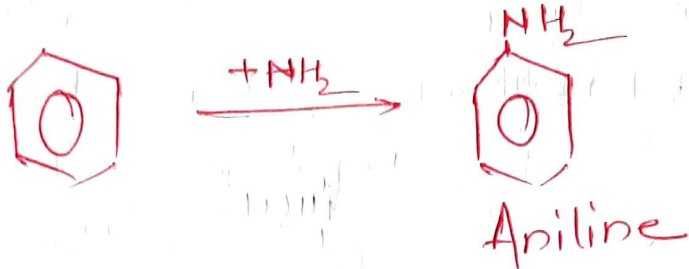
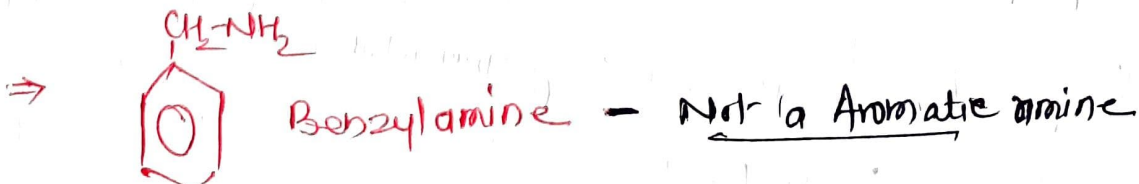
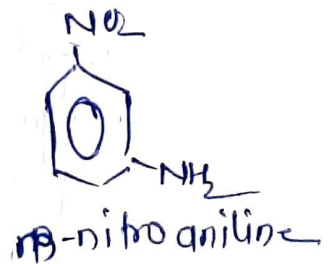
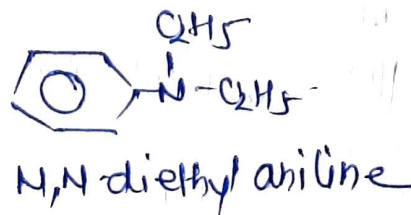
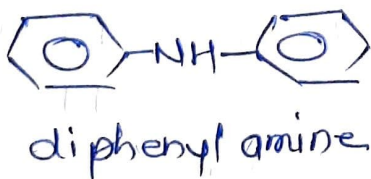
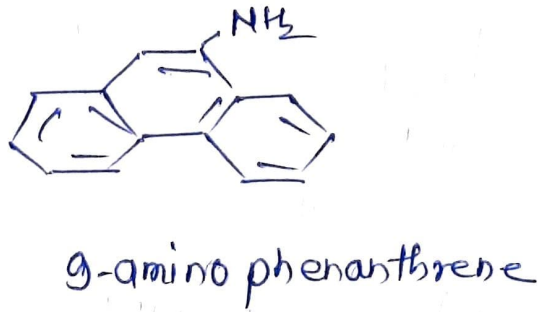
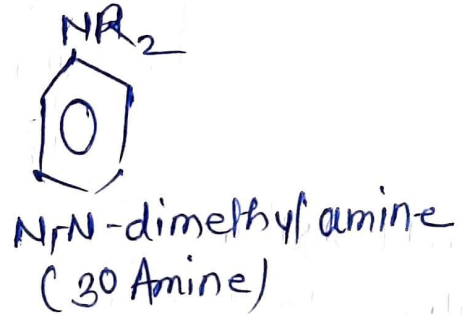
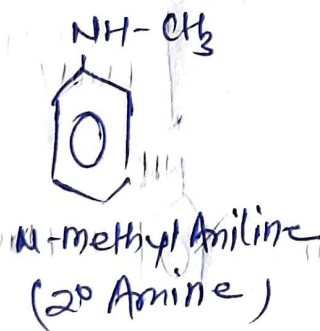
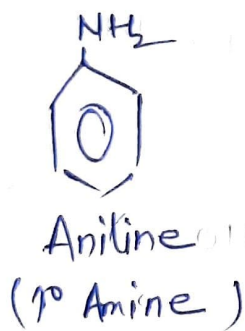


# AROMATIC AMINE


- ↳  $-NH_2$  group attached to the Aromatic ~~ring~~ hydrocarbon
- ↳ - Hydrogen of the benzene ring has been replaced by an amino group ( $-NH_2$ )



- ↳ All compounds in which an amino or substituted amino group is bonded directly to the aromatic ring are termed Aromatic Amine

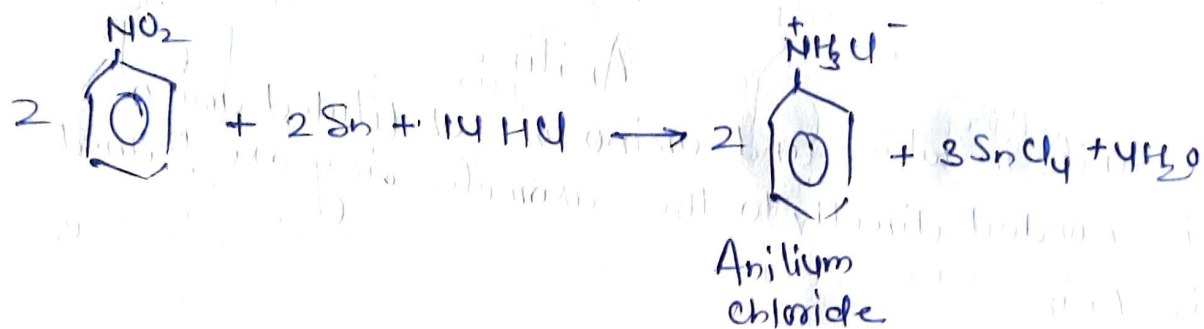


# PREPARATION METHODS OF ANILINE

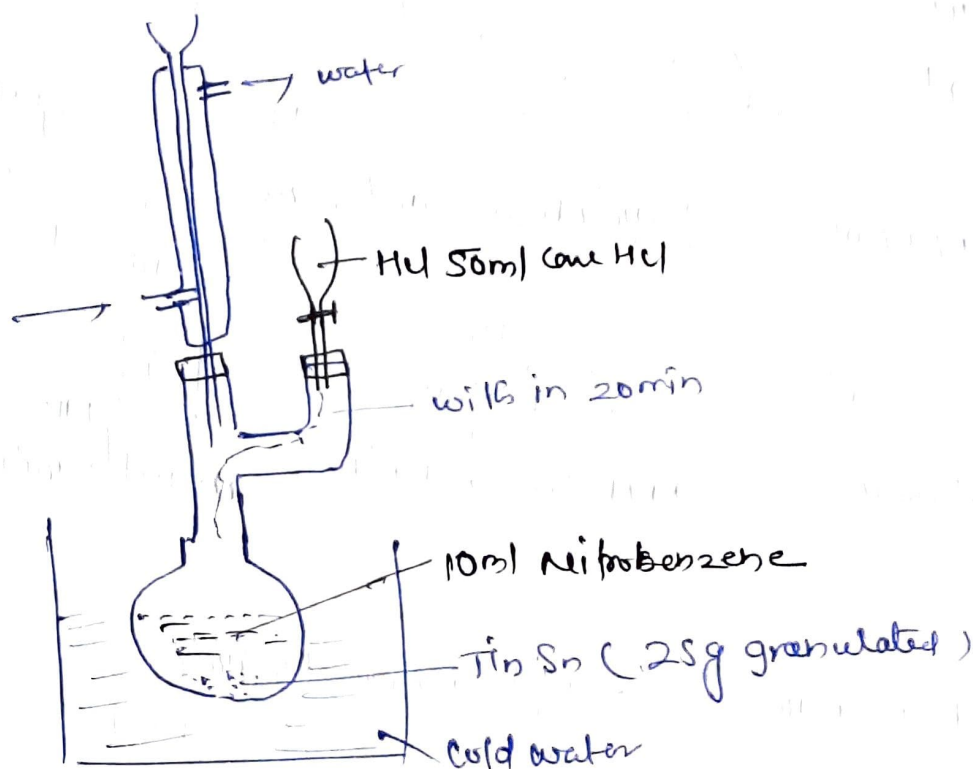
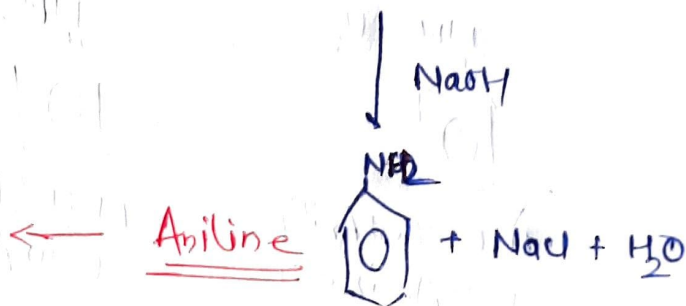
-  - Aniline,  $C_6H_5NH_2$
- Phenyl amine
- Aminobenzene

## Laboratory Preparation

- By Reduction of Nitrobenzene

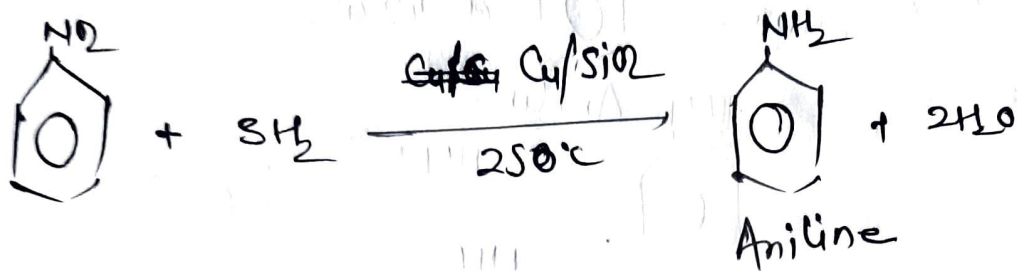


Separated by Steam distillation

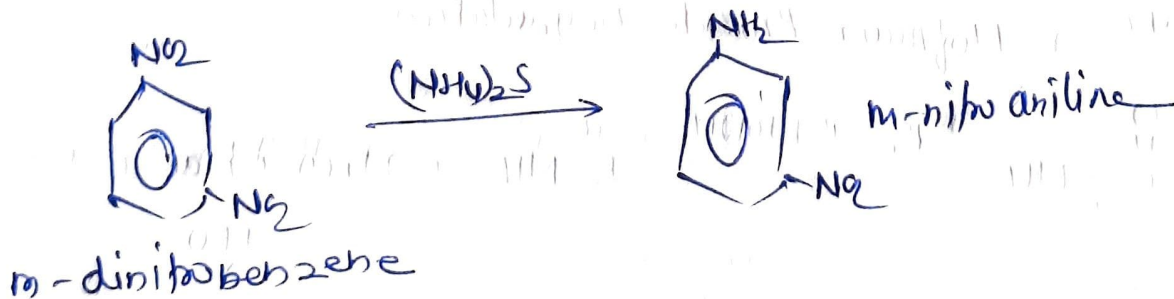
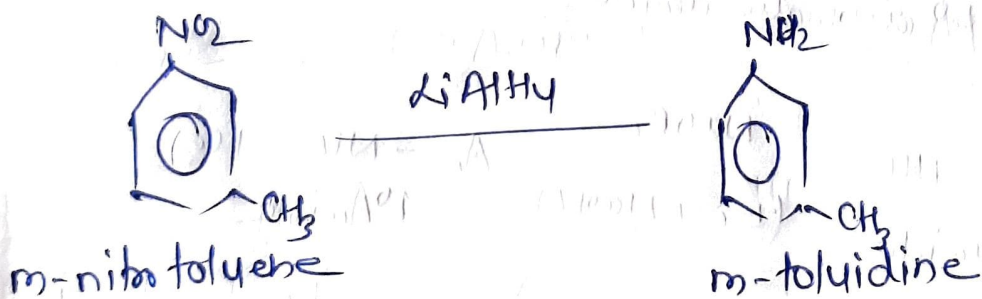
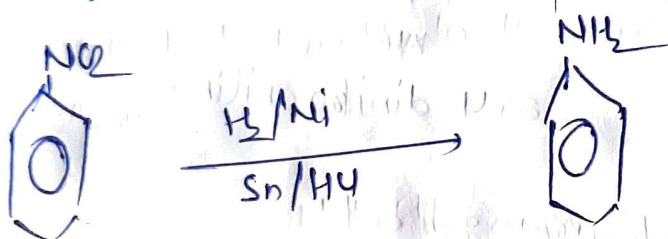


## - by Vapour-phase Reduction of Nitrobenzene

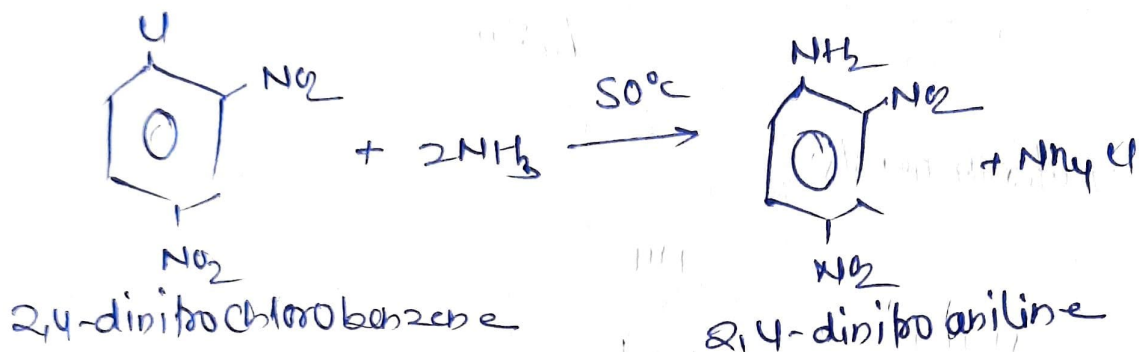
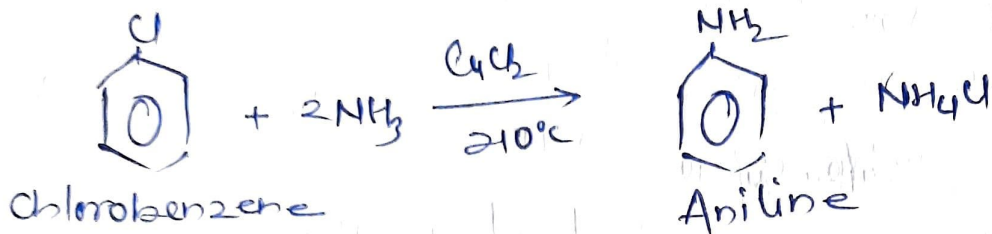
Vaporised nitrobenzene mixed with  $H_2$  is passed over a copper catalyst on silica at  $250^\circ C$



## # ① Reduction of Nitro compounds

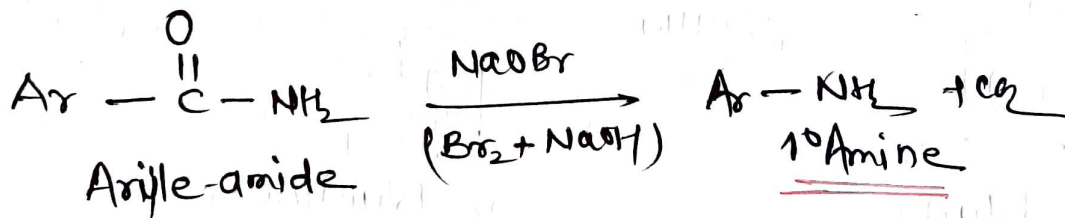


## 2. Ammonolysis of Aryl chloride

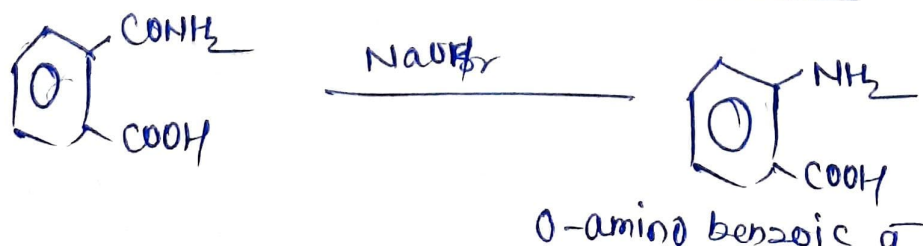
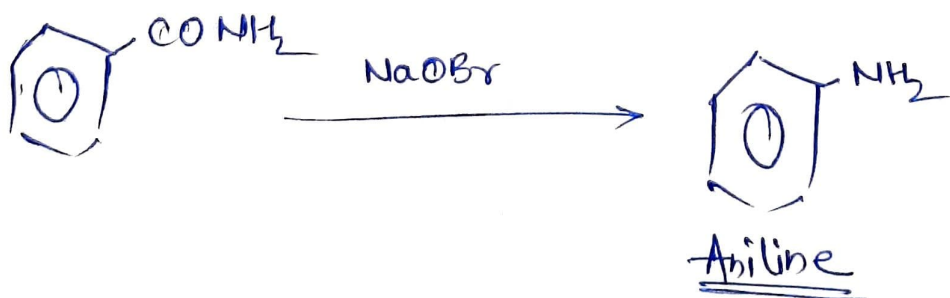
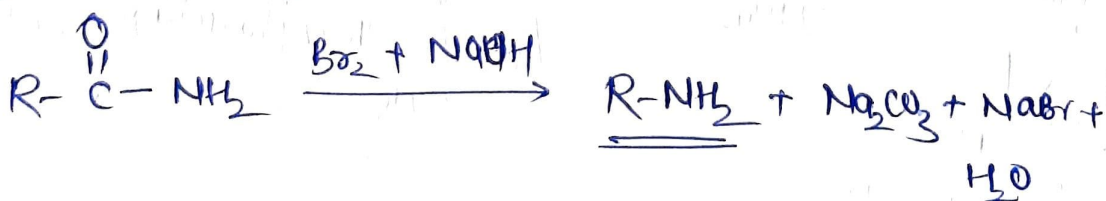


## 3. Hoffmann ~~R~~ Hofmann Rearrangement

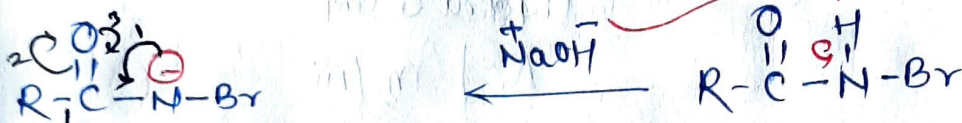
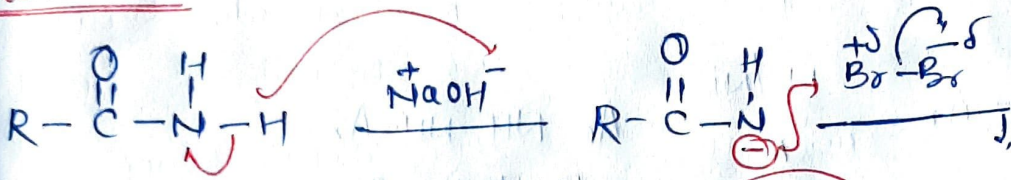
When treated with  $\text{Br}_2/\text{CH}_2$  in an alkaline solution, an aryl amide undergoes Hofmann Rearrangement to yield to a  $1^\circ$  aromatic amine.



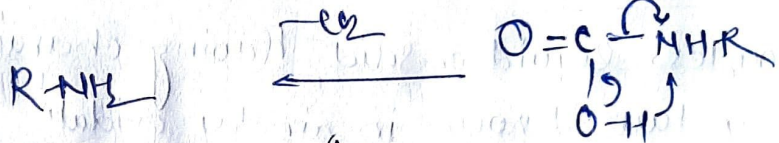
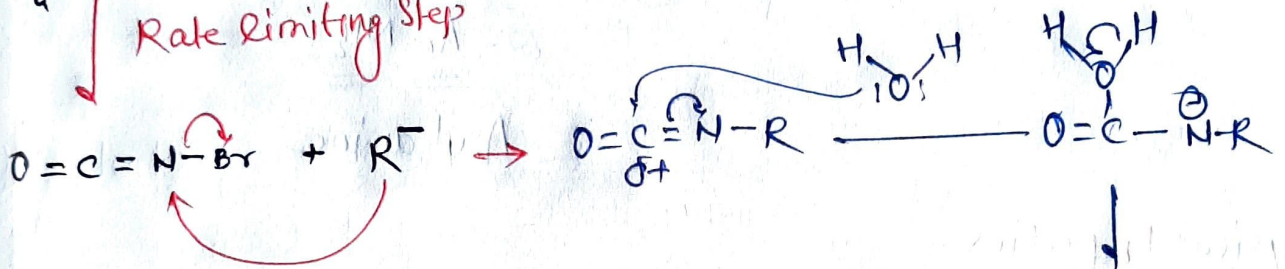
### ~~Hoffmann~~ Hofmann Bromide Degradation



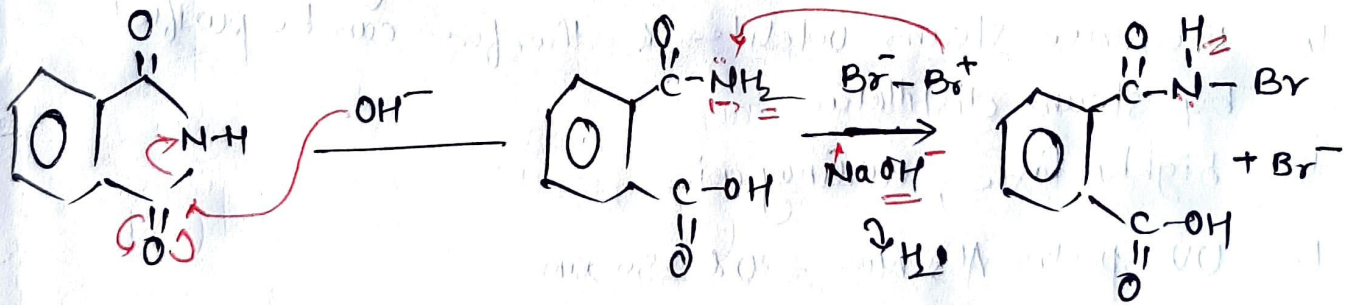
Mechanism :-



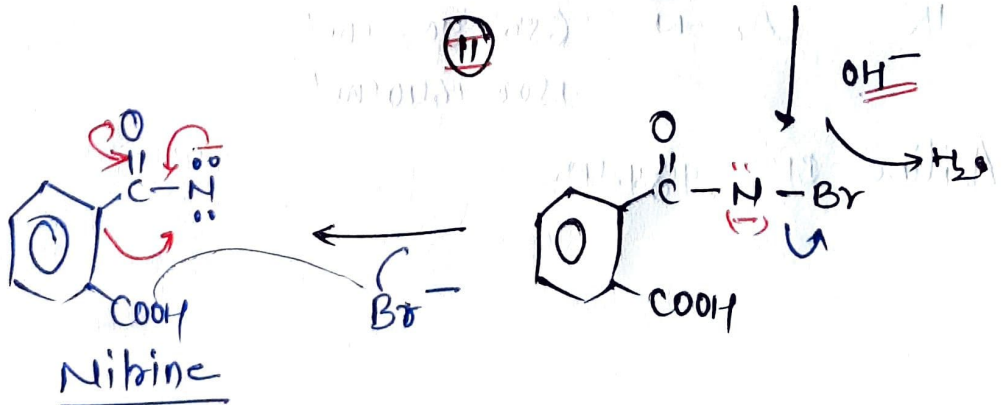
Rate limiting step



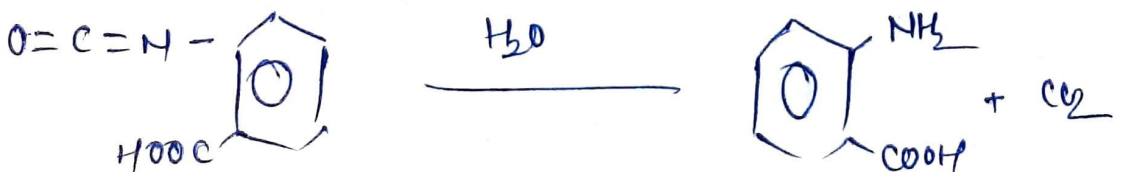
(I) step: Bromination of amide in presence of base



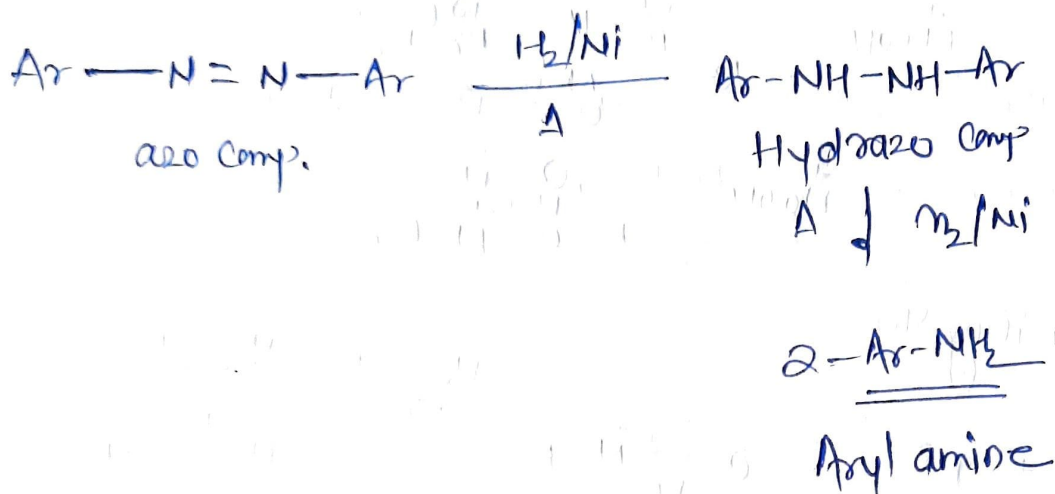
Step II



1,2, acyl shift



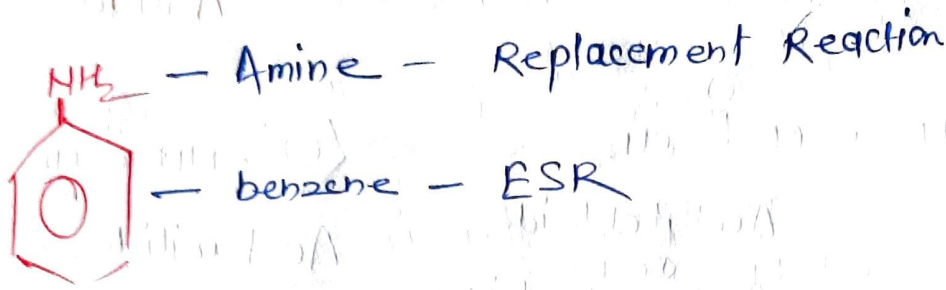
## ④ Reduction of Azo compound



### Physical Properties

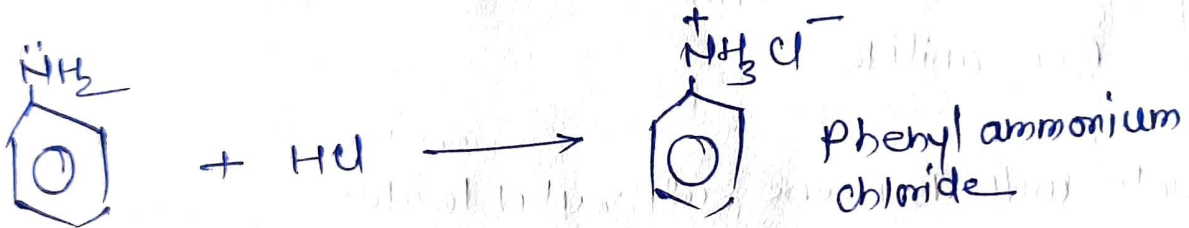
- ↳ Colourless liquid or solid, having characteristic colour, they turn brown in air by oxidation
- ↳ Sparingly soluble in water, soluble in org solvent
- ↳ They are steam volatile & therefore can be purified by steam distillation
- ↳ highly toxic, carcinogenic
- ↳ UV spectra Abs Max 230 & 280 nm
- ↳ IR = Ar-N 650-900 cm<sup>-1</sup>  
1500-1640 cm<sup>-1</sup>
- ↳ Aniline BP = 184.4°C

# CHEMICAL PROPERTIES



## A REACTION INVOLVING -NH<sub>2</sub> GROUP -

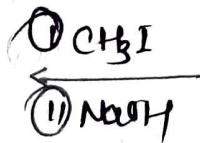
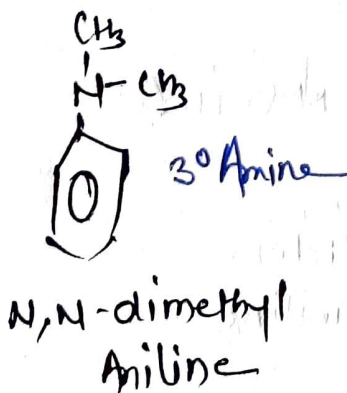
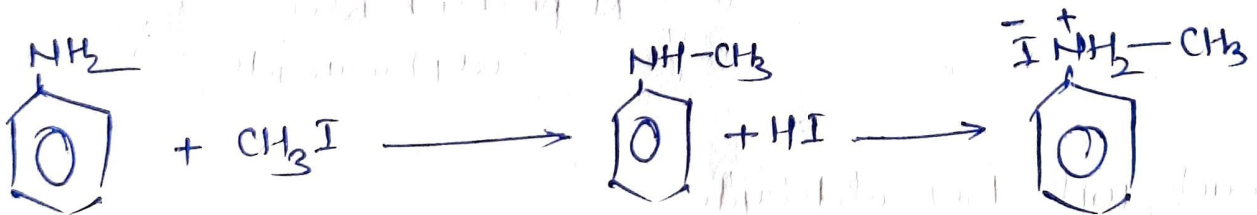
① Reaction with strong acid to form salt  
Aniline (weak base) -  $K_b = 4.2 \times 10^{-10}$



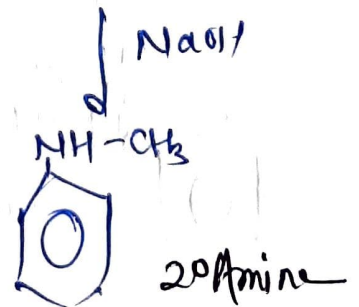
$\downarrow$  NaOH degenerate by alkali  
Aniline + NaCl + H<sub>2</sub>O

~~②~~

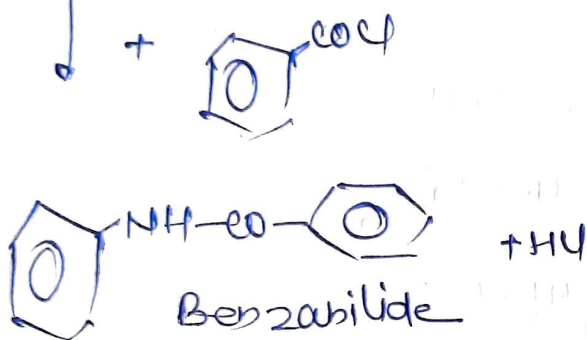
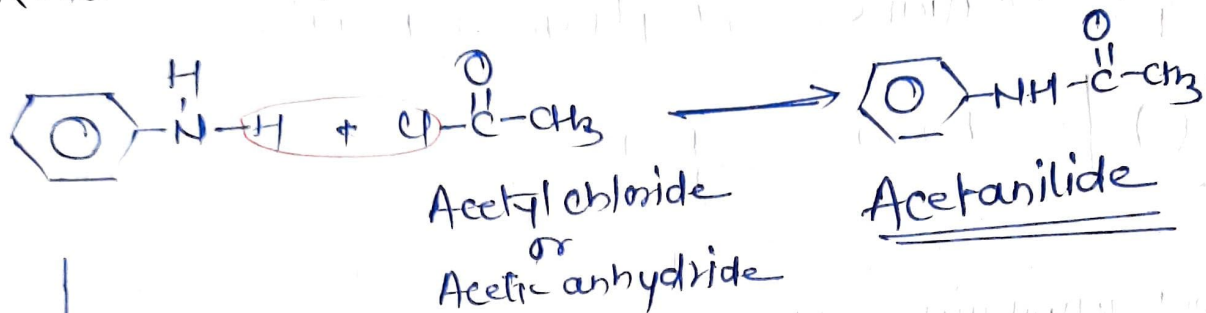
② Reacts with alkyl halide (Alkylation) - 2<sup>o</sup> Amine



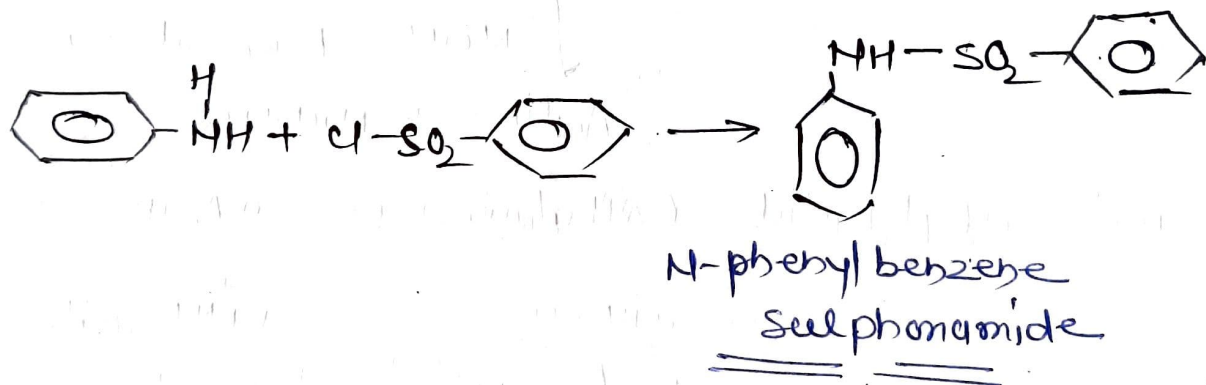
N-methyl aniline



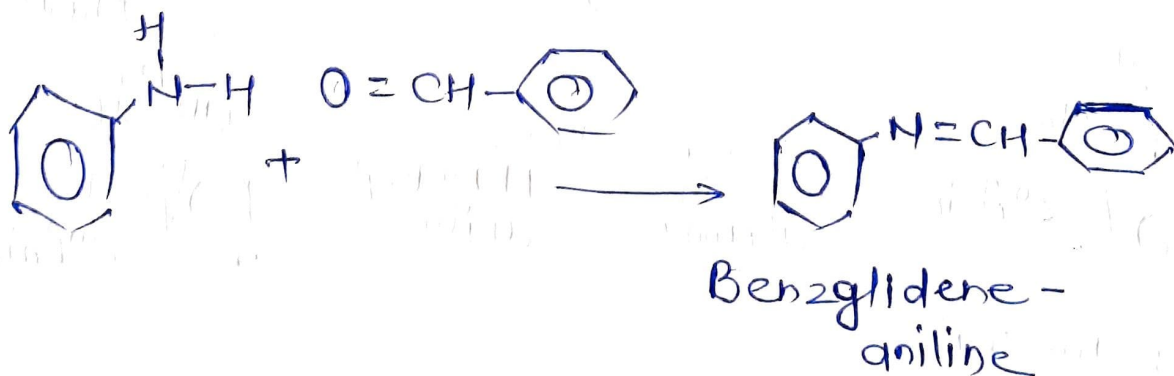
③ Reacts with Acid chloride (Acylation) → Anilides



④ Reacts with Benzene sulphonyl chloride

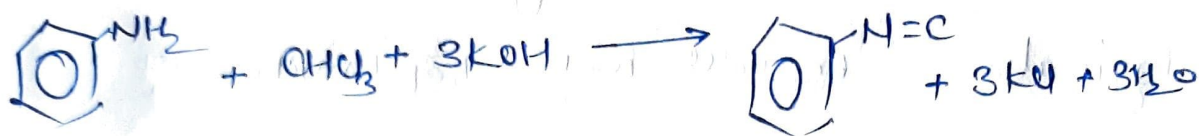


⑤ Reacts with Benzaldehyde



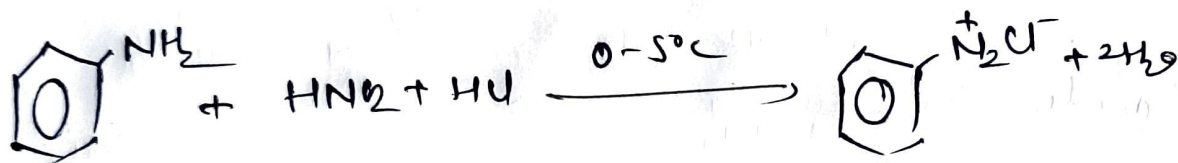


⑥ Carbylamine Reaction -



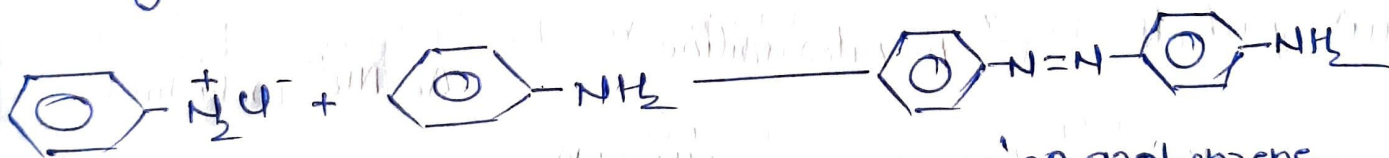
Phenyl  
isocyanide

⑦ Reaction with Nitrous Acid ( $\text{HNO}_2$ ) - ( $\text{NaNO}_2 + \text{HCl}$ )



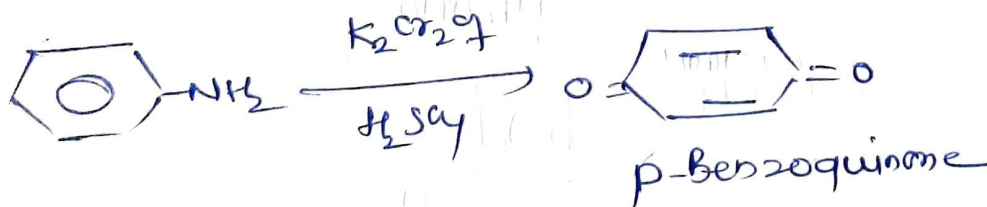
benzenium  
Benzenediazonium  
chloride

⑧ Coupling with diazonium salt



p-aminodiazobenzene

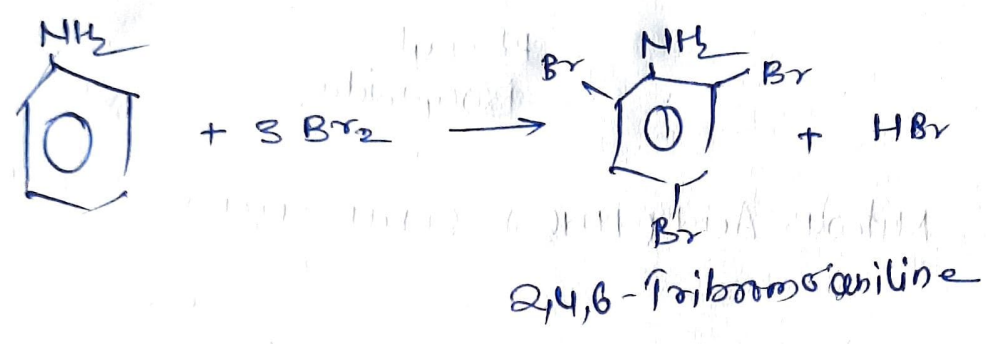
⑨ Oxidation with pot dichromate



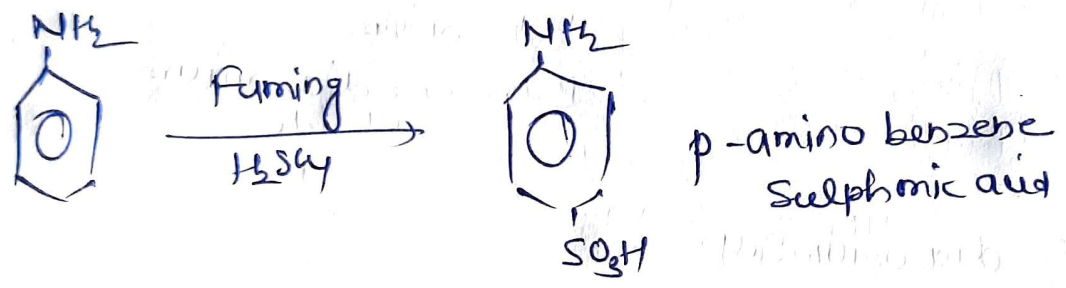
p-Benzoquinone

# Substituted Reaction of Benzene Ring

(i) Halogenation -  $Br_2$  or  $Cl_2$  water - Rapid reaction

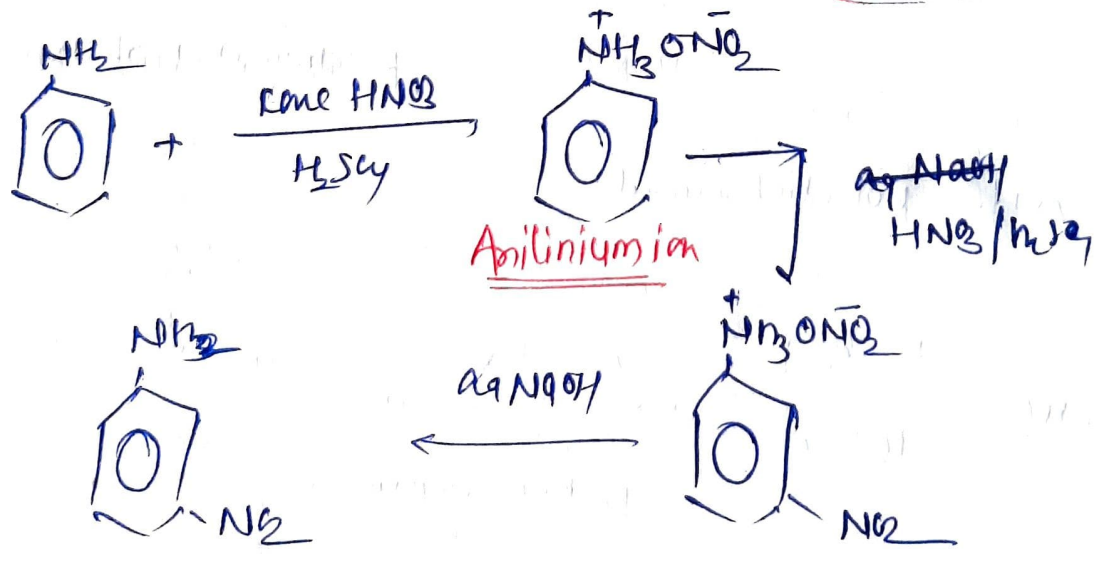


(ii) Sulphonation

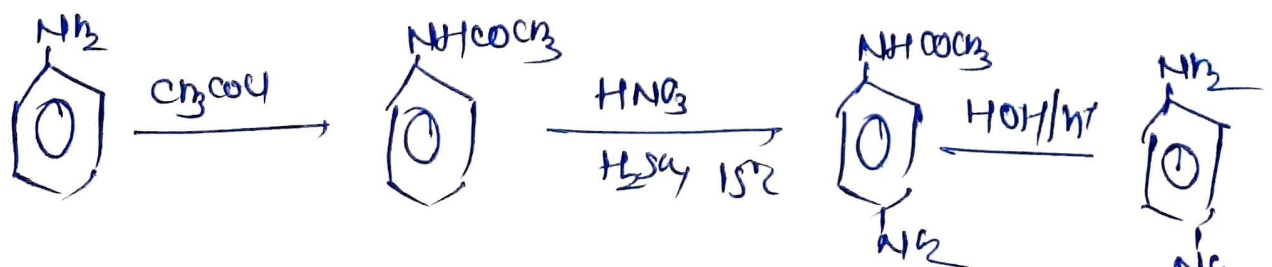


(iii) Nitration -  $m$ -nitro aniline ??

-  $Ar-NH_2^+$  - meta director



# p-nitroaniline can be obtained by first protecting  $-NH_2$  gp by acylate






## uses -

- ① preparing dye & its intermediate
- ② Antioxidant production
- ③ Rubber industries
- ④ Synthesis of self-drug
- ⑤ making of isocyanate required for polyurethane plastic used for insulators.

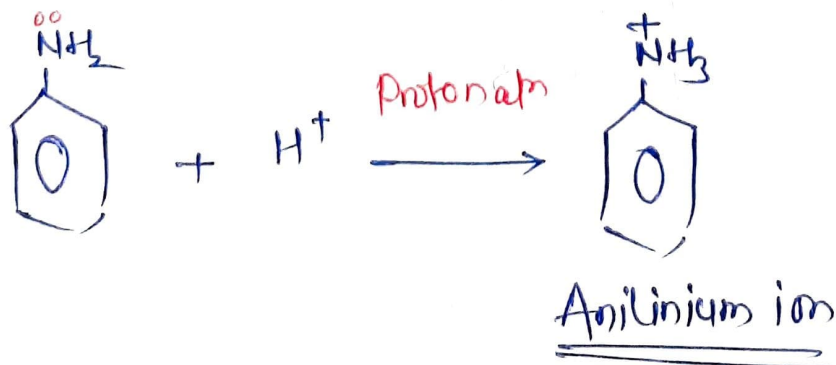
## BASICITY OF AROMATIC AMINE

# Aromatic Amines are much lesser basic than Aliphatic amine

- |   |  |   |   |
|---|--|---|---|
| ① | $\text{CH}_3\text{NH}_2$ (Methylamine)   | - | $4.4 \times 10^{-4}$  |
| ② | Aniline    | - | $4.2 \times 10^{-10}$   |
| ③ | p-toluidine<br>(e <sup>-</sup> releasing)<br>↑        | - | $4.2 \times 10^{-9}$  |
| ④ | o-nitro-aniline<br>(e <sup>-</sup> withdrawing)<br>↓  | - | <del><math>5 \times 10^{-15}</math></del> $5 \times 10^{-15}$ |



# The basicity of a compound is a measure of a compound's ability to accept a proton ( $\text{H}^+$ ). - "Proton Accepting capability"



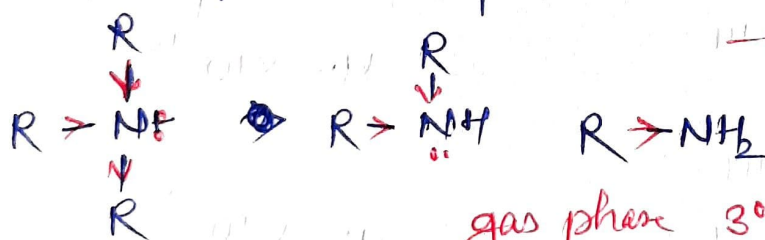
# In the Aliphatic amines ( $R-NH_2$ ), non bonding  $e^-$  pairs of N atom is localized & is fully available for co-ordination with a proton, So they easily accept the  $H^+$ . ~~Thus~~ basic

Otherhand, in Aromatic amine, non bonding  $e^-$  pair is delocalized into the benzene ring by resonance the basicity of aromatic amine is lesser than Aliphatic Amines

Aliphatic Amine

Aliphatic amine  $\rightarrow$  Aromatic Amine

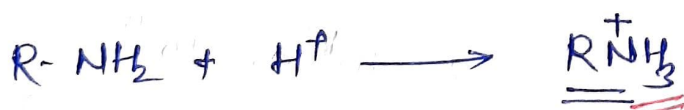
(a) +I effect -  $\uparrow$  basicity of Amine  
 $\uparrow$   $e^-$  density



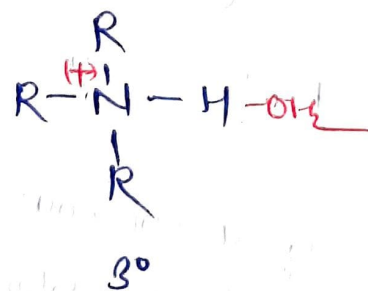
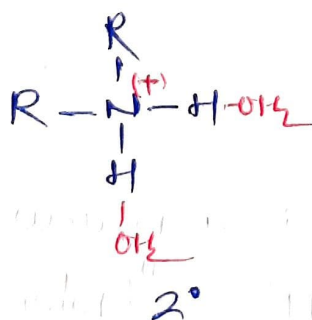
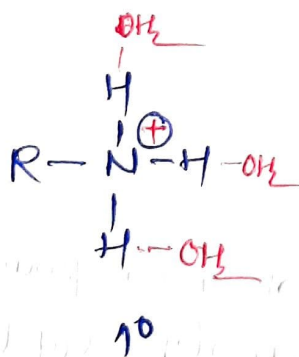
- gas phase  
 - liq phase  
 - aq. phase

gas phase  $3^\circ > 2^\circ > 1^\circ$

(b) Solvation (aq. media)



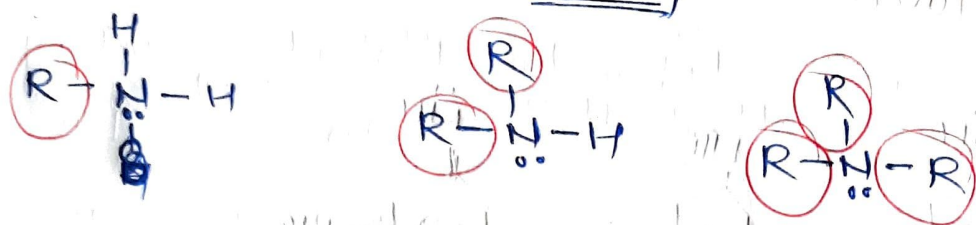
Stability -  $\uparrow$  base



Stability =  $1^\circ > 2^\circ > 3^\circ$

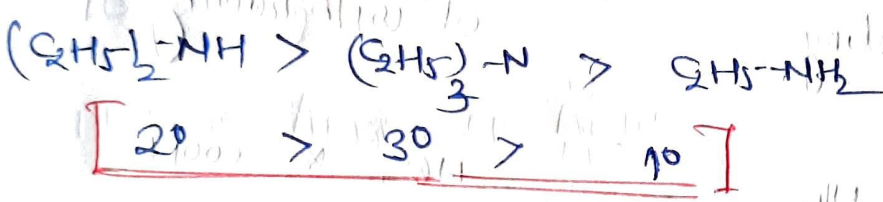
Basicity =  $1^\circ > 2^\circ > 3^\circ$

steric hindrance =  $\downarrow$  Basicity



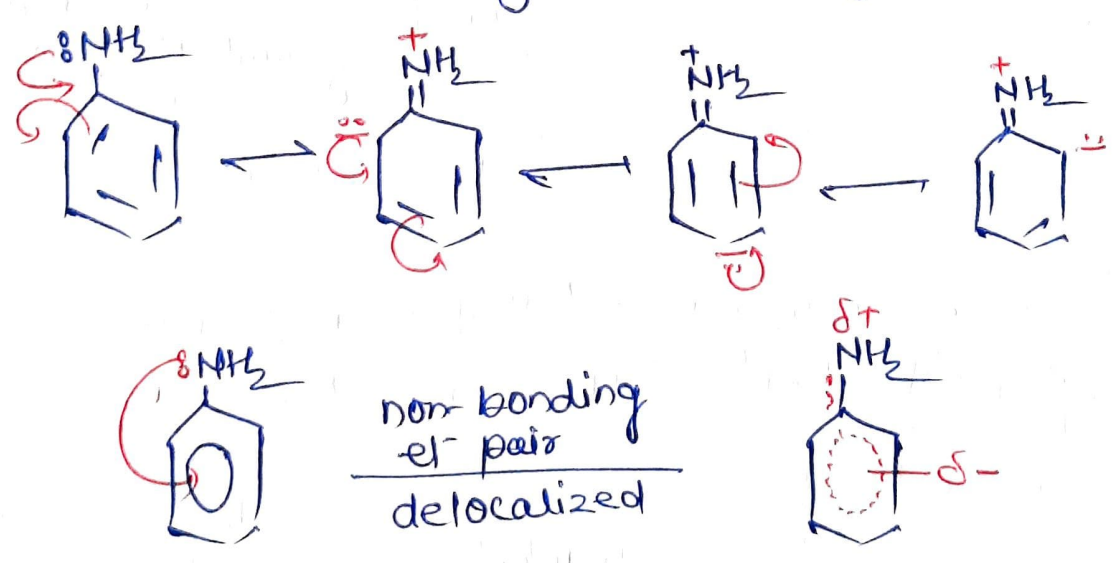
steric hindrance =  $1^\circ > 2^\circ > 3^\circ$

R =  $(C_2H_5)$



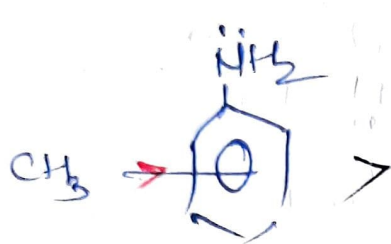
## AROMATIC Amine

Basicity of Aromatic amine is lesser than aliphatic amine because non bonding  $e^-$  at  $-NH_2$  group delocalized into benzene ring by resonance thus  $e^-$  cloud is decrease at  $-NH_2$  gp and decreasing the  $H^+$  accepting capability.



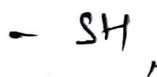
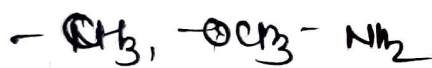
$\rightarrow$  At  $NH_2$  group -  $\downarrow e^-$  density  
 $\downarrow$  availability for protonation  
 $\downarrow H^+$  accepting capability  
 $\downarrow$  Basicity

# Effects of Substituents

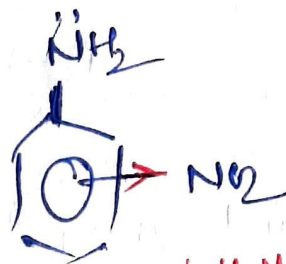


↑ e<sup>-</sup> availability  
for protonation

electron donating  
group

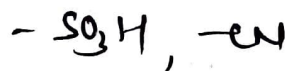
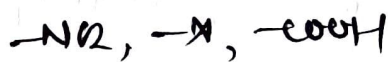


↑ Basicity



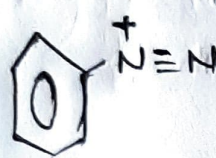
↓ e<sup>-</sup> availability  
for protonation

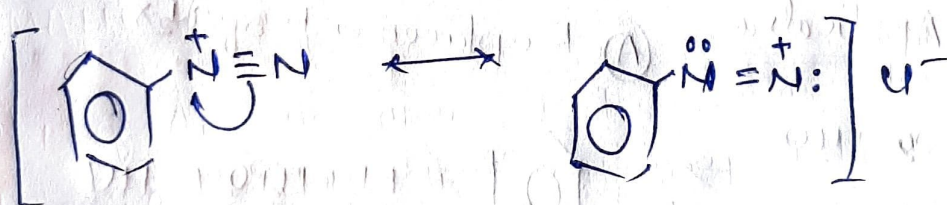
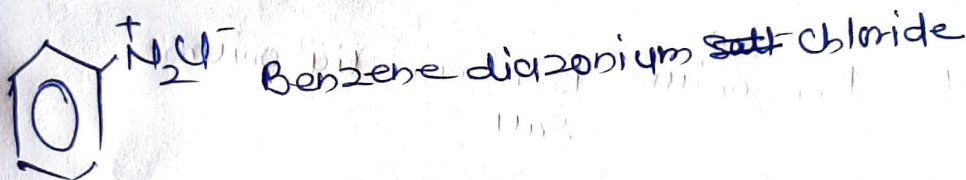
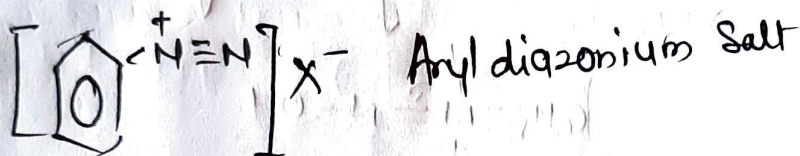
e<sup>-</sup> withdrawing gp



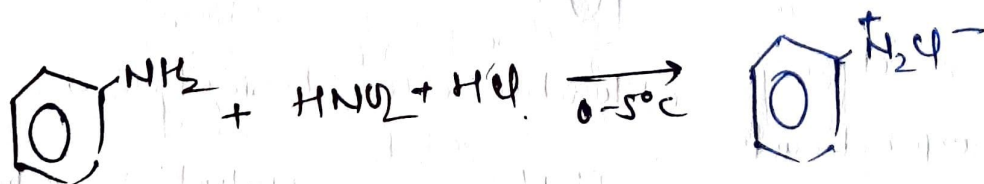
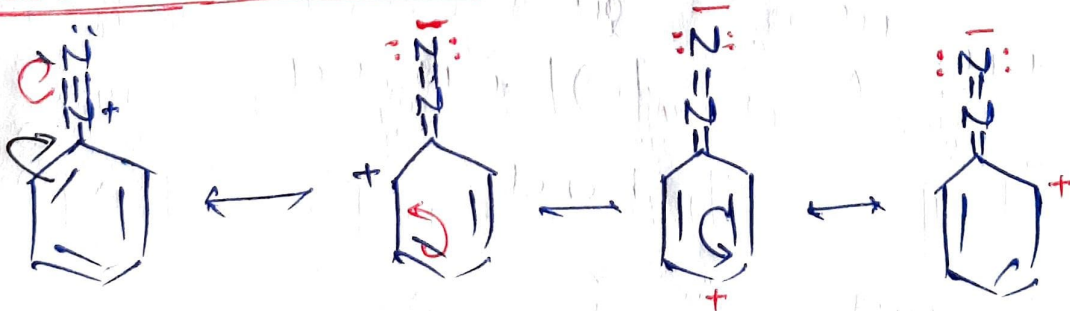
↓ Basicity

# ARYL DIAZONIUM SALTS

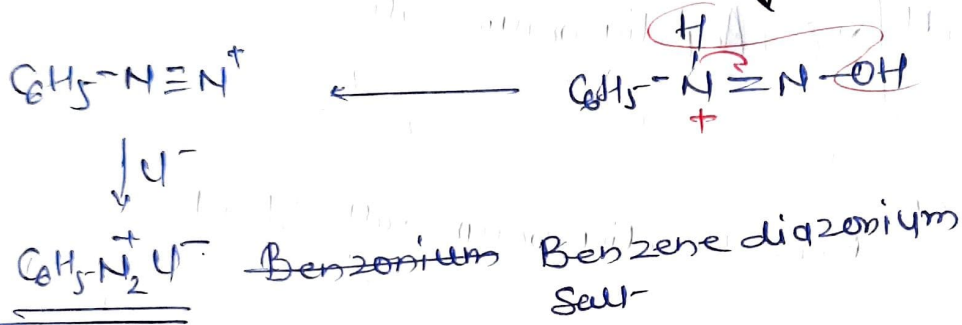
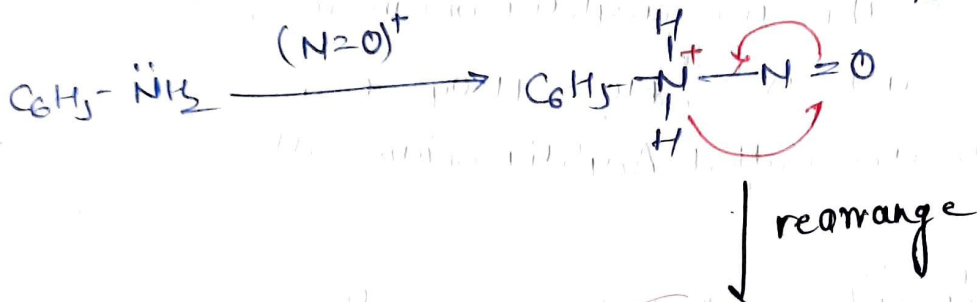
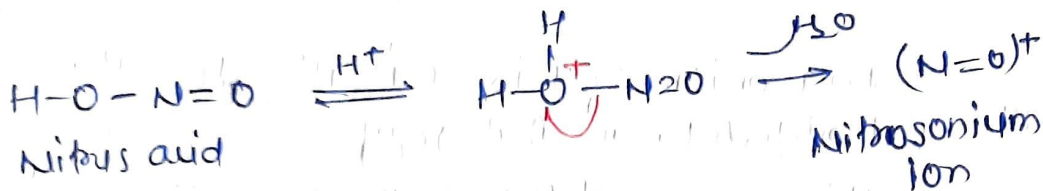
 → Diazonium salt ion ( $\text{N}^+ \equiv \text{N}^-$ ) directly bonded to an aryl group  
→ This the aryl diazonium ion, forms salt with anion such as  $\text{X}^-$ ,  $\text{NO}_2^-$ ,  $\text{HSO}_4^-$ ,  $\text{BF}_4^-$   
→ These salts are called Aryl diazonium salt



## Resonance Structure

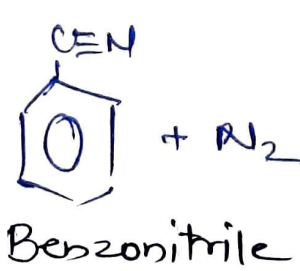
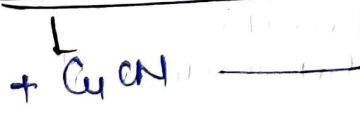
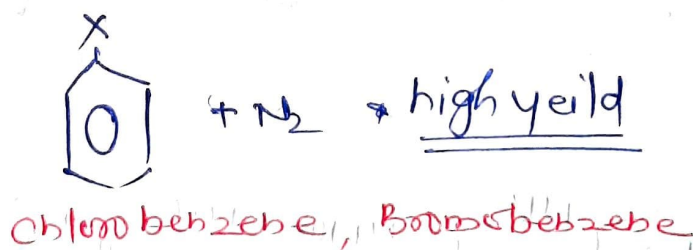
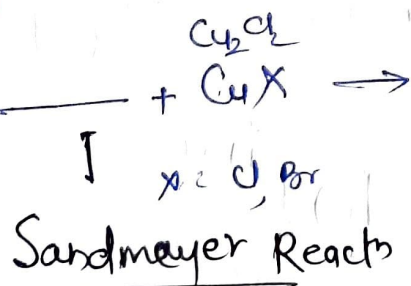
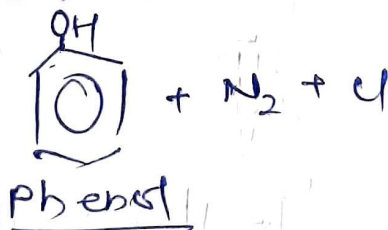
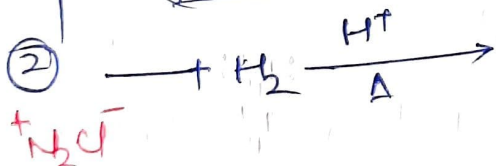
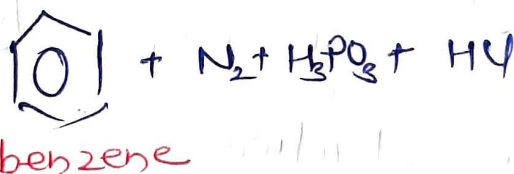
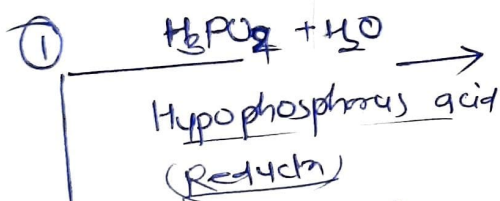


Benzene diazonium salt



### Synthetic Application

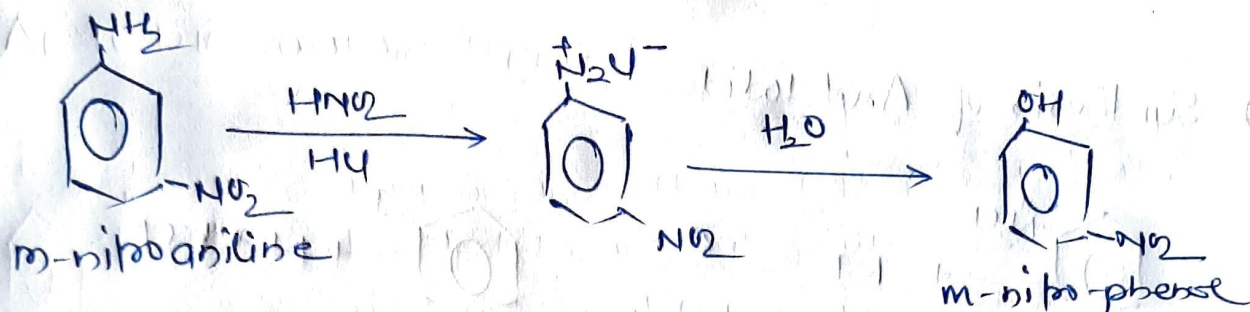
#### (A) Replacement of $\text{N}_2^+$



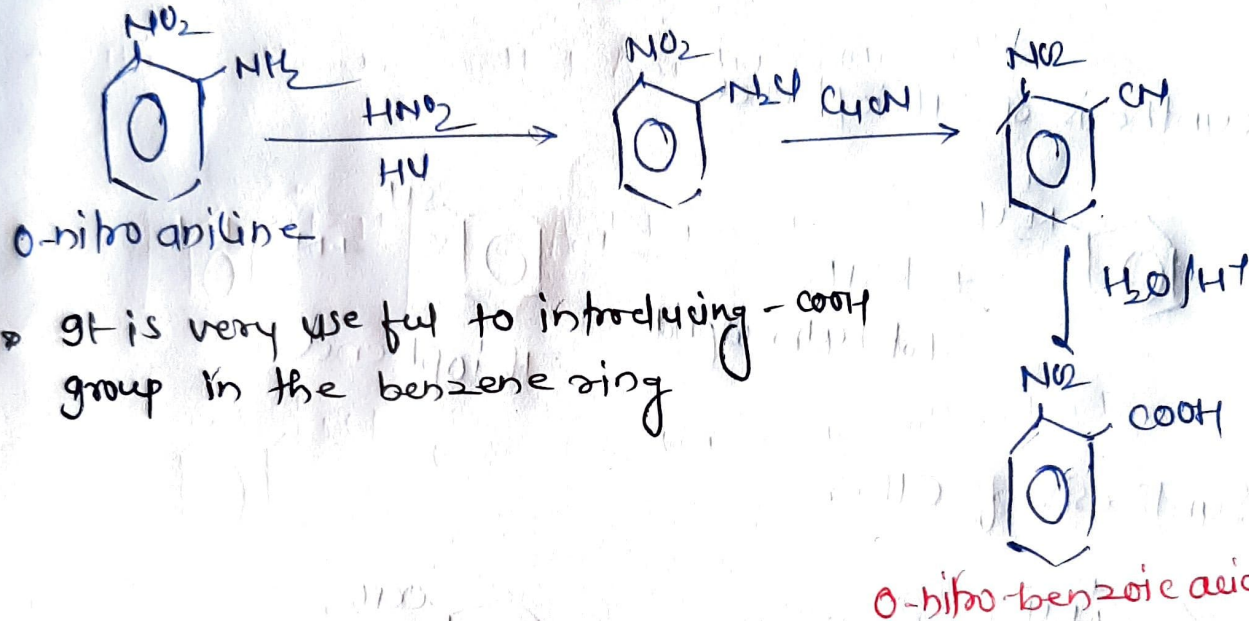
\* product of Sandmeyer Reactn is more



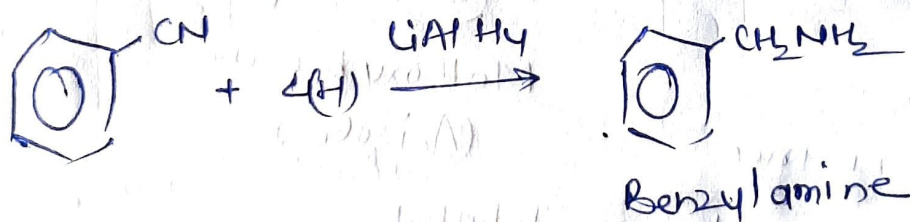




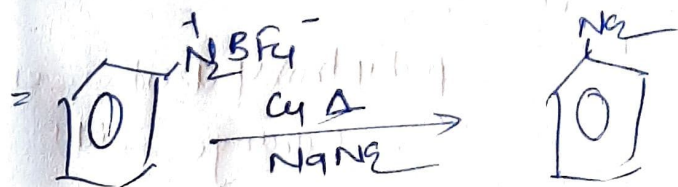
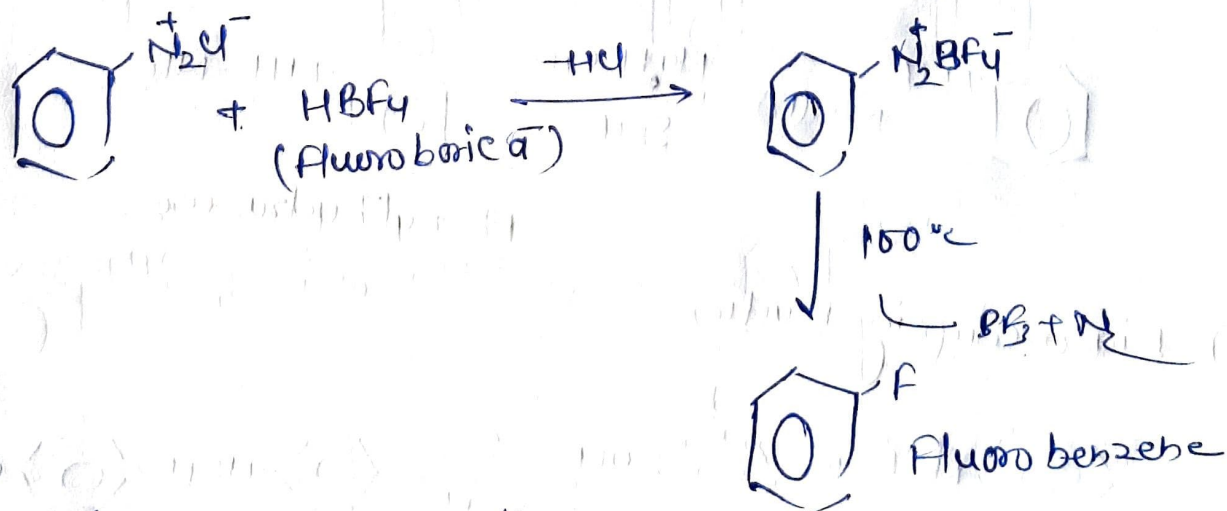
• Useful reaction for preparing of m-substituted phenol



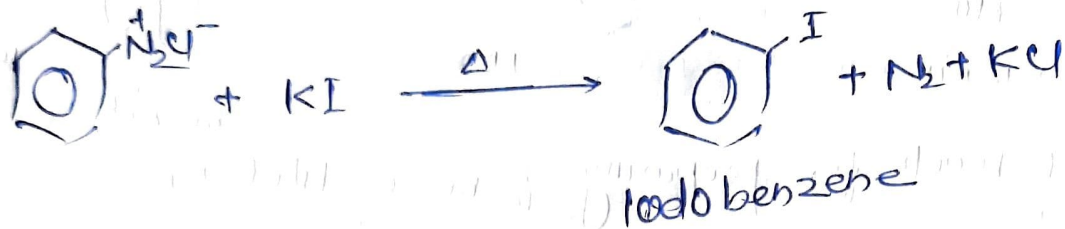
• It is very useful to introducing -COOH group in the benzene ring



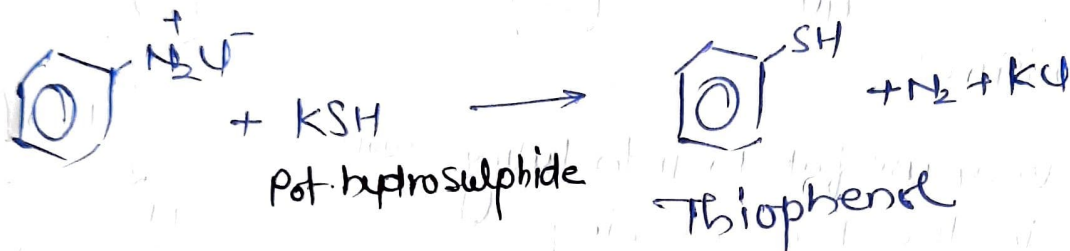
#### ④ Synthesis of Aryl Fluoride (Schiemann Reaction)



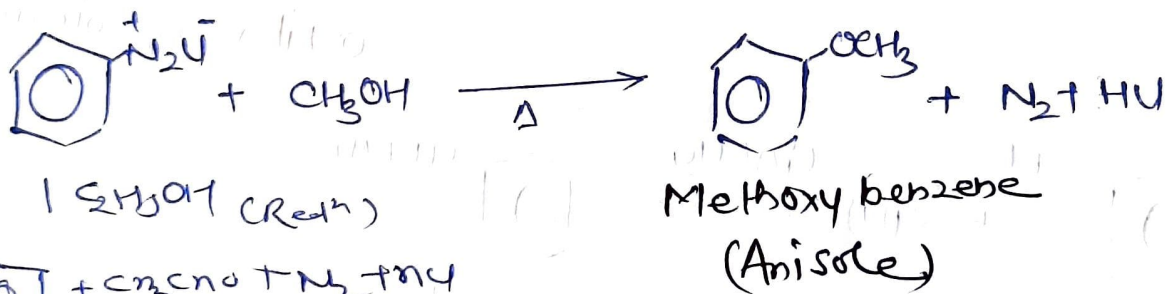
⑤ Synthesis of Aryl iodide



⑥ Synthesis of Thiophenol

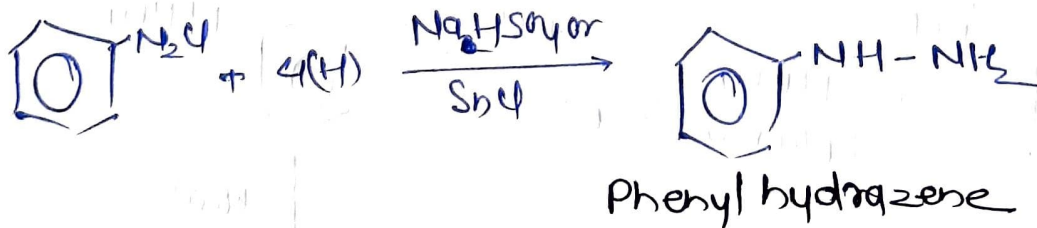


⑦ Synthesis of Ether

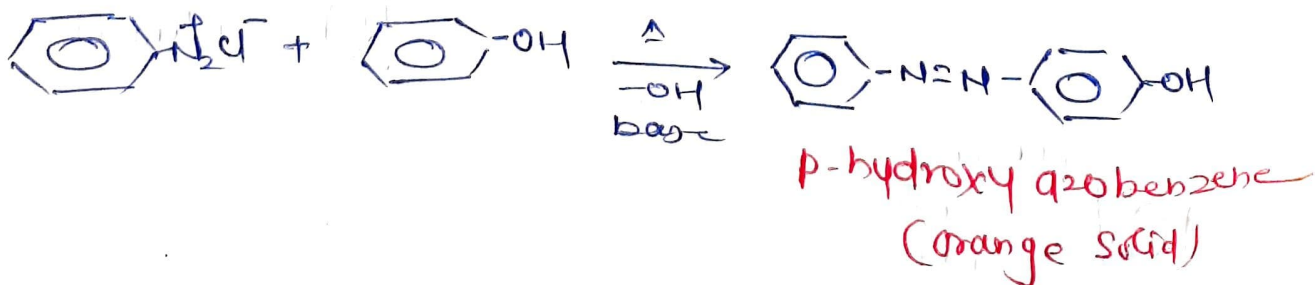


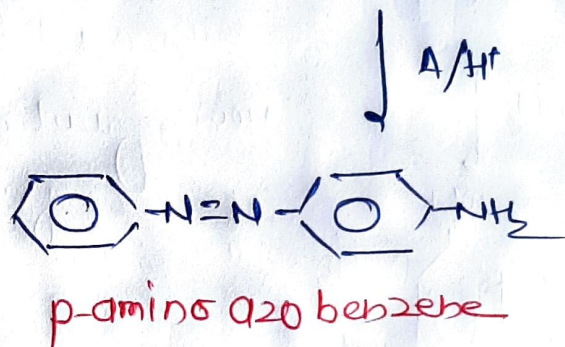
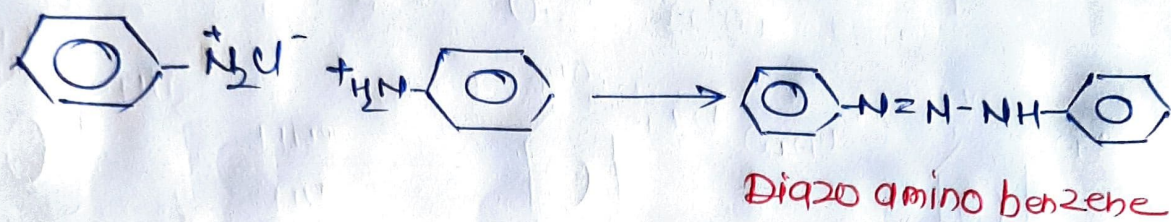
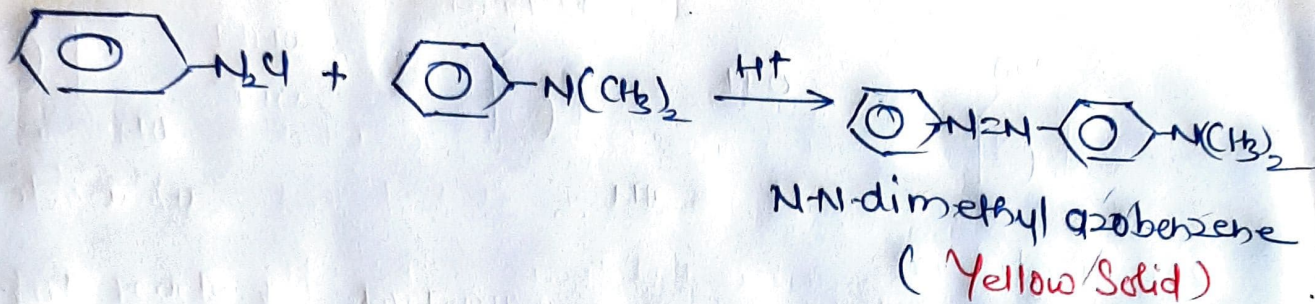
⑧ Reaction in which N atom are retained

⑧ Reduction to Arylhydrazine with Sod. bisulphide



⑨ Diazo-coupling reaction





### PHYSICAL PROPERTIES -

- ① Colourless, crystal solids which turn brown on exposure to air.
- ② Soluble in water, sparingly soluble in ethanol, glacial acetic acid & insoluble in ether.