Our country, our future

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Chapter 5: Amines

These are organic derivatives of ammonia

Classification

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
Example

CH_3NH_2 methylamine
$CH_3CH_2NH_2$ ethylamine
$CH_3CHCH_2CH_3$ (NH$_2$ on the second carbon) 2-aminobutane

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

$CH_3\ N\ CH_3$ Dimethylamine

$CH_3NHCH_2CH_3$ (H on N) 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.

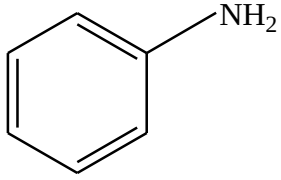
$CH_3\ N\ CH_3$ (CH_3 on N) Trimethylamine

Physical properties

1. Boiling and melting points
   (a) Amines are polar compounds and therefore 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.

3. Bacisity of amines

   Like ammonia, amines dissolve in water to form alkaline solution.
   The strength of the alkaline solution is measured by the function Kb



$< \quad NH_3 \quad < \quad (CH_3)_3N$

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

The higher the Kb the stronger the base.

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

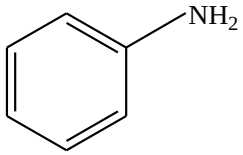
(i) Groups (such as alkyl groups) that donate electrons increase the electron density of the lone pair on the nitrogen atom. This increases the ability of alkylamine to abstract a proton from water and form stronger alkaline solutions. Thus, secondary amines are stronger bases than primary amines than ammonia because secondary amine has two electron donating groups, primary amines 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.

(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 abstract a proton from water.

Exercise

Explain the following observations

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



$< NH_3 <$ $(CH_3)_3N$

(ii) The boiling points of the following amines are

$CH_3CH_2CH_2NH_2$ = 66.8^0C

$CH_3CH_2NCH_3$ = 45.4

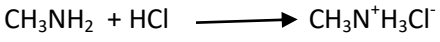
$(CH_3)_3CN$ = 7.7^0C

(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

Chemical properties

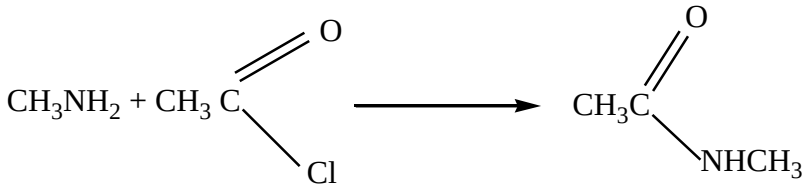
1. They react with acids to form salts
   Example



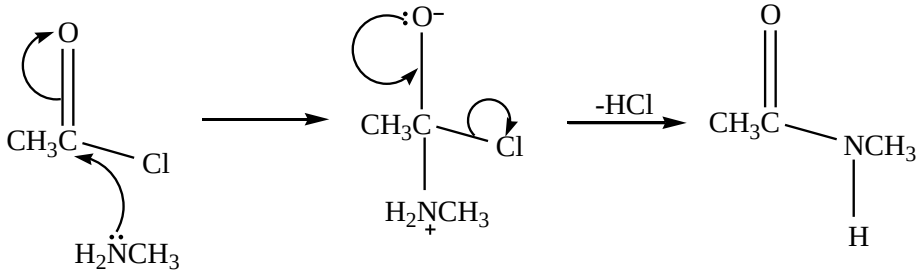
$CH_3NH_2 + HCl \longrightarrow CH_3N^+H_3Cl^-$

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

   Example



Mechanism



Exercise

Complete and write a mechanism

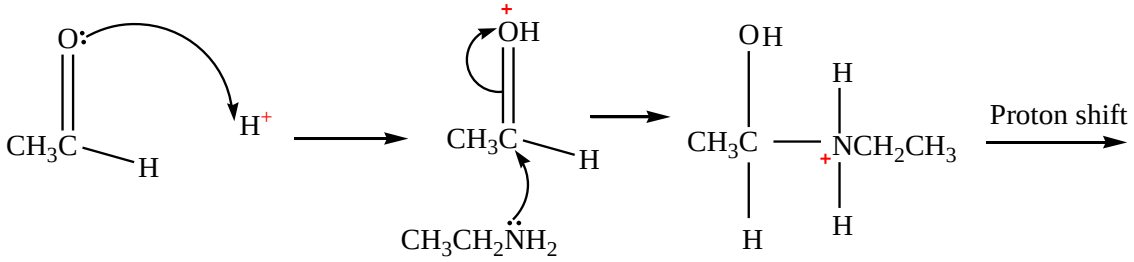
$CH_3COBr + CH_3CH_2NH_2 \longrightarrow$

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



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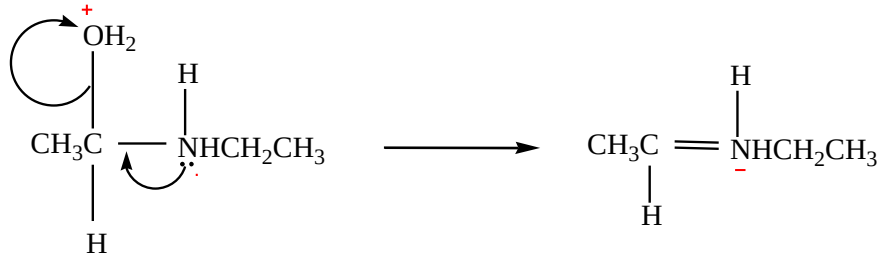

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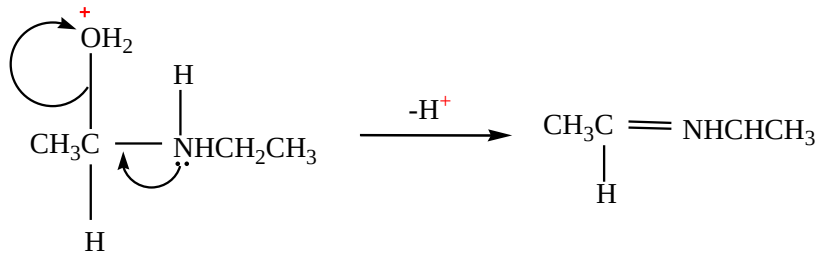
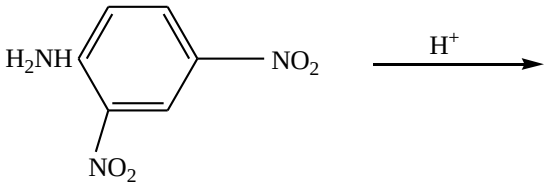


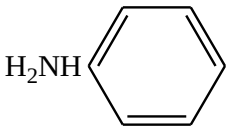
NB: Take note of the movement of the proton

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

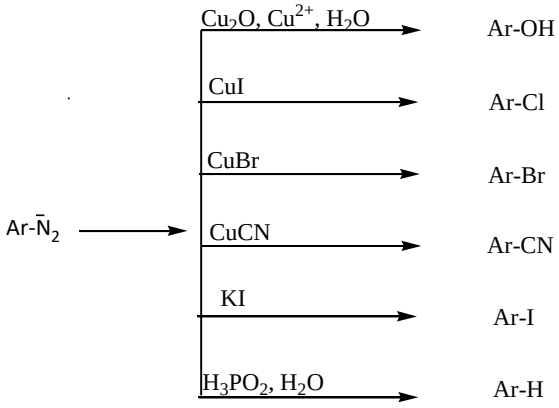
$R_3N + NaNO_2 + 4HCl \longrightarrow RN_2Cl + 2RCl + NaCl + 2H_2O$

(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

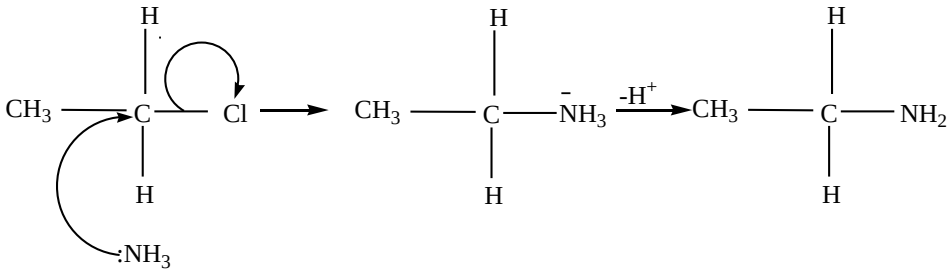
PREPARATION OF AMINES

1. Reaction of alkyl halides with ammonia

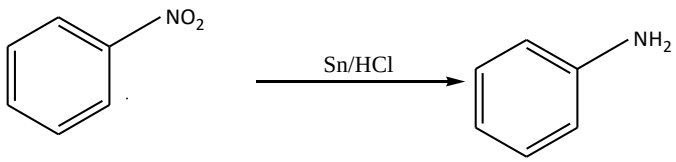
   Example

   $CH_3CH_2Cl \xrightarrow{NH_3} CH_3CH_2NH_2$

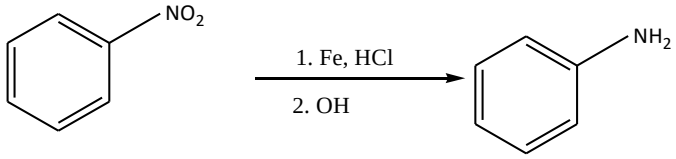
   Mechanism



2. By reduction of nitroalkane

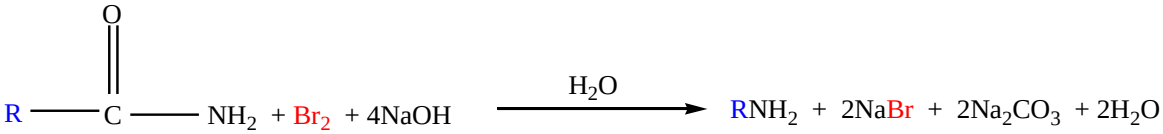


Or



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.



   Example

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

4. By reduction of nitriles

   i.e. RCN $\xrightarrow{LiAlH_4,\ dry\ ether}$ RCH_2NH_2

   nitrile

   Example

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

   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 $\xrightarrow{LiAlH_4,\ dry\ ether}$ RCH_2NH_2.

   Example

   $CH_3CH{=}NOH \xrightarrow{LiAlH_4,\ dry\ ether} CH_3CH_2NH_2$

thanx