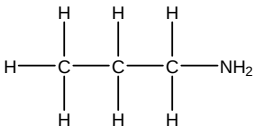
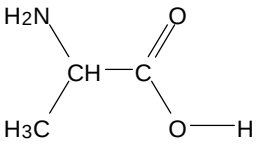
6.2.1 Amines

Naming Amines
These end in **–amine**.
There is, however, rather confusingly two ways of using this suffix.
The exam board tend to use the common version where the name stem ends in **-yl** prop**yl**amine.
The IUPAC version of the same chemical is propan-1-amine. (This is used in the same way as naming alcohols)



prop**yl**amine
Or propan-1-amine

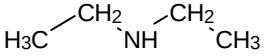
If there is another priority functional group as well as the amine group then the prefix amino is used.



2-aminopropanoic acid.

If the amine is secondary and has two alkyl groups attached to the nitrogen, then each chain is named and the smaller alkyl group is preceded by an –N which plays the same role as a number in positioning a side alkyl chain

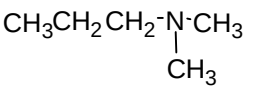
$CH_3CH_2CH_2NHCH_3$
N-methylpropylamine (common name)
N-methylpropan-1-amine (IUPAC name)



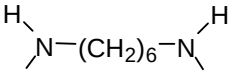
In the common naming version if the chain lengths are the same an –N is not used

Diethylamine (common name- does not use N if chains are same length)
N-ethylethanamine (IUPAC name does still use N)

If a tertiary amine similar rules apply, and each alkyl side group is given an N



N,N-dimethylpropylamine (common name)
N,N-dimethylpropan-1-amine (IUPAC name)



hexane-1,6-diamine

It could also be named
1,6-diaminohexane

Base Properties

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 H^+ and so accepting a proton.

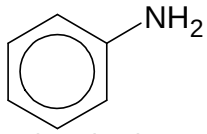
$CH_3NH_2 + H_2O \rightarrow CH_3NH_3^+ + OH^-$

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.

$NH_{3\,(aq)} + H_2O_{(l)} \rightarrow NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$

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

Reactions with acids

Amines as bases react with acids to form ammonium salts.
$CH_3NH_{2\,(aq)} + HCl_{(aq)} \rightarrow CH_3NH_3^+Cl^-{}_{(aq)}$
Methylamine methylammonium chloride

Addition of NaOH to an ammonium salt will convert it back to the amine

$CH_3CH_2NH_2 + H_2SO_4 \rightarrow (C_2H_5NH_3^+)_2SO_4^{2-}$
$CH_3CH_2NH_2 + CH_3COOH \rightarrow (C_2H_5NH_3^+)\ CH_3COO^-$

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

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

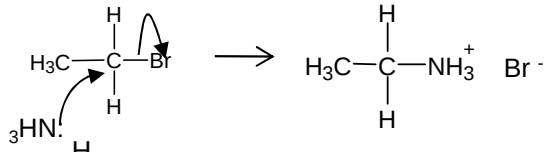
Nucleophilic properties

Primary amines can be formed by the **nucleophilic substitution** reaction between haloalkanes and ammonia.

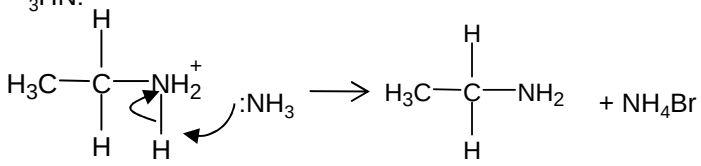
Reaction with ammonia forming primary amine

$CH_3CH_2Br + 2NH_3 \rightarrow CH_3CH_2NH_2 + NH_4Br$

Excess ammonia dissolved in ethanol is the reagent



In the first step of the mechanism the nucleophile attacks the haloalkane to form an intermediate.

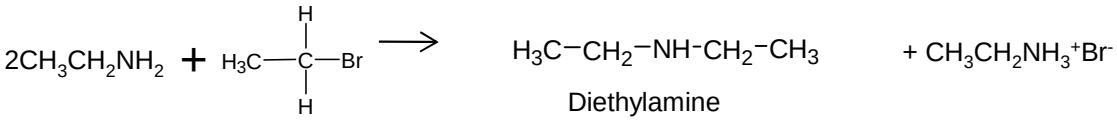


In the second step of the mechanism a second ammonia removes a proton from the intermediate (acts as base) to form the amine.

Using an **excess of ammonia** can limit further substitution reactions and will **maximise the amount of primary amine** formed

Reacting primary amines with haloalkanes forming secondary amine

Amines will react with haloalkanes in the same nucleophilic substitution reactions that ammonia does above.

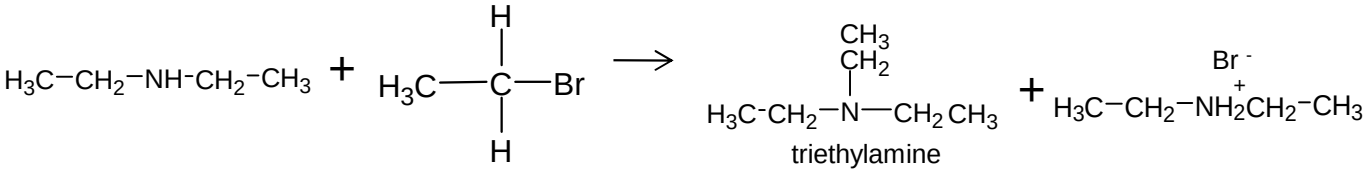


Diethylamine

A primary amine will react with a haloalkane to form a secondary amine.

Reacting secondary amines with haloalkanes to form a tertiary amine

The same reaction mechanism occurs with the secondary amine reacting to form a tertiary amine.

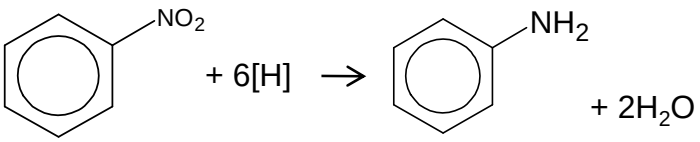


triethylamine

Reducing nitroarenes to aromatic amines

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

Reagent: Sn and concentrated HCl
Conditions: Heating
Mechanism: reduction



nitrobenzene phenylamine

As the reaction is carried out in HCl the salt $C_6H_5NH_3^+Cl^-$ will be formed. Reacting this salt with NaOH will give phenylamine.