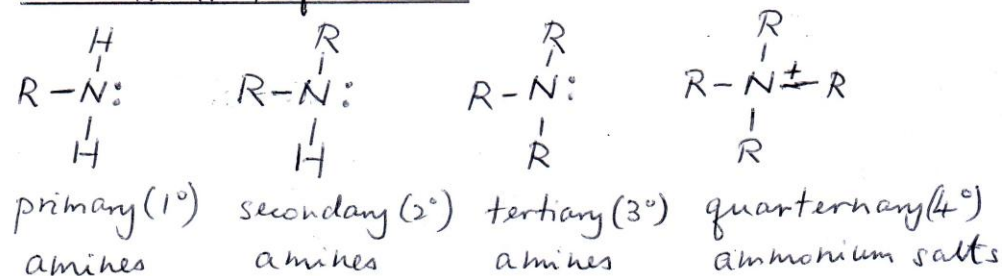


Organic Nitrogen Compounds(A2)

Amines

- amines are near relatives of ammonia, NH_3 .
- In amines, the hydrogen atoms in the ammonia have been replaced one at a time by hydrocarbon groups.

Classification of amines



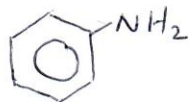
Primary amines - e.g.s

$\text{CH}_3\text{CH}_2\text{NH}_2$ ethylamine or aminoethane

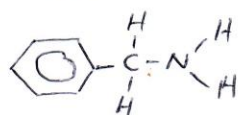
CH_3NH_2 methylamine or aminomethane

$\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ 1-aminopropane

$\begin{array}{c} \text{NH}_2 \\ | \\ \text{CH}_3\text{CHCH}_3 \end{array}$ 2-aminopropane

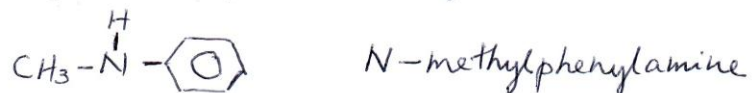


phenylamine or aminobenzene.
(aromatic amine)



(phenylmethyl)amine

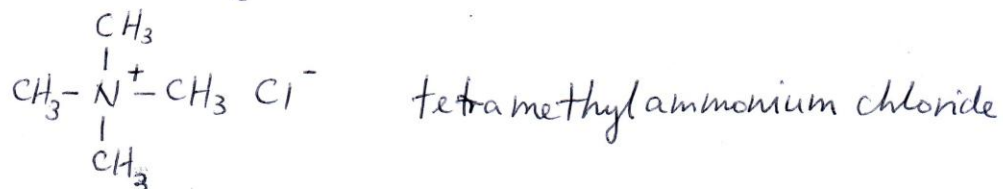
Secondary amines - e.g.s.



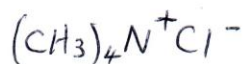
Tertiary amines - e.g.s



Quarternary ammonium salts - e.g.s



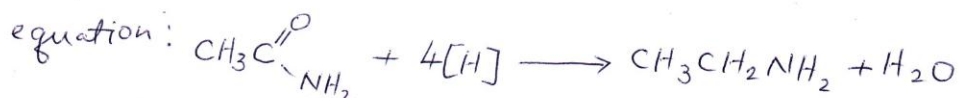
or



- quarternary ammonium salts are the organic equivalent of ammonium compounds.

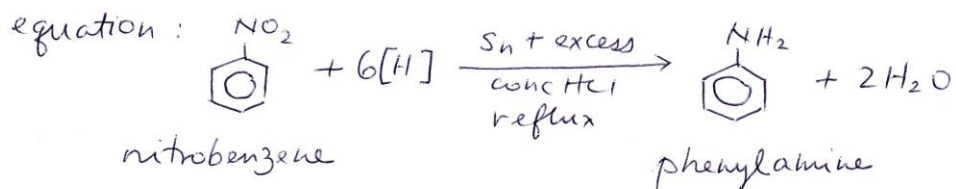
Reduction of amides

reagent & condition: LiAlH_4 in dry ether, reflux



Formation of phenylamine (by reduction of nitrobenzene)

reagent & condition: tin + conc. HCl & reflux.



note: LiAlH_4 can also be used as reducing agent in laboratory.

Basicity of amines

The lone pair on nitrogen makes amines basic.



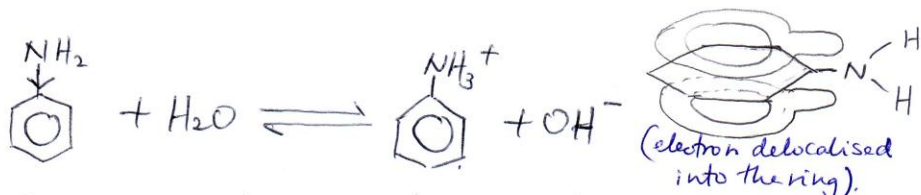
The basicity of amines depends on the availability of the lone pair and thus its ability to pick up protons

The greater the electron density on the N atom, the better its ability to pick up protons.

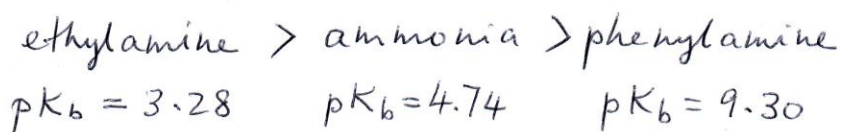
This is affected by the groups attached to the nitrogen atom.

Relative basicity of ammonia, ethylamine and phenylamine

- The strength of an amine depends on:
 1. availability of the lone pair on N to accept a proton
 2. the stability of its conjugate acid.
- electron withdrawing substituents lower the electron density on N, thus decrease the basicity of the amine.



- phenylamine is a weaker base than ammonia
- electron donating substituents increase the electron density on N, thus increase the basicity of the amine.
- $\text{CH}_3\text{CH}_2\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{CH}_2\text{NH}_3^+ + \text{OH}^-$
 $\text{H}-\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$
- ethylamine is a stronger base than ammonia
- order of base strength:



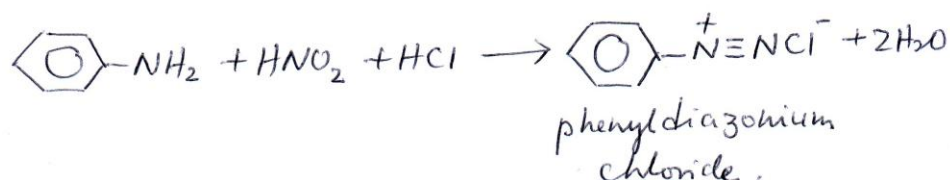
Reactions of Phenylamine

1. Formation of Diazonium Salt (diazotisation rxn)

Reactants = HNO_2 in situ ($\text{NaNO}_2 + \text{HCl}$)

Condition = 5°C

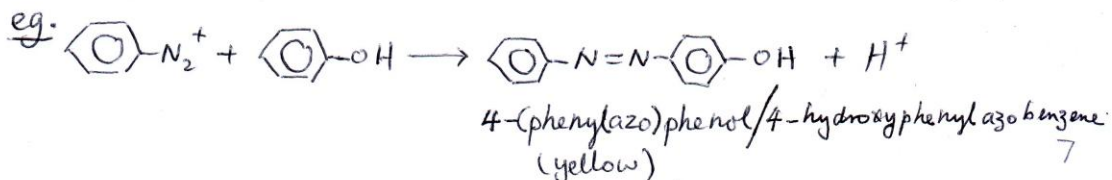
Product = diazonium salt



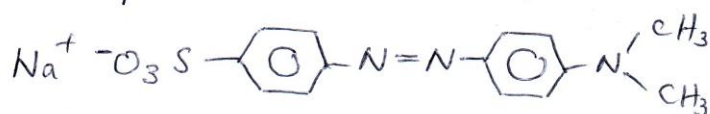
- nitrous acid (HNO_2) is unstable and is produced in situ by reacting sodium nitrite with dilute HCl .
- the diazonium salt is unstable and will decompose readily at higher temperatures and giving off nitrogen gas. So the reaction mixture must be kept below 10°C .
- at low temperatures, the delocalisation of the diazonium ion π bond electron over a benzene ring stabilises phenyldiazonium.

Coupling Reactions

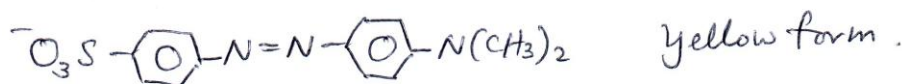
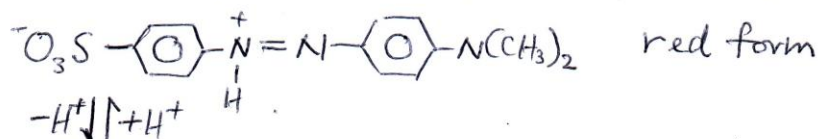
- the phenyldiazonium ion behaves as an electrophile and will attack phenols or aromatic amines in alkaline conditions.
- electrophilic substitution takes place at the 4 position.
- The reaction is known as coupling reaction.



- The compound formed is energetically stable.
Azo dye ($-N=N-$ azo group)
- the extensive delocalisation of the electrons via the nitrogen-nitrogen double bonds makes the compound stable.
- These dyes are diazonium dyes. They are very stable and do not fade. (important characteristics of a good dye)
- Example: methyl orange



- methyl orange is an azo dye which changes colour depend on the pH (concentration of H^+)



- when add acid to methyl orange, hydrogen ion attaches to methyl orange to give red form
- when add alkali to methyl orange, hydrogen ions are removed from methyl orange to give yellow form
- At end-point, there are equal amounts of the red and yellow forms, so methyl orange looks orange

2. Reaction of Phenylamine with Br₂(aq)

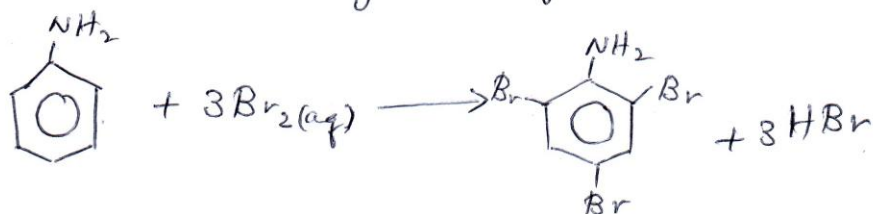
Reagents : Br₂(aq)

Condition : room temperature

product : 2,4,6-tribromophenylamine

Observation : reddish brown bromine solution decolourised

White ppt (2,4,6-tribromophenylamine) formed
steamy fumes of HBr.



- -NH₂ is ring activating group and has a 2,4-directing effect.
- this is because nitrogen's lone pair gets drawn into the delocalised ring of electrons. Enhanced delocalised electron cloud makes the benzene ring more attractive to electrophilic attack.
- Therefore bromination of phenylamine happens at less demanding conditions - room temperature.