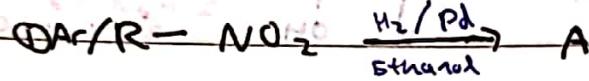


AMINES

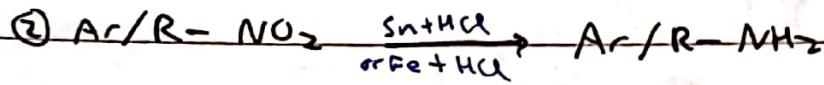
FORMATION OF ~~AMINO~~ AMINES

1. REDUCTION OF NITRO COMPOUNDS

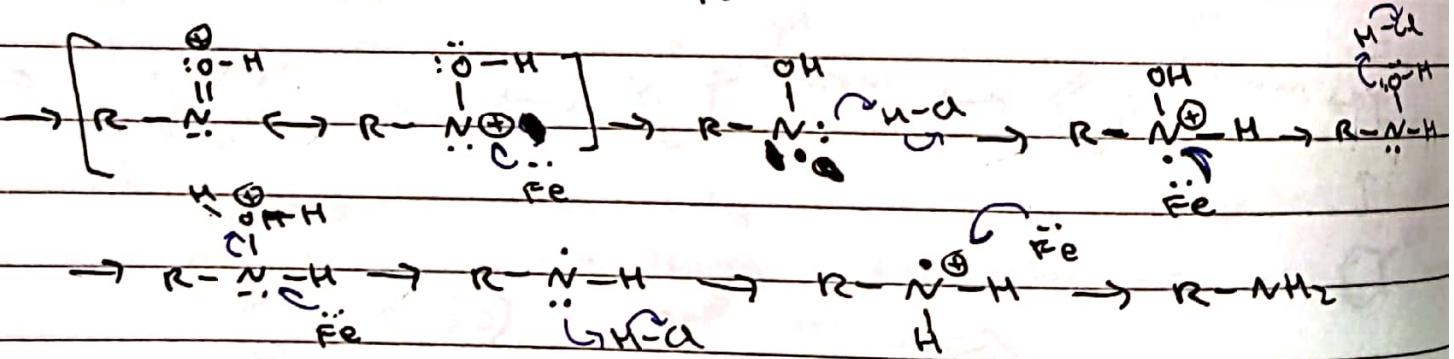
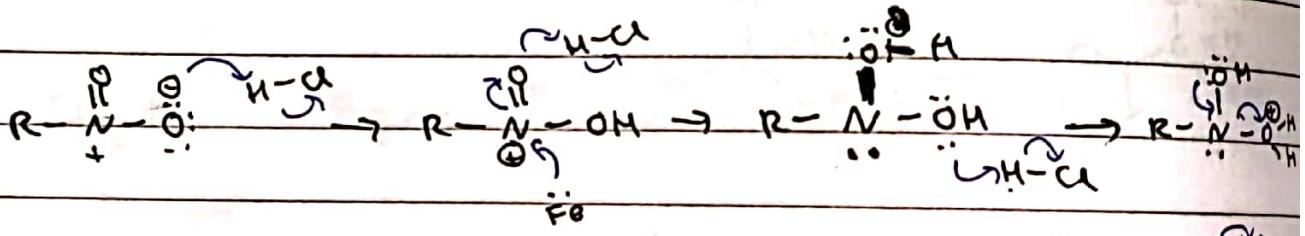
Nitro compounds are reduced to amines by passing H_2 gas in the presence of metal catalyst like finely divided nickel, palladium or platinum or by the reduction with metals in acidic medium.



Fe + HCl preferred

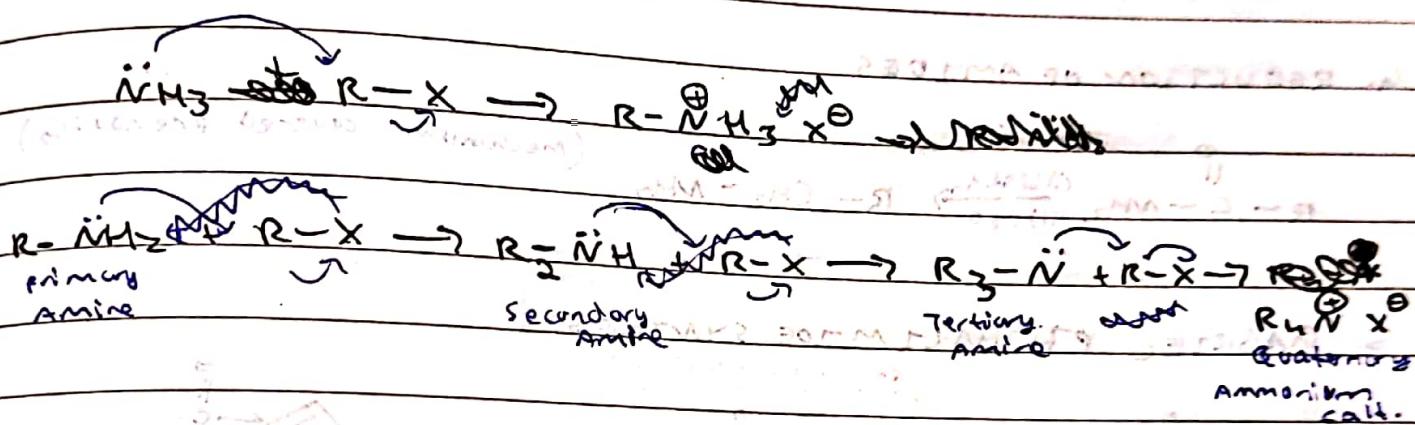


MECHANISM:

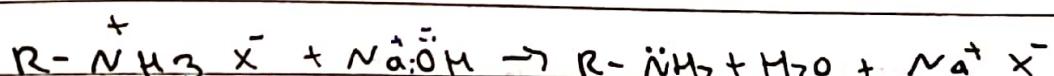


2. AMMONOLYSIS OF ALKYL HALIDES

- * The process of cleavage of Carbon-Halogen bond by ammonia (NH_3) nucleophile (standard substitution reaction) is known as ammonolysis.
- * Primary amines can also further act as a nucleophile, ~~so~~ or cleaving C-X bonds & forming secondary $\xrightarrow{\text{then}}$ tertiary $\xrightarrow{\text{then}}$ quaternary $\xrightarrow{\text{then}}$ \uparrow final.
amines



* Note: Free amine can be obtained from ammonium salt by treatment with a strong base.



* Ammonolysis has the disadvantage of yielding a mixture of primary, secondary & tertiary amines & also quaternary ammonium salt.

* But if you take large excess of ammonia, primary amine is the major product.

* To get quaternary salt as major product provide excess of alkyl halide.

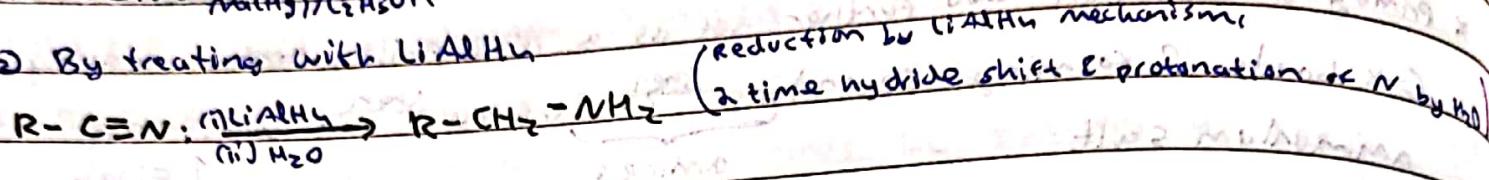
If we look at the reactions that occur, each one needs additional alkyl halide. If you provide enough chances are that reaction will go to completion. If given enough time, on the other hand, if you use a very large excess of ammonia (NH_3), the chances are greatest that a bromoethane molecule will hit an ammonia molecule rather than one of the amines formed. This helps prevent formation of higher amines / quaternary salt.

3. REDUCTION OF NITRILES

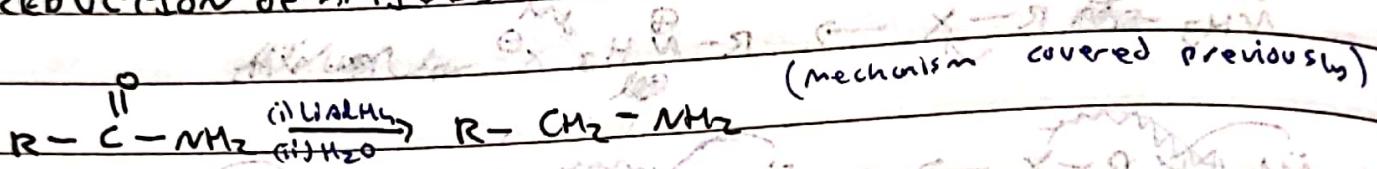
① Catalytic Hydrogenation



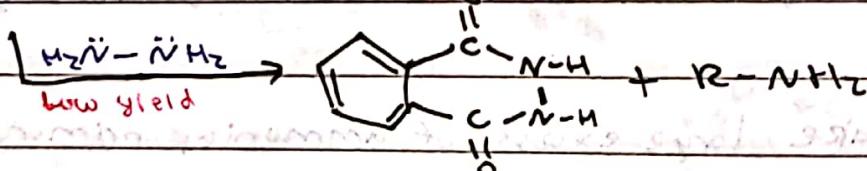
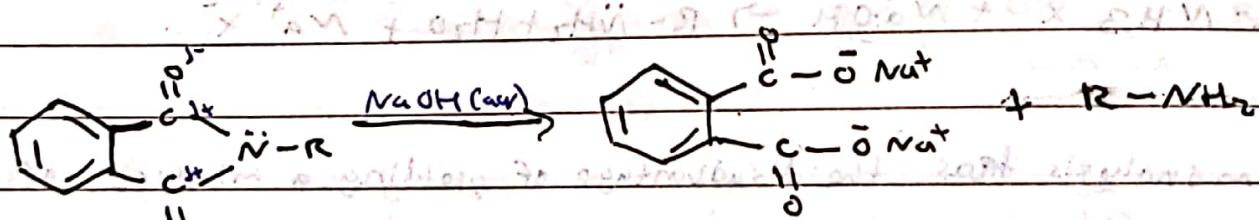
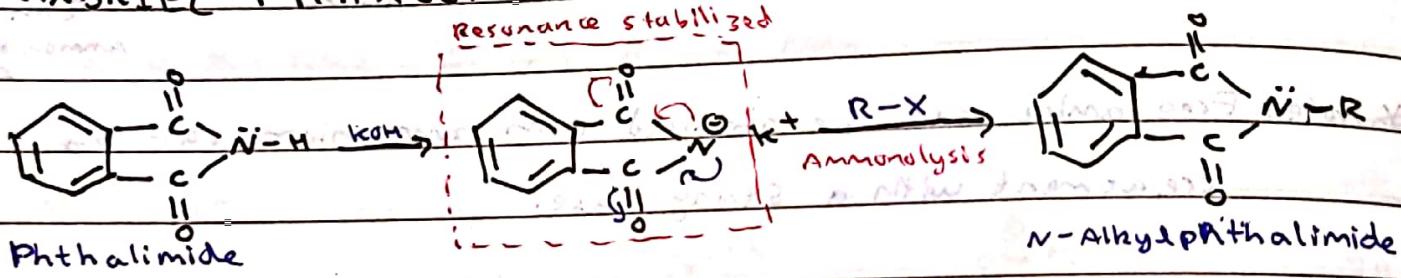
② By treating with LiAlH₄



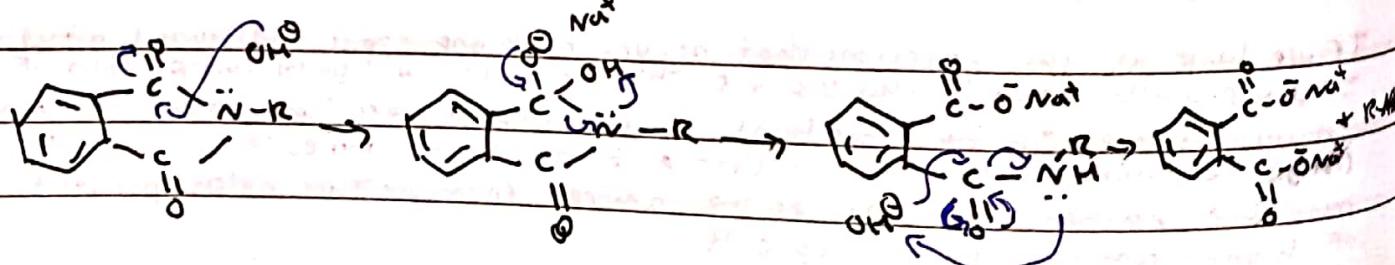
4. REDUCTION OF AMIDES



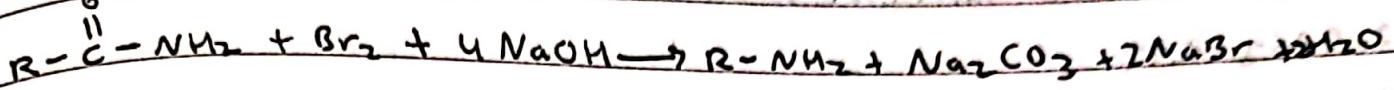
5. GABRIEL PHthalimide SYNTHESIS



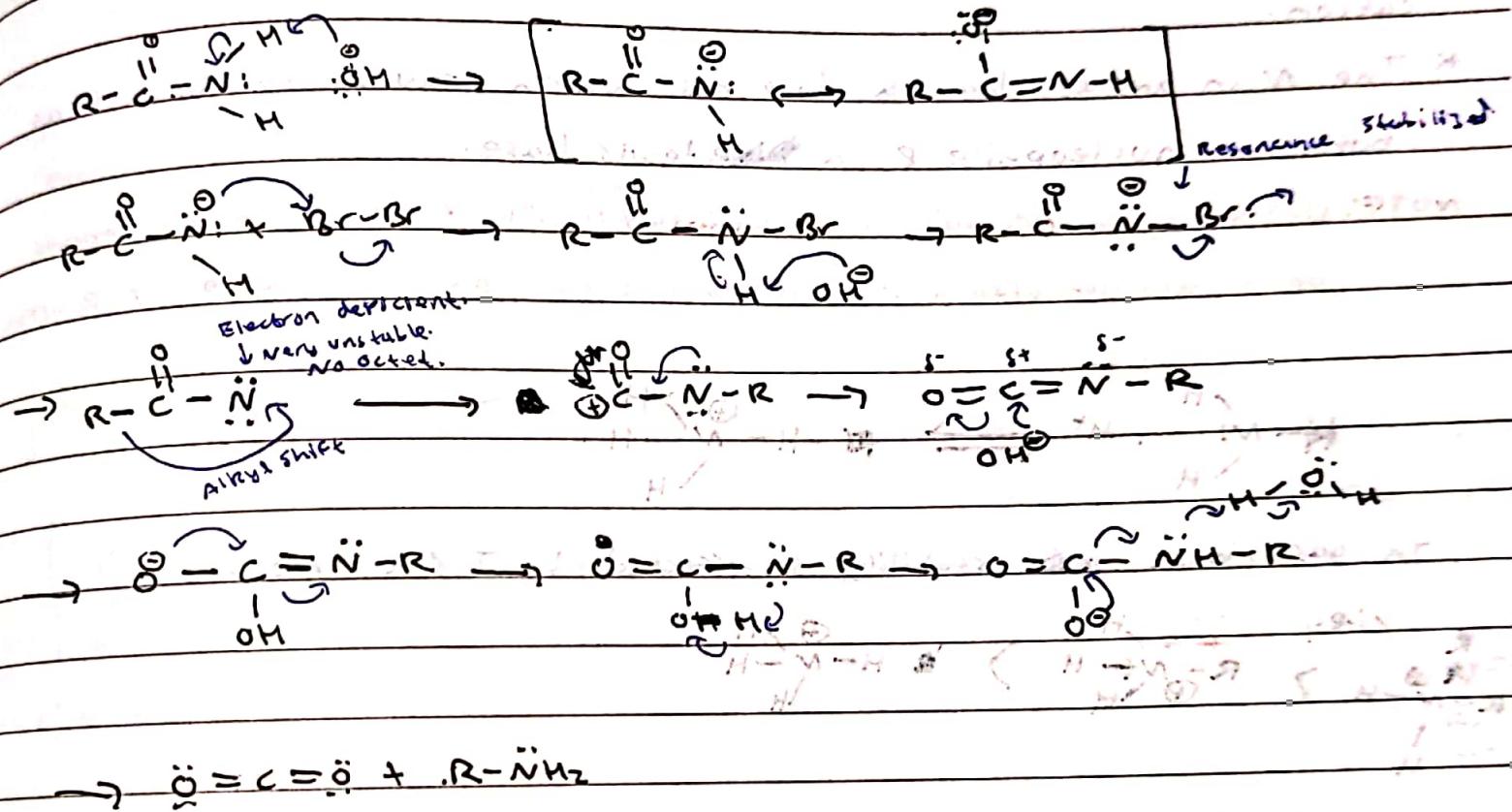
MECHANISM: Nucleophilic attack by OH^- or Hydrazine (NH_2-NH_2) ion



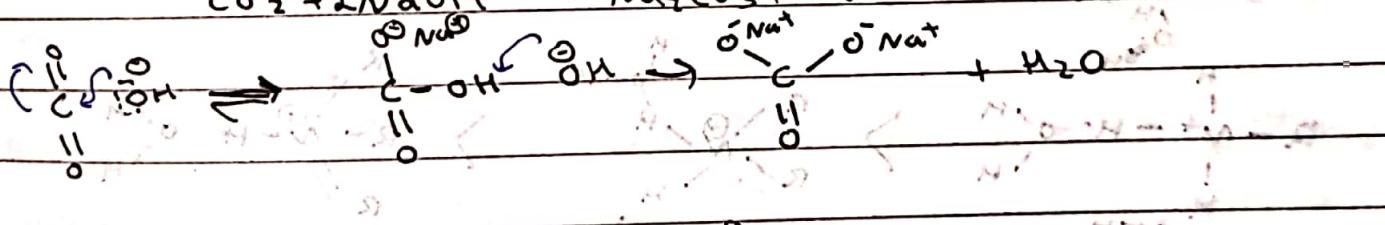
6. Hoffmann bromamide degradation reaction.



Mechanism:

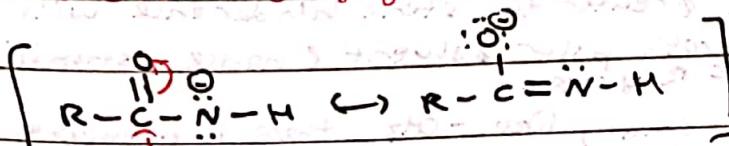


SIDE REACTION:



*NOTE: N-Hydrogen of amides ($R-\overset{\text{O}}{\underset{\text{H}}{\text{C}}}-\text{NH}_2$) is resonance stabilized

because conjugate base is resonance stabilized



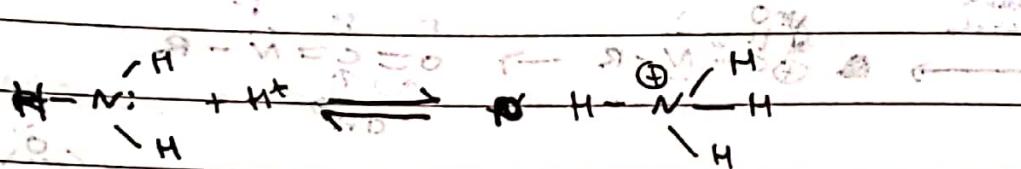
REACTIONS OF AMINES

3. LAS VEGAS

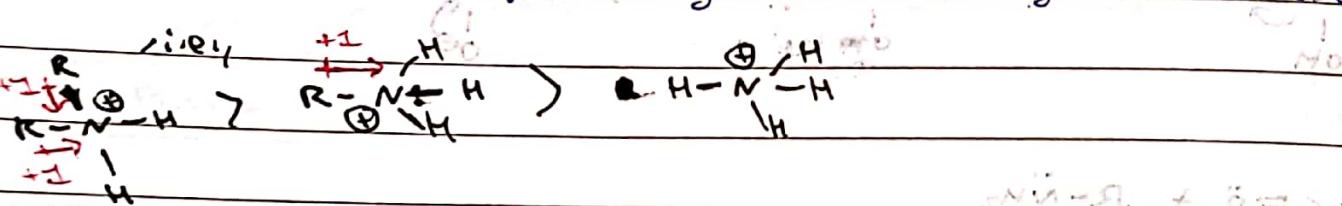
* Basicity of Amines depends upon the stability of the ammonium cation.

* The N in amines has a lone pair which causes it to act as both a nucleophile & a Lewis base.

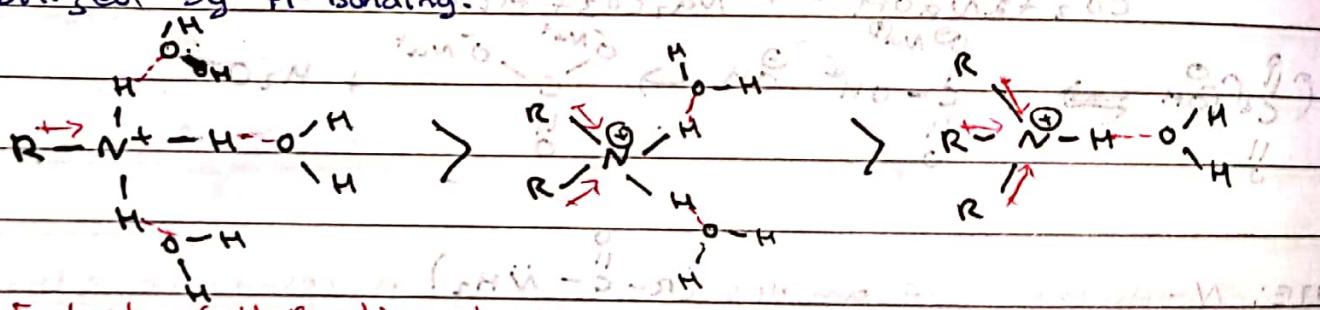
NOTE: Unlike with carboxylic acids, the stability of the cation also depends upon solvation effect, steric hindrance, etc. apart from just δ & σ factors.



In gas phase ~~only~~ stability is affected by I & R effect



However, in protic polar solvent like water, the ammonium cation is stabilized by H-Bonding.



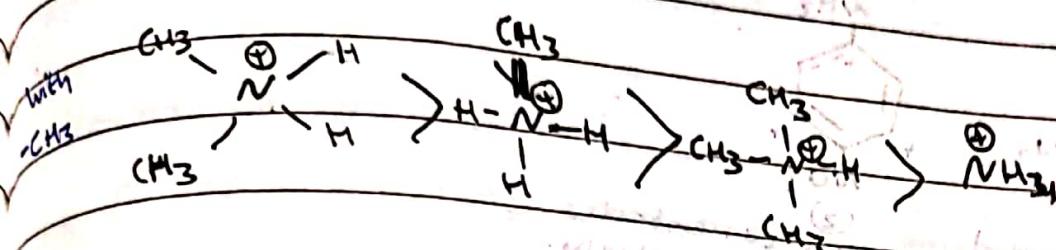
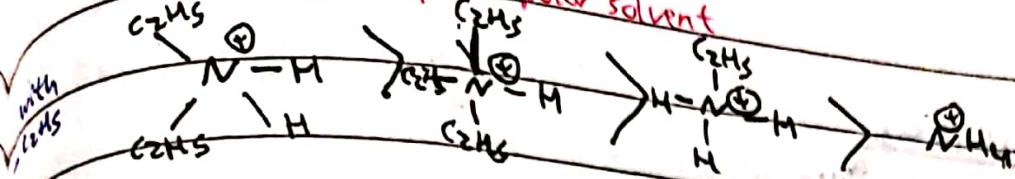
Extent of H-Bonding decreases.

+ Greater the size of the cation, greater the steric hindrance will hinder solvation effect (H-Bonding) in protic polar solvent & hence stability decreases greater the number of R groups.

* However, when the alkyl group is small, like $-\text{CH}_3$, there is negligible steric hindrance hence basicity order does not change.

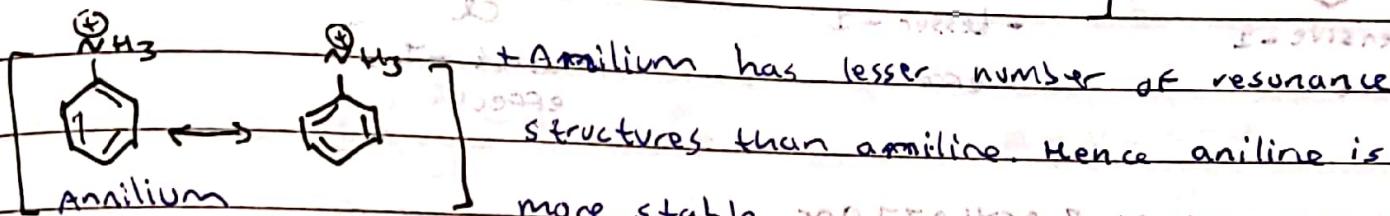
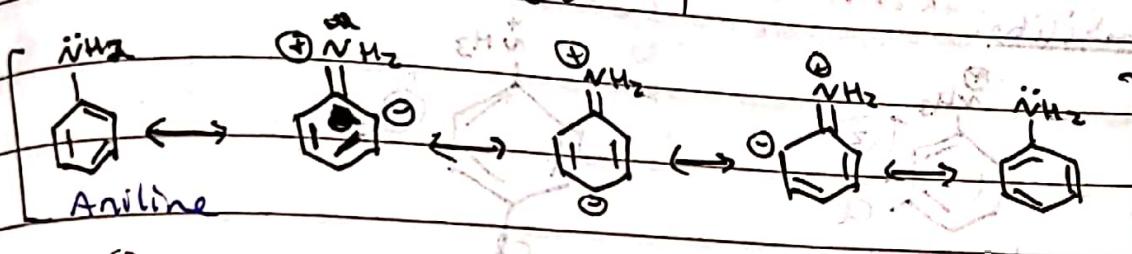
+ Hence basicity order does not change.
+ Hence, basicity of amines in protic polar solvent depends on the balance between I_R effects & solvation (steric effect).

Stability in protic polar solvent



BASICITY OF ARYL AMINES

Let us consider Aniline ($\text{C}_6\text{H}_5\text{NH}_2$)



Therefore we can infer that basicity of Aryl amines is lesser than that of alkyl amines.

BASICITY

Aryl



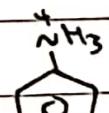
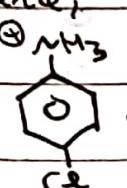
substituted

Among aryl halides, presence of ~~test~~ Electron donating groups

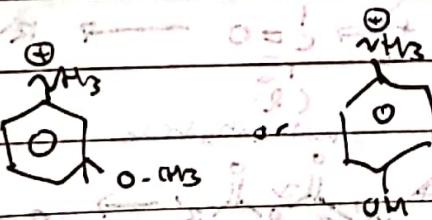
increase basicity & electron withdrawing groups reduce

stability

Hence,

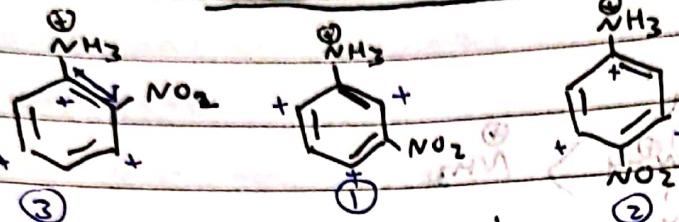


Electron withdrawing
deactivating groups



Electron donating
activating groups

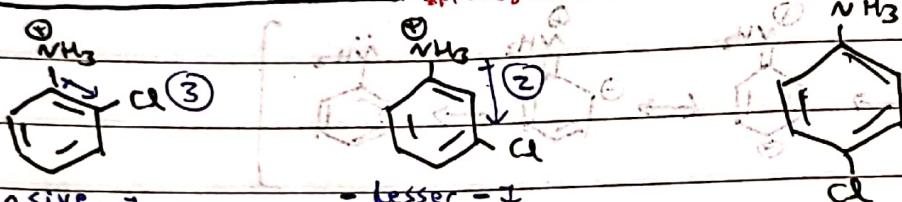
* Question: 2. Order of stability.



- R effect ~~insets~~ concentrates + charge not extensively.
- I effect concentrates +ve charge extensively.

+ R effect ~~concentrates~~
+ve charge extensively.

2. Order of stability: +R effect of halogens is extremely negligible. Halogens are deactivating species.



- Extensive -I effect produces an inductive effect and anti-parallel effect.

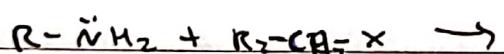
- Lesser -I effect.

- Least -I effect.

2. ALKYLATION & ACYLATION

Amines can perform alkylation & acylation (called Friedel-Crafts alkylation when done with FeCl_3 as catalyst with nucleophile $\text{R}-\text{X}$)

ALKYLATION

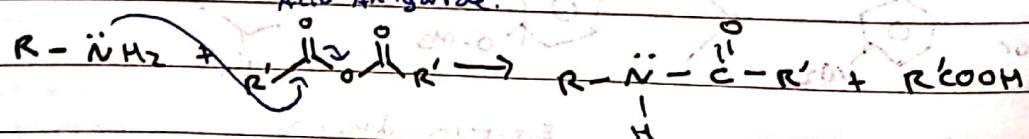
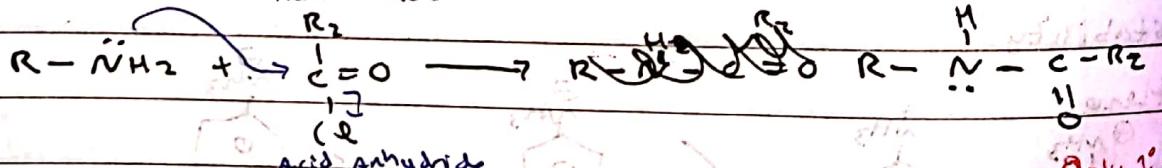


All amines ~~can~~ can perform alkylation (1° , 2° & 3°)

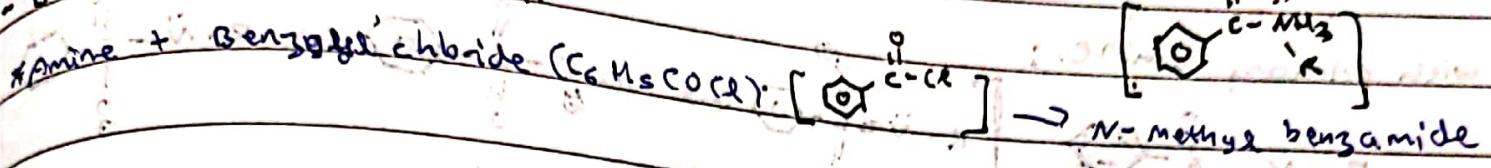


ACYLATION

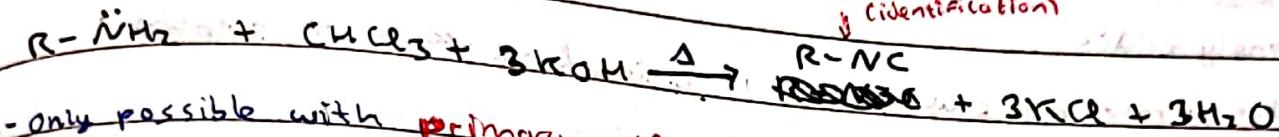
Amines can perform acylation with acid chlorides & anhydrides and chloride



- Benzoylation reaction.

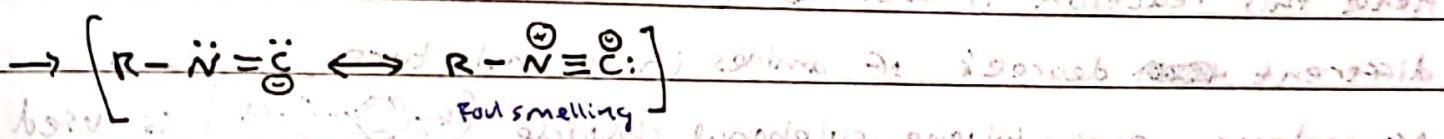
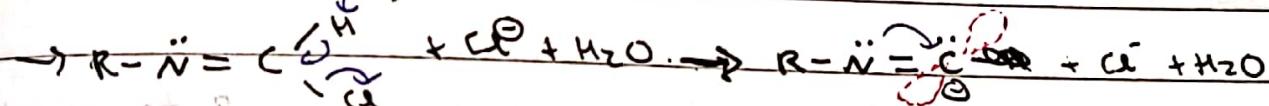
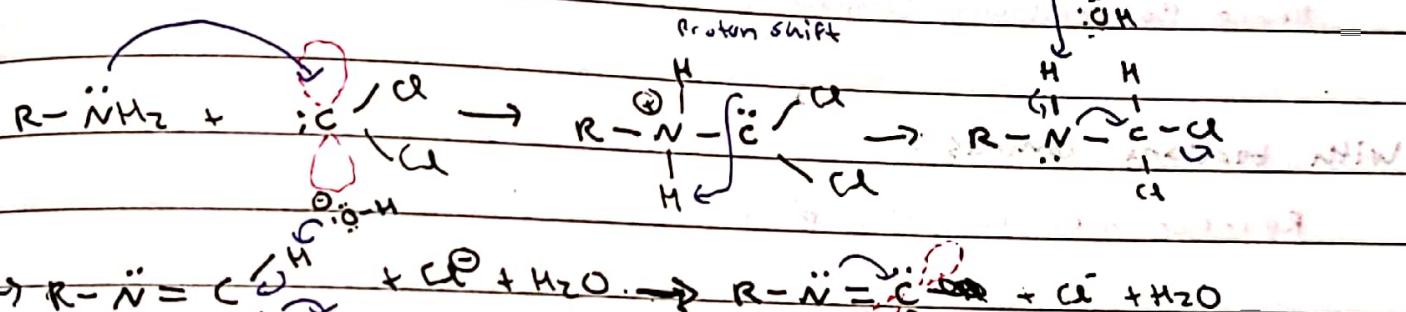
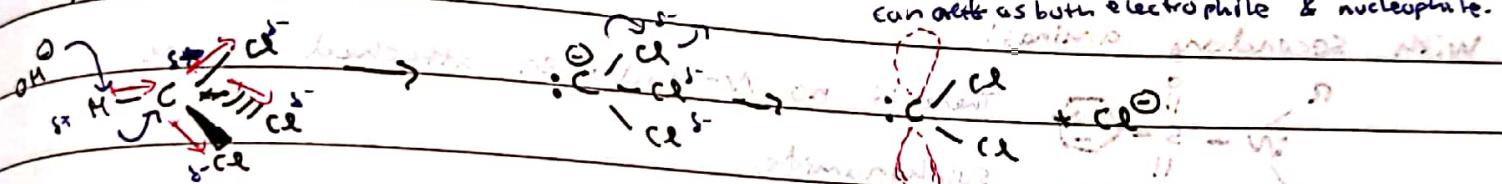


3. CARBYLAMINE REACTION



- only possible with **primary or 1° amines.**
- also called **isocyanide test**. [Test for primary amines]

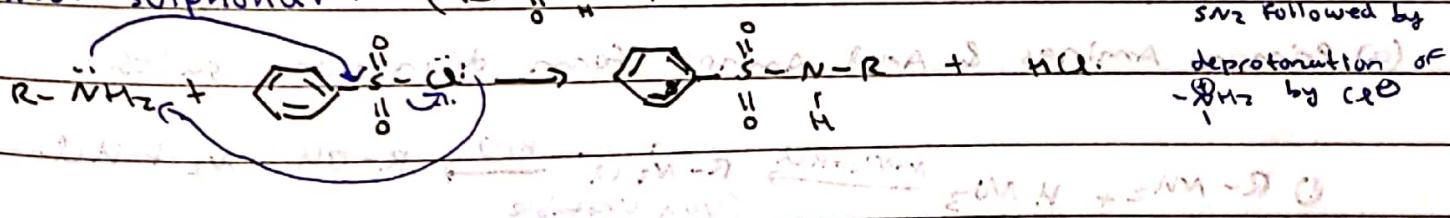
MECHANISM:



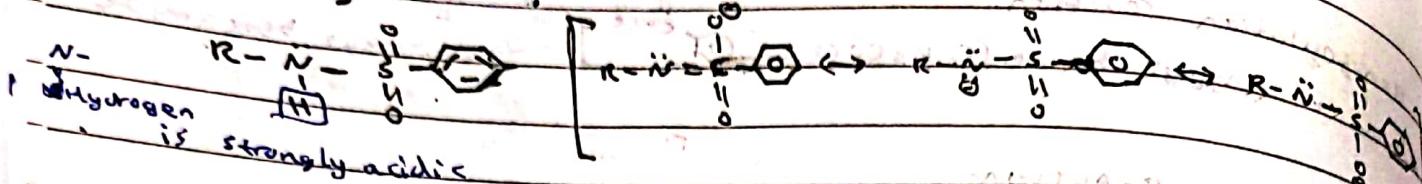
4. REACTIONS WITH ARYLSULPHONYL CHLORIDE ($(\text{C}_6H_5SO_2)_2C\text{---Cl}$)

(Hinsberg's reagent) Reacts with **primary (1°) & secondary (2°) amines**

RESULT: Sulphonamide ($(\text{C}_6H_5SO}_2)_2C\text{---NH}_2$)

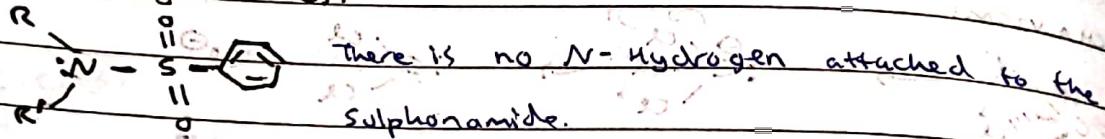


With primary amines;



Hence the resultant compound is insoluble in alkali.

With secondary amines:



Hence the resultant compound is not soluble in alkali.

With tertiary amines:

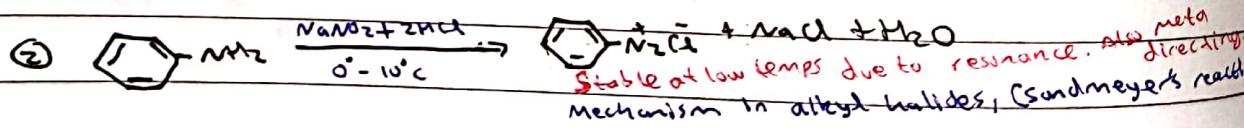
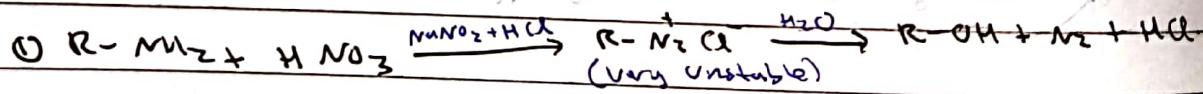
Reaction does not take place

Hence this reaction is used as an identification test & to separate different degree's of amines in a mixture.

Nowadays, para-toluene sulphonyl chloride ($\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{Cl}$) is used

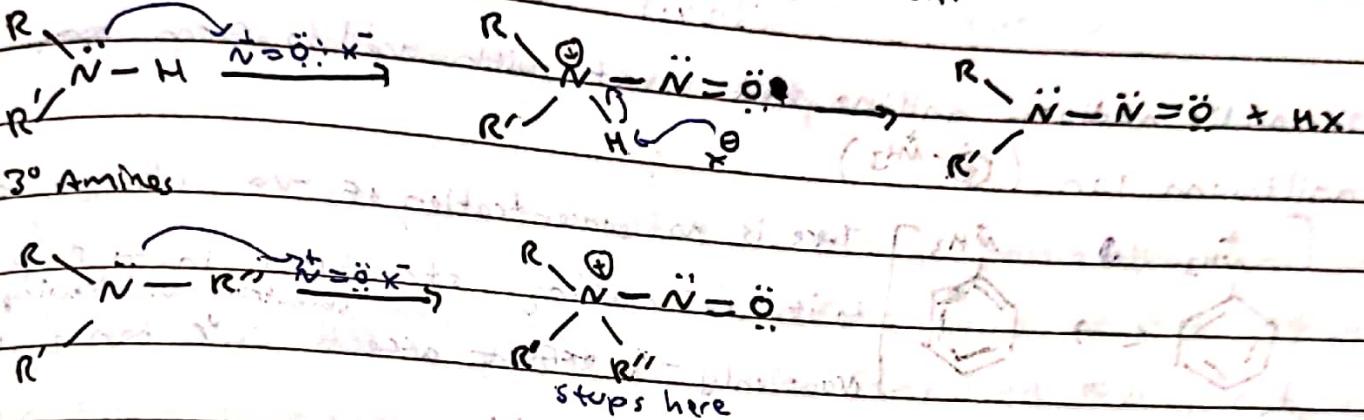
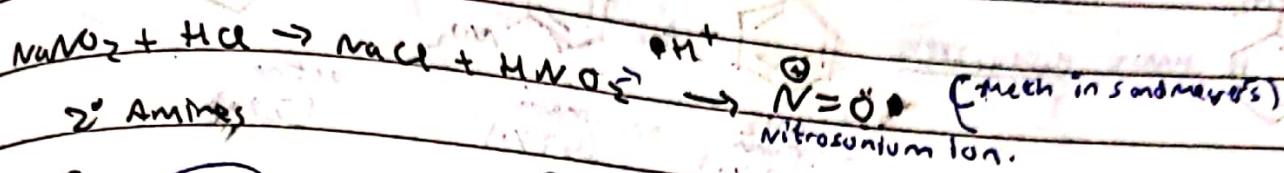
S. REACTION WITH NITROUS ACID [Diazotization]

(a) Primary Amines & Aryl Amines form diazonium salts.



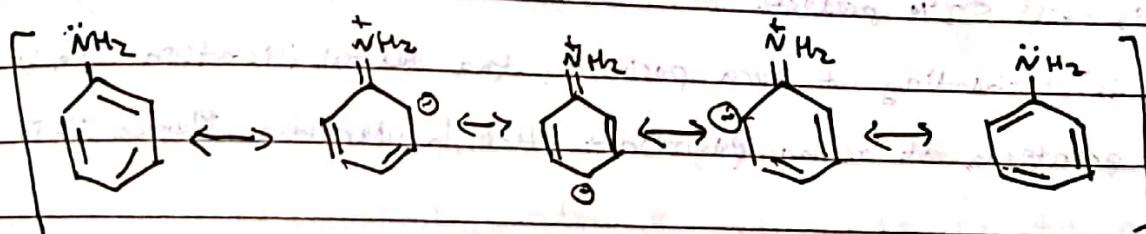
~~2°~~ Tertiary

(b) Secondary & Alliphatic Amines

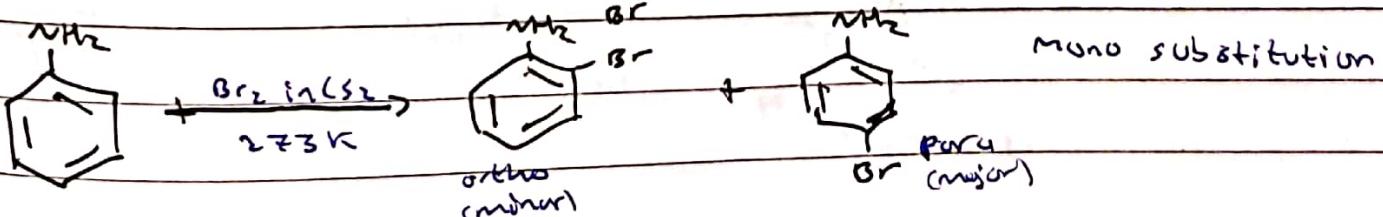
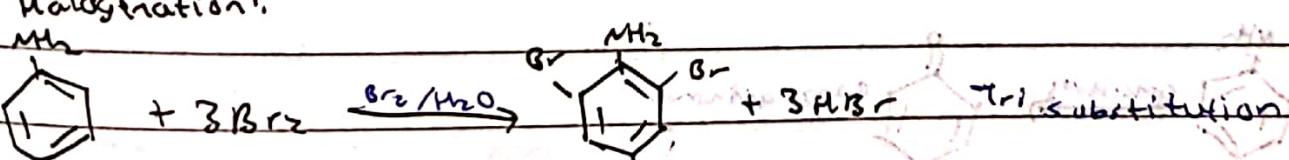


6. ELECTROPHILIC AROMATIC SUBSTITUTION (EAS)

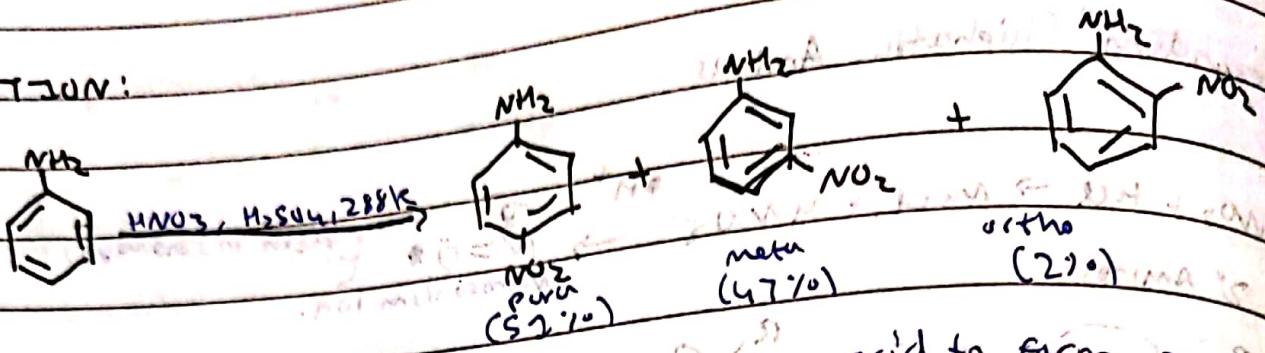
Aniline



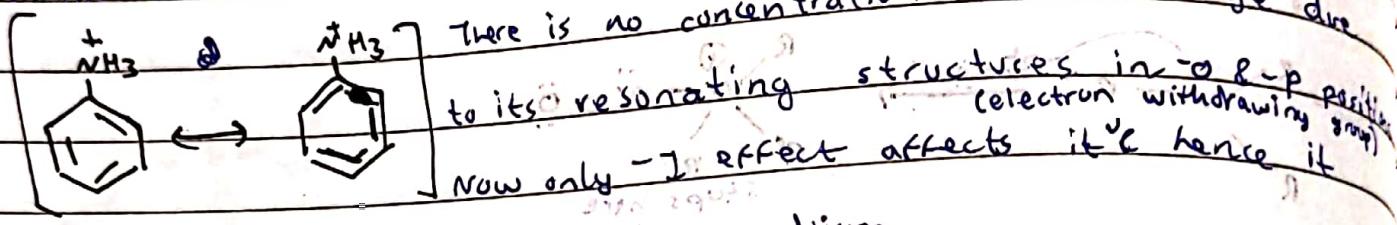
- Resonating structures concentrate -ve charge at ortho & para positions hence making aniline ortho-para directing for E.A.S.
- +R dominates $-I$, and hence NH_2 is a powerful activating group
- very similar to phenol ($\text{C}_6\text{H}_5\text{OH}$)



NITRATION:



In acidic medium, aniline reacts with acid to form an anilinium ion (NH_3^+)



Now only -I effect affects it hence it

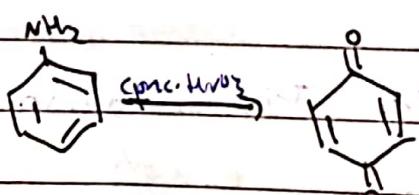
becomes meta directing in acidic medium.

- However since destabilisation is minimum due to -I effect at para position, it is still 57% product.

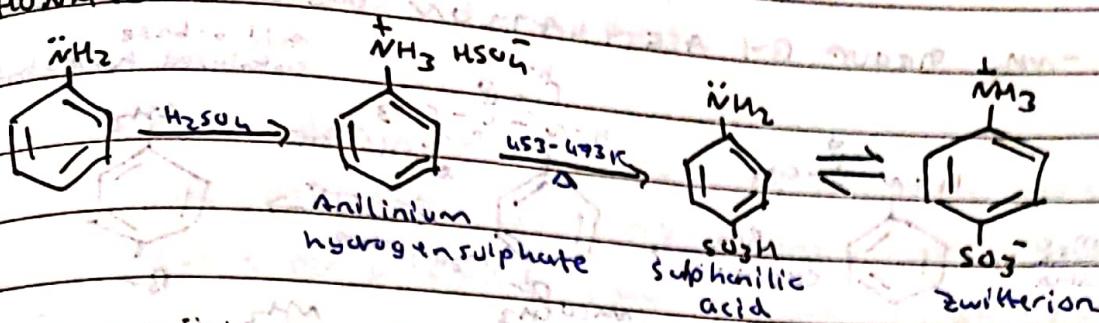
- Although there is H-bonding at para position, the destabilisation due to -I effect is greatest at ortho position + steric hindrance. Hence it is only 2%.

If nitration is attempted without strong dehydrating agents (acid) like H_2SO_4 , usually conc. HNO_3 isn't strong enough to dehydrate itself & the NO_2^+ cation cannot be formed.

Here HNO_3 acts as an oxidising agent & oxidises aniline.



SULPHONATION:



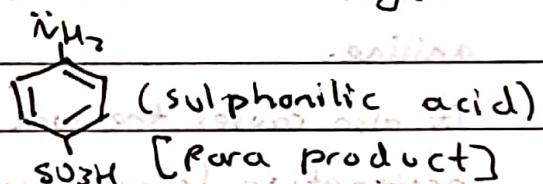
Two possible mechanisms are proposed.

① H_2SO_4 is an even weaker acid than HNO_3 , hence the conc. of NH_3^+ in solution is very low. Therefore most of the reaction occurs with NH_3^+ and hence via standard EAS, major product is para.

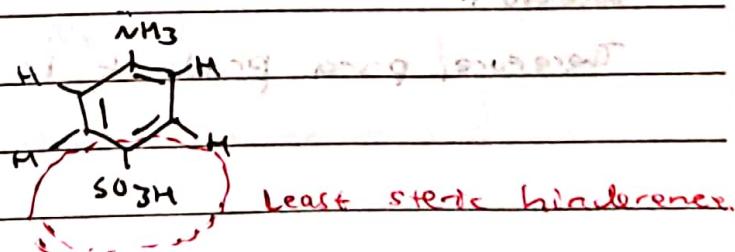
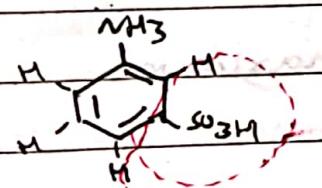
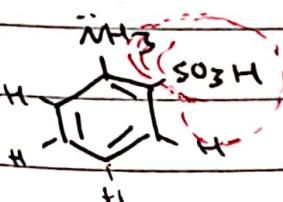
②

NH_3^+ reacts with H_2SO_4 to form HSO_4^- .

This is followed by the pi-bond attacking HSO_4^- via nucleophilic attack which leads to a rearrangement reaction to give major product



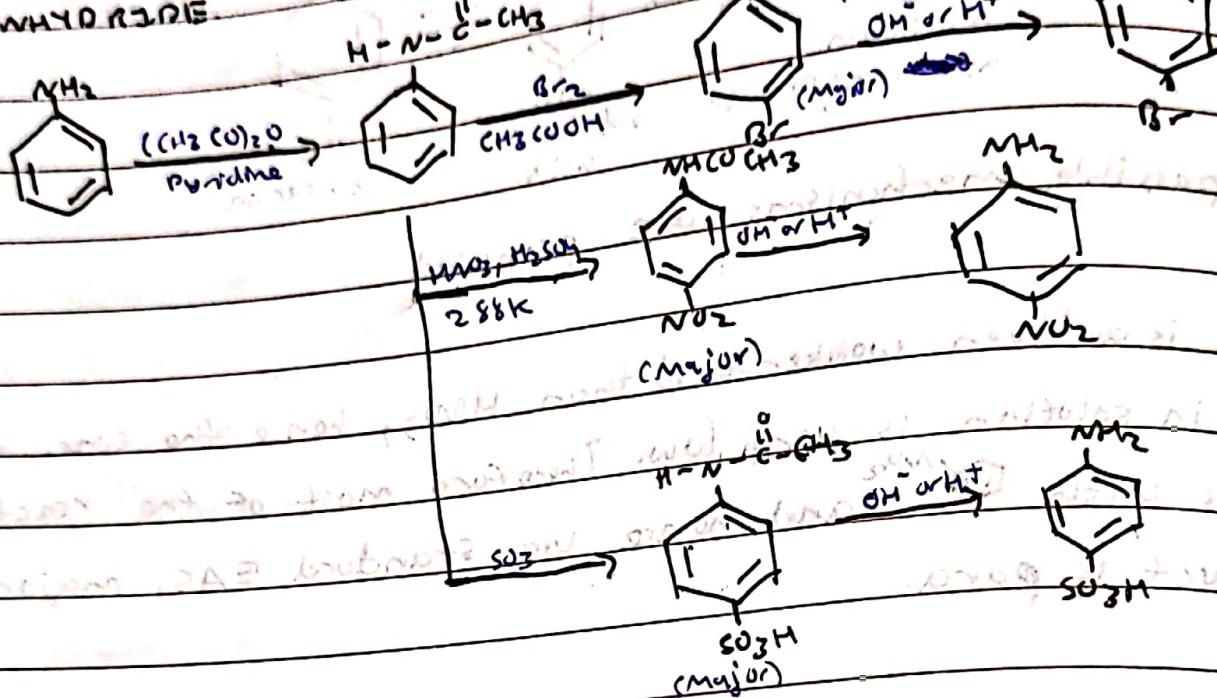
Para is major because, $\text{SO}_3^{\cdot-}$ is fairly large & provides a lot of steric hindrance.



PROTECTING NH_2 GROUP BY ACETYLATION WITH ACETIC ANHYDRIDE

acid or base
catalysed hydrolysis.

Anhydride:



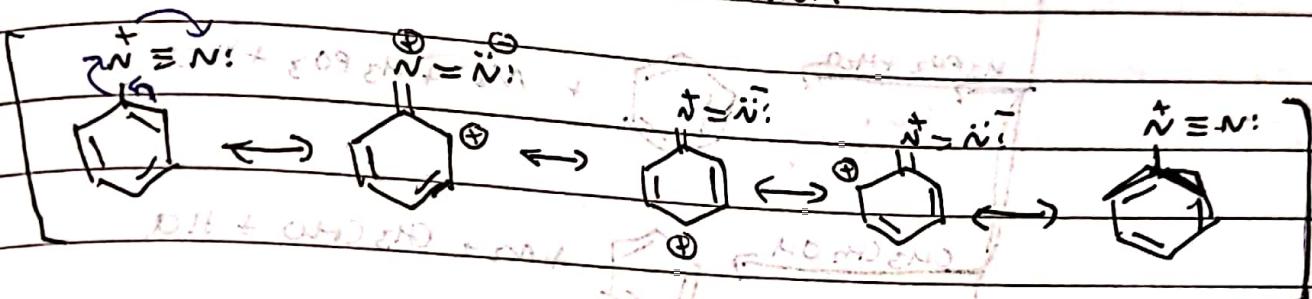
Here, $\text{H}-\ddot{\text{N}}-\text{C}-\text{CH}_3$ has this possible resonance structure. This causes the lone pair on N to be less available for donation to the benzene via resonance & hence reduces the activating effect of aniline.

It also causes the lone pair on nitrogen to be less available for protonation [since resonance structure with +ve charge on O is more electro negative atom] is very stable]. Hence meta directing ability of NH_3^+ is very low due to its low concentration in the solution.

Therefore, para product is maximum.

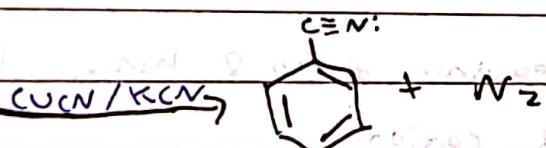
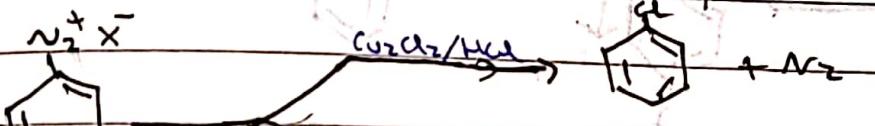
DIAZONIUM SALTS. ($R_2N_2X^-$)

For all **aliphatic diazonium salts** are ~~extremely unstable~~
and **Aromatic diazonium salts** are slightly more stable & hence
can exist for a short time in solution at low temperatures
This is due to resonance stabilisation

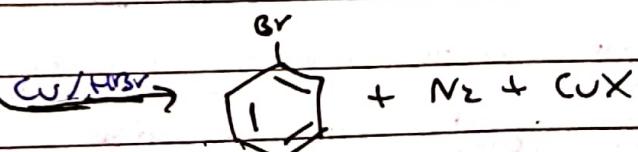
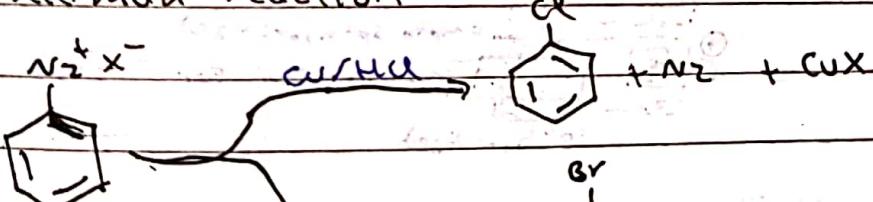


REACTIONS:

- Sandmeyer's (Covered in alkyl halides)

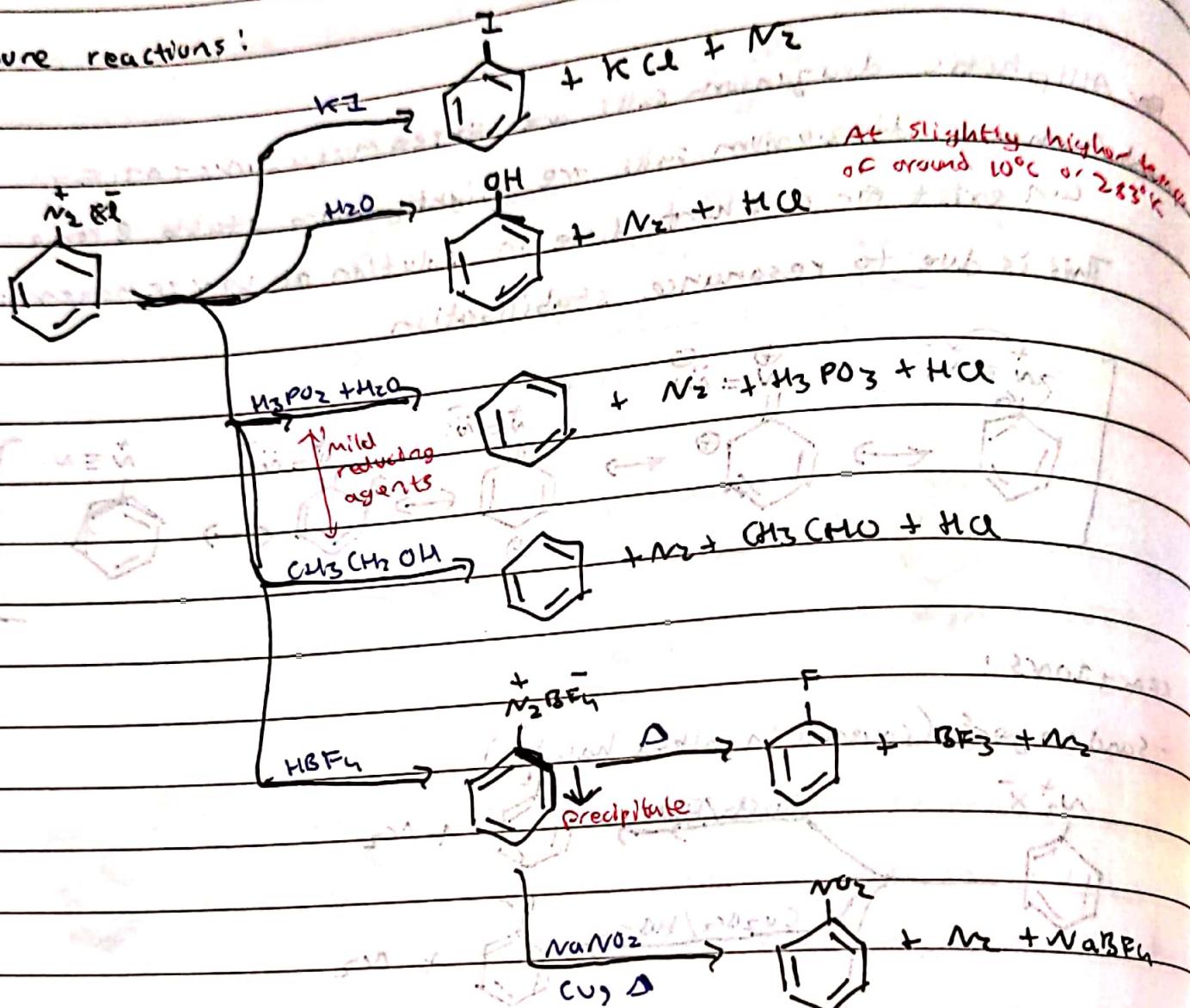


- Gatterman reaction



The yield in Sandmeyer's reaction is found to be better than in Gatterman's reaction

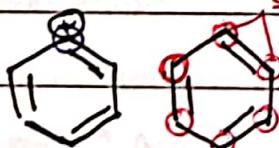
- More reactions:



N₂ is a very good leaving group & hence leaves to form a very unstable phenyl cation.

sp² hybridized

JEE NOTES

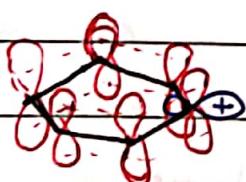


sp² hybridized \rightarrow C [1] [1 1] [1] P-orbital for π -bond

2s ~ 2p Empty sp² hybridized

C [1] [1 1] [1] P-orbital for π -bond

sp² hybridized

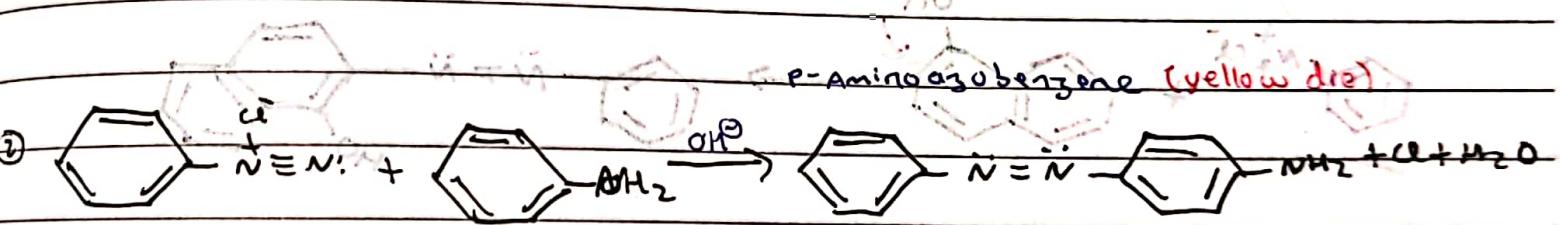
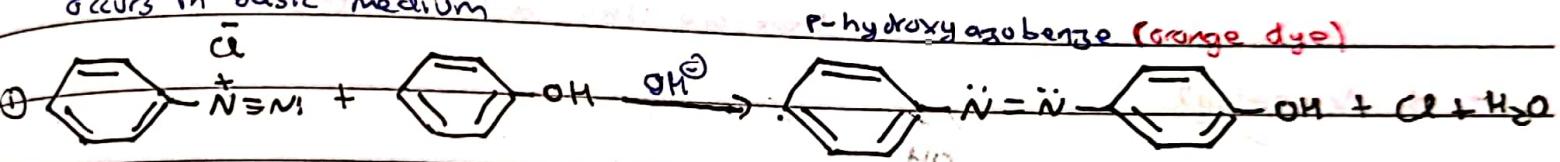


- In the phenyl carbocation, the carbocation is still sp² hybridized & the π -electron remains in the unhybridized 2p orbital so as to retain aromaticity of the ring.
- The empty (cationic) sp² orbital is orthogonal to the aromatic pi system and hence there is no resonance interaction or stabilisation in the phenyl carbocation.
- Due to the constraining effect of the 6-membered ring the cationic sp² orbital is unable to rehybridize to sp (unable to fit a full orthogonal p orbital in the ring).

- This results in considerable (low-energy) σ -character being used to stabilize an empty orbital.
- It is both this total lack of stabilization due to resonance & relatively higher energy of the molecule than what was possible if re-hybridization could occur that leads to the instability of the phenyl carbocation.
- Furthermore, since the cationic (empty) orbital is orthogonal to the benzene ring, it makes it a very good electrophile and hence very susceptible to nucleophilic attack (very low steric hindrance).

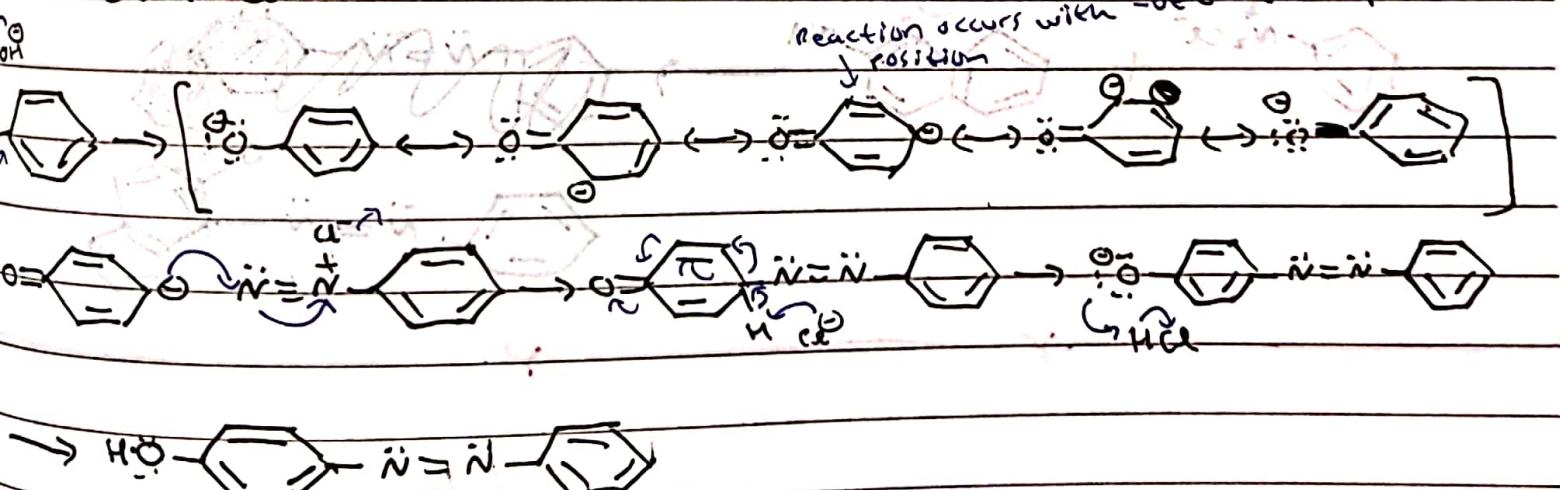
DIAZO-COUPING REACTIONS

occurs in basic medium



occurs with mechanism is EAS.

Mechanism:

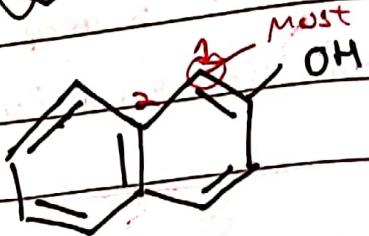
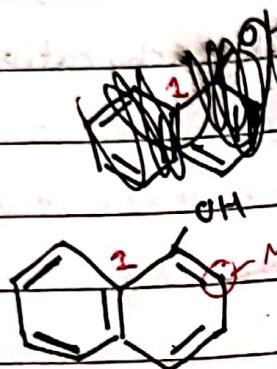


\uparrow
p bond is in conjugation.
Due to the 2 aromatic rings & p bond in conjugation,
PLenty of resonance structures are possible.

JEE NOTES

* DIACOUPLING REACTION WITH N_2 & β -naphthal.

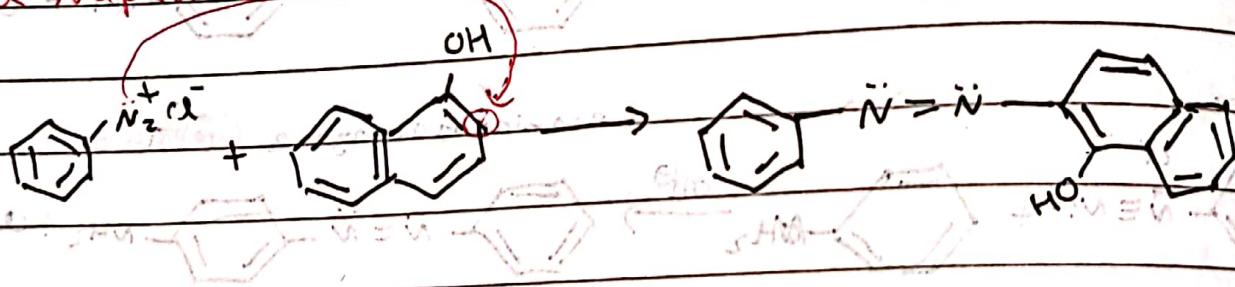
α -Naphthal or β -naphthal reacts with N_2 & β -naphthal.



Diazo coupling with

If we draw all their resonating structures we can understand that those are the most reactive sites. I haven't drawn them because there are like a lot of them.

α -Naphthal



β -Naphthal

