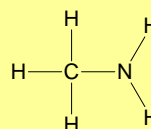


# Amines

N Goalby  
Chemrevise.org

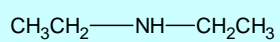
## Types of Amines

primary amine (one  
C attached to N)



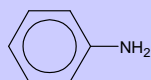
name: methylamine

Secondary amine (two C's  
attached to N)



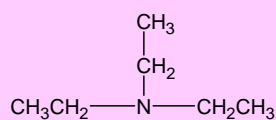
name : diethylamine

It is also possible to have  
aromatic amines



phenylamine

tertiary amine (three C's  
attached to N)

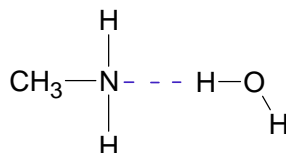


name: triethylamine

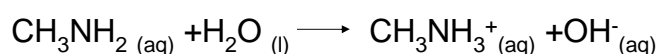
## Basic nature of amines

### Solubility in water and basic nature.

Small amines can form hydrogen bonds with water and therefore can dissolve readily in water.



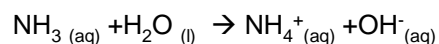
They also react with the water to form basic solutions.



Primary aliphatic amines act as Bronsted-Lowry Bases because the lone pair of electrons on the nitrogen is readily available for forming a dative covalent bond with a  $\text{H}^+$  and so accepting a proton

## Base strength

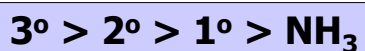
Primary aliphatic amines are stronger bases than ammonia as the alkyl groups are electron releasing and push electrons towards the nitrogen atom and so make it a stronger base.



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).

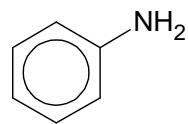
The more alkyl groups, the higher the electron density of the lone pair on the N, so the stronger the base.

Therefore  $3^\circ$  amines are stronger bases than  $2^\circ$  amines which are stronger than  $1^\circ$  amines

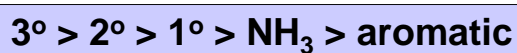
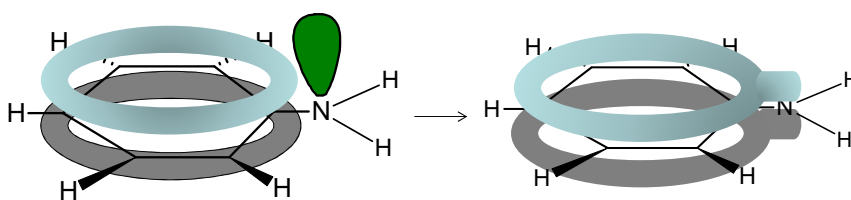


## Base strength of aromatic amines

Primary aromatic amines such as Phenylamine do not form basic solutions because the lone pair of electrons on the nitrogen delocalise with the ring of electrons in the benzene ring. This means the N is less able to accept protons.



phenylamine



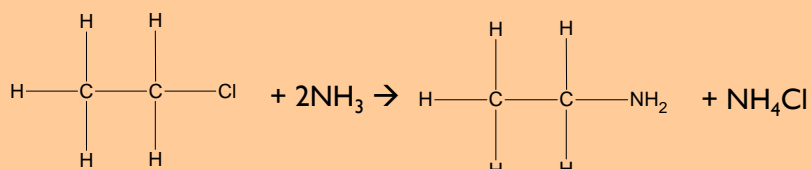
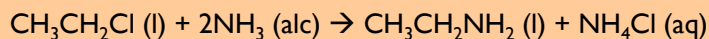
## Methods of preparing amines

### Method 1: Preparation from haloalkanes

**Change in functional group:** haloalkane  $\rightarrow$  amine

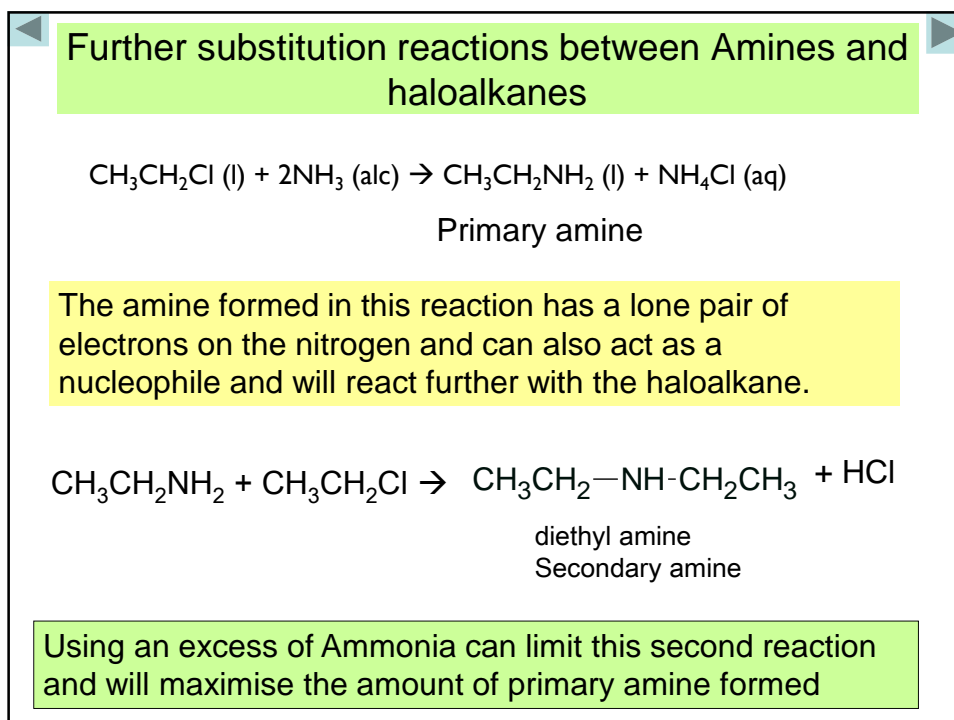
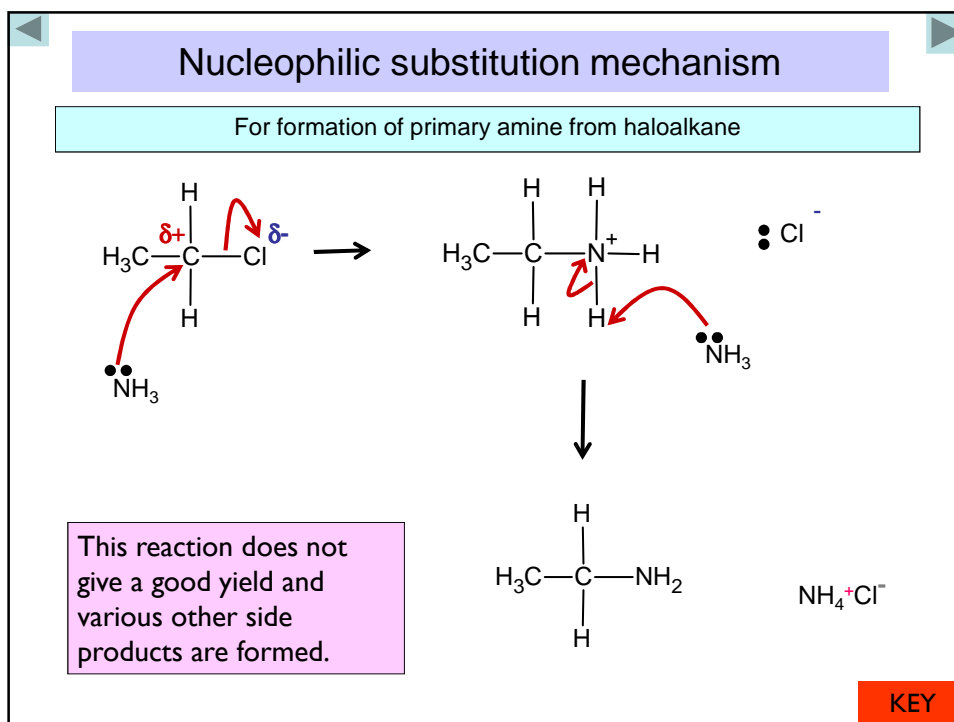
<b>Reagent:</b>	$\text{NH}_3$ dissolved in ethanol
<b>Conditions:</b>	Heating under pressure (in a sealed tube)
<b>Mechanism:</b>	Nucleophilic Substitution
<b>Type of reagent:</b>	Nucleophile, $:\text{NH}_3$

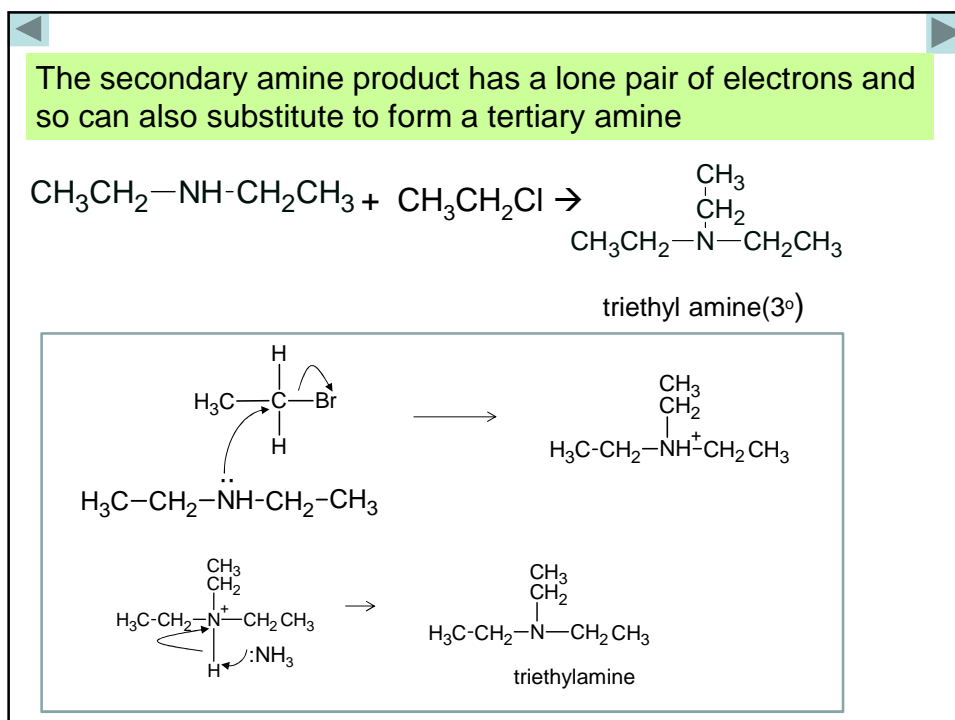
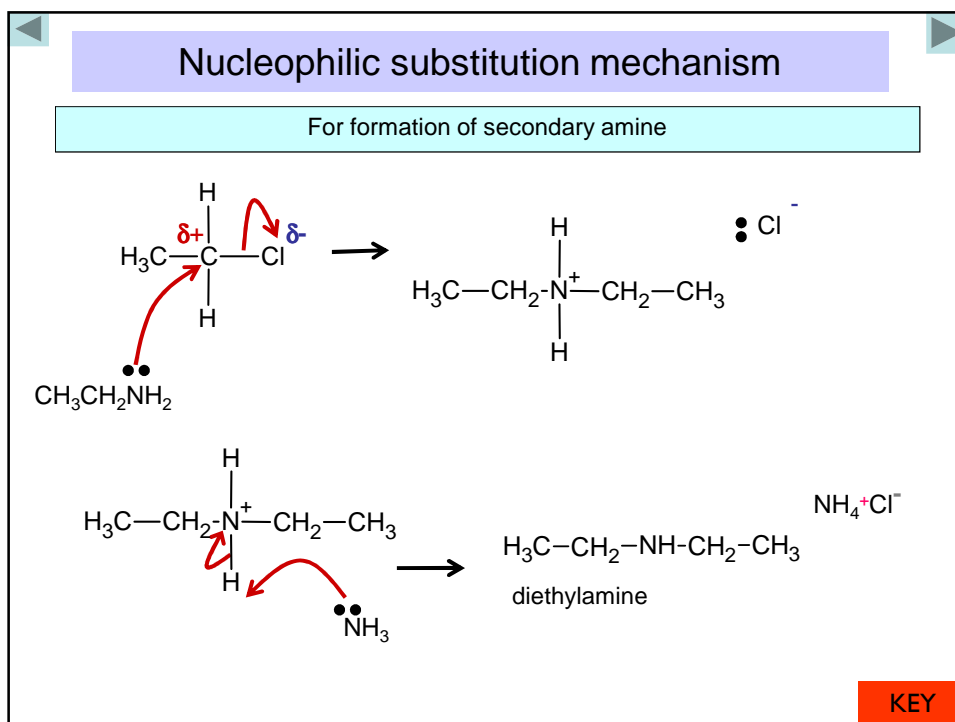
### Equation:



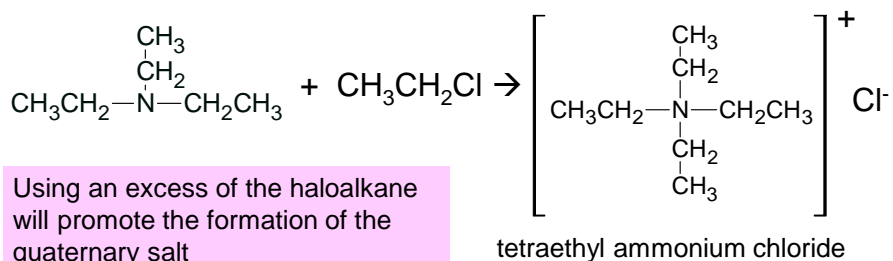
**1-chloroethane**

**ethylamine**

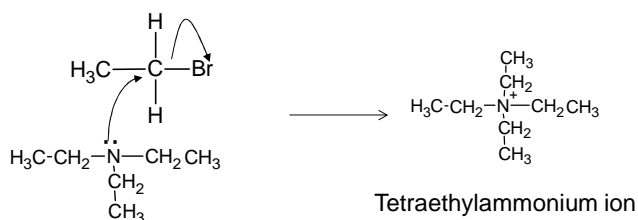




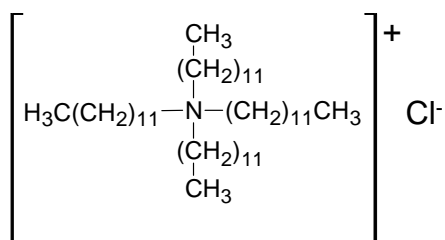
The tertiary amine product has a lone pair of electrons and so can also substitute to form a quaternary ammonium salt



Using an excess of the haloalkane will promote the formation of the quaternary salt



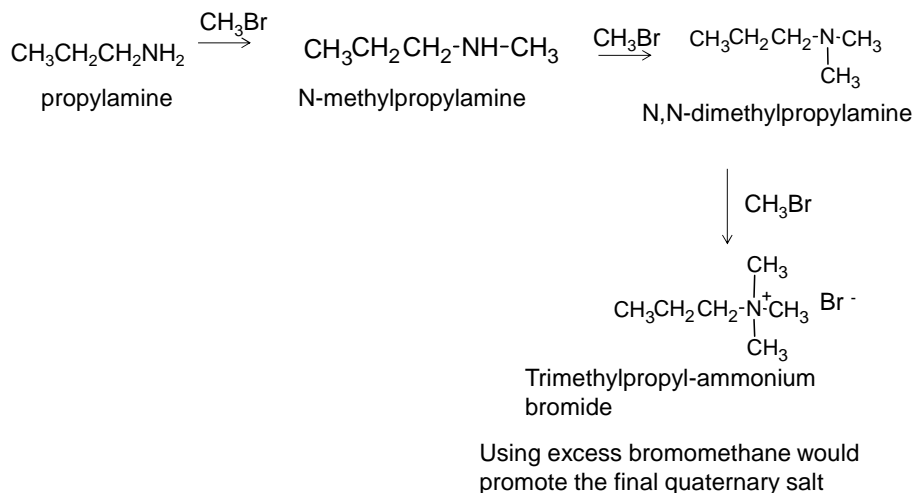
## Quaternary salts



Quaternary Salts can be used as **cationic surfactants**

The positive nitrogen is attracted toward negatively charged surfaces such as glass, hair, fibres and plastics. This helps in their uses as fabric softeners, hair conditioners and sewage flocculants

Some questions will involve substituting an amine onto a haloalkane which has a different length of carbon chain from the amine



## Methods of preparing amines 2

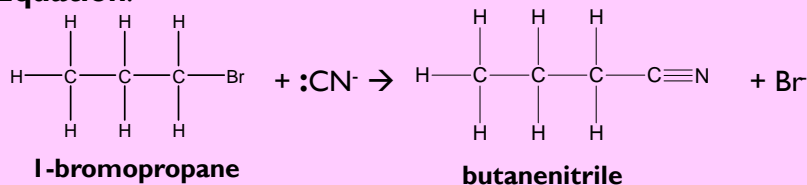
Using haloalkanes and ammonia is not an efficient method for preparing primary amines because of the further substitution that occurs.

A better method is to use the following two step method

Step 1: Conversion of a haloalkane → nitrile

<b>Reagent:</b>	KCN dissolved in ethanol	
<b>Conditions:</b>	Heating under reflux	
<b>Mechanism:</b>	Nucleophilic Substitution	$:\text{C}\equiv\text{N}^-$
<b>Type of reagent:</b>	Nucleophile, $:\text{CN}^-$	

**Equation:**



## Methods of preparing amines 2

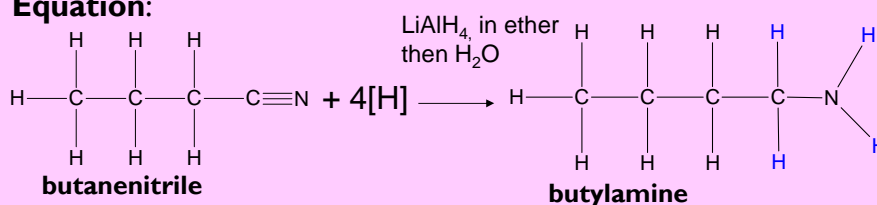
### Step 2: Reduction of the nitrile $\rightarrow$ amine

**Reagents:** **LiAlH<sub>4</sub> dissolved in ether** (diethylether)  
(followed by hydrolysis with water)

**Mechanism:** Reduction

**Type of reagent:** Reducing Agent LiAlH<sub>4</sub>

#### Equation:



A disadvantage of this method is that it is a two step reaction that may therefore have a low yield. Also KCN is toxic

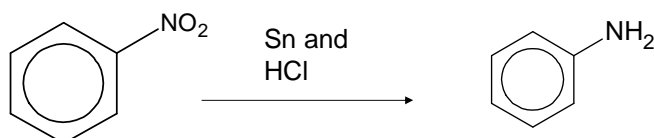
## Reducing nitro-arenes to amines

The nitro group on an arene can be reduced an amine group as follows

**Reagent:** Sn and HCl or Fe and HCl

**Conditions:** Heating

**Mechanism:** reduction

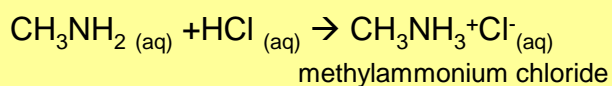


These amines can be converted to other compounds that are used as dyes

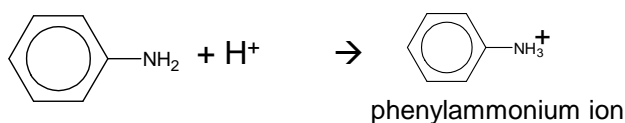


## Reaction with acid

Amines react with acids to form ammonium salts.



Phenylamines react with acid



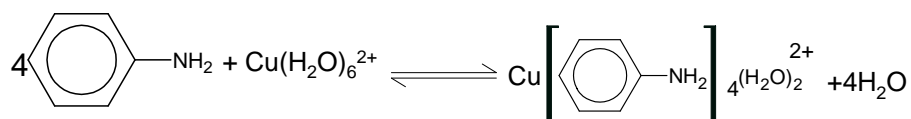
The ionic salts formed in this reaction means that the compounds are soluble in the acid.

e.g. Phenylamine is not very soluble in water but phenylammonium chloride is soluble

These ionic salts will be solid crystals, if the water is evaporated, because of the strong ionic interactions.

## Formation of complex ions

The lone pair of electrons on the nitrogen enable amines to act as ligands and bond into transition metal ions to form coloured complex ions.



Ammonia can also act as a ligand and forms complex ions

