ORGANIC MICROANALYSIS

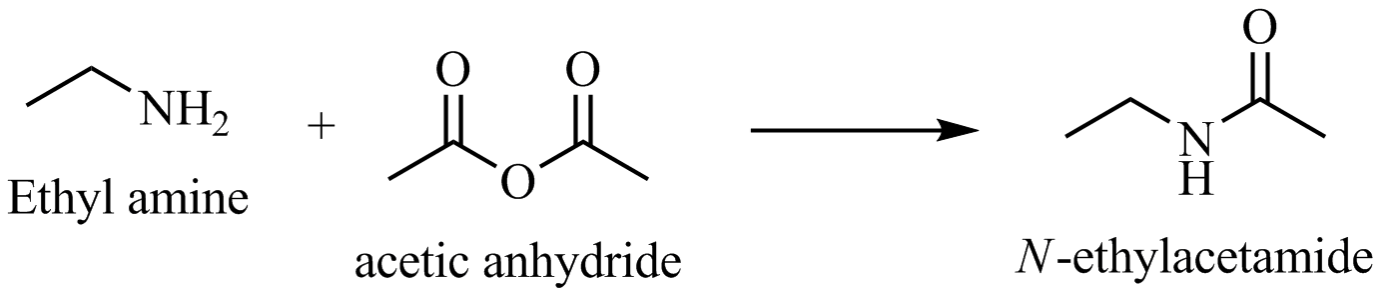
Amino compounds

Amino compounds

- Amino compounds can be determined by:
- Titration (aqueous and non-aqueous).
- Aliphatic amines are alkaline compounds which can be titrated(in aqueous medium) against standard acids (dissociation constant (K)= (10^{-6} to -10^{-3}).
- Aromatic amines are week alkaline compounds which can be successfully titrated(in non-aqueous medium) with dissociation constant (K)= (10^{-12} to -10^{-9}).
- The basicity of amines depends on the chemical structure.
- Alicyclic amines like pyridine and pyrrole are week amino compounds.
- Saturated cyclic amines like piperidine and pyrrolidine are strong amines

Reaction with anhydrides

For °1 & °2 amines in presence of °3



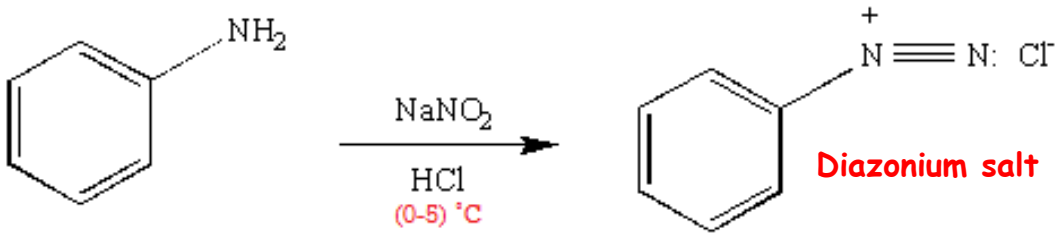
Excess

Hydrolysis

RCOOH → **Titration with NaOH using ph.ph**

- This type of reactions is more rapid than reactions with alcohols.

Using diazonium salts



- Direct titration with $NaNO_2$ in HCl

$$NO_2^- + 2I^- + H^+ \xrightarrow{\text{Starch}} I_2$$

λ_{max}= 600 nm

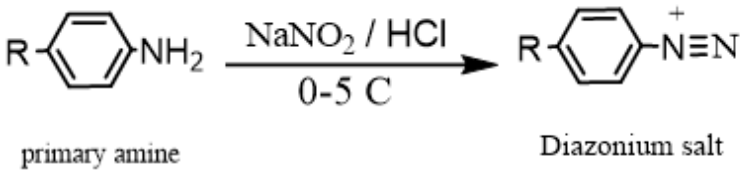
- For °1 & °2 aliphatic and aromatic amines

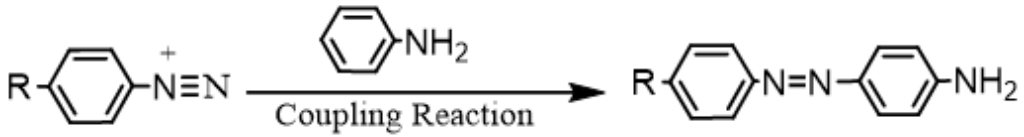
- Indirect titration with NaS_2O_3(for aromatic only)

$$NO_2^-{}_{(unreacted)} + 2I^- + H^+ \longrightarrow I_2$$

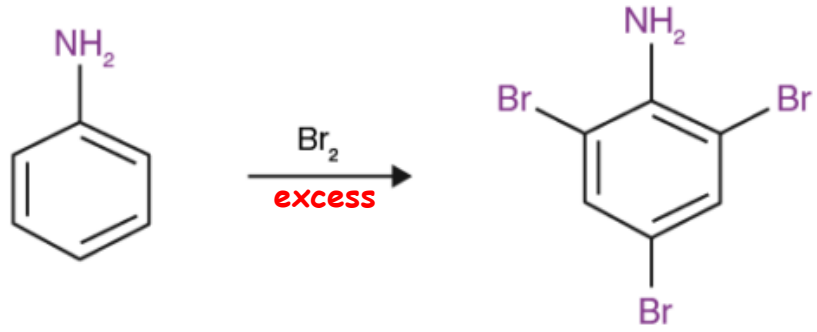
$$I_{2\ (unreacted)} + 2Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2NaI$$

- Or I_2 $\xrightarrow{\text{Starch}}$ blue complex (λ_{max}= 600 nm)





Bromination



$$(\text{unreacted})Br_2 + KI \longrightarrow KIO_3 + 2KBr$$

$$IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$$

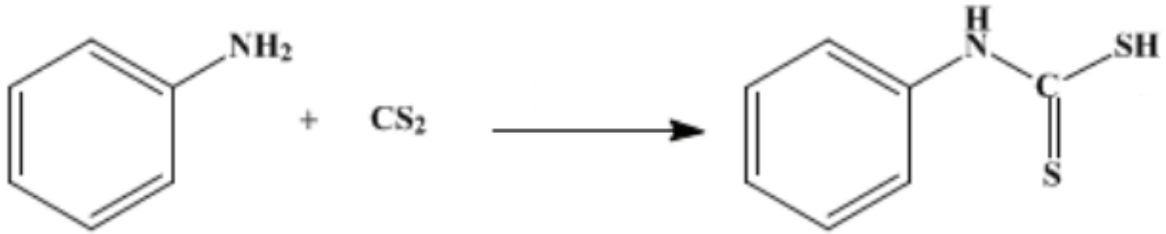
Direct addition of starch and Spectrophotometric determination at λ_{max}= 600 nm

Titration with $Na_2S_2O_3$ using starch as an indicator

Potentiometric titration

- Small amounts (ppm) of aromatic and aliphatic amines can be determined by potentiometric titration against HCl using glass electrode as a reference.

Using carbon disulphide

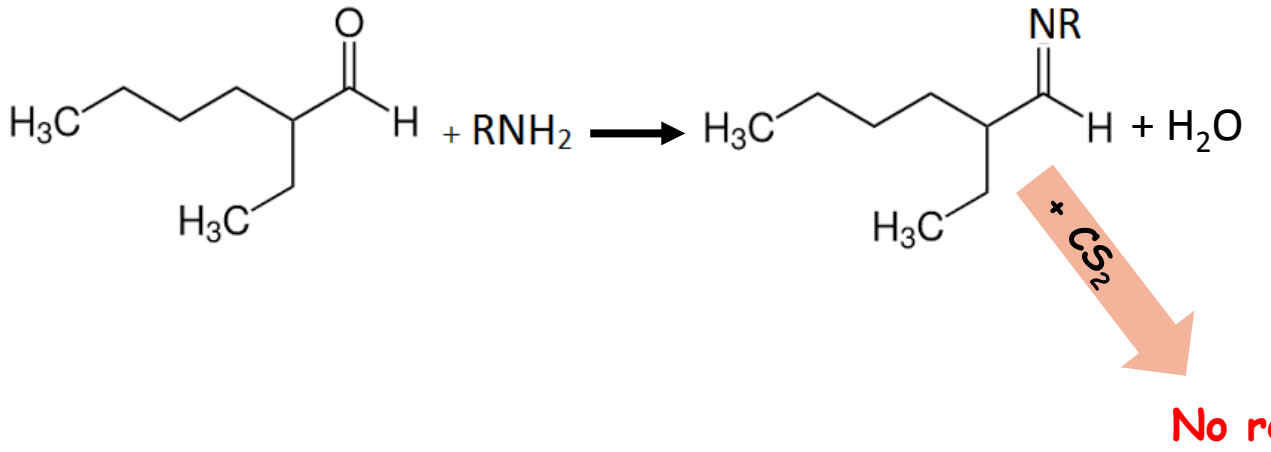


- The produced dithiocarbamic acid is:
- Directly titrated against NaOH in (pyridine + water + 2-propanol) medium using ph.ph indicator.This method is used to determine most of **primary and secondary** amines.
- Potentiometrically titrated against NaOH.
- Monitoring of molecular emission of S_2

Using CS_2-2-ethyl hexaldehyde

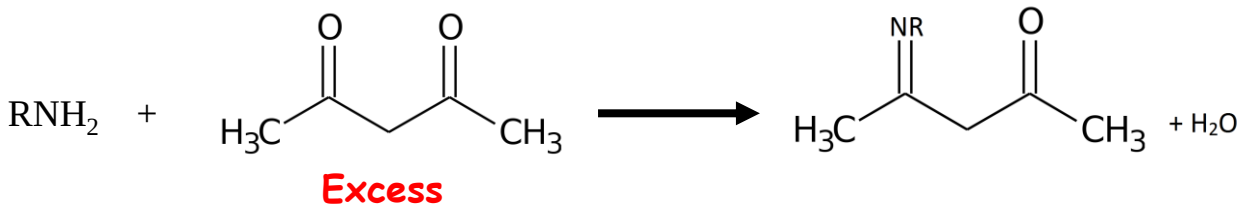
- This method is used to determine °2 amines in presence of °1 amines.
- It can be done by:

1. masking °1 amines by adding 2-ethyl hexaldehyde to form imine.
2. Adding CS_2 which reacts **only** with °2 amines.
3. The produced dithiocarbamic acid is directly titrated against NaOH in (pyridine + water + 2-propanol) medium using ph.ph.



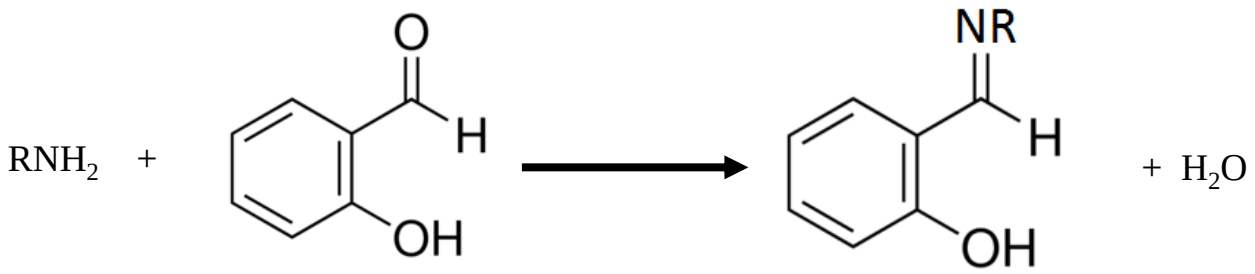
Using 2,4 pentadione

- This method is used to determine °1 amines in presence of °2 amines.



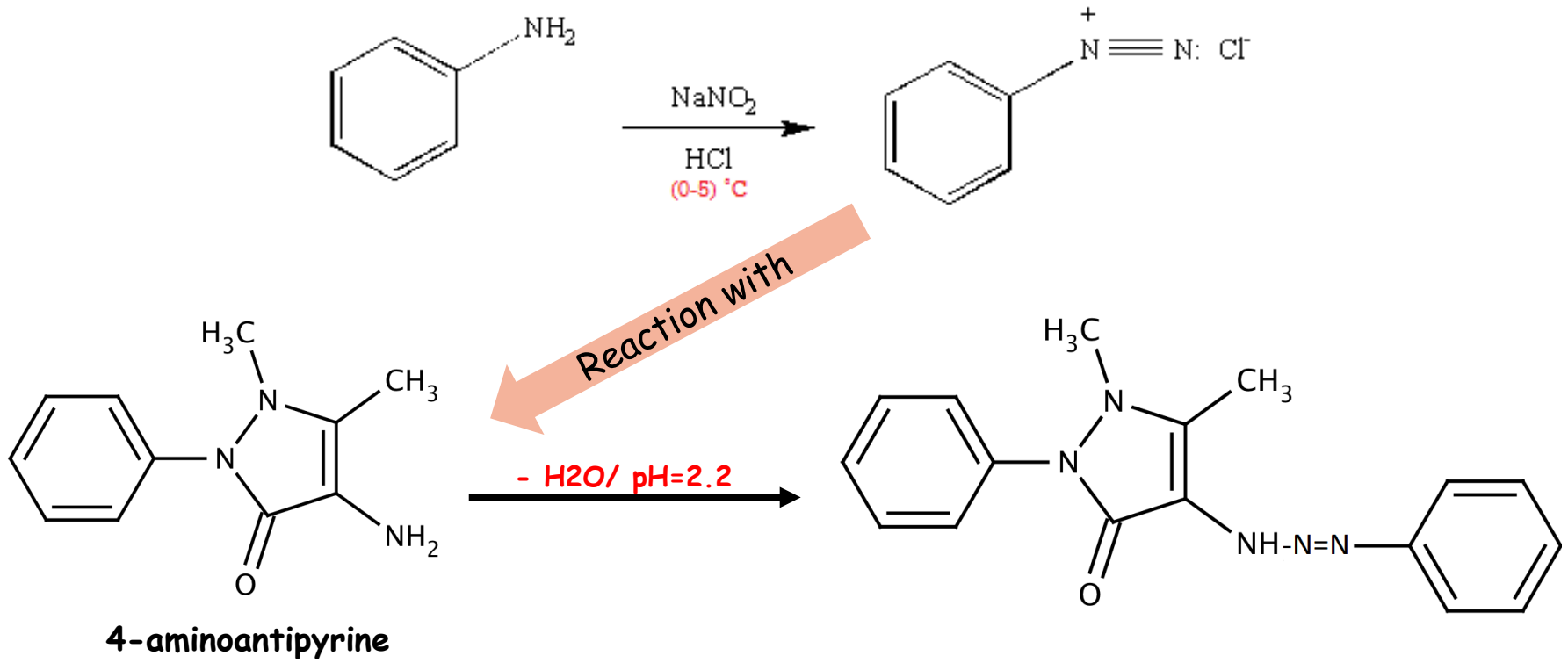
Titration with $NaOCH_3$ using ph.ph indicator

Using salicylaldehyde



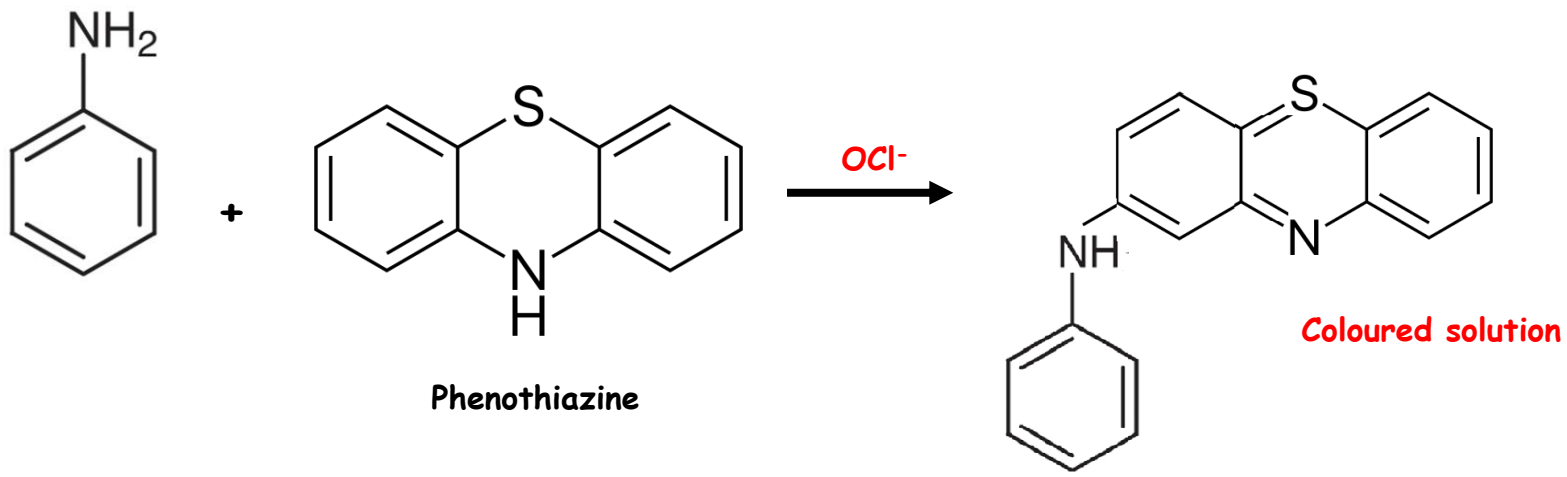
- Salicylaldehyde is used to mask °1 amines as it reacts with them only.
- This method is used to determine °2 & °3 aliphatic and aromatic amines (after removing or masking °1 amine), then they are potentiometrically titrated against (HCl in 2-propanol medium).
- **Spectrophotometrically**, °1 amines can react, in a small amounts, with salicylaldehyde in presence of Cu to produce a colour complex which can be determined.

Diazonium-coupling reactions



4-aminoantipyrine

Oxidation coupling reactions



Phenothiazine