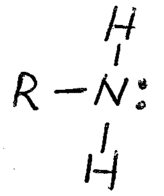
Organic Nitrogen Compounds (A2)

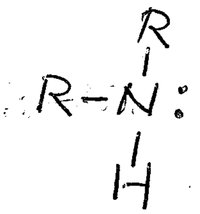
Amines

- 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.

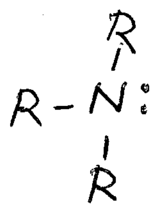
Classification of amines


$R-NH_2$

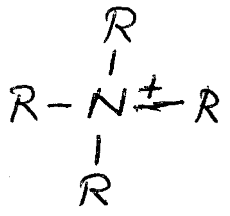
primary (1°) amines


R_2NH

secondary (2°) amines


R_3N

tertiary (3°) amines


R_4N^+

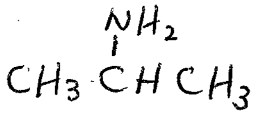
quarternary (4°) ammonium salts

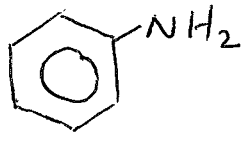
Primary amines – e.g.s

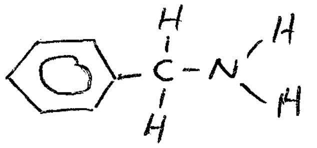
$CH_3CH_2NH_2$ ethylamine or aminoethane

CH_3NH_2 methylamine or aminomethane

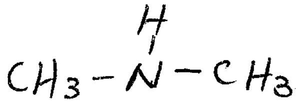
$CH_3CH_2CH_2NH_2$ 1-aminopropane


$CH_3CH(NH_2)CH_3$ 2-aminopropane

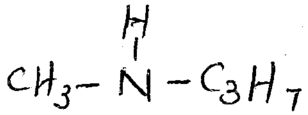

phenylamine or aminobenzene.
(aromatic amine)


(phenylmethyl)amine

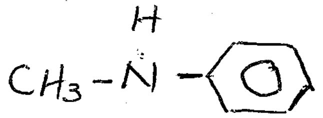
Secondary amines – e.g.s



$CH_3-NH-CH_3$ dimethylamine

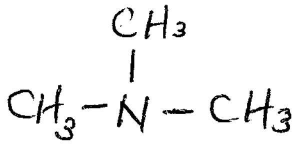


$CH_3-NH-C_3H_7$ methylpropylamine



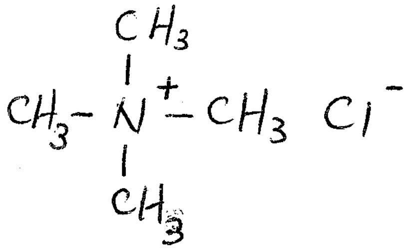
$CH_3-NH-C_6H_5$ N–methylphenylamine

Tertiary amines – e.g.s



$(CH_3)_3N$ trimethylamine

Quarternary ammonium salts – e.g.s



$(CH_3)_4N^+\ Cl^-$ tetramethylammonium chloride

or

$(CH_3)_4N^+Cl^-$

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

Formation of ethylamine

1. Reduction of nitrile

2. Substitution reactions of bromoethane with ammonia

Reduction of Nitrile

lithium tetrahydridoaluminate(III)
(litium aluminium hydride).

Reagent & condition : $LiAlH_4$ in dry ether or
pass H_2 over Ni at 140°C or
sodium + ethanol

$$CH_3CN + 4[H] \longrightarrow CH_3CH_2NH_2$$

Substitution reactions of bromoethane with ammonia

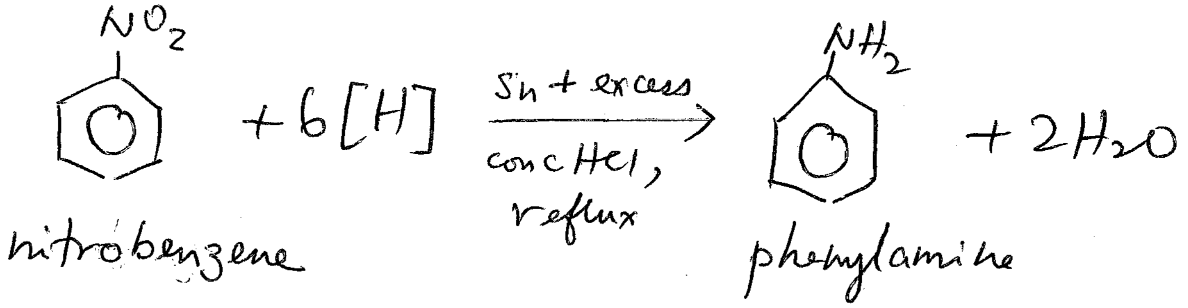
Reagent & condition : excess $NH_{3(aq)}$ + alcohol,
reflux with pressure or
conc. NH_3, heat and pressure

$$CH_3CH_2Br + 2NH_3 \longrightarrow C_2H_5NH_2 + NH_4Br$$

XS NH_3 so that the chances are always greatest that a bromoethane molecule will hit an ammonia molecule rather than one of the amines being formed. That will help to reduce the formation of second (etc) amines through further substitution reaction.

Formation of phenylamine - by reduction of nitrobenzene

Reagent & Condition: tin + conc. HCl & reflux



- $LiAlH_4$ can also be used as reducing agent in laboratory.

Basicity of Amines

- The lone pair on nitrogen makes amines basic.

$$R\ddot{N}H_2 + H^+ \rightleftharpoons RNH_3^+$$

- 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, the better its ability to pick up protons.
- this is affected by the groups attached to the nitrogen.

Reactions of amines as base

1. Amines in water

$$CH_3CH_2NH_2 + H_2O \rightleftharpoons CH_3CH_2NH_3^+ + OH^-$$

ethylamine — ethylammonium ion

2. Amines dissolves in acids, forming salts

$$CH_3CH_2NH_2 + HCl \longrightarrow CH_3CH_2NH_3^+Cl^-$$

ethylamine — ethylammonium chloride

3. Quarternary ammonium sats + alkali to liberate free amines

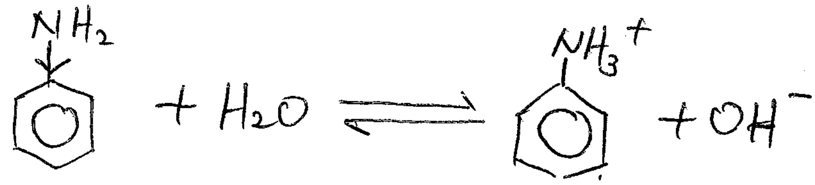
$$CH_3CH_2NH_3^+ + OH^- \longrightarrow CH_3CH_2NH_2 + H_2O$$

ethylammonium ion — ethylamine

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.

- $$\underset{\underset{H}{|}}{N}H_2 + H_2O \rightleftharpoons NH_4^+ + OH^-$$



(electron delocalised into the ring).

- phenylamine is a weaker base than ammonia
- **electron donating** substituents increase the electron density on N, thus increase the basicity of the amine.
- $CH_3CH_2 \rightarrow NH_2 + H_2O \rightleftharpoons CH_3CH_2NH_3^+ + OH^-$

  $H-NH_2 + H_2O \rightleftharpoons NH_4^+ + OH^-$
- ethylamine is a stronger base than ammonia
- order of base strength:

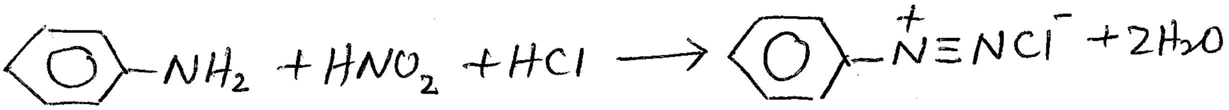
  ethylamine > ammonia > phenylamine

  $pK_b = 3.28$ $pK_b = 4.74$ $pK_b = 9.30$

Reactions of Phenylamine

1. Formation of Diazonium Salt. (diazotisation rxn)

Reactants : HNO_2 in situ ($NaNO_2 + HCl$)
Condition : 5°C
Product : diazonium salt



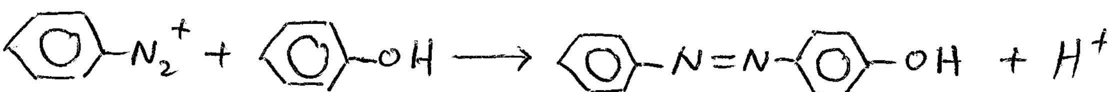
phenyldiazonium
chloride.

- 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.

eg.

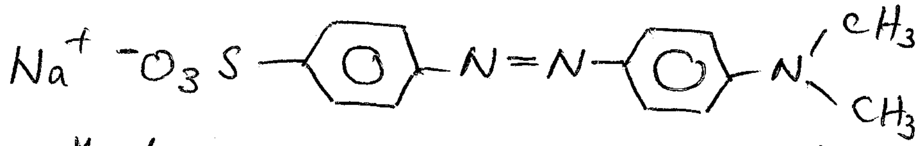


4-(phenylazo)phenol/4-hydroxyphenylazobenzen
(yellow)

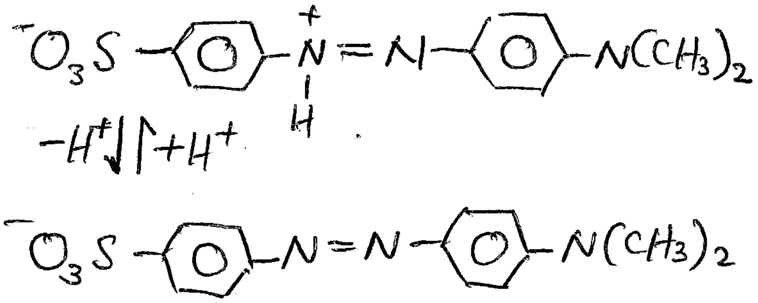
- The compound formed is energetically stable.

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 <u>stable</u> and <u>do not fade</u>. (important characteristics of a good dye)
- Example : <u>methyl orange</u>



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



red form

yellow form.

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

2. Reaction of Phenylamine with $Br_{2(aq)}$

Reagnts : $Br_{2(aq)}$

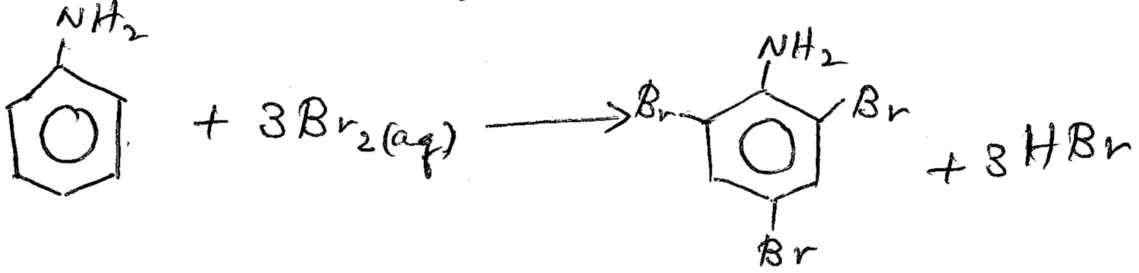
Condition : room temperature

product : 2,4,6-tribromophenylamine

observation : reddish brown bromine solution decolourised

White ppt (2,4,6-tribromophenylamine) formed

steamy fumes of HBr.



- $-NH_2$ is ring activating group and has a <u>2,4- directing</u> effect.
- this is because nitrogen's lone pair gets drawn into the delocalised ring of electrons. Enhanced delocalised electron clound makes the benzene ring more attractive to electrophilic attack.
- Therefore bromination of phenylamine happens at less demanding condition – room temperature.