

***Topic 4.7***

***AMINES***

***Preparation of primary, secondary and tertiary amines***

***Basic properties of amines***

***Uses of quaternary ammonium salts***

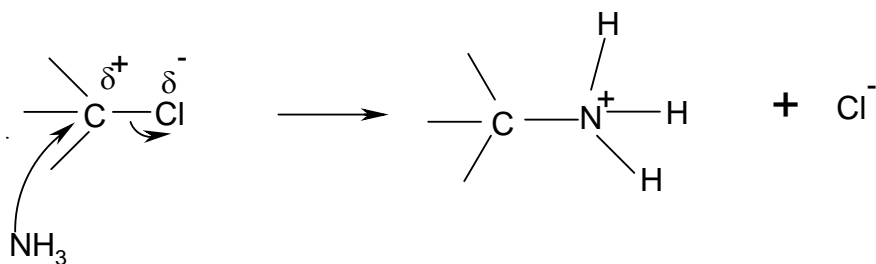
## PREPARATION OF AMINES

Amines can be prepared in two ways: by nucleophilic substitution of a haloalkane and by reduction from nitriles. The preparation from a haloalkane results in a mixture of primary, secondary and tertiary amines and their salts. The preparation from a nitrile results in the formation of primary amines only.

### a) Preparation of amines from haloalkanes

Haloalkanes react with nucleophiles. If ammonia is used as the nucleophile then amines are formed. It is possible to make primary, secondary and tertiary amines and also quaternary ammonium salts by this method, depending on the relative quantities of ammonia and the haloalkane used. **It is therefore not considered an effective method for the preparation of primary amines.**

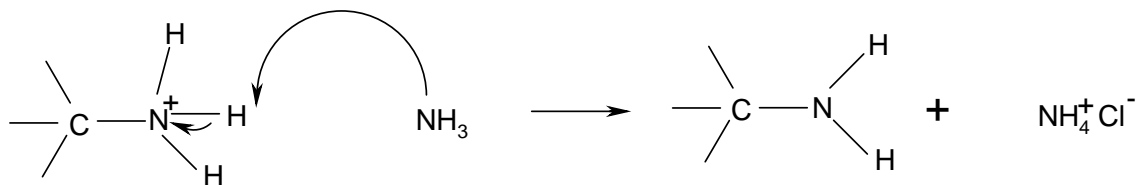
The mechanism for the reaction is nucleophilic substitution and it proceeds as follows:



The second step will vary depending on which of the reactants is present in excess.

#### i) primary amines

If the reaction takes place in excess ammonia, the H will be removed by another ammonia molecule:

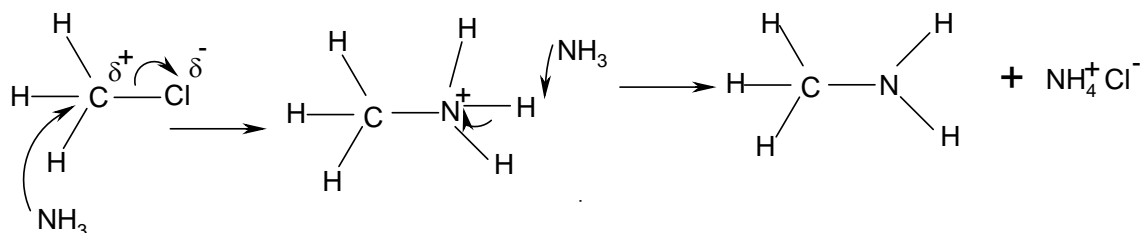


A primary amine is formed and ammonium chloride is the other product.

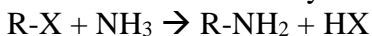
So primary amines are formed by the addition of **excess ammonia to a haloalkane**:



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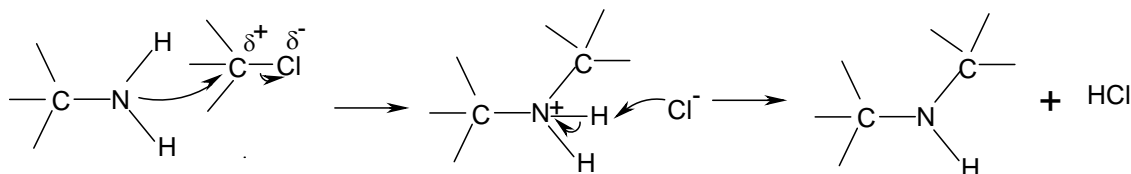


Primary amines will also be formed if haloalkanes and ammonia are mixed in a 1:1 ratio. In this case HCl is likely to be the second product as the  $\text{Cl}^-$  will pull off the extra H:

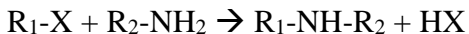


## ii) secondary amines

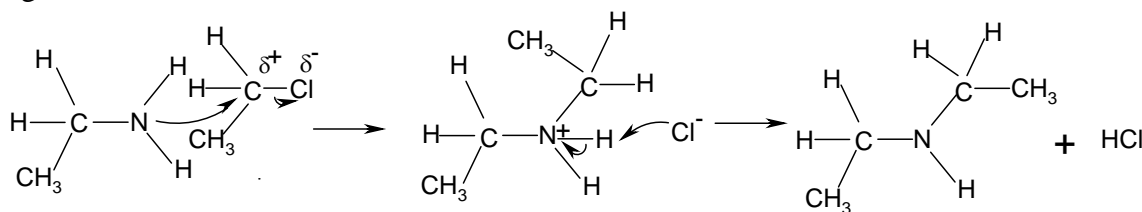
If the reaction takes place in excess haloalkane, the primary amine will attack the remaining haloalkane to form a secondary amine:



So secondary amines are formed by reacting **haloalkanes and ammonia in a 2:1 ratio** or by reacting a **haloalkane with a primary amine in a 1:1 ratio**:

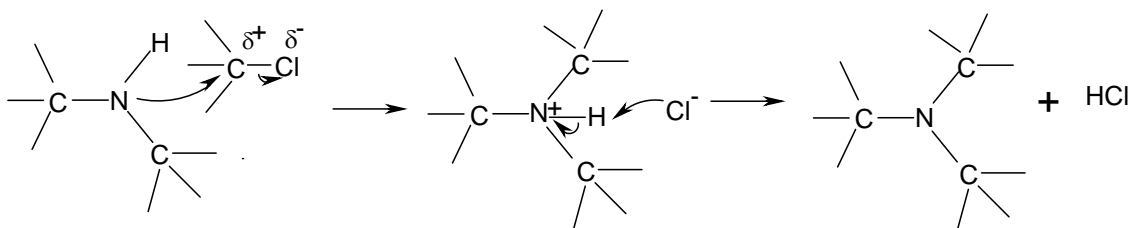


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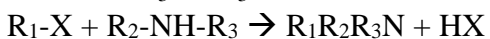
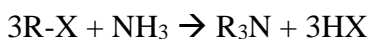


### iii) tertiary amines

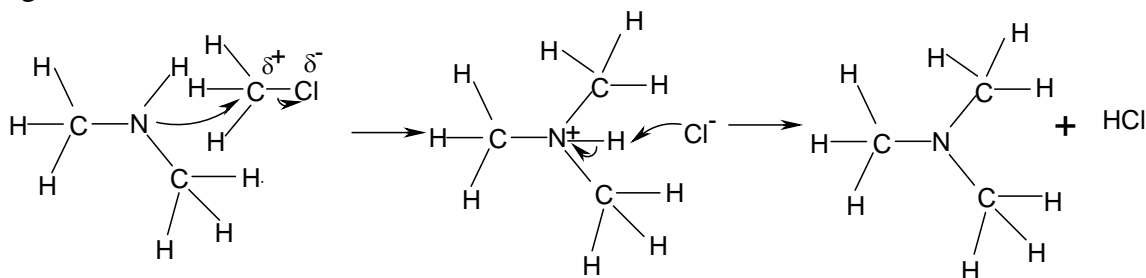
If any haloalkane is present after the secondary amine has been formed, it can be attacked by the secondary amine to form a tertiary amine:



So tertiary amines are formed by reacting **haloalkanes and ammonia in a 3:1 ratio** or by reacting a **haloalkane with a secondary amine in a 1:1 ratio**:

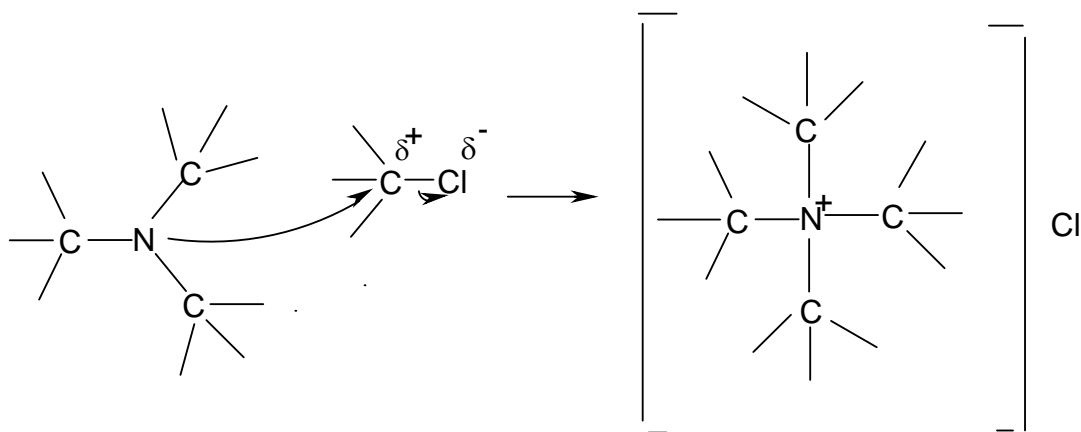


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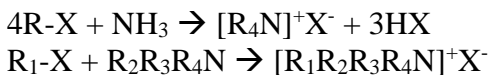


### iv) quaternary ammonium salts

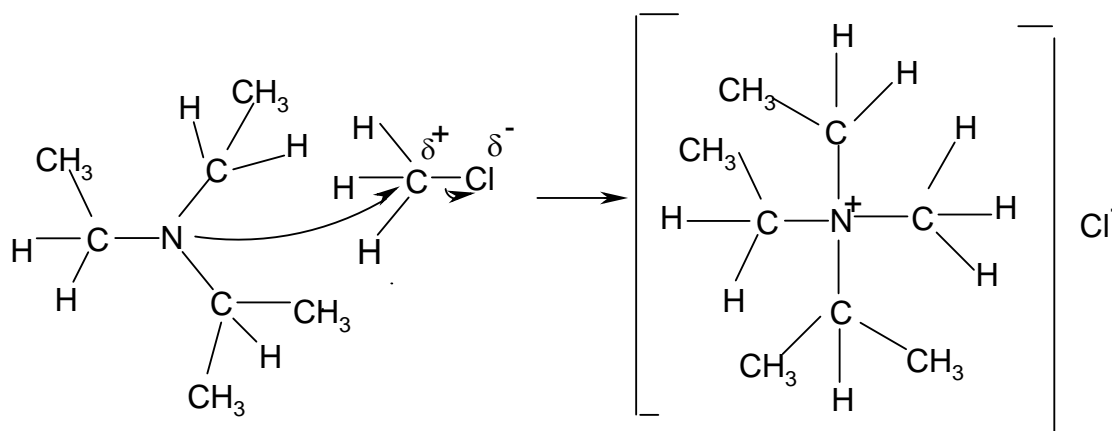
If there is any haloalkane left after the tertiary amine has been formed, it will be attacked by the tertiary amine to form a quaternary ammonium salt:



So quaternary ammonium salts can be made by **reacting haloalkanes and ammonia in a 4:1 ratio** or by **reacting tertiary amines and haloalkanes in a 1:1 ratio**.

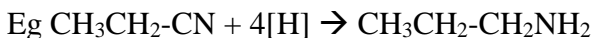
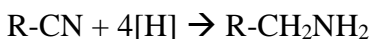


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b) **preparation of primary amines from nitriles**

Primary amines can be made by treating nitriles with a strong reducing agent such as  $\text{LiAlH}_4$ :



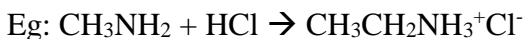
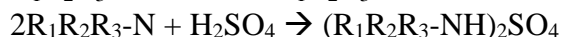
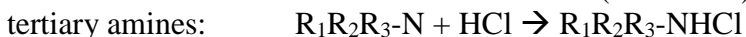
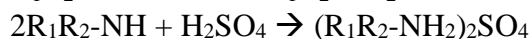
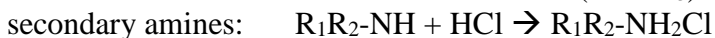
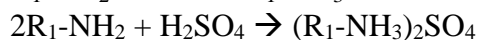
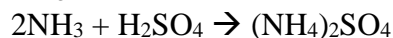
**Secondary and tertiary amines cannot be prepared in this way; the primary amine is the only product. As a result this preparation produces a very good yield of the primary amine.**

## BASIC PROPERTIES OF AMINES

Amines are weak bases; the lone pair of electrons on the nitrogen atom can behave as a proton acceptor. The strength of amines varies, but all react with strong acids to make alkylammonium salts.

### a) Reaction of amines with acids

Amines react with acids in the same way as ammonia:



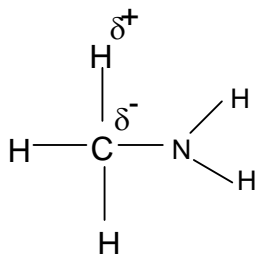
The charges on the ions are often shown, eg  $\text{R}_1\text{R}_2\text{-NH}_2^+\text{Cl}^-$

### b) Comparison of base strength of different amines

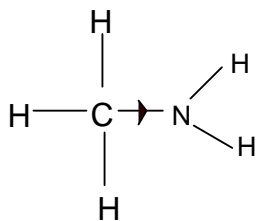
The basicity of ammonia and amines depends on the availability of the lone pair of electrons on the nitrogen atom. The more available the lone pair, the stronger the base.

The availability of the lone pair in turn depends on how much electron density is on the nitrogen atom, and this depends on the adjacent atoms.

Primary amines have one alkyl group attached to the N atom:



The hydrogen atom is slightly more electropositive than the carbon atom. This means that the carbon atom has a slight surplus of electrons which the nitrogen atom can attract towards itself. This effect is known as a “positive inductive effect” and it means that the N atom has an excess of electron density:

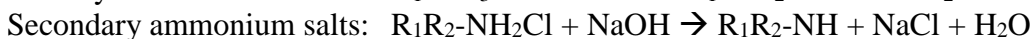


The greater the electron density on the N atom, the more likely the lone pair is to be released for bonding. **Primary amines are thus stronger bases than ammonia, as the alkyl groups push electron density onto the N atom, making the lone pair more available for bonding.**

It follows that secondary amines, which have two electron-pushing alkyl groups, are stronger bases than primary amines and that tertiary amines are stronger bases than secondary amines.

#### c) **Reaction of alkylammonium salts with bases**

The alkylammonium salts are slightly acidic and can be converted back into amines on addition of alkalis:

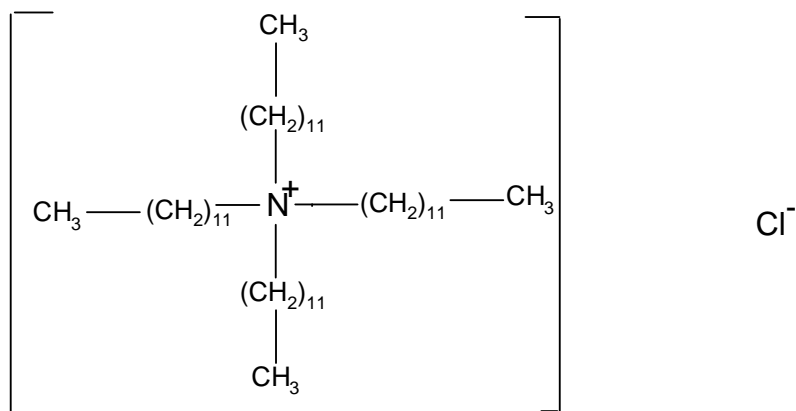


Quaternary ammonium salts are not acidic as the N atom is not bonded to any hydrogen atoms.

## USES OF QUATERNARY AMMONIUM SALTS

Quaternary ammonium salts are principally used as cationic surfactants. Long-chain ammonium salts are mainly used for this purpose:

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A surfactant is a substance which can be added to a liquid to reduce its surface tension.

Cationic surfactants can also be added to solids which tend to attract negative charge, such as glass, hair and fibres. The cation helps cancel out the negative charge and hence acts as an anti-static agent. This is just one of a variety of functions performed by surfactants.



#### 4. Summary of preparation and acid-base properties of amines

Type of reaction	Mechanism
<p><b>1. haloalkane → primary amine</b></p> <p>reagents: haloalkane and excess ammonia  conditions: heat  equation: <math>R-X + 2NH_3 \rightarrow R-NH_2 + NH_4X</math>  or  reagent: haloalkane and ammonia (1:1 ratio)  conditions: heat  equation: <math>R-X + NH_3 \rightarrow R-NH_2 + HX</math></p> <p><b>2. haloalkane → secondary amine</b></p> <p>reagents: haloalkane and ammonia (2:1 ratio)  conditions: heat  equation: <math>2R-X + NH_3 \rightarrow R-NH-R + 2HX</math>  or  reagents: haloalkane and primary amine  conditions: heat  equation: <math>R_1-X + R_2-NH_2 \rightarrow R_1-NH-R_2 + HX</math></p> <p><b>3. haloalkane → tertiary amine</b></p> <p>reagents: haloalkane and ammonia (3:1 ratio)  conditions: heat  equation: <math>3R-X + NH_3 \rightarrow R_3N + 3HX</math>  or  reagents: haloalkane and secondary amine  conditions: heat  equation: <math>R_1-X + R_2-NH-R_3 \rightarrow R_1R_2R_3N + HX</math></p> <p><b>4. haloalkane → quaternary ammonium salt</b></p> <p>reagents: haloalkane and ammonia (4:1 ratio)  conditions: heat  equation:  <math>4R-X + NH_3 \rightarrow [R_4N]^+X^- + 3HX</math>  or  reagents: haloalkane and secondary amine  conditions: heat  equation: <math>R_1-X + R_2R_3R_4N \rightarrow [R_1R_2R_3R_4N]^+X^-</math></p>	Nucleophilic substitution (required)
<p><b>2. reduction: nitrile → primary amine</b></p> <p>reagents: <math>LiAlH_4</math> in dry ether  conditions: room temperature  equation: <math>R-CN + 4[H] \rightarrow R-CH_2NH_2</math></p>	n/a
<p><b>3. acid-base:</b></p> <p>a) amines with acids  equations: <math>R_1-NH_2 + HCl \rightarrow R_1-NH_3Cl</math>  <math>R_1R_2-NH + HCl \rightarrow R_1R_2-NH_2Cl</math>  <math>R_1R_2R_3-N + HCl \rightarrow R_1R_2R_3-NHCl</math></p> <p>b) alkyl ammonium salts with alkalis  equations: <math>R_1-NH_3Cl + NaOH \rightarrow R_1-NH_2 + NaCl + H_2O</math>  <math>R_1R_2-NH_2Cl + NaOH \rightarrow R_1R_2-NH + NaCl + H_2O</math>  <math>R_1R_2R_3-NHCl + NaOH \rightarrow R_1R_2R_3-N + NaCl + H_2O</math></p>	n/a