

AMINES

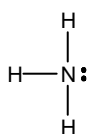


Name Form

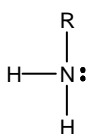
TYPES OF AMINES

- Amines can be classed as primary, secondary and tertiary.
- Ammonia can be regarded as the simplest amine.
- Aromatic amines have the N joined directly to the benzene ring.
- Quaternary ammonium salts contain quaternary ammonium ions and are related to amines, but they are not amines and do possess a lone pair of electrons on the N.
- There is some H-bonding between molecules, but this is weaker than in alcohols (e.g. CH_3NH_2 is a gas).

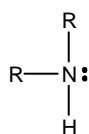
ammonia



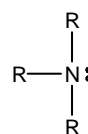
primary amine



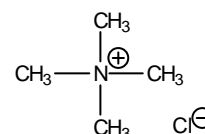
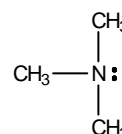
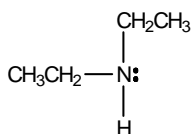
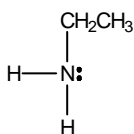
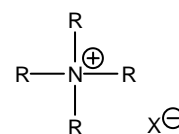
secondary amine



tertiary amine

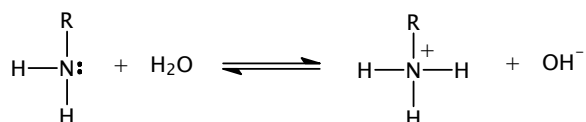


quaternary ammonium salt (NOT amines)



BASE STRENGTH OF AMINES

- Amines are Brønsted-Lowry bases (proton acceptors).
- They are weak bases, and act as bases because the lone pair on the N atom can readily accept a proton.



- The ability of ammonia or an amine to act as a base depends on how well the lone pair on the N atom can accept H^+ .
- The higher the electron density of the lone pair on the N, the better it will be able to accept H^+ , so the stronger the base.

In general, the order of base strength is:

3^y, 2^y and 1^y amines compared to ammonia

- Compared to ammonia, the more alkyl groups that are substituted onto the N atom in place of H atoms, the more electron density is pushed onto the N atom (as the inductive effect of alkyl groups is greater than that of H atoms - so alkyl groups push electron density towards the N atom better than H atoms).
- So the more alkyl groups, the higher the electron density of the lone pair on the N, so the stronger the base.

Aromatic amines compared to ammonia

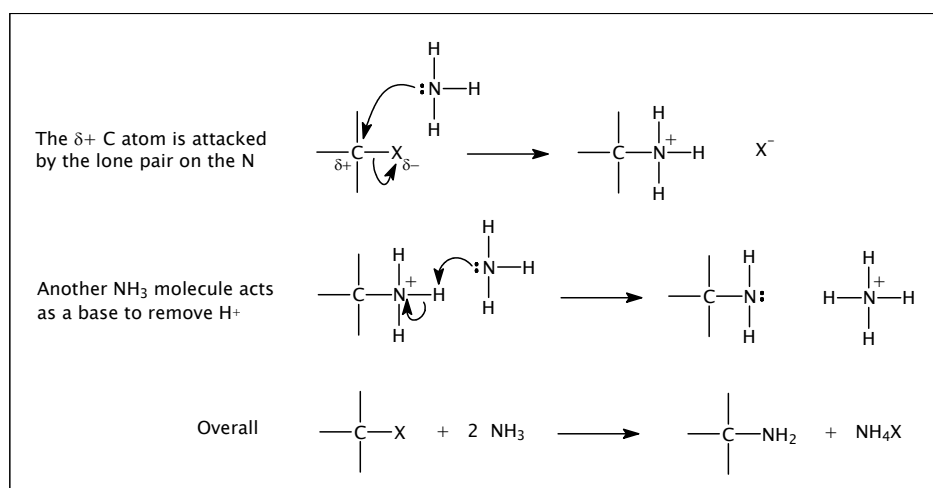
- The lone pair on this N is partially delocalised into the benzene ring, leading to a reduction in the electron density on the N atom, so weaker base strength.

For each of the following pairs of amines, draw the structures, state which is the stronger base and explain why it is the stronger base.

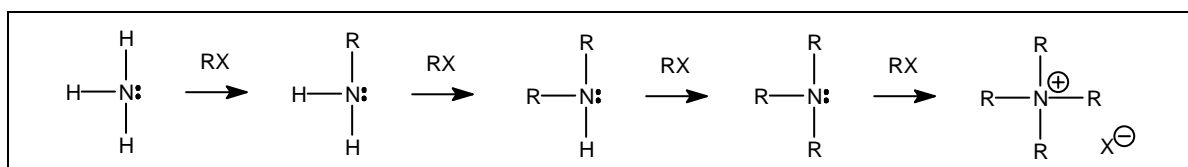
	amine	amine	stronger base	reason
1	methylamine	diethylamine		
2	propylamine	phenylamine		
3	ammonia	phenylmethylamine ($C_6H_5CH_2NH_2$)		
4	ammonia	cyclohexylamine		

NUCLEOPHILIC SUBSTITUTION

- NH_3 reacts with haloalkanes to form 1^o amines initially.
- The overall reaction is **nucleophilic substitution**, with ammonia acting as a nucleophile through the lone pair on the N atom attacking the electron deficient δ^+ C atom of the C-halogen bond.



- However, as well as ammonia, the amines produced also have a lone pair on the N atom, so they can react with haloalkanes.
- This means that the H's on the N can be successively replaced by the R group from the haloalkanes, right through to quaternary ammonium salts.



- This greatly complicates the reaction, because any amine produced in such a reaction can react with more haloalkane and undergo further substitution.
- Due to the problems of further substitution in this reaction, it is not often used to prepare amines, as a mixture of amines and ammonium salts is produced which would have to be separated.
- However, if a large excess of ammonia is used, then a 1^y amine is the main product.
- Similarly, if a large excess of the haloalkane is used, then the 4^y ammonium salt is the main product.

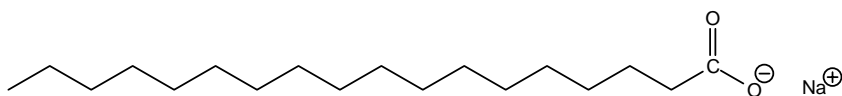
a) i) Give all the organic products formed when methylamine reacts with chloroethane.

ii) Give mechanism for the formation of the tertiary amine in this reaction.

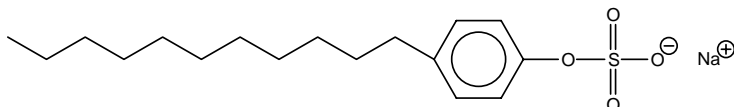
b) Give all the organic products formed when diethylamine reacts with 2-bromopropane

Use of quaternary ammonium salts

- Soap and detergent molecules are called surfactants and consist of
 - an ionic "head" – this will dissolve in water and is known as being hydrophilic
 - a long alkyl chain ("tail") – this dissolves grease (grease is not soluble in water) and is known as being hydrophobic.
- Micelles are formed as the soap/detergent molecules surround the dirt/grease molecules, with the hydrophobic tails in the centre dissolving the grease, and the hydrophilic heads around the outside dissolving in the water.
- This is an example of a soap:



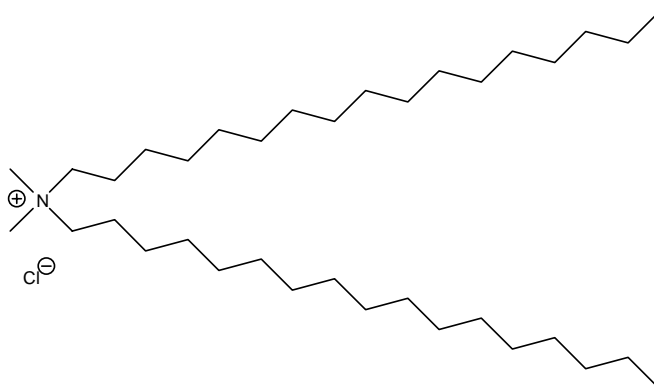
- This is an example of a detergent:



Cross-section of a spherical detergent micelle.

- Quaternary ammonium salts with some long chain alkyl groups are used as cationic surfactants.
- Fabric softeners often contain cationic surfactants as the surface of most materials is -ve charged.

e.g. $(\text{CH}_3)_2\text{N}[(\text{CH}_2)_{16}\text{CH}_3]_2^+ \text{Cl}^-$



PREPARATION OF AMINES

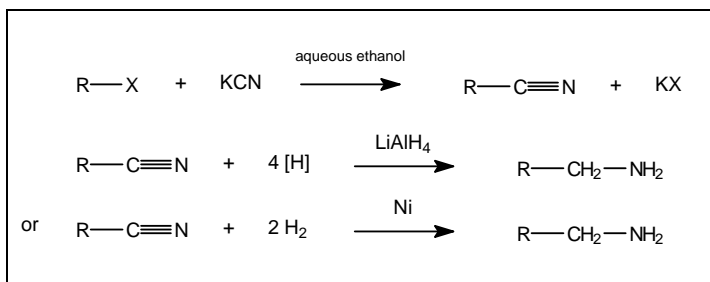
Primary aliphatic amines

a) By reaction of NH_2 with haloalkanes

- This method is not usually used due to the difficulties already described with the amines produced reacting further due to further substitution, giving a mixture of products.
- The desired amine could be separated, but this is time-consuming.

b) Reduction of nitrile compounds

- This is the commonest way and is usually done in two steps:
 - a) producing a nitrile compound from a haloalkane
 - b) then reducing the nitrile compound
- Note that the final amine has one more C than the original haloalkane.



Give two synthetic paths to making butylamine. Give equations for all reactions.

Primary aromatic amines

- These are usually prepared by the reduction of nitro compounds:

