Chapter 5: Amines

These are organic derivatives of ammonia

Classification of animes

According to the number of alkyl groups attached to the nitrogen atom

(a) Primary amines: have only one alkyl group attached. i.e. RNH_2
Examples

CH_3NH_2	methylamine
$CH_3CH_2NH_2$	ethylamine
$CH_3CHCH_2CH_3$ (with NH_2 on C-2)	2-aminobutane

(b) Secondary amines: have two alkyl groups attached to a nitrogen atom, R_2NH
Examples

CH_3 N CH_3 Dimethylamine

H
|
$CH_3NHCH_2CH_3$ Ethylmethylamine

(in alphabetical order)

(c) Terrtiary amine: have 3 alkyl groups on the nitrogen atom i.e, R_3N, where R is an alkyl group.

CH_3 N CH_3 Trimethylamine
|
CH_3

Physical properties of amines

1. Boiling and melting points

(a) Amines are polar compounds and therefore have higher melting and boiling points than non-polar compounds of similar molecular mass due to dipole-dipole intermolecular forces or hydrogen bonding,
(b) Primary and secondary amines have higher melting points and boiling points than tertiary amines because tertiary amine do not form intermolecular hydrogen bonds
(c) Primary amines have higher melting and boiling points than secondary amines because they form many hydrogen bonds per molecule.

2. Solubility

Amines are soluble in water because they can form hydrogen bonds with water but the solubility decrease with alkyl chain length. Generally, primary amines are stronger bases than secondary amines than tertiary amines because they form many hydrogen bonds in water.

3. Basicity of amines

Like ammonia, amines dissolve in water to form alkaline solution.

$RNH_2 + H_2O \leftrightarrow RN^+H_3 + OH^-(aq)$

The strength of the alkaline solution is measured by the function Kb

$$Kb = \frac{[RN^+H_3][OH^-]}{[RNH_2]}$$

The higher the Kb the stronger the base or the higher the hydroxyl ion concentrations.

The ability to form alkaline solution, by amines, is due to the presence of a lone pair of electron on the nitrogen atom.

(i) Groups (such as alkyl groups) that donate electrons increase the electron density of the lone pair on the nitrogen atom. This increases the ability of alkylamine to attract a proton from water to release hydroxide ions.

Thus, secondary amines are stronger bases than primary amines than ammonia because secondary amine has two electron donating groups, primary amines has one, whereas, amines have none.

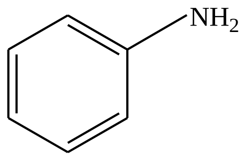
However, tertiary amines are weaker bases than either secondary or primary amines because their iminium ions are poorly solvated or hydrated or are unstable.

(ii) Groups that withdraw electrons from nitrogen atoms like phenyl group, make amines weaker bases because they reduce the ability of the lone pair of electron on the nitrogen atom and its ability to attract a proton from water.

Exercise

Explain the following observations

(i) The basic strength of the following amine is in order.



$<$ NH_3 $<$ $(CH_3)_3N$

Solution

Trimethylamine is a stronger base than ammonia because the methyl groups donate electrons to the nitrogen atom. This increases the density of alone pair of electron on the nitrogen atom on trimethylamine and its ability to attract a proton from water and form hydroxyl ions.

Phenylamine is a weaker base than ammonia because the phenyl group pulls electrons from the nitrogen atom. The reduction of electron density of alone pair on the nitrogen atom reduces the ability of the lone pair to attract a proton from water and form hydroxyl group.

(ii) The boiling points of the following amines are

$CH_3CH_2CH_2NH_2$	$= 66.8^0C$
$CH_3CH_2NHCH_3$	$= 45.4^0C$
$(CH_3)_3CN$	$= 7.7^0C$

Solutions

Propylamine has the highest boiling point has the highest boiling point because it has two hydrogen atoms on the nitrogen atom which form many intermocular hydrogen bonding. The hydrogen bonds necessitate high temperature to break; hence high boiling point.

Ethylmethylamine has one hydrogen bond on the nitrogen atom and thus forms fewer hydrogen bonds leading to lower boiling point.

Trimethylamine lack a hydrogen atom on a nitrogen atom and is incapable of forming inter-molecular hydrogen bond leading to the lowest boiling point.

(iii) The acid constants Ka for the following amines are:

Amine	Ka ($moldm^{-3}$)
$(CH_3)_3N$	9.70
$CH_3CH_2CH_2NH_2$	10.67

Solution

Trimethylamine $(CH_3)_3N$ is a weaker base than propylamine because it form unstable aqueous ammonium ions

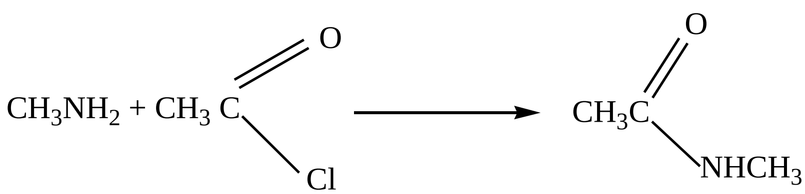
Chemical properties

1. They react with acids to form salts
   Example

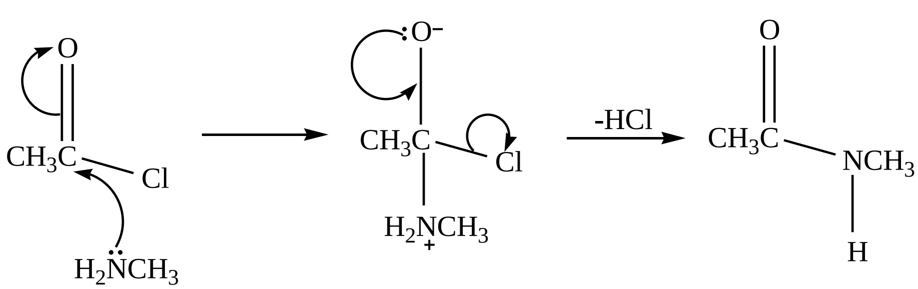
   $CH_3NH_2 + HCl \longrightarrow CH_3N^+H_3Cl^-$

2. Primary and secondary amines react with alkanoyl halides to form amides

   Example



Mechanism



Exercise

Complete and write a mechanism

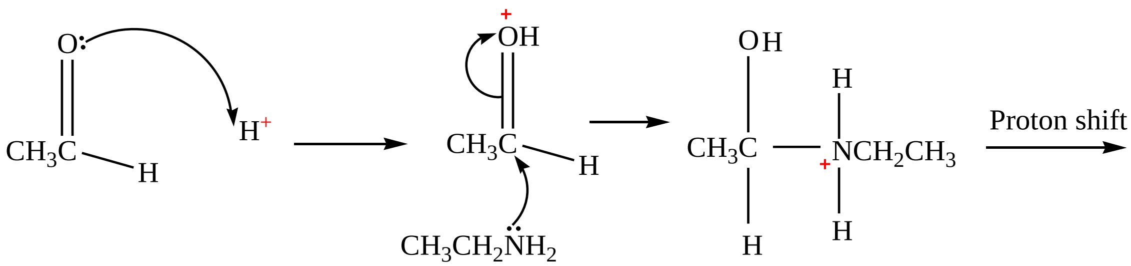
$CH_3COBr + CH_3CH_2NH_2 \longrightarrow$

3. Primary amines undergo condensation reaction with carbonyl compounds between pH 4 -5 to form **imines**. At lower pH the **amine is protonated** as well making it a weaker nucleophile.

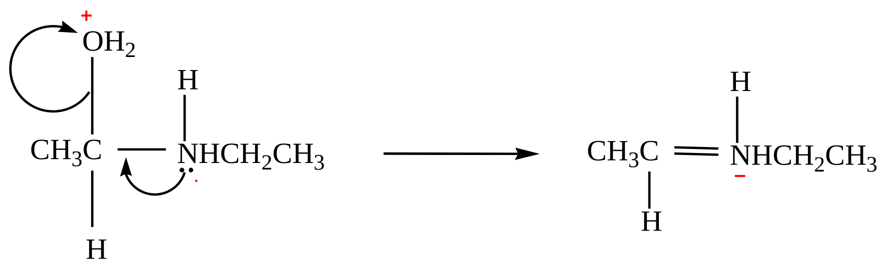
Example

$CH_3CH_2NH_2 + CH_3CHO \xrightarrow{H^+} CH_3CH_2N{=}CHCH_3$

MECHANISM



Then



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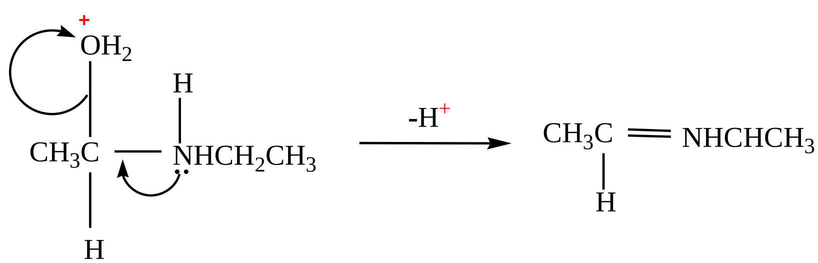
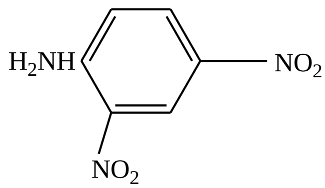


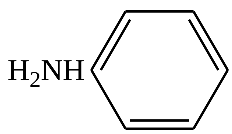
NB: Take note of the movement of the proton

Exercise

Complete the following equations and write appropriate mechanism.

1. CH_3COCH_3 + RNH_2 $\xrightarrow{H^+}$

2. CH_3CH_2CHO +  $\xrightarrow{H^+}$

3. CH_3COCH_3 +  $\xrightarrow{H^+}$

Distinguishing between primary, secondary and tertiary amines

A. Reagent: nitrous acid ($NaNO_2$, HCl (0-5^{0}C))

Observation

(i) Primary amine: effervescence

Equation

$RNH_2 + NaNO_2 + 2HCl \longrightarrow RCl + N_2(g) + H_2O + NaCl$

(ii) Secondary amines: yellow oil liquid

Equation

$R_2NH + NaNO_2 + HCl \longrightarrow R_2N\text{-}NO + NaCl + H_2O$

(iii) Tertiary amines: no observable change du to the formation of soluble diazonium salts

Equation

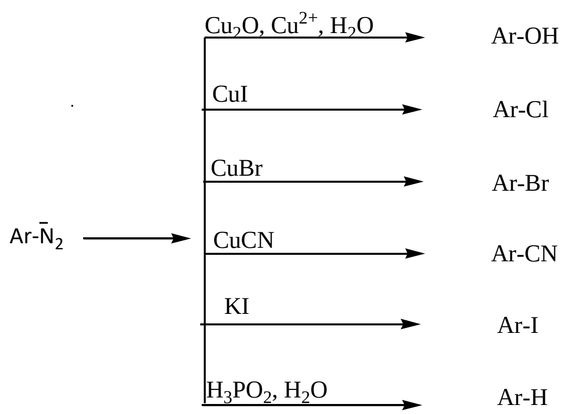
$R_3N + NaNO_2 + 4HCl \longrightarrow RN_2Cl + 2RCl + NaCl + 2H_2O$

(iv) Aromatic amine: no observable change du to the formation of soluble diazonium salts

Equation

$ArNH_2 + NaNO_2 + 2HCl \longrightarrow ArN_2Cl + NaCl + 2H_2O$

Reaction of aromatic diazonium salts



B. The Hinsberg test

Procedure: a mixture of small amount of the amine and benzenesuplfonyl chloride is shaken potassium hydroxide, time allowed for the reaction to take place and then the mixture is acidified.

Primary amine for a colorless solution with potassium hydroxide, forming a precipitate when the mixture is acidified.

Secondary amine: forms a precipitate with potassium hydroxide insoluble when the mixture is acidified

Tertiary amine: no observable change

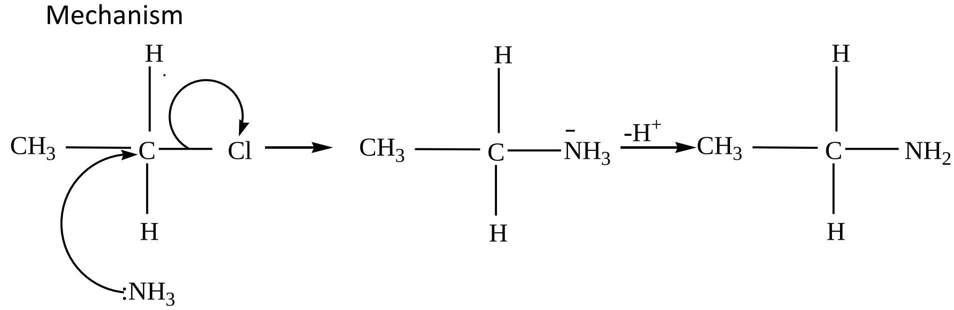
Preparation of amines

1. Reaction of alkyl halides with ammonia

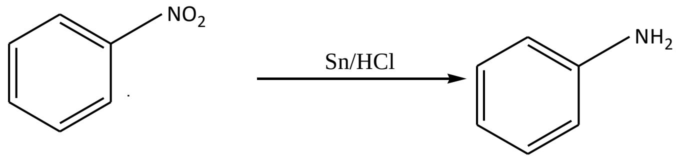
   Example

   $$CH_3CH_2Cl \xrightarrow{NH_3} CH_3CH_2NH_2$$

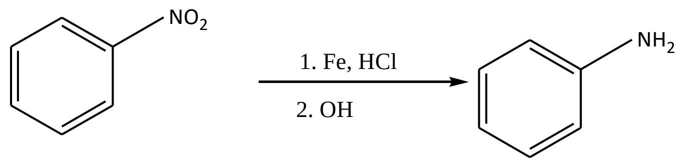
Mechanism



2. By reduction of nitroalkane



Or



3. By Hofmann degradation
Amides with no substituent on the nitrogen atom react with solution of bromine or chlorine in sodium hydroxide to yield amines.

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 + Br_2 + 4NaOH \xrightarrow{H_2O} RNH_2 + 2NaBr + 2Na_2CO_3 + 2H_2O$$

Example
$CH_3CONH_2 \xrightarrow{Br_2 / {}^-OH} CH_3NH_2$

4. By reduction of nitriles
i.e. $RCN \xrightarrow{LiAlH_4\text{, dry ether}} RCH_2NH_2$
nitrile

Example
$CH_3CN \xrightarrow{LiAlH_4\text{, dry ether}} CH_3CH_2NH_2$

Nitrile can be obtained by reacting alkyl halides with potassium cyanide.

i.e. $RCl + KCN \longrightarrow RCN + KCl$

5. By reduction of oximes
i.e. $RCH{=}NOH \xrightarrow{LiAlH_4\text{, dry ether}} RCH_2NH_2$.
Example
$CH_3CH{=}NOH \xrightarrow{LiAlH_4\text{, dry ether}} CH_3CH_2NH_2$
Thank you
Dr. Bbosa Science