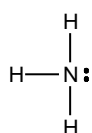




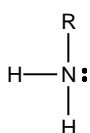
## 1) TYPES OF AMINES

- Amines can be classed as primary, secondary and tertiary.
- Amines are related to ammonia (NH<sub>3</sub>).
- 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 **NOT** possess a lone pair of electrons on the N.
- There is some hydrogen bonding between molecules and many simple amines are liquids at room temperature, but this is weaker than in alcohols (e.g. CH<sub>3</sub>NH<sub>2</sub> is a gas). Note that there is no hydrogen bonding between tertiary amine molecules (as there is no H attached to the N)

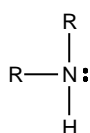
ammonia



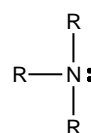
primary amine



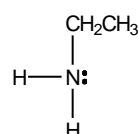
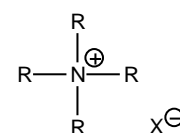
secondary amine



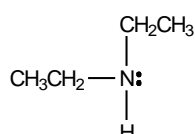
tertiary amine



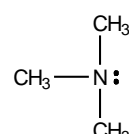
quaternary ammonium salt (**NOT** amines)



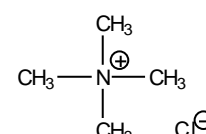
ethylamine



diethylamine



trimethylamine

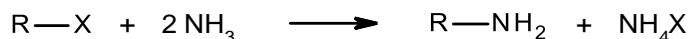


tetramethylammonium chloride

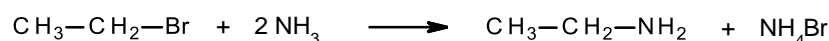
## 2) PREPARATION OF 1° ALIPHATIC AMINES

### a) By reaction of NH<sub>3</sub> with halogenoalkanes

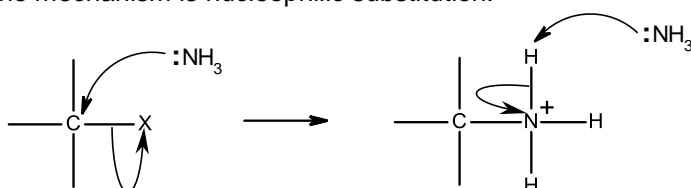
- Halogenoalkanes are reacted with an excess of concentrated ammonia dissolved in ethanol at pressure in a sealed container.



e.g. making ethylamine: bromoethane + excess conc NH<sub>3</sub>



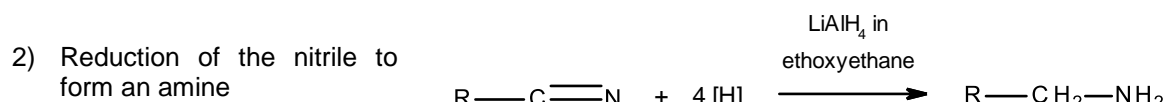
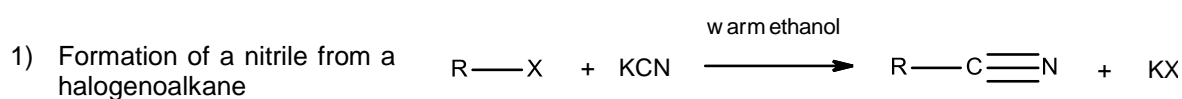
- The mechanism is nucleophilic substitution.



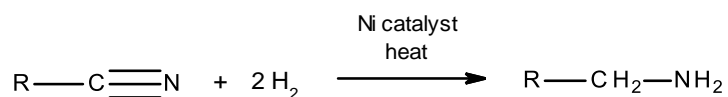
- This method is not usually used due to make primary amines however as the amine produced can react further with more of the halogenoalkane to form secondary and tertiary amines and quaternary ammonium salts. This problem is minimised by using an excess of concentrated ammonia, but it is still a problem.

### **b) By reduction of nitrile compounds**

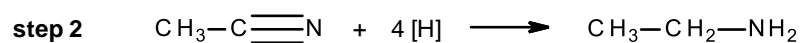
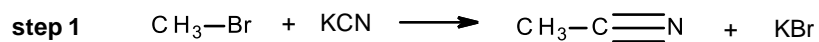
- This is the commonest way as it only forms one amine rather than a mixture.
- It is done in two steps.
- Note that the product has one more C atom than the starting material.



OR



e.g. making ethylamine



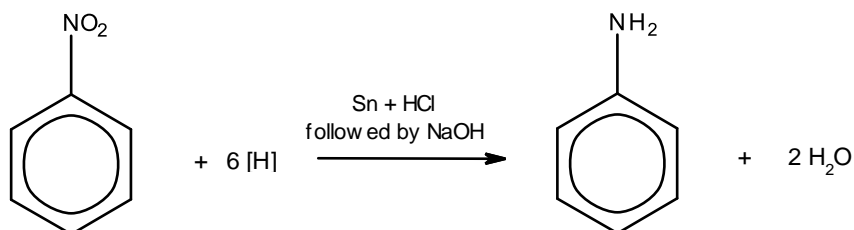
**TASK 1** – Give two synthetic paths to making butylamine. Give equations for all reactions.

Route 1

Route 2

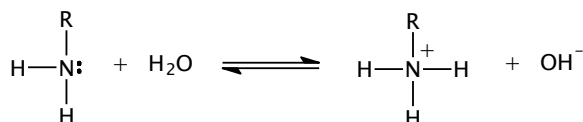
### 3) PREPARATION OF 1<sup>y</sup> AROMATIC AMINES

- These are usually prepared by the reduction of nitro compounds using tin and concentrated hydrochloric acid. (this would actually form the ammonium salt and so NaOH is added to give the amine).



### 4) 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.



**TASK 2** – Write equations for the following reactions of amines as bases. Show the structure of all organic substances

1) *Methylamine + nitric acid*

2) *Diethylamine + sulfuric acid*

- 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:

tertiary amine > secondary amine > primary amine >  $NH_3$  > aromatic amine

### $3^y$ , $2^y$ 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

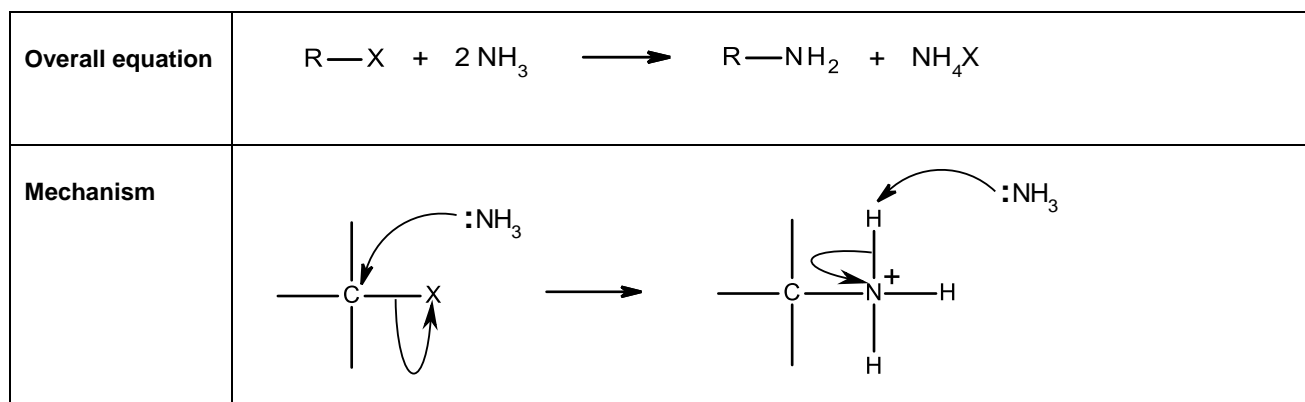
- The lone pair on this N is partially delocalised into the benzene ring, leading to a reduction in the electron density on the N atom, so weaker base strength.

**TASK 3** – Draw the structure of the two amines and then identify and explain which is the stronger base.

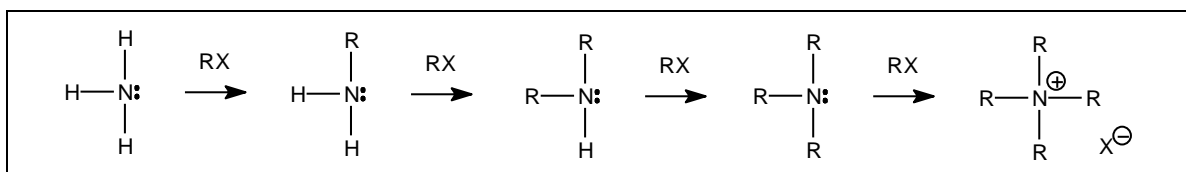
	amine	amine	stronger base	reason
1	methylamine	diethylamine		
2	propylamine	phenylamine		
3	ammonia	phenylmethylamine ( $C_6H_5CH_2NH_2$ )		
4	ammonia	cyclohexylamine		

## 5) NUCLEOPHILIC SUBSTITUTION REACTIONS

- $\text{NH}_3$  reacts with halogenoalkanes to form  $1^\text{y}$  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  $\delta^+$  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 halogenoalkanes. (in fact, the product has a greater electron density on the N lone pair and is even better at reacting with halogenoalkane than the original molecule).
- 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  $1^\text{y}$  amine is the main product.
- Similarly, if a large excess of the haloalkane is used, then the  $4^\text{y}$  ammonium salt is the main product.

**TASK 4** – Give two synthetic paths to making butylamine. Give equations for all reactions.

- 1) Draw the structure of and name the main organic product when ethylamine reacts with a large excess of chloromethane.
- 2) Draw the structure of and name the main organic product when a large excess of propylamine reacts with a chloromethane.

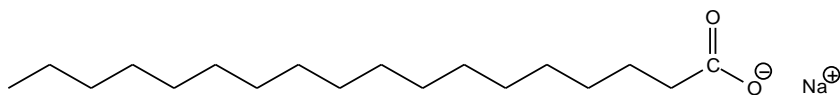
3) a) Draw the structure of and name the organic products formed when methylamine reacts with chloroethane.

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

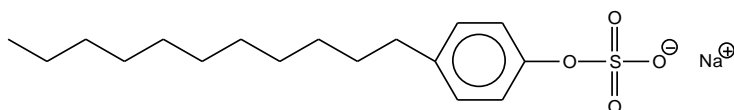
4) Draw the structure of all the organic products formed when diethylamine reacts with 2-bromopropane

### Use of quaternary ammonium salts

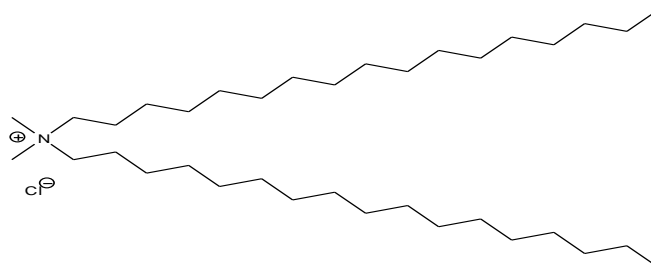
- Soap and detergent molecules are called surfactants and consist of
  - an ionic "head" – this will dissolve in water and is known as being hydrophilic
  - a long alkyl chain ("tail") – this dissolves grease (grease is not soluble in water) and is known as being hydrophobic.
- Micelles are formed as 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:



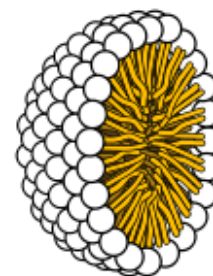
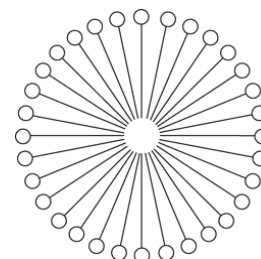
- This is an example of a detergent:



- 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.

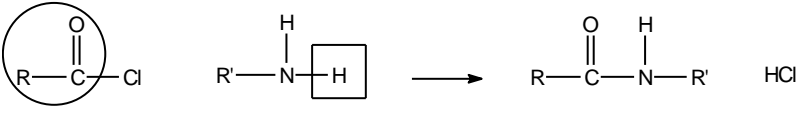
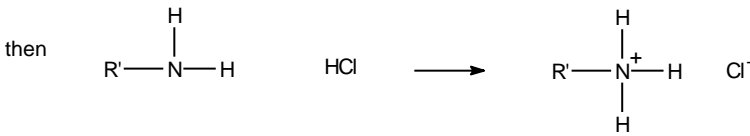
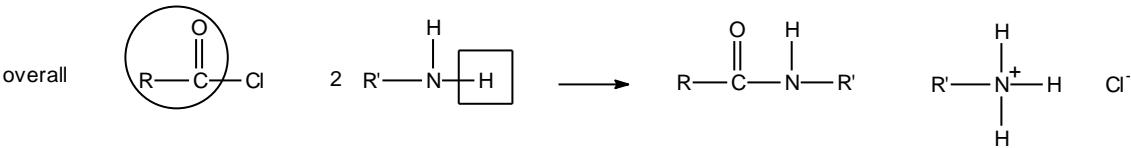
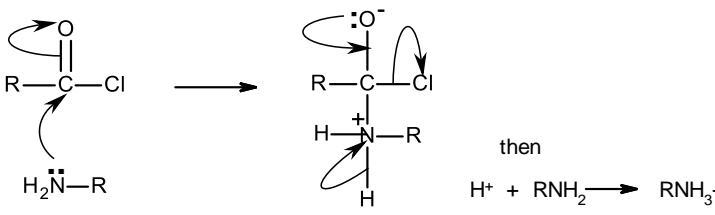


e.g.  $(\text{CH}_3)_2\text{N}[(\text{CH}_2)_{16}\text{CH}_3]_2^+ \text{Cl}^-$



## 6) NUCLEOPHILIC ADDITION-ELIMINATION REACTIONS (ACYLATION)

- Amines react with acyl chlorides and acid anhydrides to replace an H on the N with the acyl group.
- This produces an amide and a molecule of HCl or a carboxylic acid.
- A second molecule of the amine reacts with the HCl / carboxylic acid to form a salt.

<p><b>Equation</b></p>	<p>e.g. acylation of an amine (using an acyl chloride)</p>  <p>then</p>  <p>overall</p> 
<p><b>Mechanism (for acyl chlorides)</b></p>	<p>nucleophilic addition-elimination</p>  <p>then</p> $\text{H}^+ + \text{RNH}_2 \rightarrow \text{RNH}_3^+$

### TASK 5

- Give balanced equation for: ethylamine + propanoic anhydride
- Give balanced equation and mechanism for: propylamine + butanoyl chloride