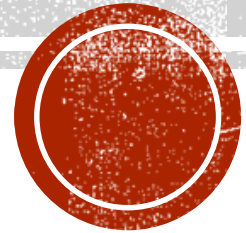
ORGANIC MICROANALYSIS

Carboxyl compounds and their derivatives

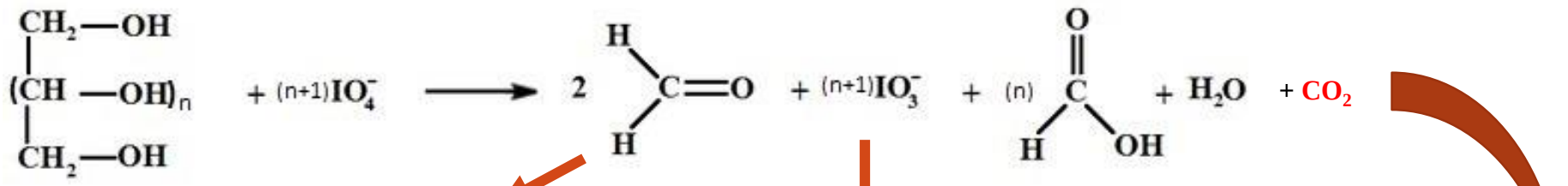


Carboxyl compounds

- Carboxyl compounds and their derivatives can be determined by:
- Titration (colourimetrically or potentiometrically) with standard base.
- Titration depends on the strength of the acid and its solubility in different solvents.
- Existing electron attracting groups like halogens and nitrogen in carboxylic acids can enhance the strength of this organic acid
- Carboxylic acids which contain small alkyl group is soluble in water, and the solubility decreases with the increasing of carbon atoms.

In poly-hydroxyl compounds

- Malaprade reaction or Malaprade oxidation is a glycol cleavage reaction in which a vicinal diol is oxidized by periodic acid or a periodate salt to give the corresponding carbonyl functional groups.



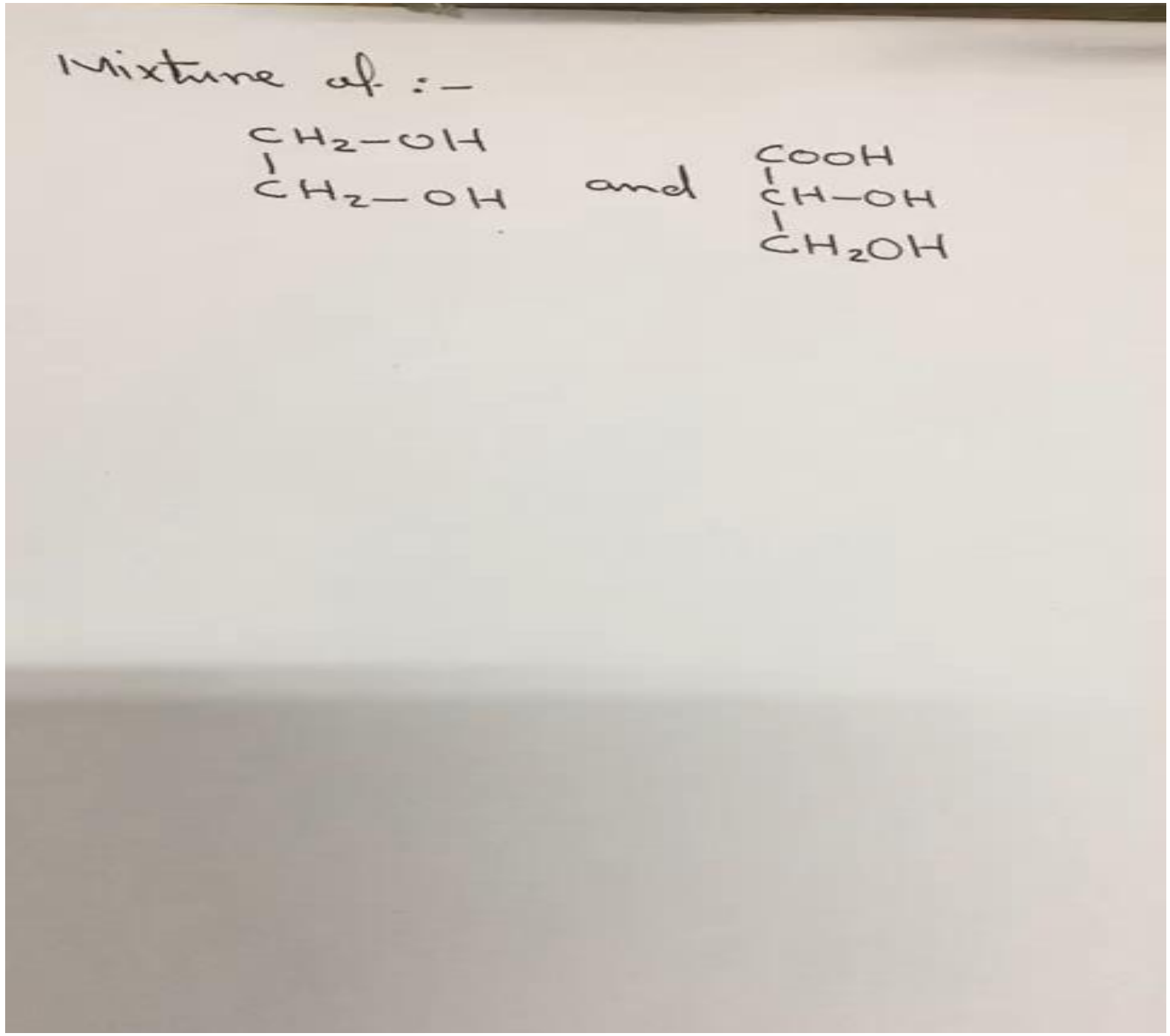
Carbonyl methods

Reaction with molybdate ion (hydroxyl methods)

Titration with NaOH using ph.ph as (indicator) OR Potentiometric titration

$$CO_2 + Ba(OH)_2 \longrightarrow BaCO_3 + H_2O$$

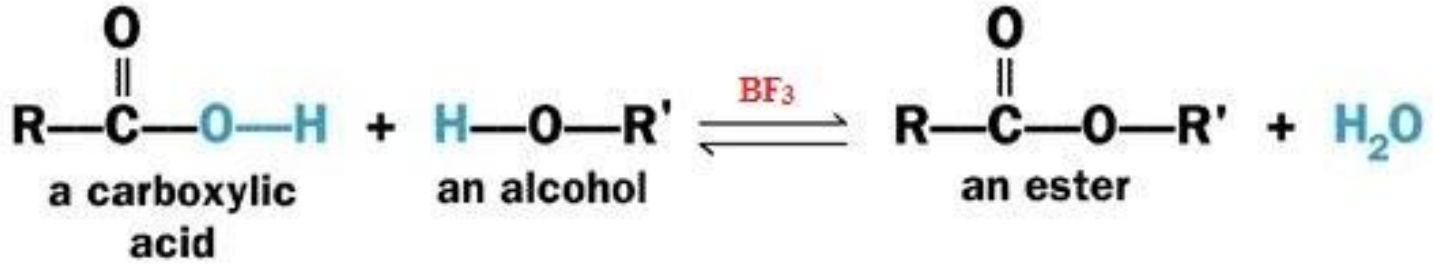
$$Ba(OH)_{2\ unreacted} + 2HCl \longrightarrow BaCl_2 + 2H_2O$$

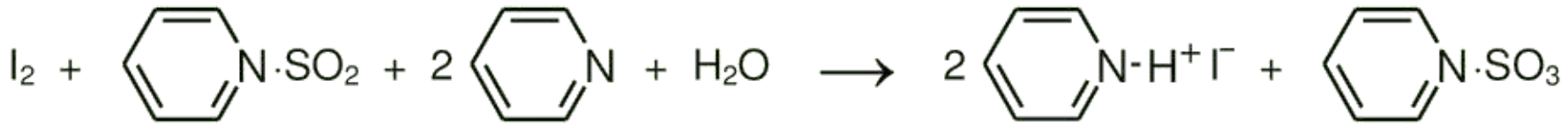


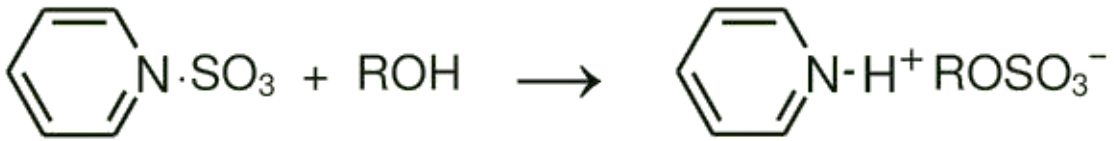
How to determine two compounds in a mixture?

Esterification of carboxylic acids

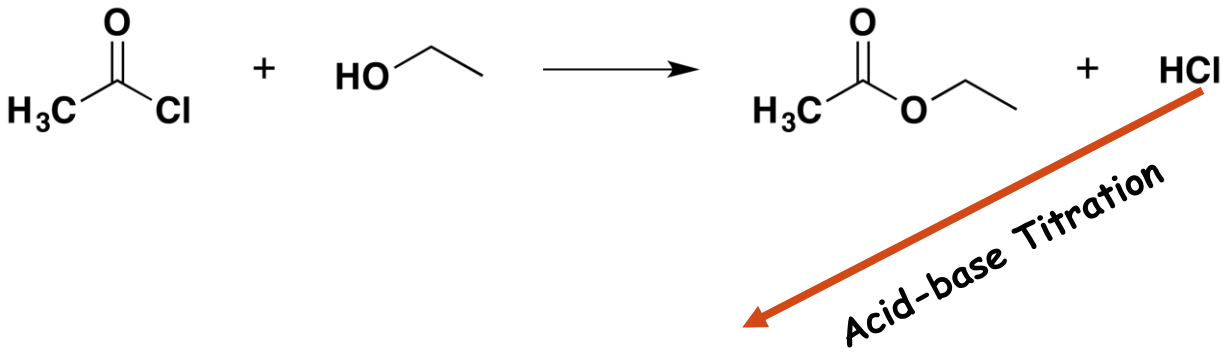
- Esterification can be done by an alcohol in addition to a catalyst such as boron tri fluoride (BF_3) to produce an equivelant quantity of H_2O which can be estimated by **Karl Fischer** titration.



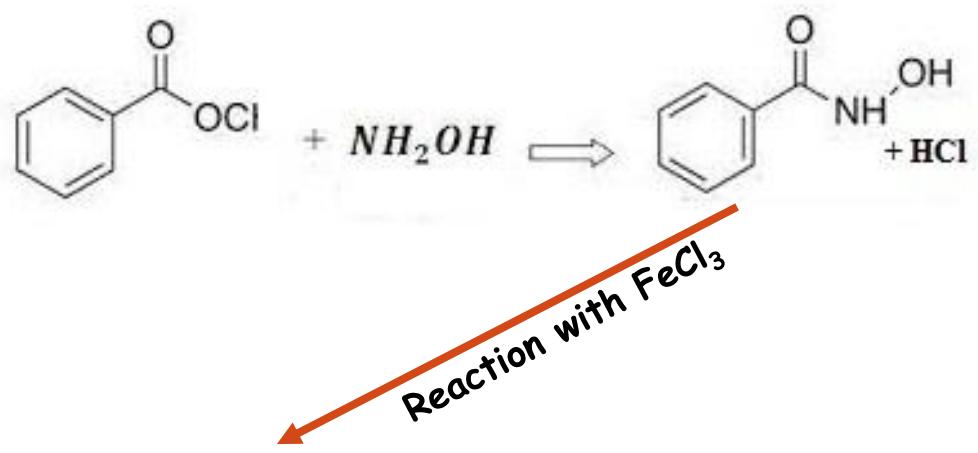




Chlorides of carboxylic acids

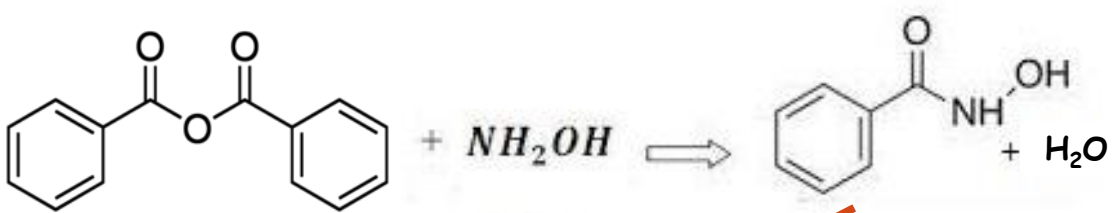


$$HCl + NaOH \xrightarrow{\text{methyl red}} NaCl + H_2O$$



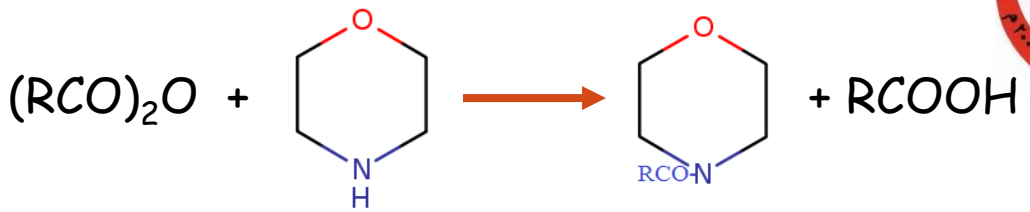
Red complex

Anhydrides of carboxylic acids



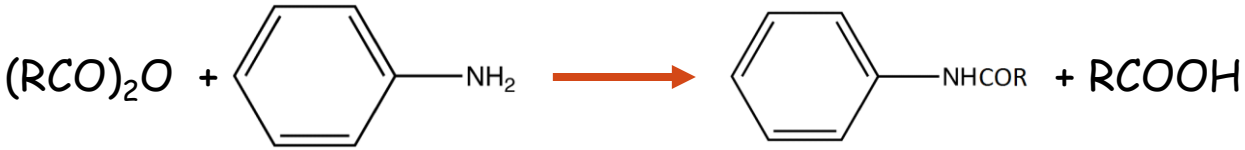
Reaction with $FeCl_3$

Red complex



Excess

Titration with methanolic HCl using (methylene blue +methylene yellow) indicator

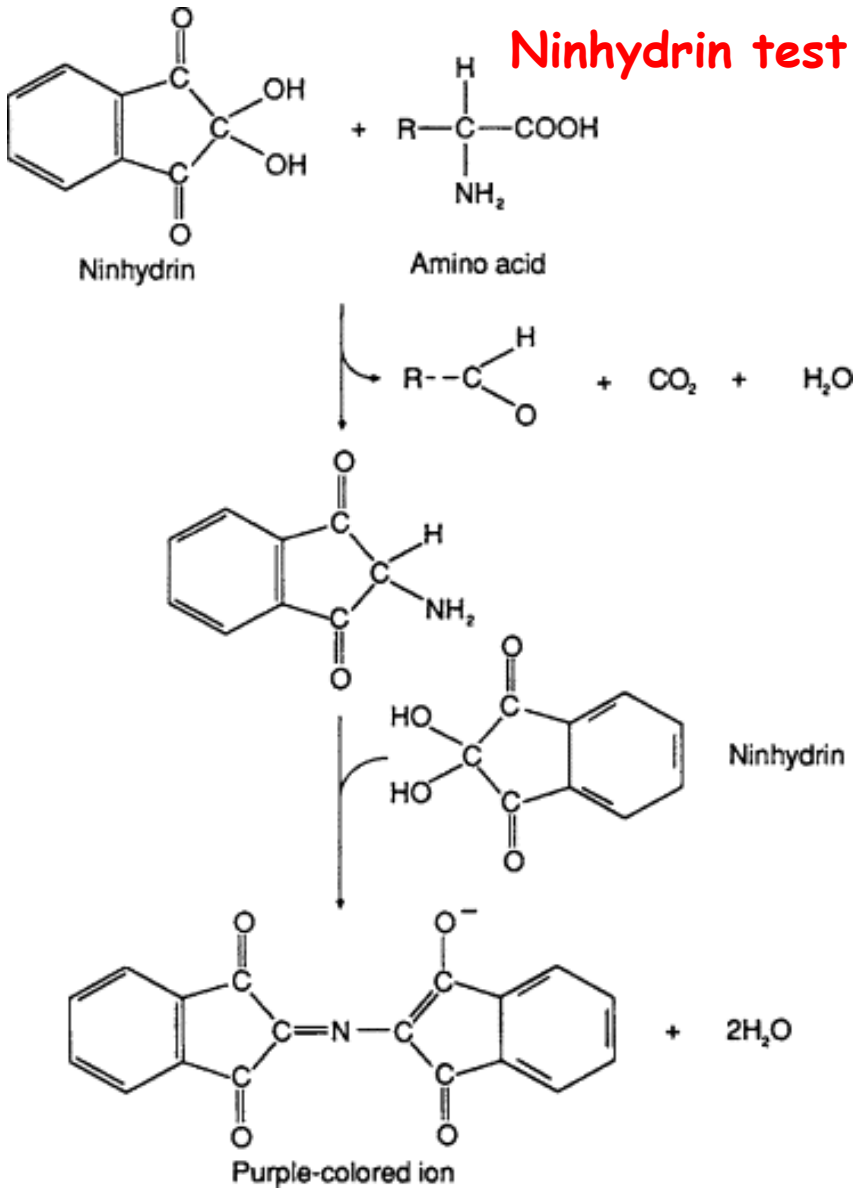


Excess

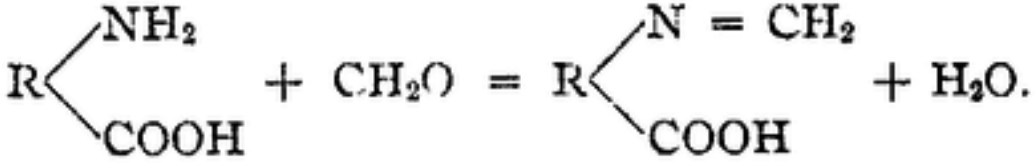
Unreacted aniline can be potentiometrically titrated with (o.2N) HCl in a mixture of (ethylene alcohol + isopropyl alcohol) as a solvent

Determination of amino acids

Ninhydrin test

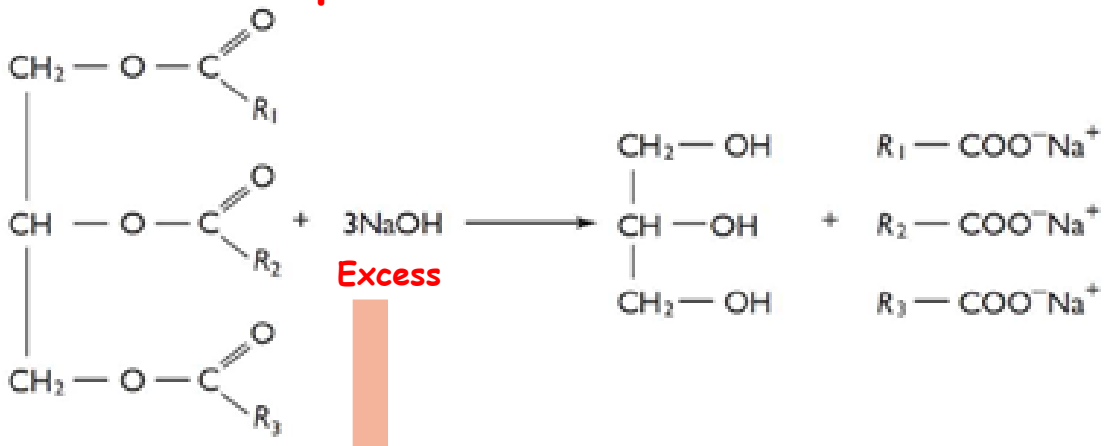


- Carboxylic group in amino acids is not too strong to be determined directly because of the effect of amino group, so it is important to mask the amino group firstly with formaldehyde then direct titration with NaOH and ph.ph indicator can be done.



Esters of carboxylic acids

Saponification method



$$HCl + NaOH \xrightarrow{\text{methyl red}} NaCl + H_2O$$

- Cyclic esters react with NaOH rapidly, while Long chain esters do not,
- This reaction is used to determine esters with conc. More than 100 ppm.

Hydroxamic acid method

RCOOR
RCOCl
$(RCO)_2O$
$RCONH_2$
RCOOH

$$+ NH_2OH \xrightarrow{OH^-} RCONHOH$$

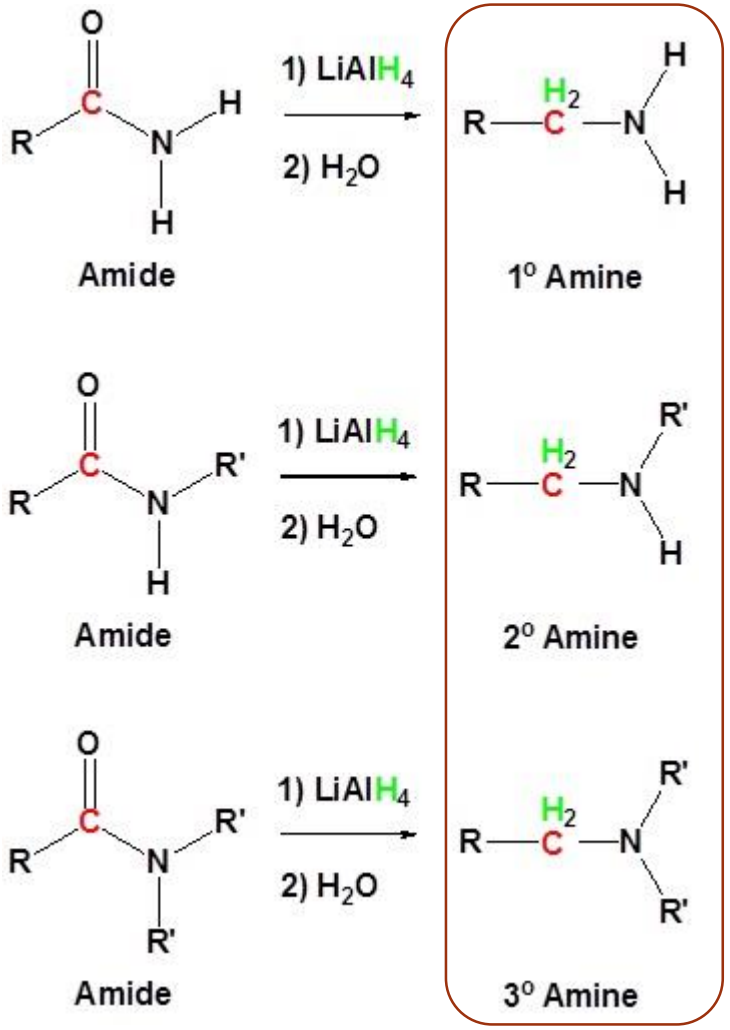
ROH
HCl
RCOOH
NH_3
H_2O

Reaction with $FeCl_3$

Red to purple complex (λ_{max}= 520 nm)

Amides of carboxylic acids

Reduction of amides



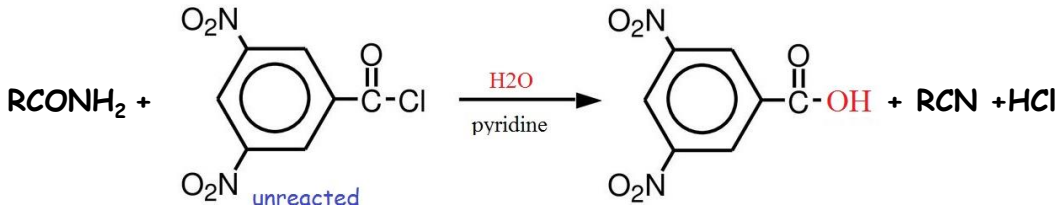
- The produced amine is separated by steam distillation, and titrated with H_2SO_4 directly.

Direct titration with $HClO_4$

$$RCONH_2 + HClO_4 \xrightarrow{\text{Acetic anhydride}} RCONH_3^+ \, ClO_4^-$$

Determination of °1 amides

With 3,5-dinitrobenzoyl chloride



- Non-aqueous titration with sodium methaxide in a mixture of (benzene + anhy.ethanol) with ph.ph indicator.
- This method is used to determine °1 in presence of °2 & °3

Photometric titration with hypobomite

$RCONH_2 + OBr^- \rightarrow RCONHBr + OH^-$

(high absorption) (λ_{max}=350 nm) (low absorption)

Flame method

- This method is used to determine °1 (aliphatic and aromatic) amides in presence of °2 & °3

$$RCONH_2 + 2Ba(OH)_2 + Br_2 \longrightarrow RNH_2 + BaCO_3 + BaBr_2 + 2H_2O$$

- Dissolved in HNO3 then determine Ba by flame emission photometry

Colorimetric method

Hydroxamic acid method

$$RCONH_2 + NH_2OH \xrightarrow{OH^-} RCONHOH + NH_3$$

Reaction with $FeCl_3$

Red to purple complex (λ_{max}= 520-540 nm)

Flame method

- This method is used to determine °1 (aliphatic and aromatic) amides in presence of °2 & °3

$$RCONH_2 + 2Ba(OH)_2 + Br_2 \longrightarrow RNH_2 + BaCO_3 + BaBr_2 + 2H_2O$$

- Dissolved in HNO3 then determine Ba by flame emission photometry

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