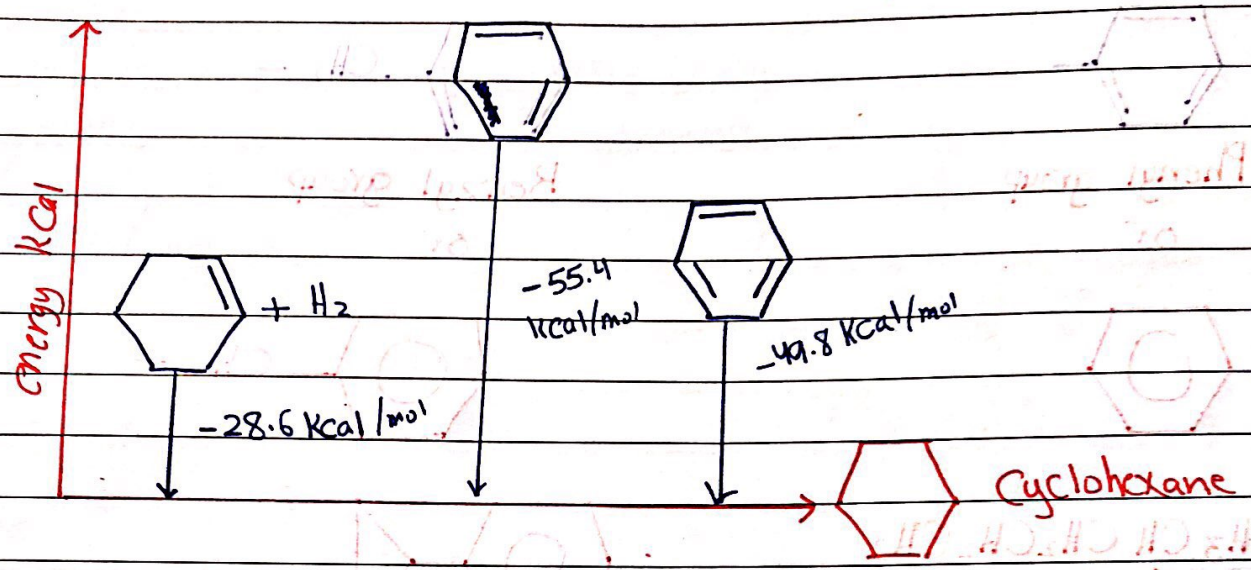


m-nitrobenzyl alcohol.



O-benzylphenol.

* The resonance energy of Benzene:-
Resonance Hybrid is always more stable than any of its Contributing Structures.



real benzene molecules are more stable than the Contributing resonance Structures.

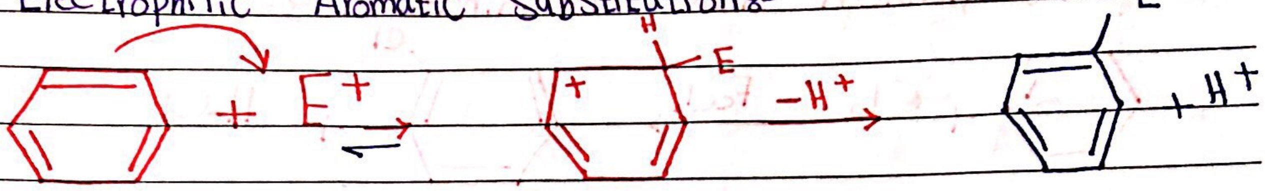
Stabilization energy: (resonance energy):-
The difference between the actual energy of the real molecule (The resonance hybrid) and the Calculated energy of the most Contributing Structure.

For benzene this value is: 36 KCal/mol

$(28.6 \times 3) - 49.8 = 36$ KCal mol

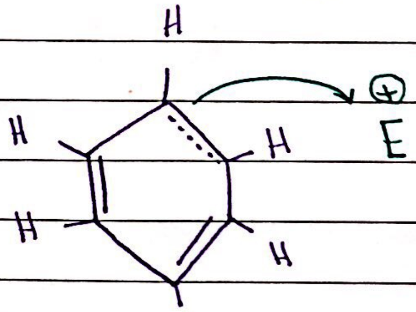
* Benzene and other aromatic compounds usually react in such a way as to preserve their aromatic Structure and therefore retain their resonance energy.

* Electrophilic Aromatic Substitutions-

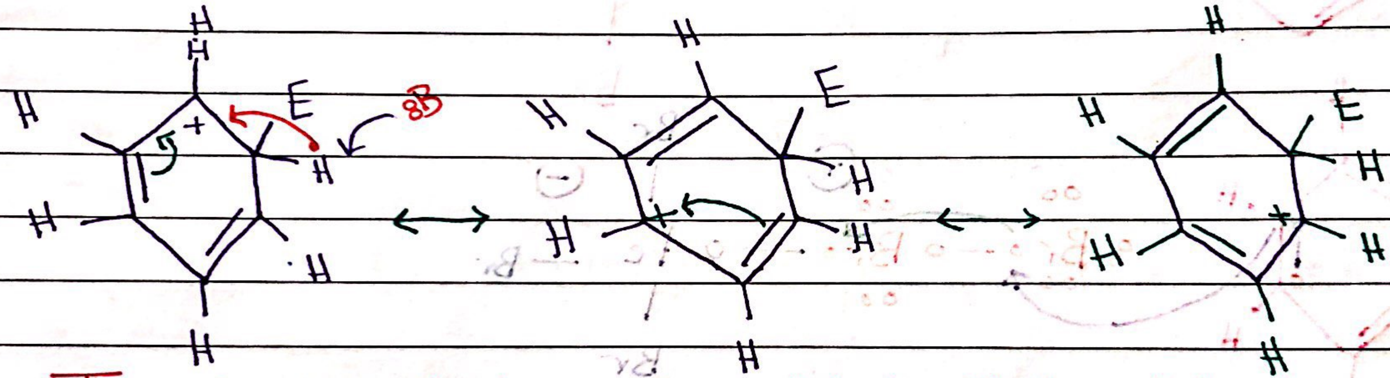


Benzenonium
ion

((EAS))



E good at getting electrons



These resonance structures ~~are~~ ↓ have relatively stable carbocations,

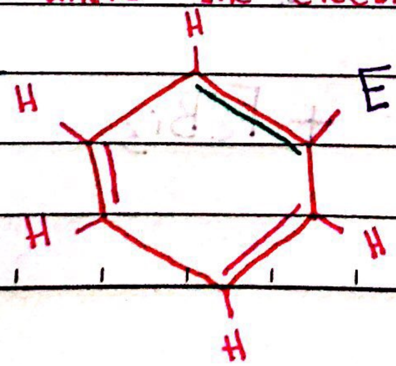
beause electrons can move around the positive charge is dispersed between carbons.

to get back to being aromatic and stable → adding electron . + $\bar{e}$

we need a Base :B to nab the proton which is on the same carbon where the electrophile is attached

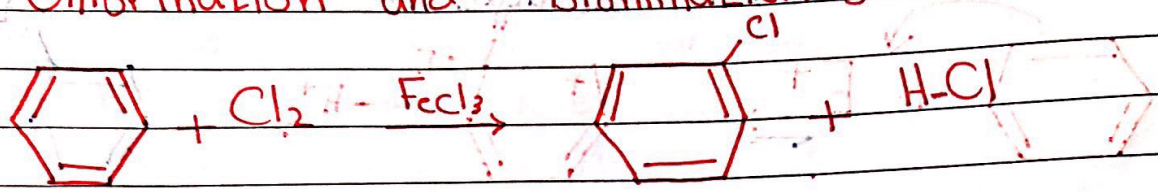
(Finally resonance stable)

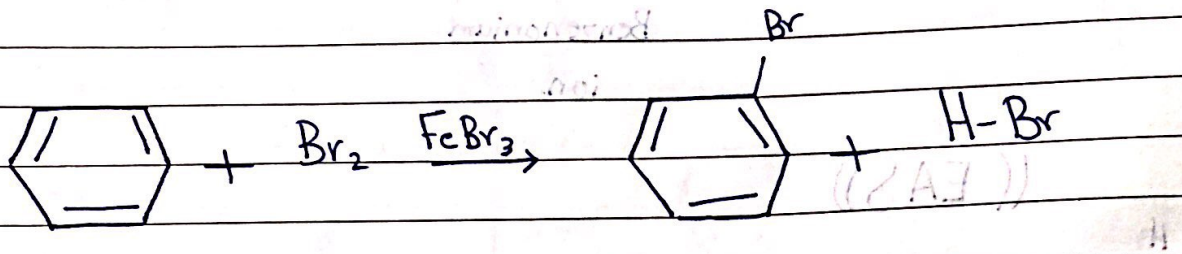
electron ← is returned ☺



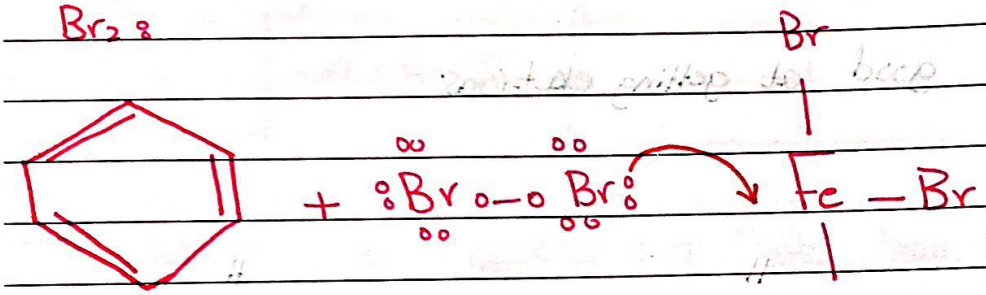
+ H—B

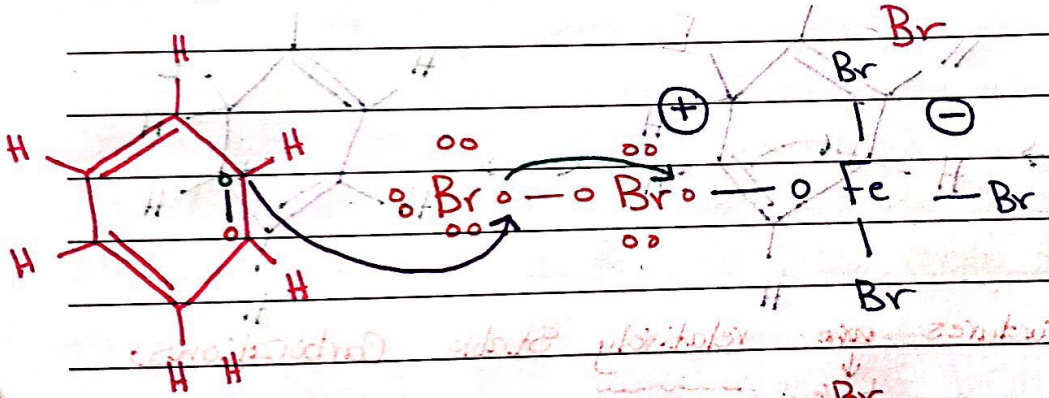
* Chlorination and Bromination :-

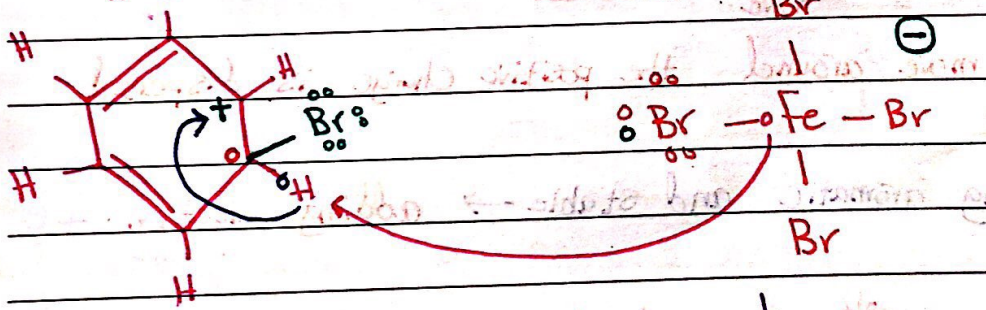




Br_2 :

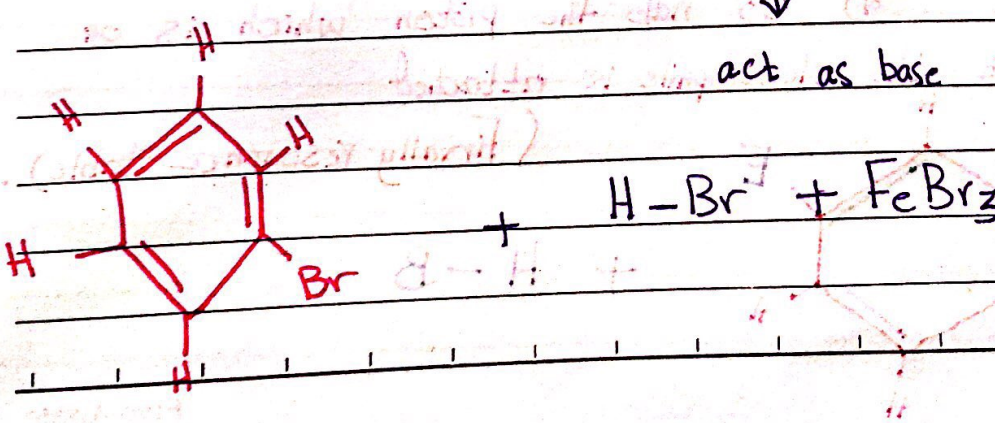


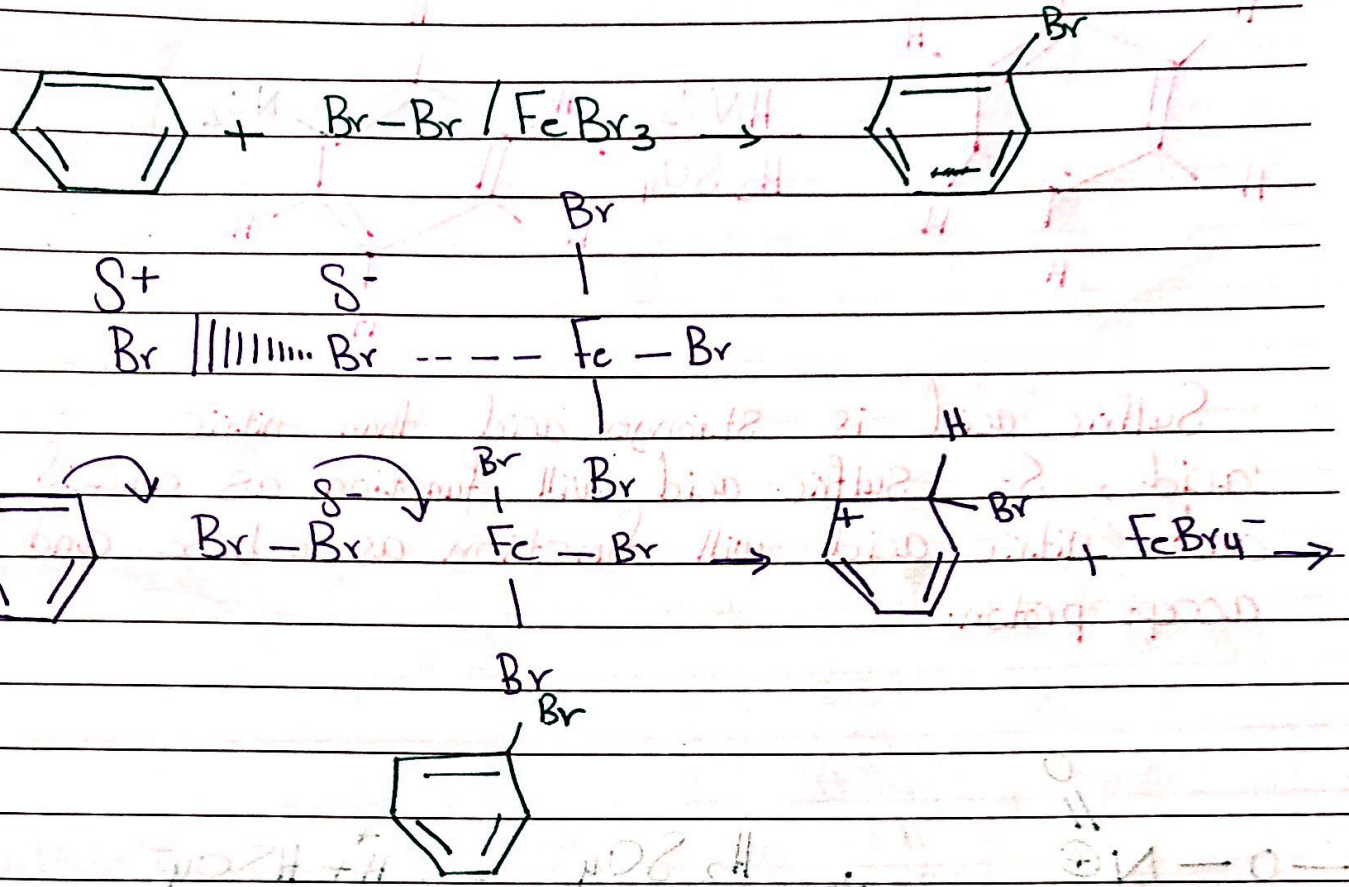




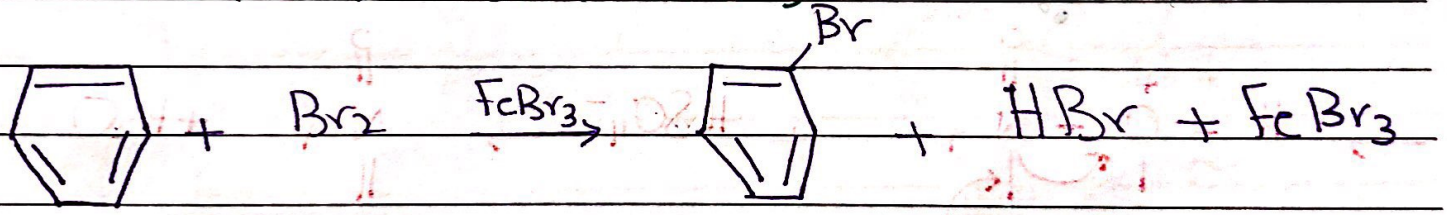
↓

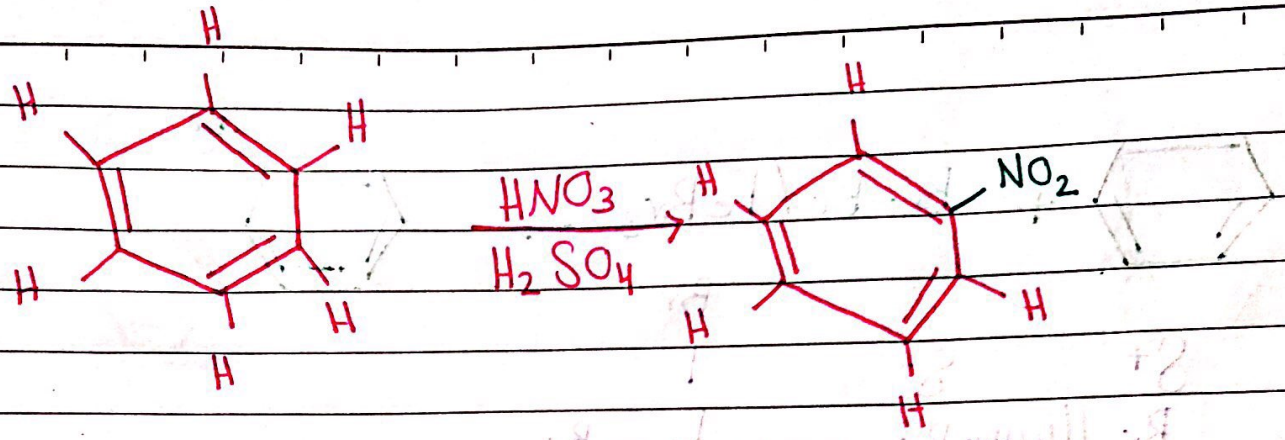
act as base



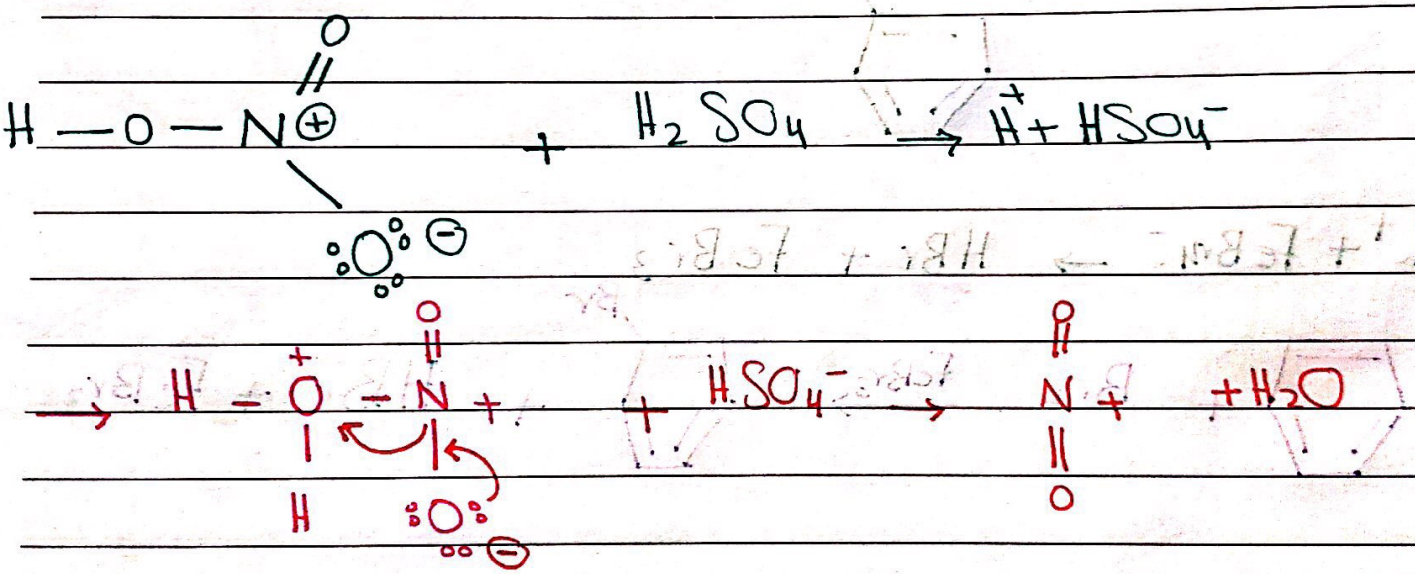


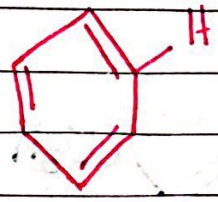
$H^+ + FeBr_4^- \rightarrow HBr + FeBr_3$





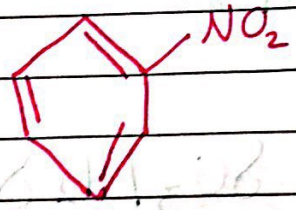
Sulfric acid is stronger acid than nitric acid, So sulfric acid will function as an acid and nitric acid will function as a base and accept proton.

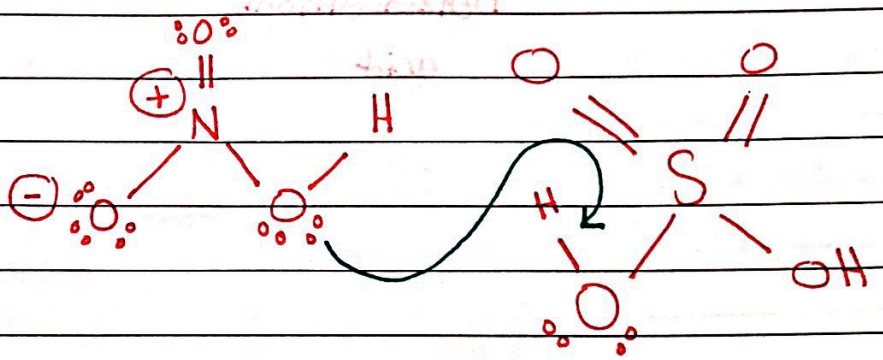


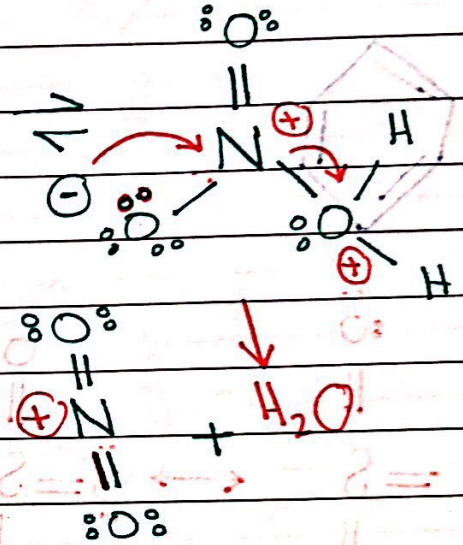


HNO_3

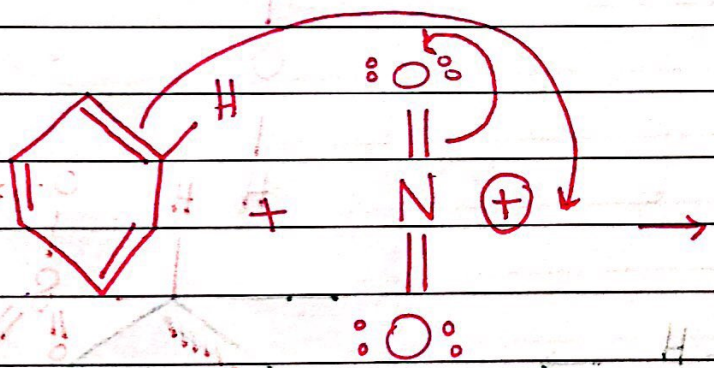
H_2SO_4

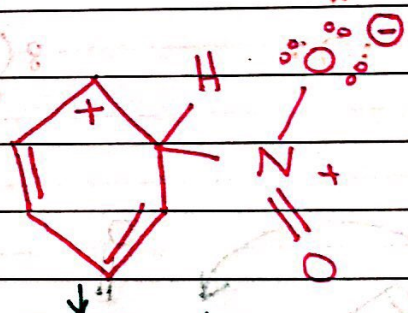




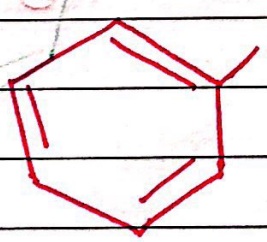


electrophile $\rightarrow E^+$ = nitronium ion





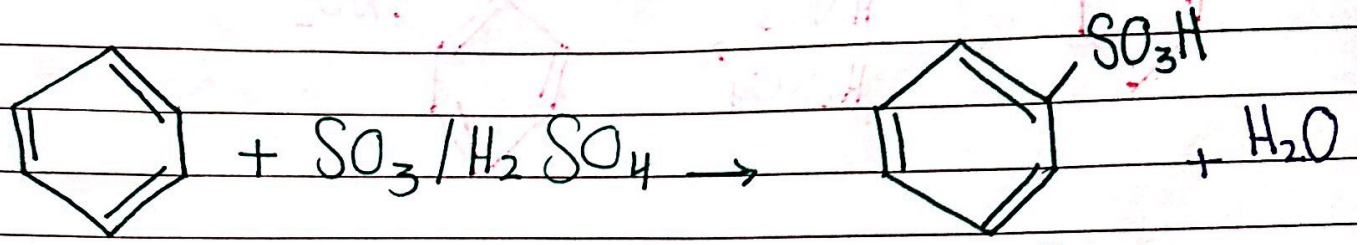
This has resonance structures.



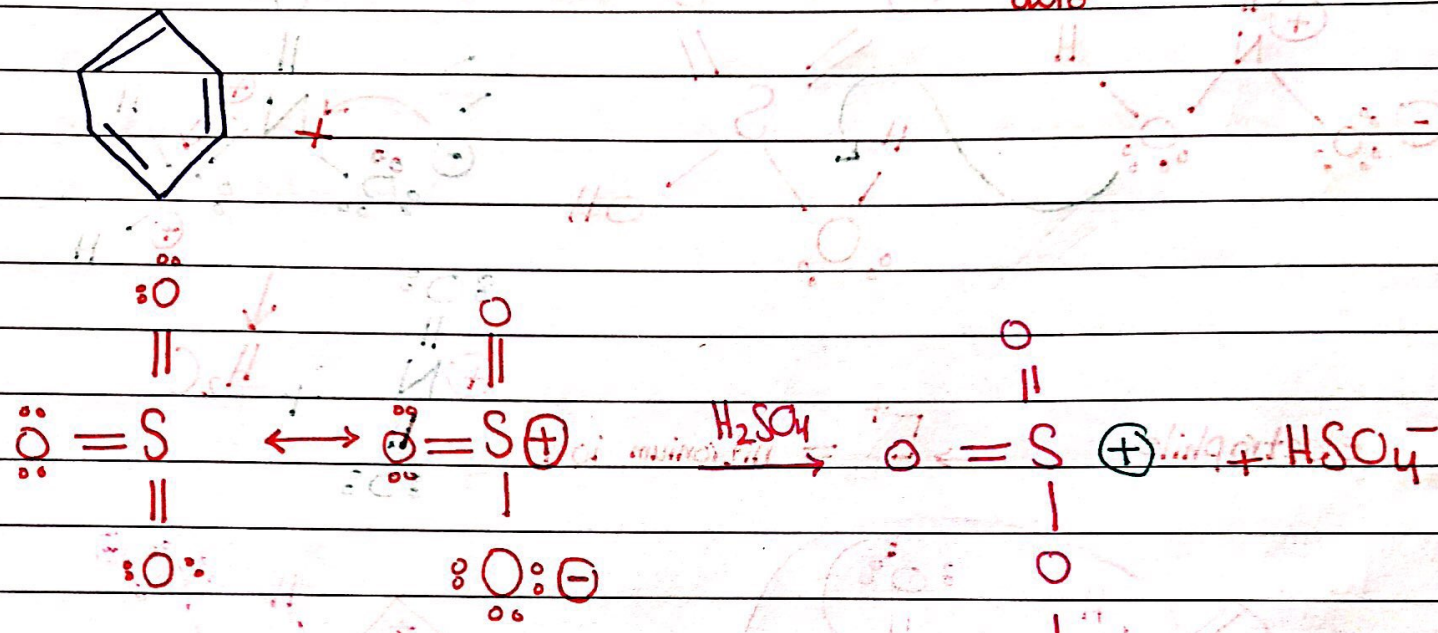
$+ H_2O$

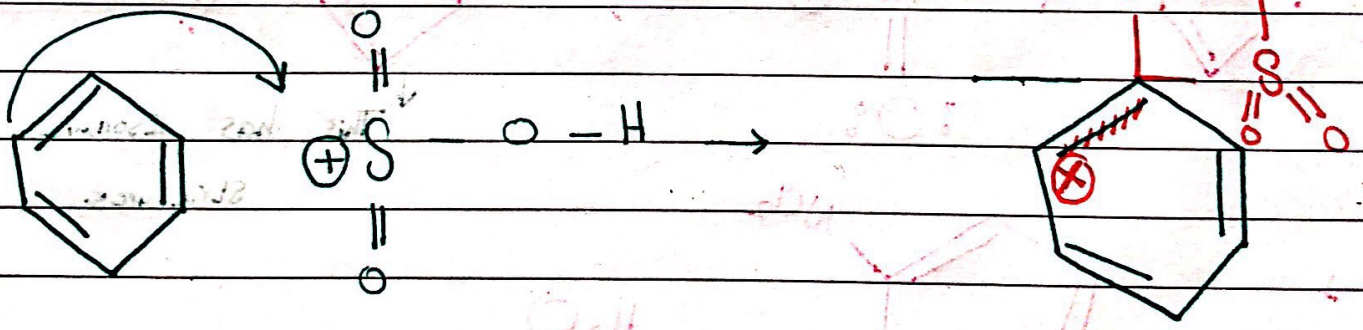
$H^+ + HSO_4^- \rightarrow H_2SO_4$

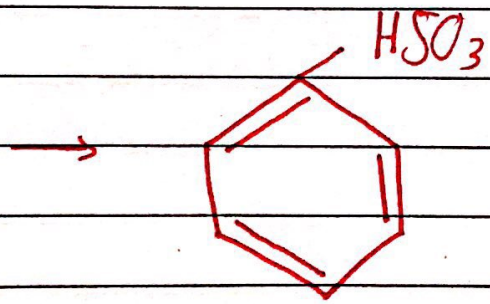
Sulfonation :-



benzenesulfonic acid

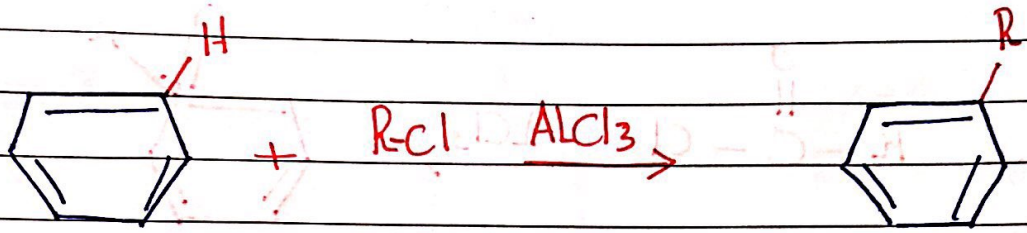




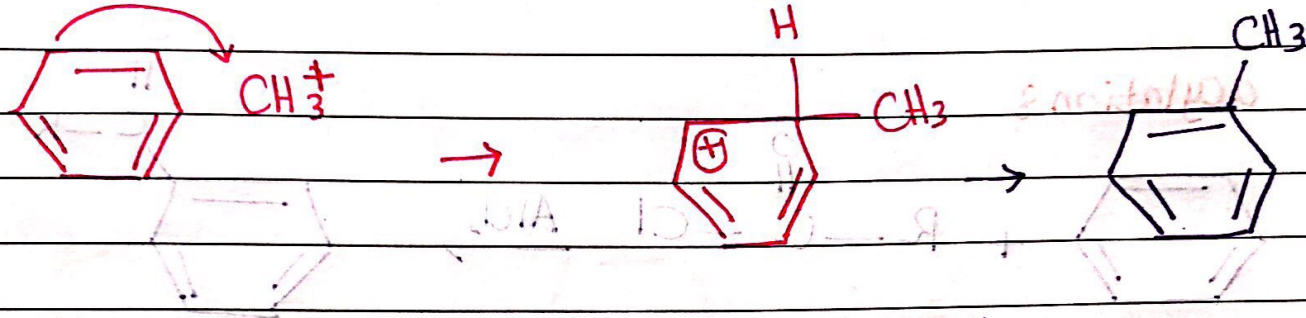


$H^+ + HSO_4^- \rightarrow H_2SO_4$

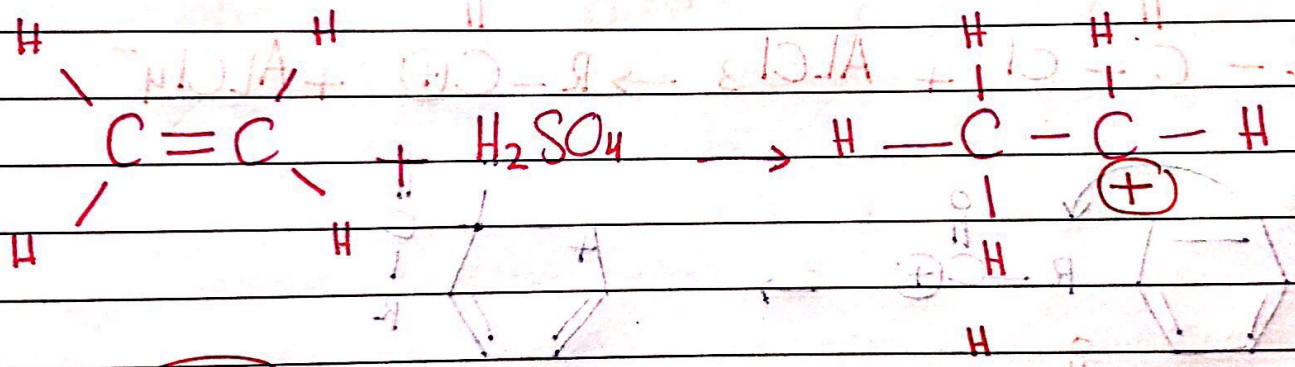
* Alkylation :-

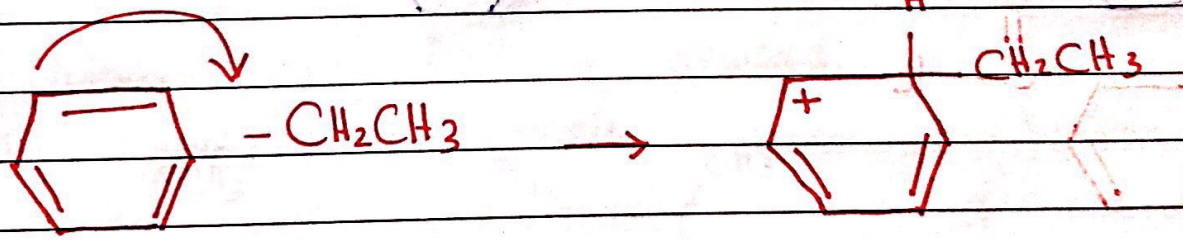


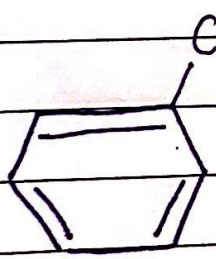
$$CH_3-Cl \longrightarrow AlCl_4^- + CH_3^+$$



$$H^+ + AlCl_4^- \rightarrow AlCl_3 + HCl$$

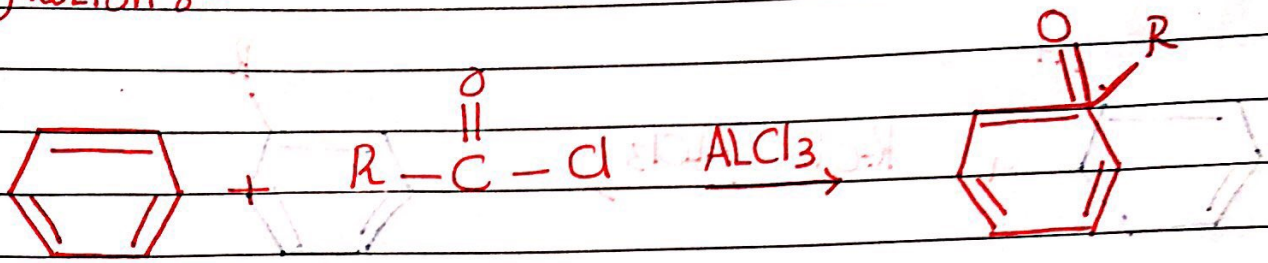




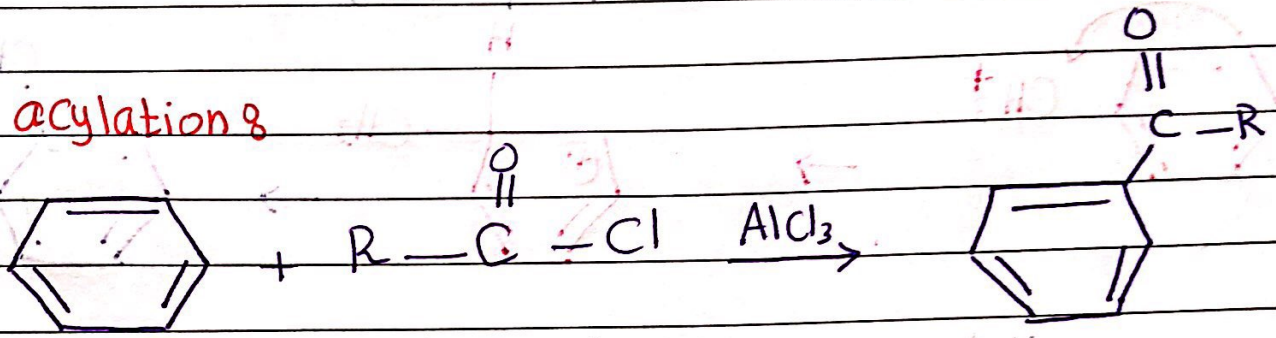


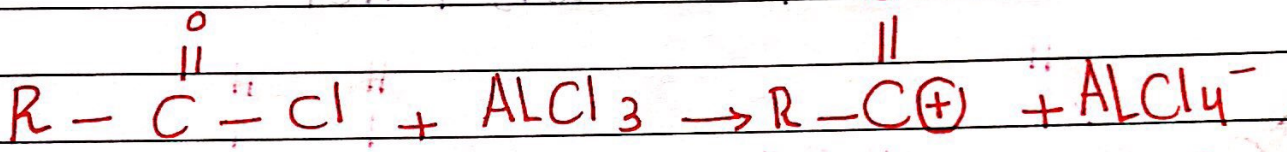
$$H^+ + HSO_4^- \rightarrow H_2SO_4$$

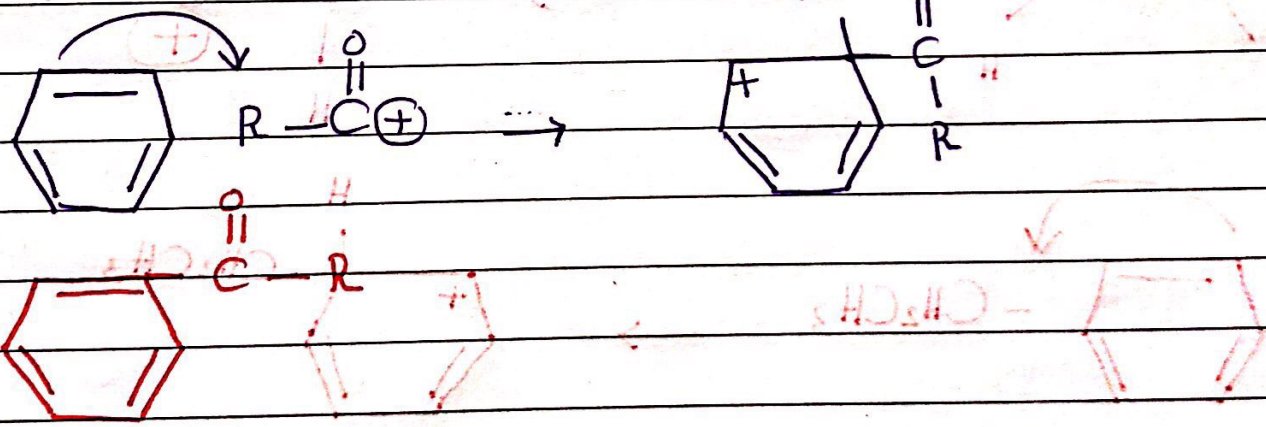
acylation :-



* acylation :

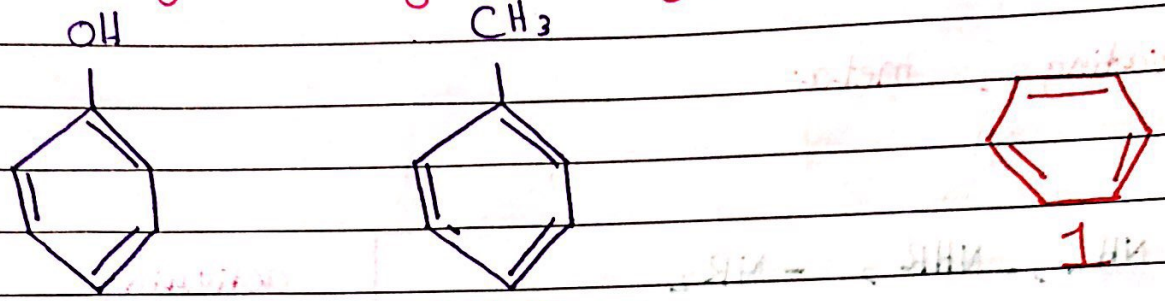




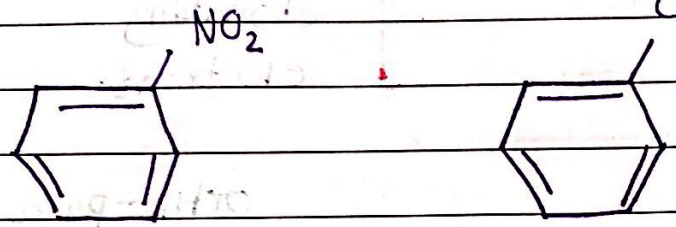


$$H^+ + AlCl_4^- \rightarrow AlCl_3 + HCl$$

4.10 ring-activating and ring-deactivating groups:-



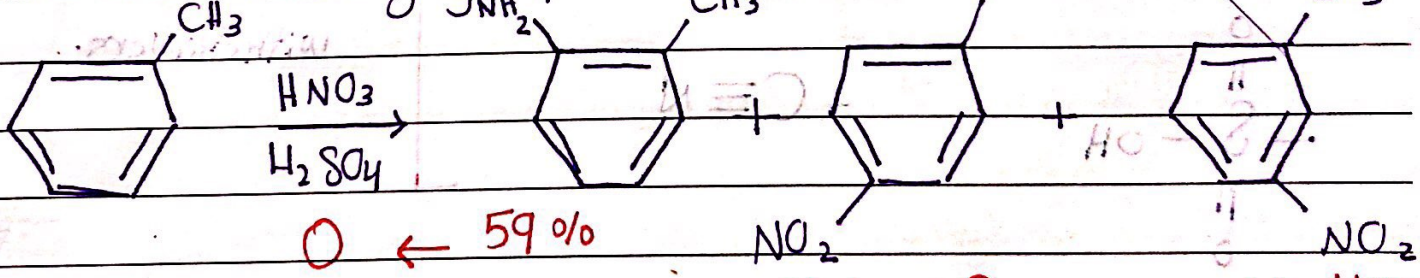
activating



deactivating

⊖ relative nitration rate

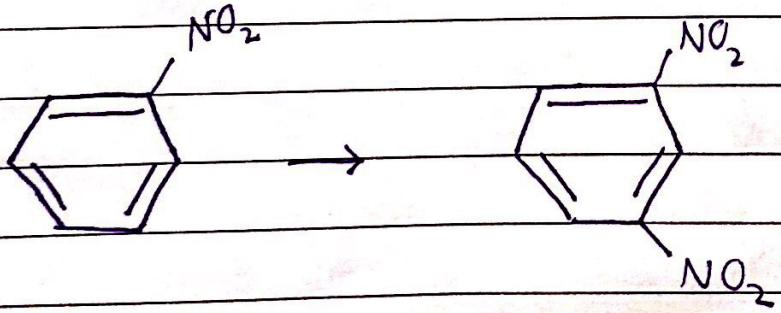
4.11 (Ortho, ~~Para~~ para) directing groups :- and meta directing groups:-



O ← 59%

37% → P

m X 4%



93%

meta

activating → ortho – para

deactivating → meta.

– NH_2, – NHR, – NR_2

– $\ddot{O}H$, ~ O – CH_3, ~ $\ddot{O}$ – R

~ N(H) – C(=O) – R

~ CH_3

activating.

ortho – para directing.

donating electrons.

(ortho-para deactivating.) ✓

– F, – Cl, – Br, – I]

YEAH g

O

||

– C – R

O

||

– C ➡ OH

O

||

– C – NH_2

– NO_2

O

||

– S – OH

||

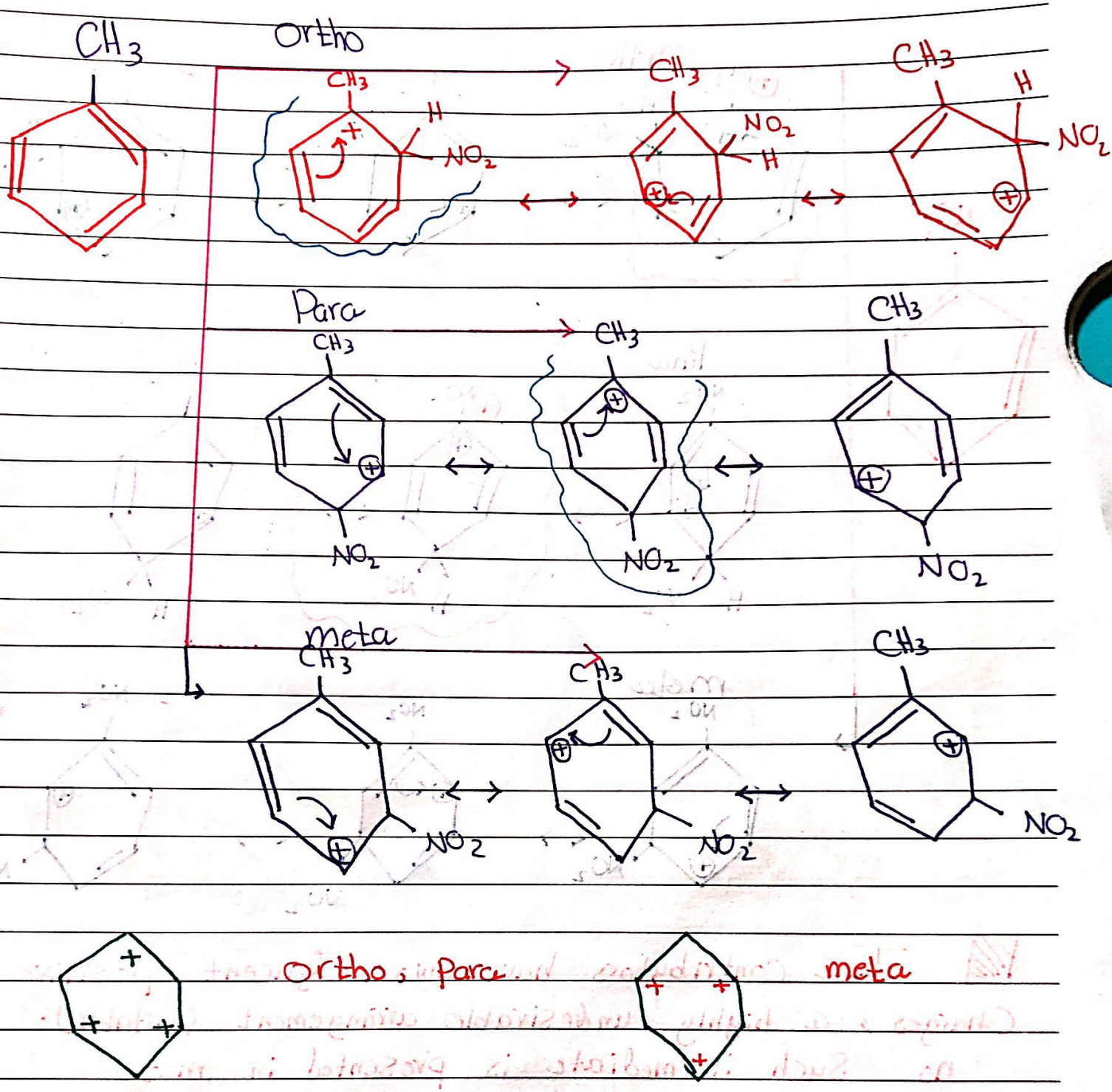
O

– C ≡ N

deactivating

meta-directing.

electrons withdrawers.



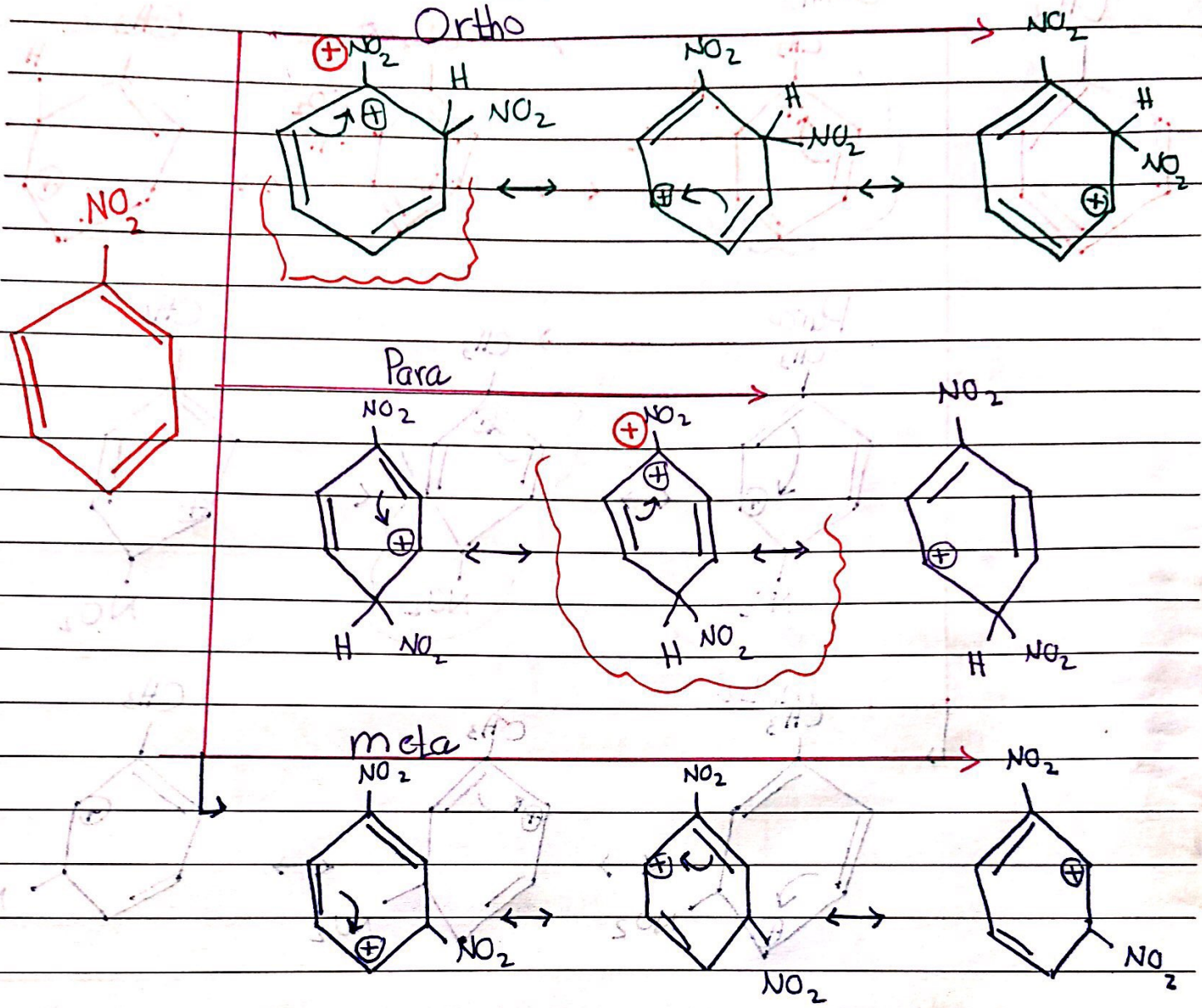
ortho ; Para

meta

■ Carbocation adjacent to methyl group (tertiary) more stable → less energy.

In meta it's always secondary carbocation which much ↓ less stable than the tertiary.

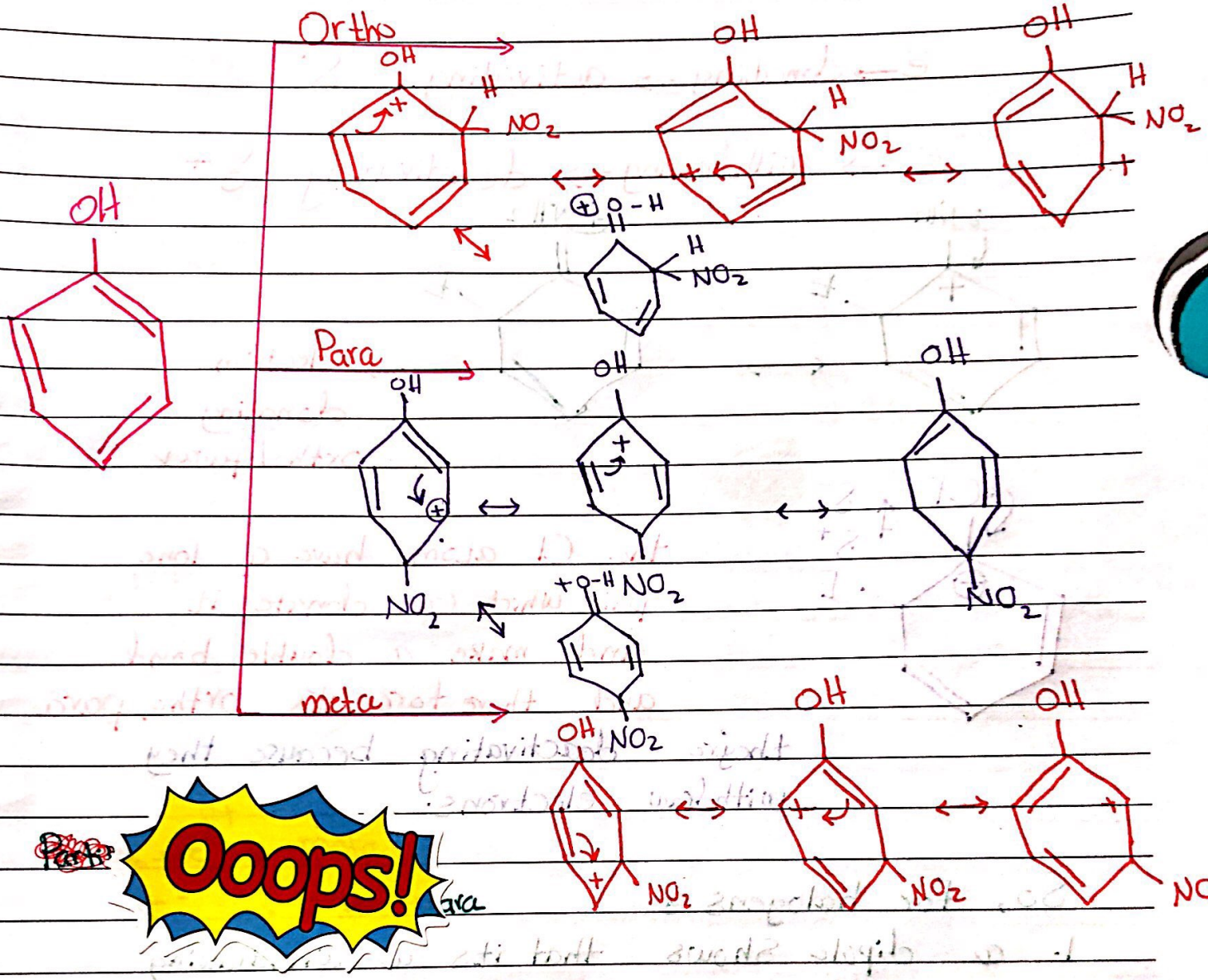
All alkyl groups are ortho-para Directors.



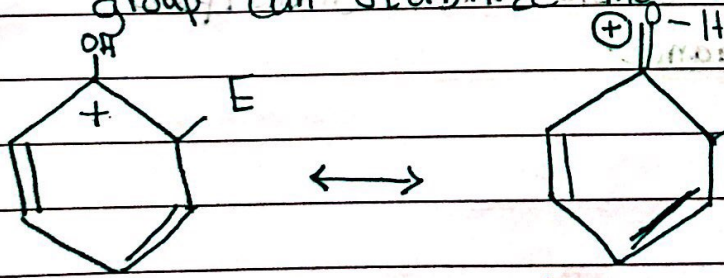
These contributors have two adjacent positive Charges, a highly undesirable arrangement (unstable).
no Such itermediate is presented in meta Substitution.

meta directing groups → the atom attached to the benzene ring will carry a partial positive Charge.

* All groups in which the atom directly attached to the aromatic Compound ring is positively Charged or is a part of a multiple bond to a no EN element will Be Meta directing.



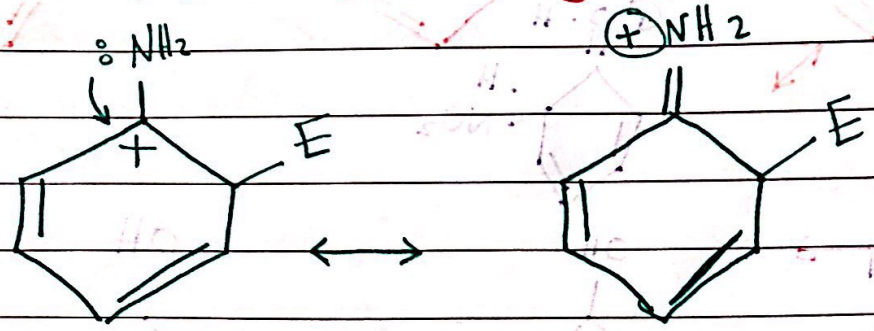
Ortho/para give rise to a situation where -OH group can stabilize the molecule by donating ($\bar{e}$).



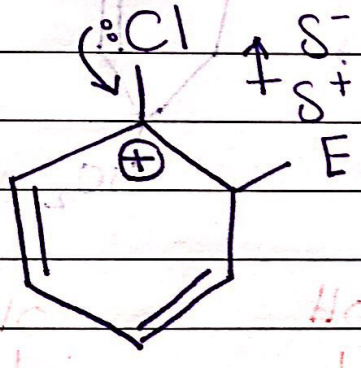
All groups with unshared electrons on the atom attached to the ring are Ortho-para directing.

$\bar{e}$ → donating → activating δ^-

$\bar{e}$ → withdrawing → deactivating δ^+



→ electron donating ortho/para ✓

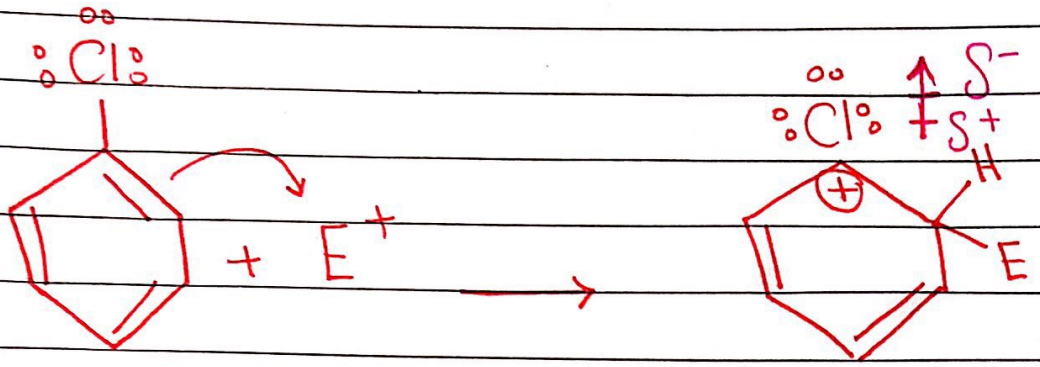


the Cl atom have a lone pair which can donate it and make a double bond and therefore it's ortho, para

they're deactivating because they withdraw electrons.

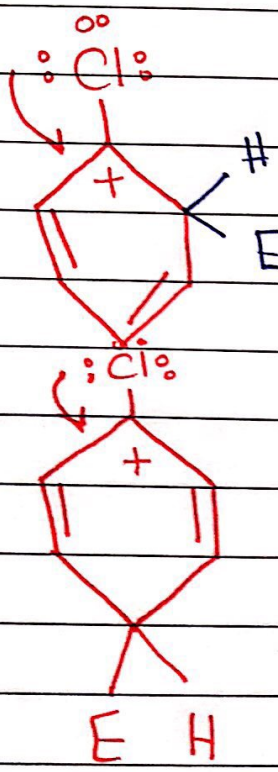
So, For halogens 🙂

1. a dipole shows that its a withdrawing group (deactivating)
2. Because of its potential for resonance it's actually more stable with ortho/para to do resonance.



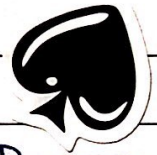
deactivating

Because they're strongly withdrawing for electrons.



ortho

Para



Because halogens have unshaired ē pairs, they're ortho/para directing.