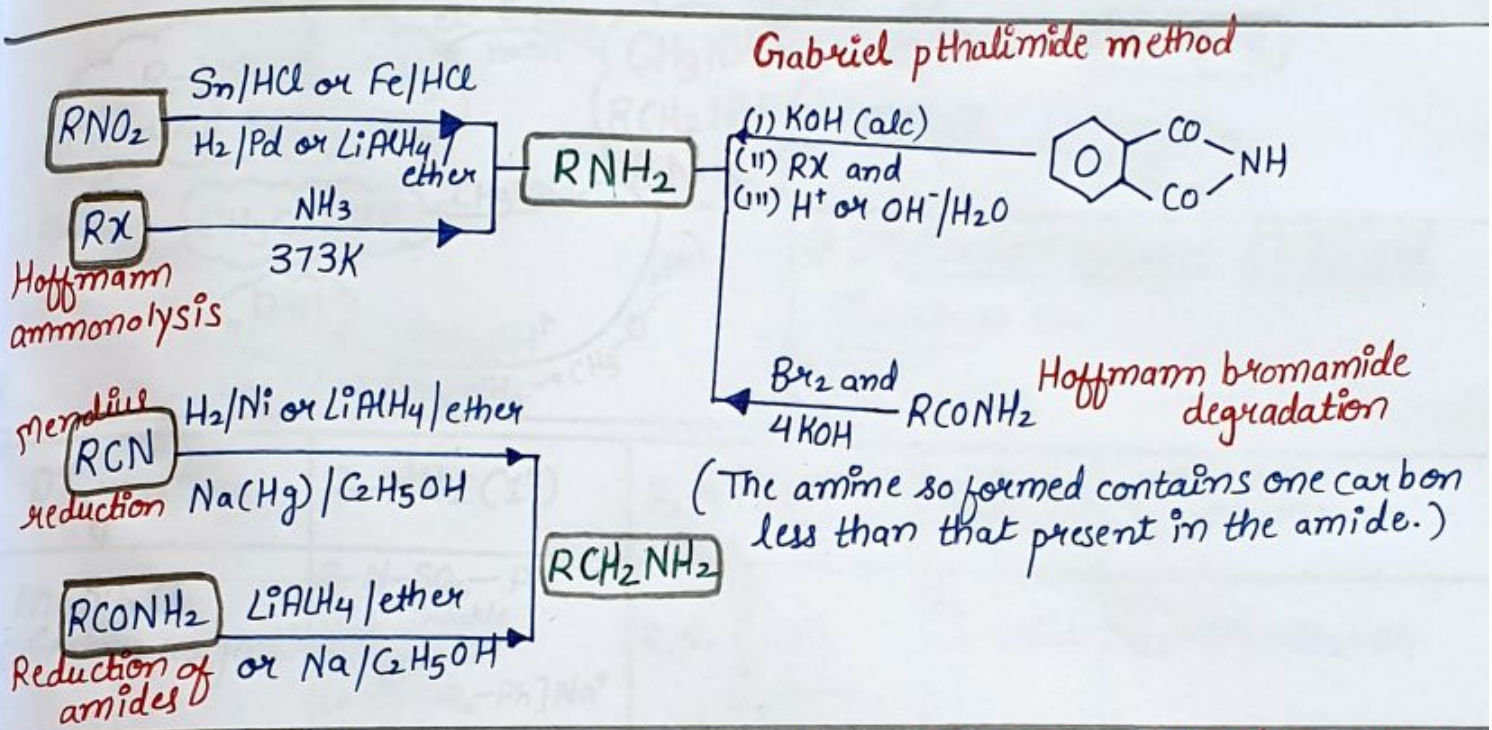
AMINES

Introduction
→ Derivatives of ammonia in which one or more hydrogen atoms have been replaced by alkyl groups.

Classification
→ On basis of number of alkyl groups attached to nitrogen atom.

$R-NH_2$ (alkyl amine), 1° amine; R_2NH (Dialkyl amine), 2° amine; R_3N (Trialkyl amine) 3° amine.

preparation Of Amines



(The amine so formed contains one carbon less than that present in the amide.)

Aromatic 1° amines cannot be prepared by Gabriel pthalimide synthesis method because aryl halides do not undergo nucleophilic substitution with anion formed by pthalimide.

Chemical Reactions of Amines...

- **Basic character of Amines:-**
- Larger the value of K_b, stronger is the base.
- Aliphatic amines are stronger base than ammonia due to +I effect of alkyl groups leading to high electron density on nitrogen atom.
- Order of basicity of amines in gaseous phase follows the expected order:

  3° amine > 2° amine > 1° amine > NH_3

- In aqueous phase, substituted ammonium cation gets stabilized not only by electron releasing effect of the alkyl group (+I) but also by solvation with water molecules.

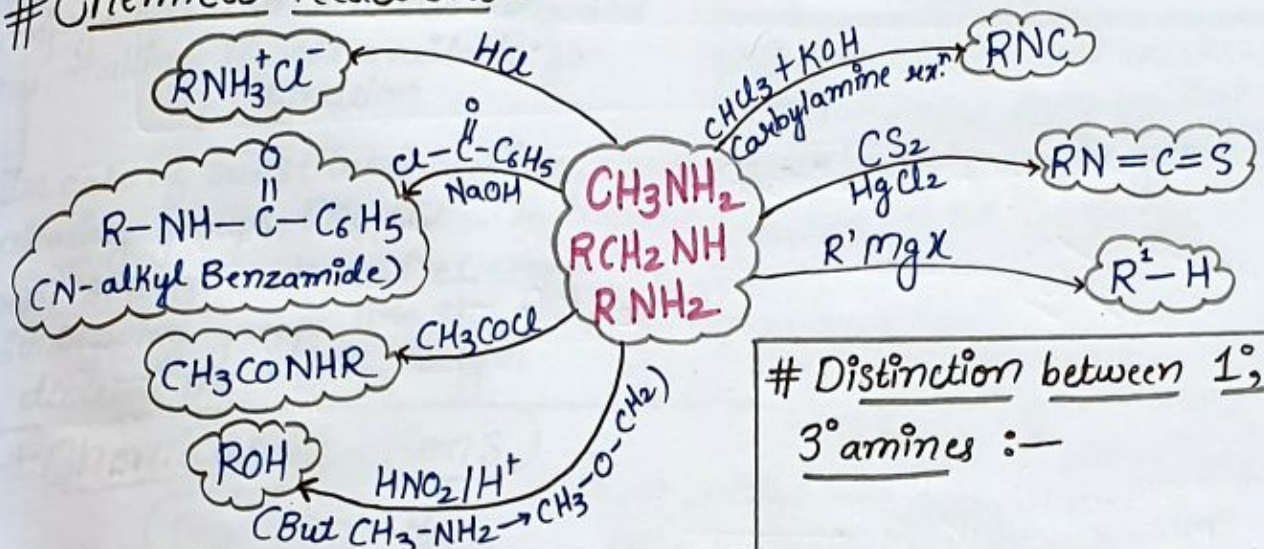
  Greater the size of ion, lesser will be the solvation and the less stabilised is the ion.

- Order of basic strength in aqueous solution :—

  $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$.

  $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$.

Chemical Reactions :—

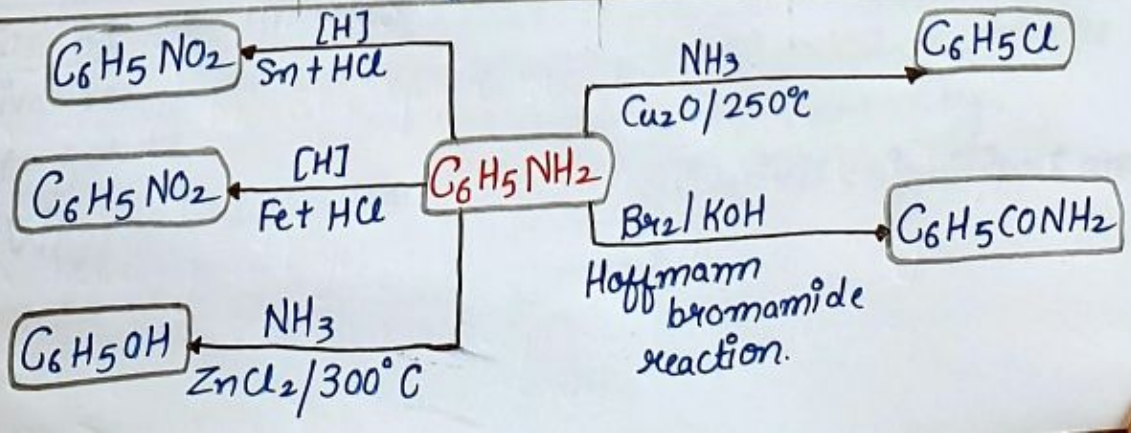


Distinction between 1°, 2°, and 3° amines :—

Reagent	$R-\ddot{N}H_2$ (1°)	$R_2\ddot{N}H$ (2°)	$R_3\ddot{N}$ (3°)	$C_6H_5-\ddot{N}H_2$
$Ph-SO_2Cl$ (Hinsberg reagent)	$R-N(H)-SO_2-Ph$ Soluble ↓ NaOH $[R-N^-(Na^+)-SO_2-Ph]Na^+$	$R_2N-S(=O)_2-Ph$ ↓ NaOH Insoluble	No reaction.	$C_6H_5-NH-SO_2-Ph$
$C(=S)=S$ Δ/$HgCl_2$ Mustard oil test	$R-NH-C(=S)-SH$ $HgCl_2$ ↓ Δ $R-N=C=S + HgS$	$R_2N-C(=S)-SH$ $HgCl_2$ ↓ Δ No reaction.	No reaction.	KOH → $Ph-N=C=S + HgS$
HNO_2 nitrous acid	$ROH + N_2$	$R_2N-N=O$ (Nitrosoamine) Yellow oily liquid	No reaction	$C_6H_5-N_2^+Cl^-$

Aniline

Preparation :—



Chemical Properties :-

* Basicity of aniline.

- Aromatic amines are less basic than Aliphatic Amines.

$C_6H_5NH_2 < NH_3 < CH_3NH_2$.

- pK_b value of aniline is quite high bcoz in aniline or other arylamines, the $-NH_2$ group is attached directly to the benzene ring. It results in unshared electron pair on nitrogen atom to be in conjugation with benzene ring and thus, making it less available for protonation.

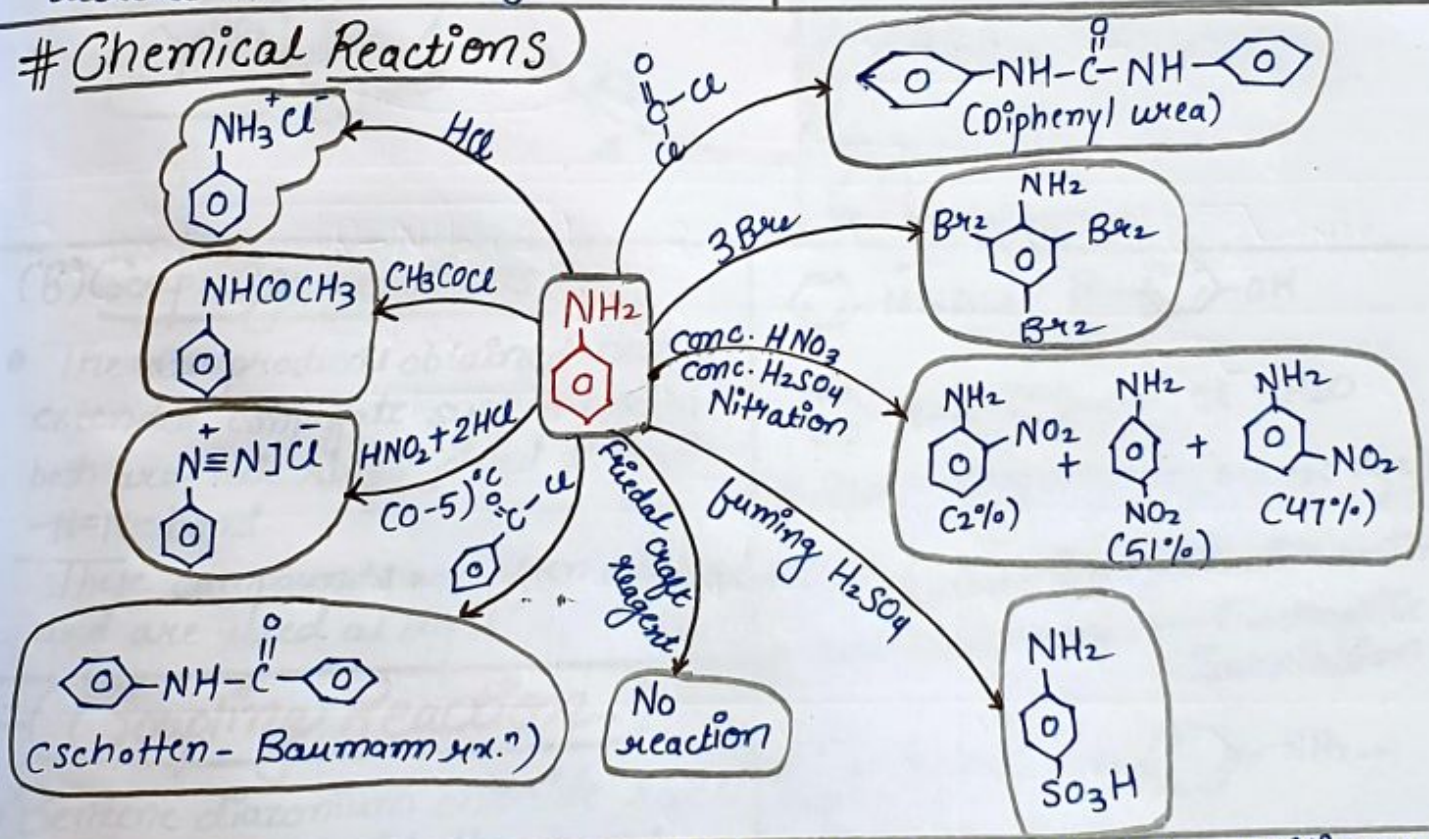
- In case of substituted aniline, electron releasing groups like OCH_3, CH_3 increase basic strength whereas electron withdrawing groups like NO_2, $-SO_3H$, $-X$ decrease the basic strength

Basic strength of substituted aniline

S.no.	Grp. attached to benzene ring of aniline	Basic strength
1.	Methyl	p > m > o
2.	Cl	p > m > o
3.	Br	p > m > o
4.	Methoxy	p > o > m
5.	NH_2	p > m > o
6.	NO_2	m > p > o

- Ortho substituted anilines are weaker bases than aniline irrespective of the nature of the group which is known as Ortho effect.

Chemical Reactions



- Direct nitration of aniline yields oxidation products in addition to the nitro derivatives. Moreover, in strongly acidic medium, aniline is protonated to form anilinium ion which is meta directing.

That's Why, besides ortho and para derivatives, significant amt. of meta derivative is also formed.

Tests for Aniline :-

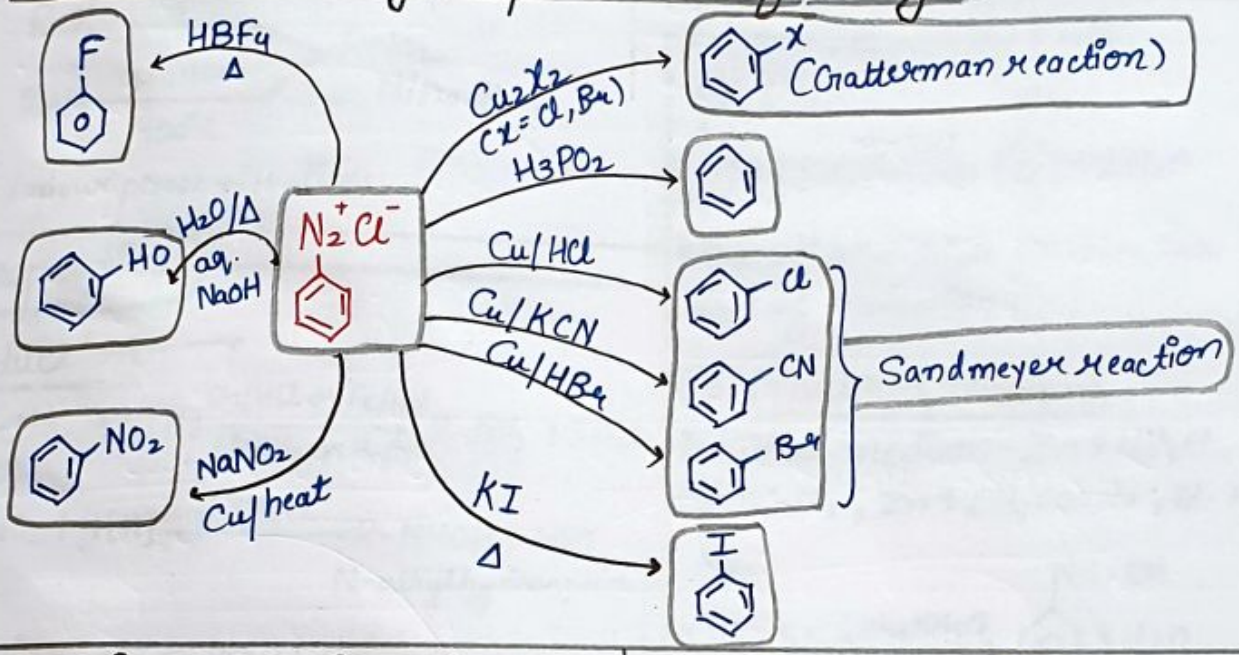
(i) **Isocyanide (Carbylamine) test:**
C_6H_5NC (pungent odour) is formed on treating aniline with $CHCl_3 + KOH$.

(ii) **Bromine water test:**
White ppt. (2,4,6-tribromoaniline) is formed on reaction of aniline with bromine water.

Diazonium Salt

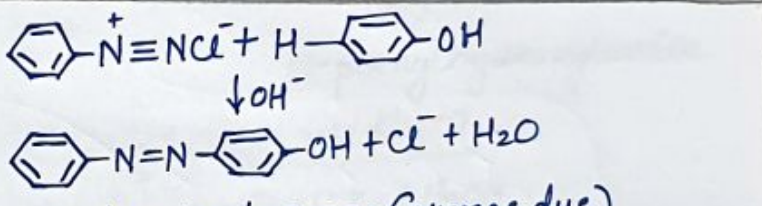
- Benzenediazonium chloride is obtained by treating aniline with nitrous acid (HNO_2) at 0-5°C (ice bath temperature).
- Diazonium salt containing aryl group directly linked to the nitrogen atom is stable due to resonance stabilization between the benzene nucleus and N-atom.

(A) Reactions involving displacement of Nitrogen :-



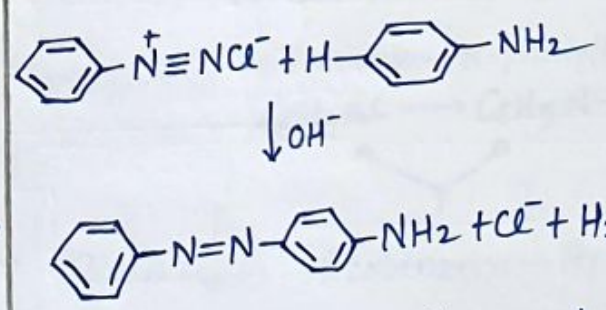
(B) Coupling Reactions :-

- The azo products obtained have an extended conjugate system having both aromatic rings joined through $-N=N-$ bond.
- These compounds are often coloured and are used as dyes.



p-hydroxyazobenzene (orange dye)

- Rx.n of diazonium salt with aniline yields p-aminoazobenzene. — Electrophilic Substitution Rx.n



p-Aminoazobenzene (yellow dye)

Coupling Reaction..

- Benzene diazonium chloride reacts with phenol in which the phenol molecule at its para position is coupled with diazonium salt to form p-hydroxyazobenzene.
  This rx.n is Coupling rx.n

Nitroalkanes

These are classified as 1°, 2°, and 3° depending upon nature of carbon atom to which nitro group is attached.

$R-CH_2-NO_2$ — 1° Nitro alkane

R_2CH-NO_2 — 2° nitro alkane

$R-\overset{R}{\underset{R}{C}}-NO_2$ — 3° nitroalkane

Preparation

$R-X \xrightarrow{AgNO_2} RNO_2$

$R-H \xrightarrow[400°C]{HONO_2} RNO_2$

Nitroalkane

(Vapour phase nitration)

Properties

1. Reduction →

(i) $R-NO_2 + 6[H] \xrightarrow[LiAlH_4 \text{ or } H_2/Ni]{Sn/HCl \text{ or } Fe/HCl} R-NH_2 + 2H_2O$

(ii) $R-NO_2 + 4[H] \xrightarrow{Zn/NH_4Cl} R-NHOH + H_2O$

N-alkylhydroxylamine

2. Action of nitrous acid. →

Different products are formed from 1°, 2° and 3°-nitroalkanes.

- $R-\underset{NO_2}{\underset{|}{CH_2}} + O=N-OH \xrightarrow[(-H_2O)]{} R-\underset{NO_2}{\underset{|}{C}}=N-OH$

1° nitroalkane — Nitrolic acid

$\xrightarrow{NaOH}$ $R-\underset{NO_2}{\underset{|}{C}}=N-ONa$ Red Colour (Sodium salt)

- $R_2\underset{NO_2}{\underset{|}{CH}} + HONO \longrightarrow R_2\underset{NO_2}{\underset{|}{C}}-NO$

2°-Nitroalkane — pseudonitrol

$\xrightarrow{NaOH}$ (Blue Colour)

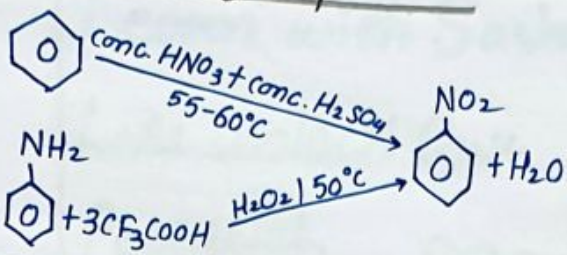
- $R_3C-NO_2 \xrightarrow{HNO_2}$ No rx.ⁿ

3°-Nitroalkane

→ These rx.ⁿ distinguish b/w 1°, 2°, 3° nitro alkanes

Nitrobenzene, $C_6H_5NO_2$

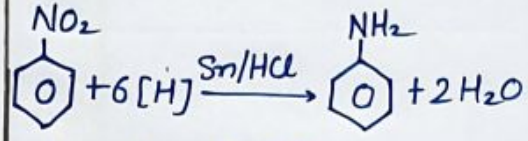
Methods Of Preparation :—



Chemical Reactions :—

(a) Reduction in acidic medium.

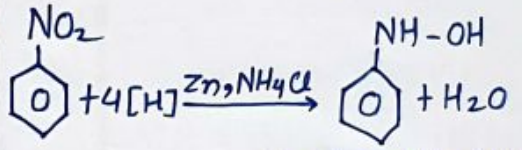
Acidic medium – Zn + HCl



- Low pH and high temperature ↑ses Rate of reduction.

(b) Neutral medium.

Neutral medium – $Zn + NH_4Cl$, $Zn + CaCl_2$, $Zn + CH_3COONa$; Al-Hg + NH_4Cl etc.



N-phenylhydroxylamine

(c) Alkaline medium.

Alkaline medium : Zn + NaOH.

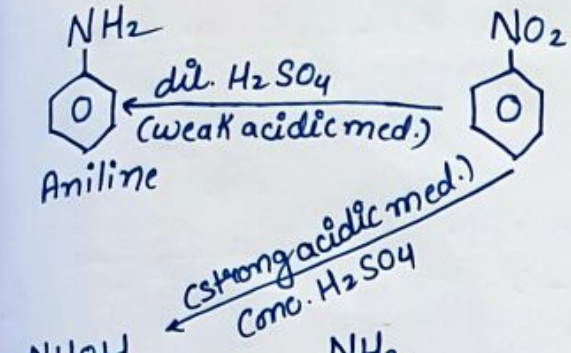
Nitrosobenzene and N-phenylhydroxylamine are formed, which interact to form dinuclear products like azoxybenzene → azobenzene and finally hydrazobenzene.

Nitrobenzene $C_6H_2NO_2 \longrightarrow$ Nitrosobenzene $C_6H_5NO \longrightarrow$ N-phenylhydroxylamine C_6H_5NHOH

Azoxybenzene → Azobenzene → Hydrazobenzene

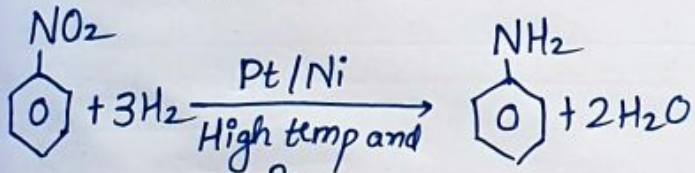
NEET SLAYER... Unlock Your Potential...

(d) Electrolytic reduction:

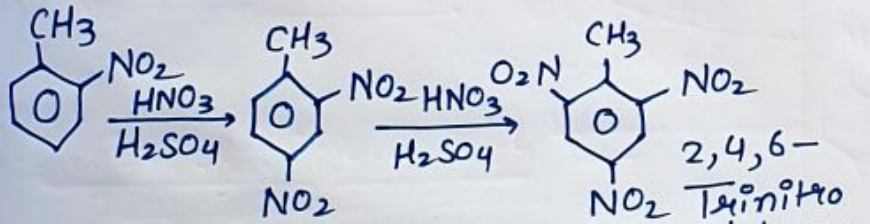


p-Amino phenol

(e) Catalytic Reduction:



(f) Electrophilic Substitution Reaction:



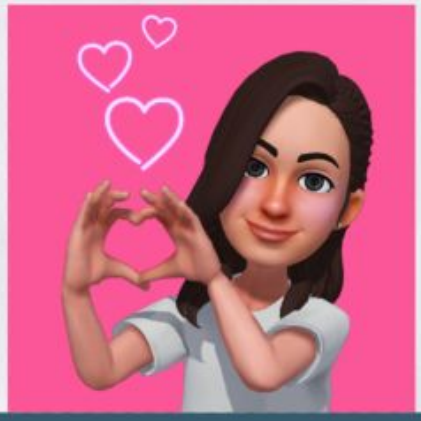
2,4,6-Trinitro toluene (TNT)

Used as explosive.

NEET SLAYER...

Learn with Sasha..

Let's unlock Our Potential, Together..



NEET SLAYER