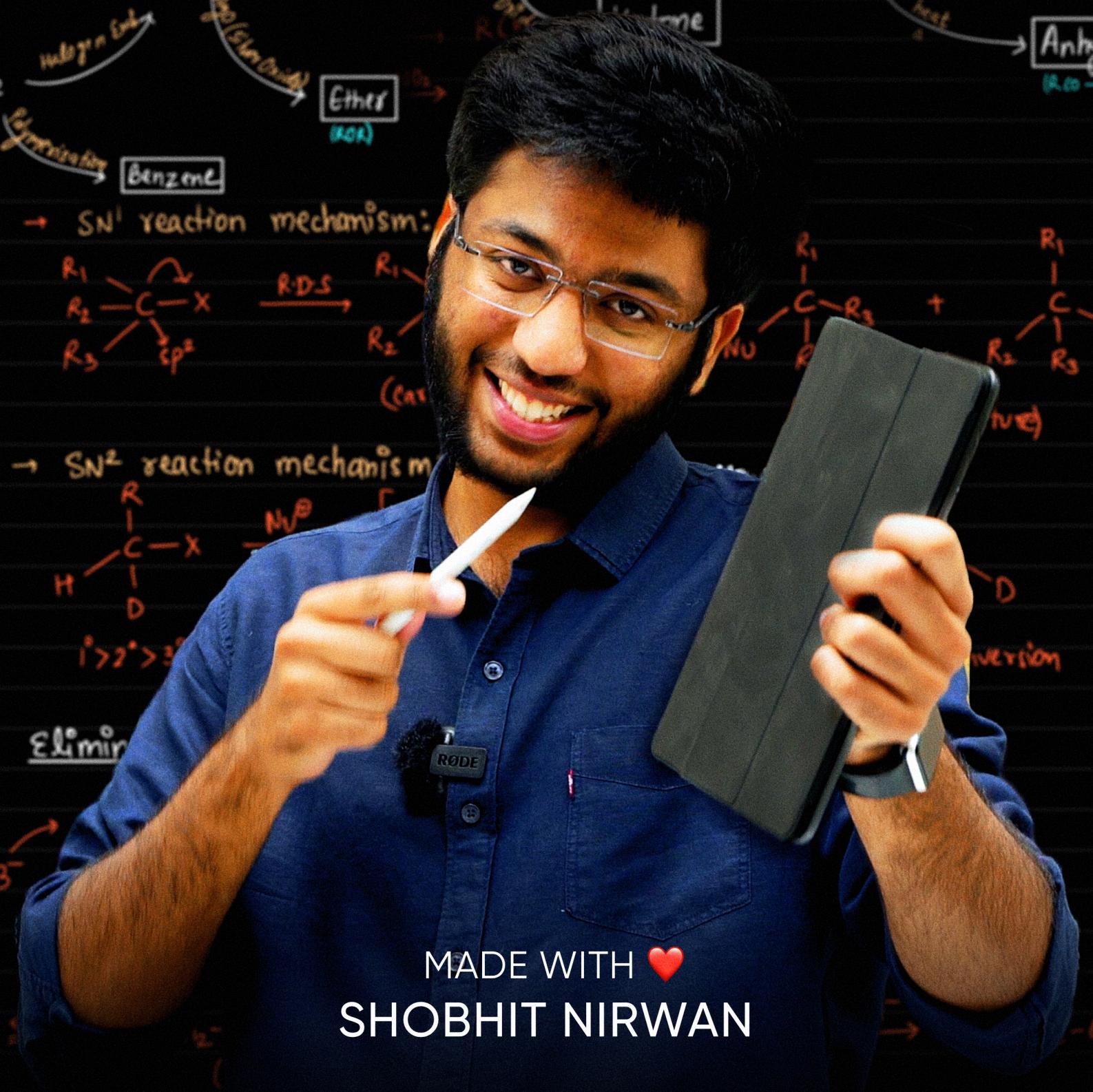


AMINES

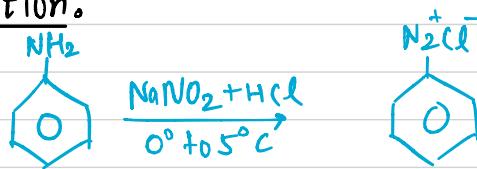
REVISION NOTES



MADE WITH ❤
SHOBHIT NIRWAN

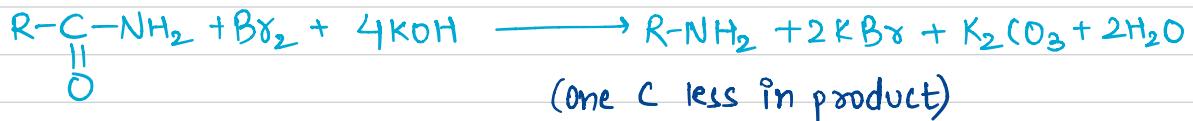
NAME REACTIONS OF THIS CHAPTER

[1] Diazotisation Reaction:



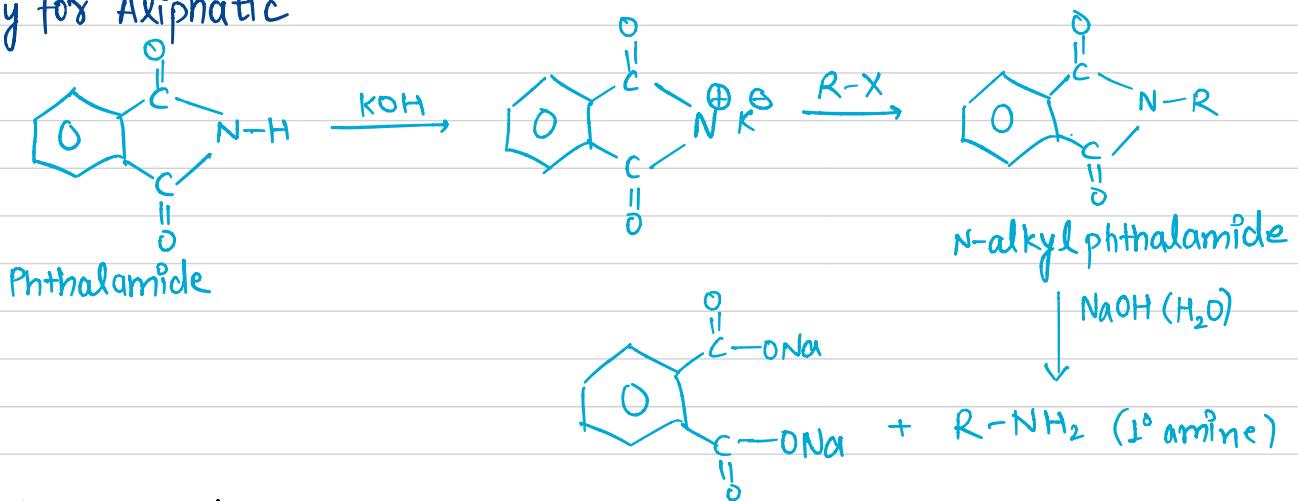
[2] Hofmann Bromide Reaction:

→ for both aliphatic and aromatic 1° amines

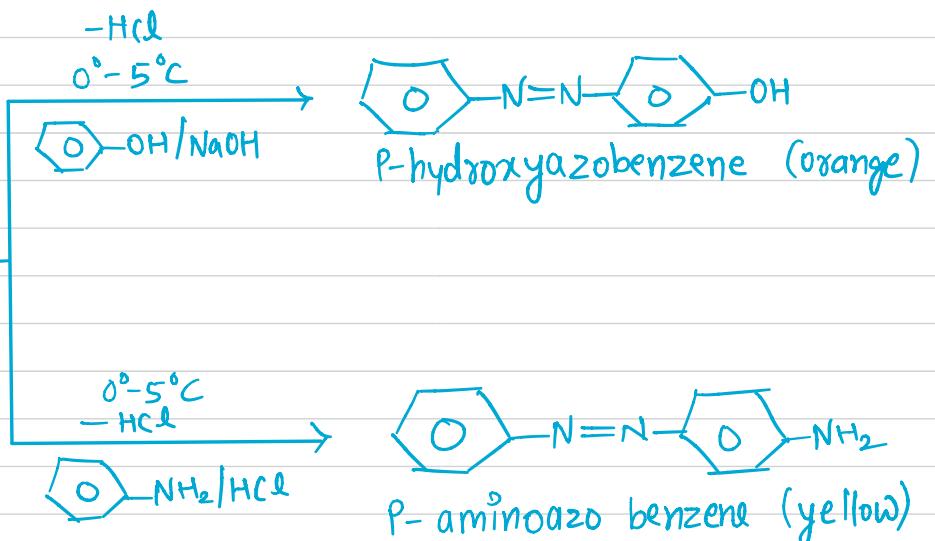


[3] Gabriel Phthalamide Synthesis: (1° formed)

→ Only for Aliphatic



[4] Coupling Reaction:



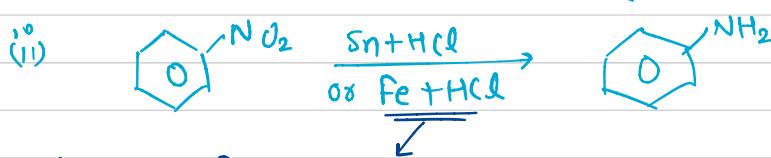
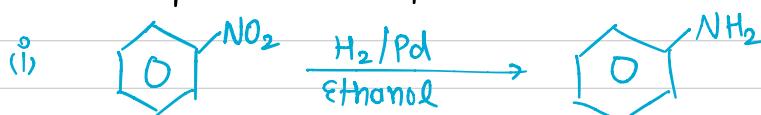
[5] Carbylamine Reaction / Isonitrile test:



↳ use to differentiate b/w 1° amine from 2° & 3° .

PREPARATIONS

(1) Reduction of Nitro Compounds:

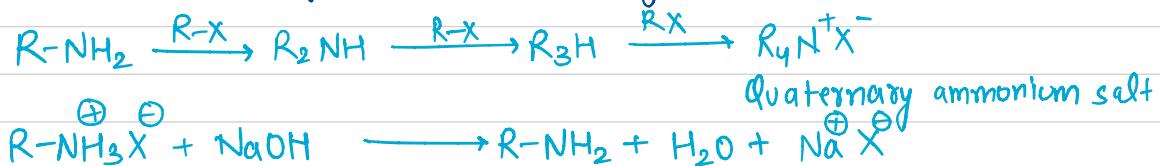


Reduction with iron scrap and HCl is preferred because FeCl_2 formed gets hydrolysed to release HCl.

→ only small amount of HCl is required to initiate reaction.

(2) Ammonolysis of Alkyl halides:

The process of cleavage of C-X bond by ammonia molecule is Ammonolysis



↳ Disadvantage: It yields mixture of 1° , 2° , 3° and 4° salt.

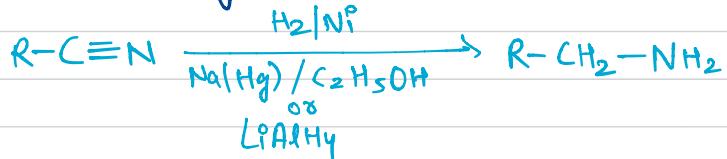
1° is major product by taking large excess of ammonia.

Order of Reactivity of halides with Amine \Rightarrow $\boxed{\text{R-I} > \text{R-Br} > \text{R-Cl}}$

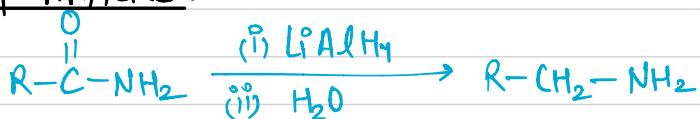
(3) Reduction of Nitriles:

→ 1° amine produced

→ This reaction is used for ascent of amine series i.e. preparation of amines containing one carbon atom more than starting amine.



(4) Reduction of Amides:



(5) Gabriel Phthalamide Synthesis: Aromatic 1° amines cannot be prepared by this method because aryl halides do not undergo nucleophile substitution with anion formed by phthalamide.

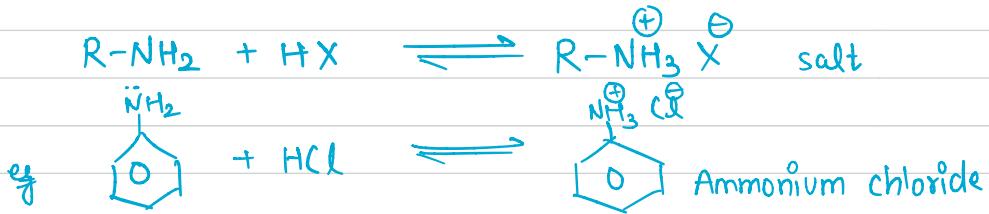
(6) Hoffman Bromide degradation Reaction: (One carbon less in product)

CHEMICAL REACTIONS

* Amines behave as nucleophile.

(I) Basic character of Amines:

They are basic in nature, react with Acid \rightarrow Salt



→ Amine salts are soluble in H_2O and not in org. sol. like ether.
salt + base \rightarrow parent amine



→ This reaction is basis for separation of amines from non-basic org. compounds insoluble in water.

$$\rightarrow p(K_b) \text{ of ammonia} = 4.75$$

$$[p(K_b) = -\log K_b]$$

$\uparrow K_b \text{ or } \downarrow pK_b \rightarrow \text{strong base}$

→ Aliphatic amines are strong base due to +I

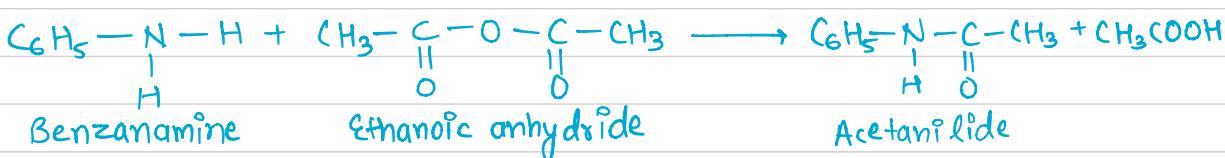
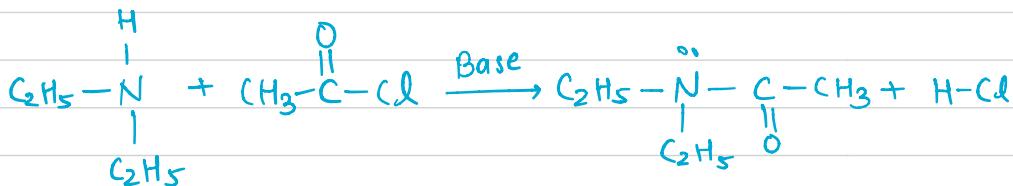
↪ pK_b b/w 3-4.22.

pK_b of aniline is high
aromatic amine $pK_b <$ ammonia.

→ Structure - basicity related to Amines: basicity depends on ease of formation of cation by accepting a proton from the acid.

More stable cation, more basic amine

→ Acylation





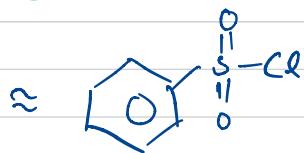
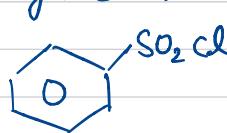
Carbylamine reaction

Reaction with nitrous acid

Reaction with aryl Sulphonyl chloride

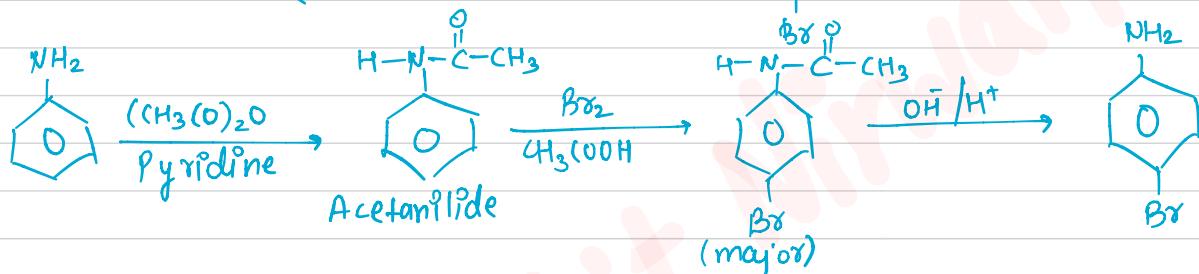
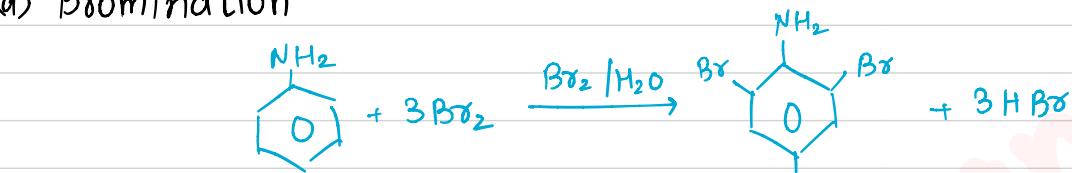
} at last in easy way

Hinsberg's reagent :



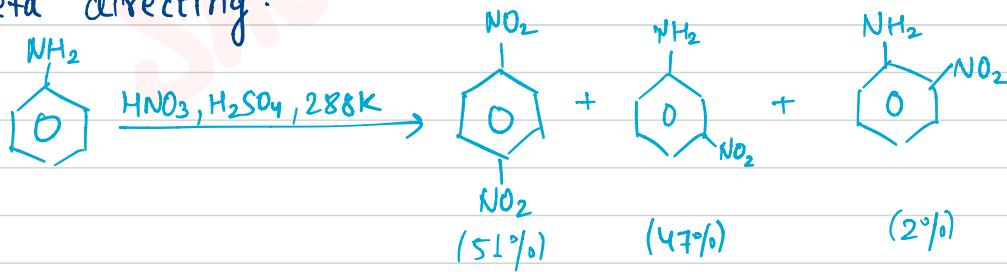
(2) Electrophilic Substitution:

(a) Bromination

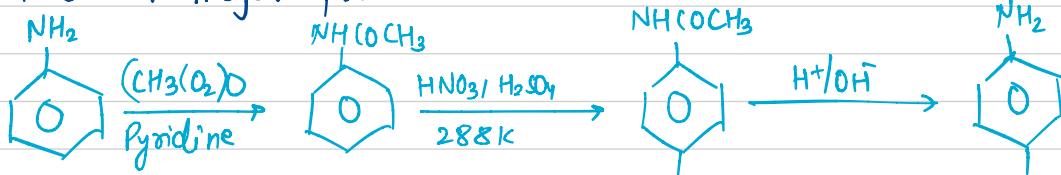


(b) Nitration:

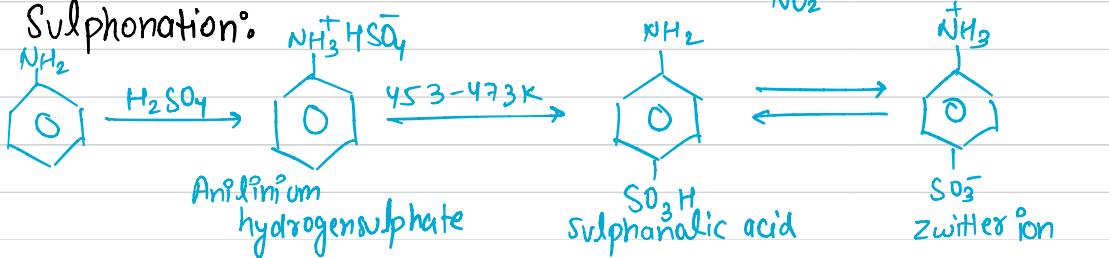
In strongly acidic medium, aniline is protonated to form anilinium ion which is meta directing.



→ By acetylation reaction with acetic anhydride reaction can be controlled and one can obtain major product



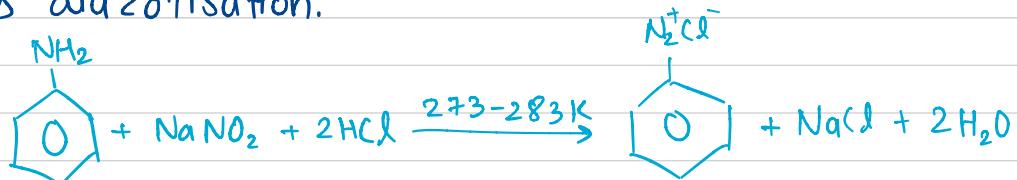
(c) Sulphonation:



Diazonium Salts

PREPARATIONS:

→ The conversion of primary aromatic amines into diazonium salts is known as diazotisation.



PHYSICAL PROPERTIES:

Benzene diazonium chloride - colourless crystalline solid

- It is readily soluble.
- Stable in cold but reacts with water when warmed.
- decomposes easily in dry state.

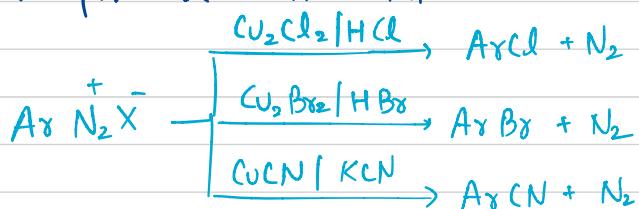
Benzene diazonium fluoborate is water insoluble and stable at room temp.

CHEMICAL REACTIONS:

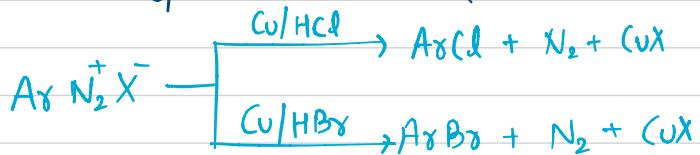
A. Reactions involving displacement of Nitrogen-

I. Replacement by halide or cyanide ion.

→ Sandmayer's reactions aka ↗



→ OR, Br or Cl can be introduced by halogen acid in presence of Cu powder, this is called Gatterman reaction.



Sandmayer is better than Gatterman

2. Replacement by iodide ion:

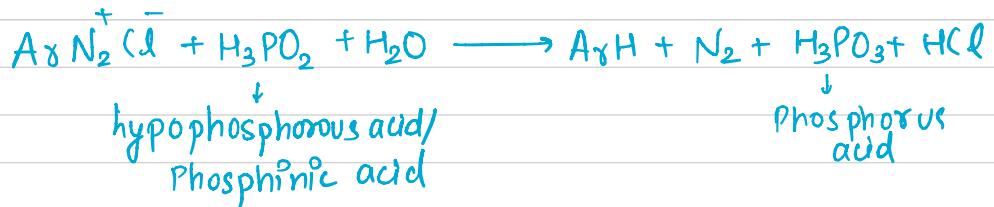
Iodine not easily introduced in benzene ring directly, but when diazonium salt solution is treated with potassium Iodide, Iodobenzene is formed.



3. Replacement by Fluoride ion:



4. Replacement by H

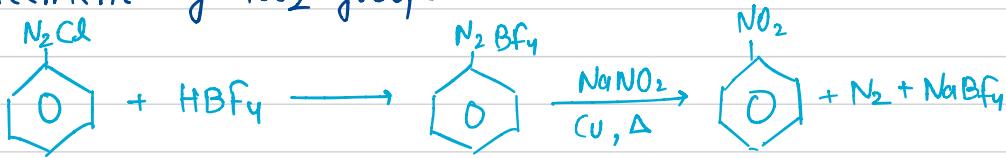


5. Replacement by Hydroxyl group:

Temp. get \uparrow then 283K \longrightarrow Phenol form



6. Replacement by NO_2 group:



B. Reactions involving retention of diazo grp. → Coupling reaction

IMPORTANCE:

- Diazonium salts are good intermediate for intro of F, Cl, Br, I, CN, OH, NO_2 grp.
- Help in forming compound which cannot substitute directly.

3 TESTS:

1) Carbylamine Reaction / Isocyanide Test (differentiate 1° from others)

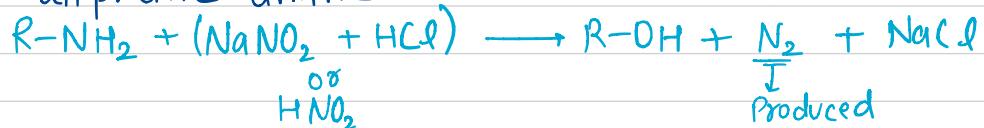
→ Aliphatic / Arom 1° amine on heating with chloroform and ethanoic potassium hydroxide forms isocyanide or carbylamine, foul in smell.

→ distinguish 1° amine from 2° and 3°

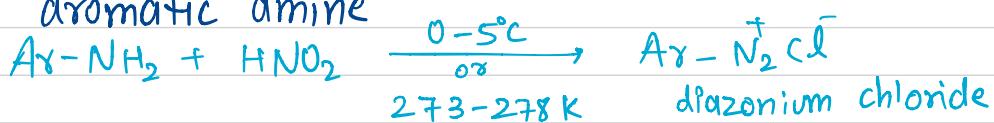


2) Reaction with Nitrous acid (test 2) (diff. b/w aliphatic & aromatic from 1° only)

i) 1° aliphatic amine



ii) 1° aromatic amine



→ Hinsberg Reagent (HR)

3) Reaction with Aryl Sulphonyl chloride test (Separates 1°, 2° & 3°)

