# Edexcel Chemistry A-Level

## Topic 18: Organic Chemistry III

Detailed Notes

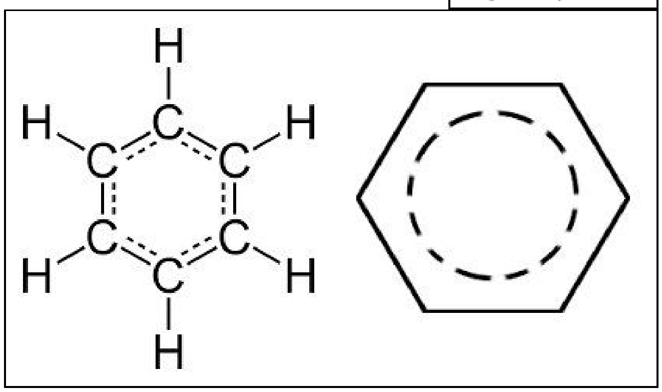
# Topic 18A: Arenes - Benzene

## Bonding in Aromatic Compounds

Arenes are aromatic compounds that **contain benzene as part of their structure**. They have **high melting points** due to the high stability of the delocalised ring, but **low boiling points** as they are **non-polar** molecules and **cannot often be dissolved** in water. Benzene is an **arene** consisting of a ring of **six carbon atoms** with **six hydrogen atoms** and a ring of **delocalised electrons**:

*Example:*

Image courtesy of Quora




Each bond in the benzene ring has an **intermediate length** in between that of a double and single bond.

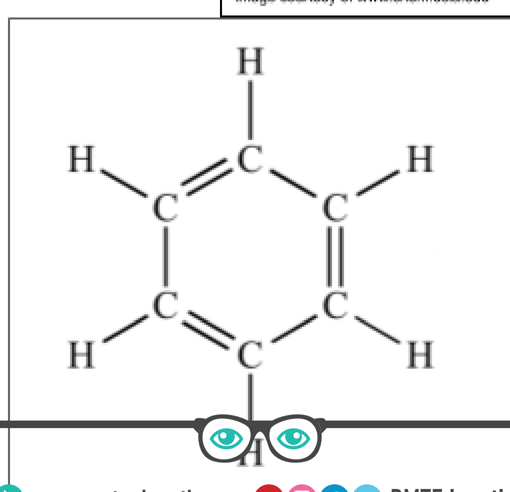
The outer electron from the **p-orbital** of each carbon atom is **delocalised** to form the central ring. This ring structure makes benzene **very stable** compared to other molecules of a similar size.

**Cyclohexatriene vs. Benzene**

When benzene was first discovered its structure was not known. It was predicted from empirical measurements that it had the structure similar to that of **cyclohexatriene**, with three double bonds and three single bonds.

*Example:*

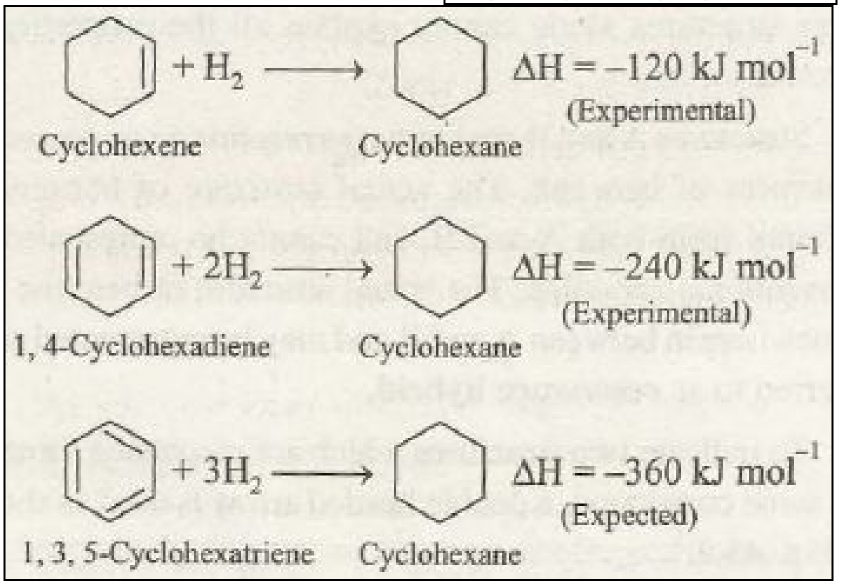
Image courtesy of www.chem.ucla.edu



Therefore the enthalpy change of hydrogenation for benzene was **predicted to be -360kJmol$^{-1}$**, three times the enthalpy change change of cyclohexene.

*Example:*

Image courtesy of chemistry-assignment.com




It was later discovered that the enthalpy change of hydrogenation of benzene was **actually -208kJmol$^{-1}$** leading to the conclusion of its **different, unusual structure**.

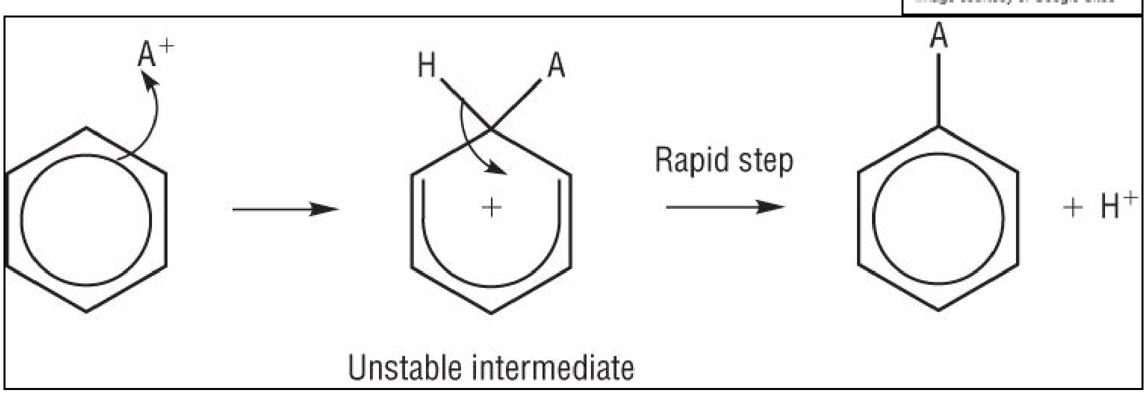
## Reactions of Benzene

### Electrophilic Substitution

The delocalised ring in benzene is an **area of high electron density** making it susceptible to attack from **electrophiles**. When these species attack the electron ring, it is **partially destroyed** then **restored** in the process of **electrophilic substitution**. This mechanism means aromatic amines and nitrobenzene can be produced from benzene.

**Mechanism**

Image courtesy of Google Sites




***The nucleophile is shown as A$^{+}$.***

## Nitration

In this form of electrophilic substitution, the electrophile is the **$NO_2^+$ ion**. This is a **reactive intermediate**, produced in the reaction of concentrated sulfuric acid ($H_2SO_4$) with concentrated nitric acid ($HNO_3$).

*Example:*

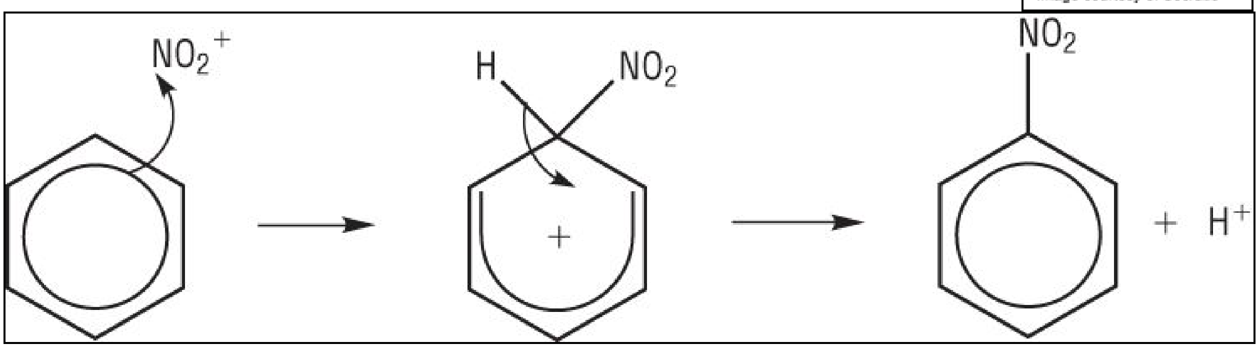
$$H_2SO_4 + HNO_3 \longrightarrow H_2NO_3^+ + HSO_4^-$$

$$H_2NO_3^+ \longrightarrow H_2O + \boxed{NO_2^+}$$

When heated with benzene these reagents lead to the **substitution of the $NO_2^+$ electrophile** onto the benzene ring, **removing a hydrogen** ion.

### Mechanism

Image courtesy of Socratic




This reaction shows a **mono-substitution** of a single $NO_2^+$ electrophile which takes places when the reaction temperature is **55°C**. At temperatures greater than this, multiple substitutions can occur. It is vital that only one substitution occurs for the production of **aromatic amines**.

## Friedel-Crafts Acylation

The delocalised electron ring in benzene can also act as a **nucleophile**, leading to the **attack on acyl chlorides**. This reaction is known as **Friedel-Crafts acylation**.

In order for it to take place, a **reactive intermediate** must be produced from the acyl chloride and an **aluminium chloride catalyst**.

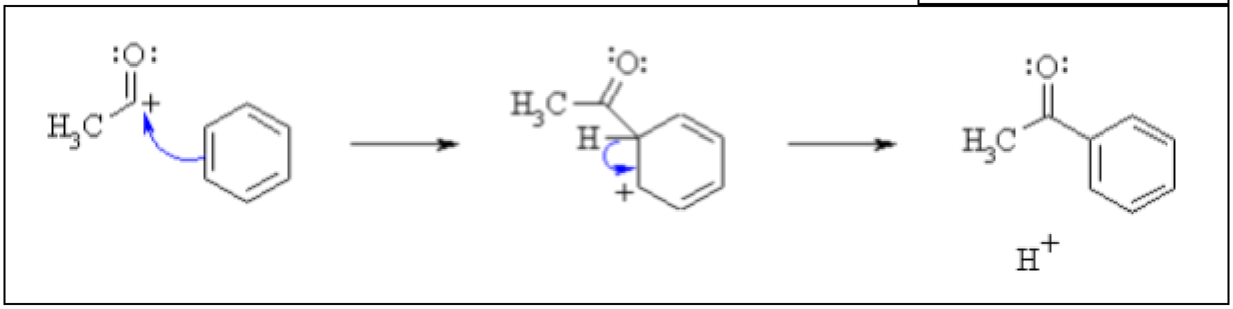
*Example:*

$$R\text{-}COCl + AlCl_3 \longrightarrow \boxed{R\text{-}CO^+} + AlCl_4^-$$

This reactive intermediate is then attacked by the benzene ring.

**Mechanism**

Image courtesy of the University of Calgary




At the end of the reaction, the **$H^+$ ion** removed from the ring reacts with the **$AlCl_4^-$ ion** to reform the aluminium chloride, showing it to be a **catalyst**.

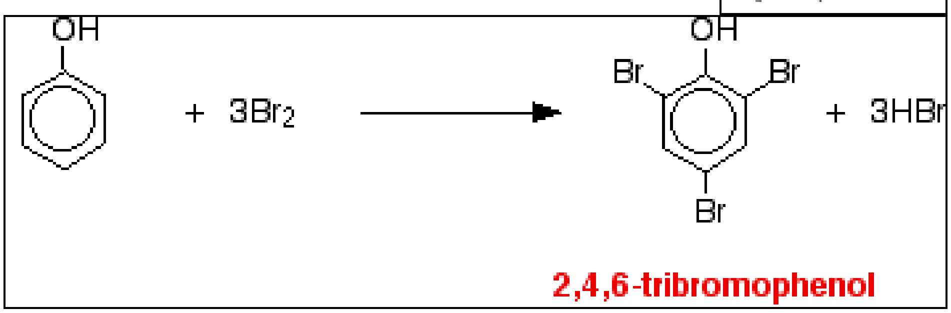
The product of this reaction is a **phenylketone**. In this case, the benzene group is called a **phenyl group**. These molecules are commonly used in the industrial production of dyes, pharmaceuticals and even explosives.

## Bromine Water

Phenol, produced in electrophilic substitution reactions with benzene can then react with bromine water via multiple substitutions to produce 2,4,6-tribromophenol which forms as a white precipitate with a distinct smell of antiseptic.

*Example:*

Image courtesy of ChemGuide



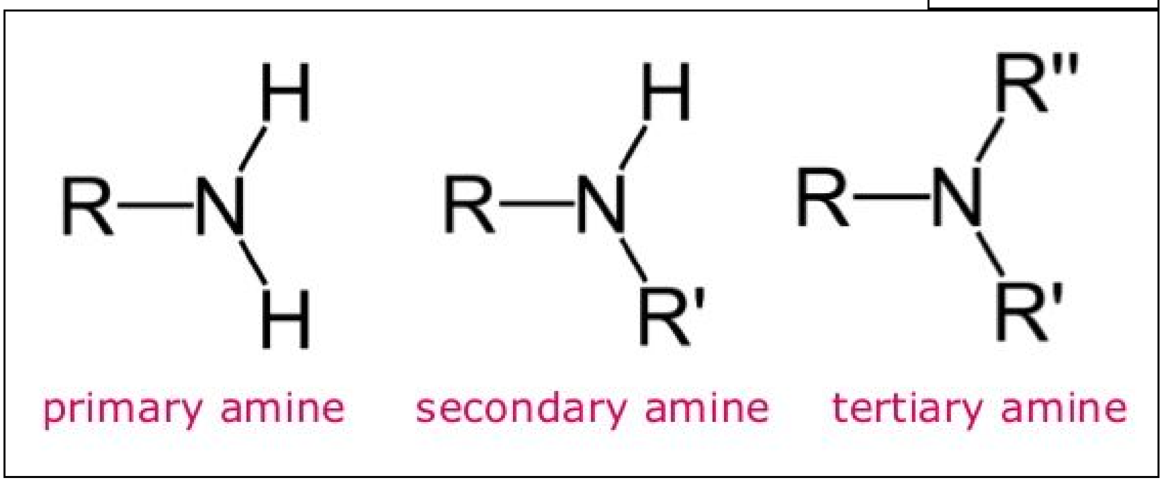
# Topic 18B: Amines, Amides, Amino Acids and Proteins

## Aliphatic Amines

Amines are produced when one or more of the hydrogen atoms in ammonia is **replaced with an organic group**. They can be **1°, 2° or 3° amines** depending on how many hydrogen atoms are replaced.

*Example:*

Image courtesy of SlideShare




Amines can be produced in two ways:

### Nucleophilic Substitution

This reaction produces amines from the reaction of a **halogenoalkane with ammonia** in a sealed tube. One mole of halogenoalkane reacts with two moles of ammonia producing a **primary amine** and an **ammonium salt** **(ammonium ion and bromide ion)**.

*Example:*

Image courtesy of chemguide.co.uk

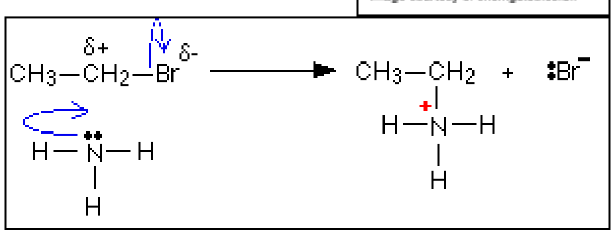
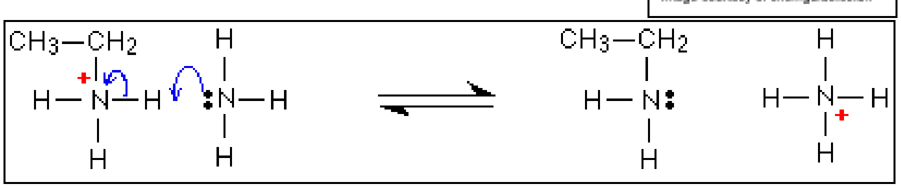


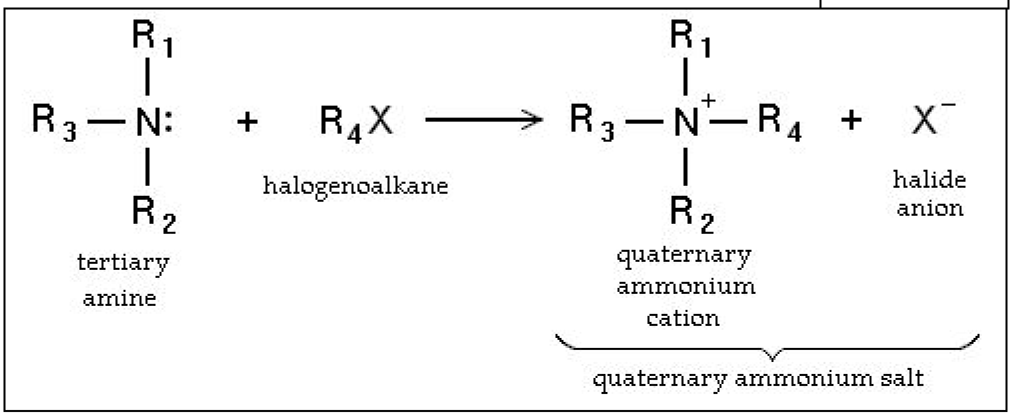
Image courtesy of chemguide.co.uk



This substitution reaction can continue until **all the hydrogen atoms have been replaced** with organic groups. Following this, an additional substitution can occur, producing a **quaternary ammonium salt**.

*Example:*

Image courtesy of Wikibooks



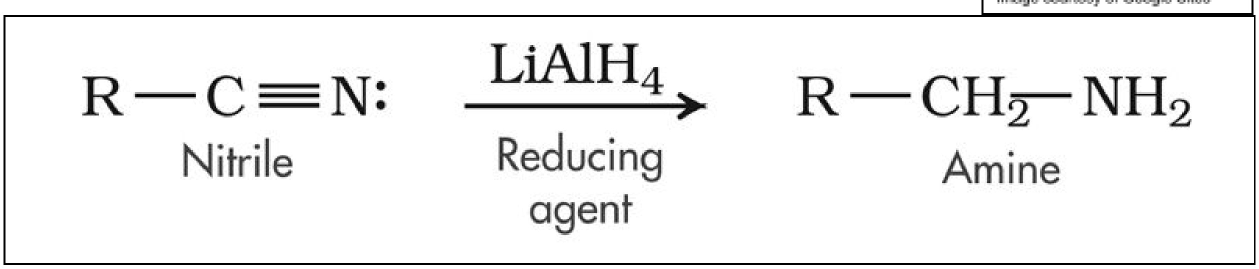

The multiple number of possible substitutions means that a **mixture of products** are produced. Therefore the reaction has **low efficiency** and reaction conditions have to be changed so that only a single substitution occurs. Ammonia can be added **in excess** in order to achieve only the primary amine, or the mixture of products can be **separated using fractional distillation**.

### Reduction of Nitriles

Reducing nitriles via **hydrogenation** can produce amines. This reduction requires **$LiAlH_4$**, a reducing agent, and **acidic conditions** or a combination of **hydrogen and nickel** (catalytic hydrogenation).

*Example:*

Image courtesy of Google Sites

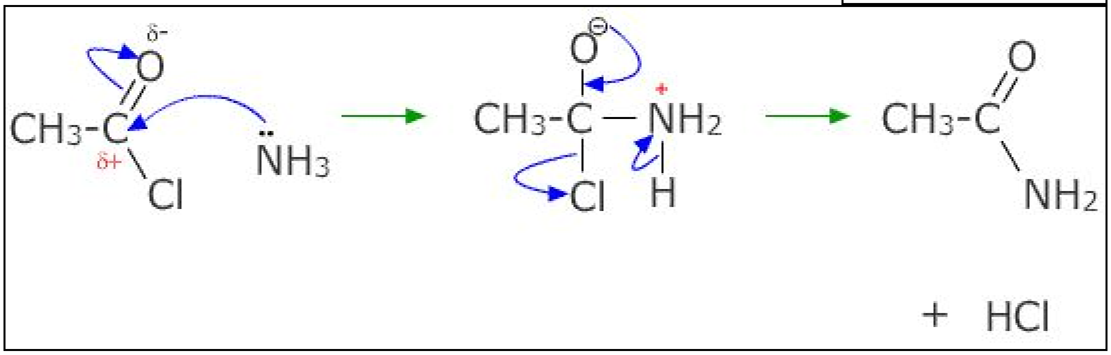



## Amides

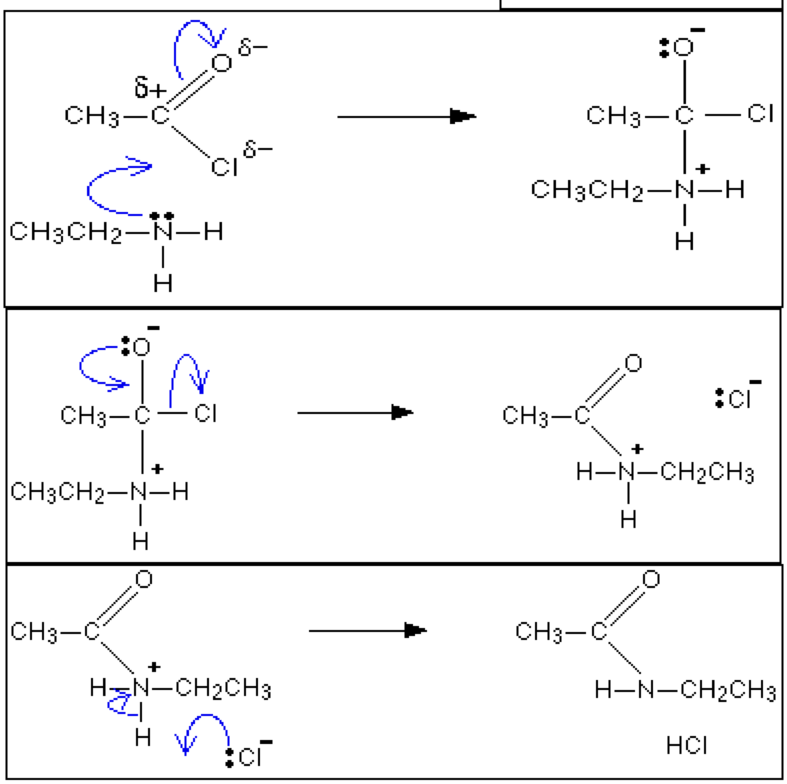
Amines can also undergo **nucleophilic addition-elimination** reactions with acyl chlorides to produce **amides** and **N-substituted amides**.

**Mechanism**

Image courtesy of alevelchem.com




Images courtesy of chemguide.co.uk

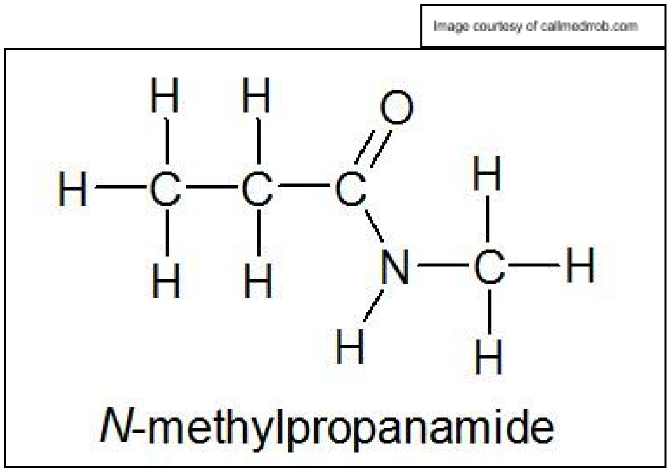



This same reaction mechanism can also occur with **acid anhydrides** to produce an amide and a carboxylic acid.

**N-substituted Amides**

When naming n-substituted amides, they are treated in a similar way to esters.

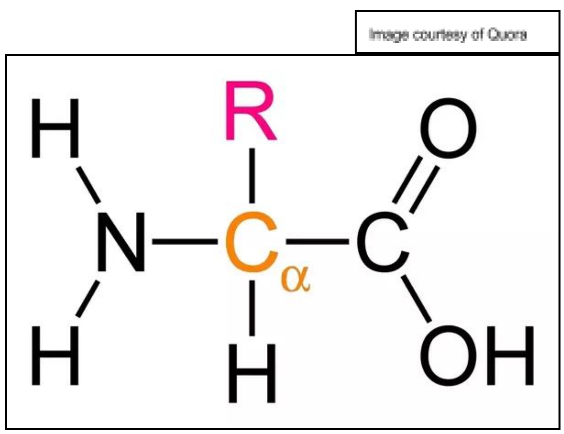
*Example:*




## Amino Acids

An amino acid is a compound with an **amine group and a carboxylic acid group** within the molecule. The amine group is always on the **second carbon** in the chain meaning they are always named as **'2-amino acids'**. As this is always the case, amino acids with this structure are also known as **'$\alpha$-amino acids'**.

*Example:*

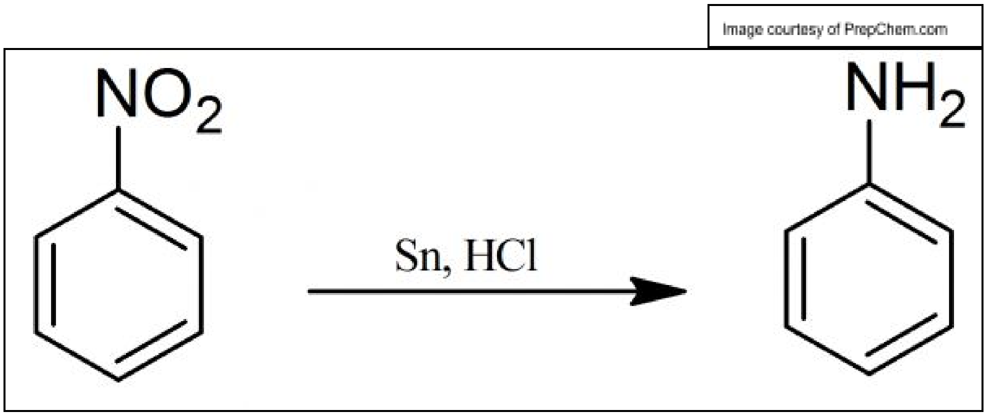



This second carbon is often **chiral** as it has four different groups bonded to it meaning amino acids exist as **optical isomers**. However in nature, nearly all amino acids exist as **a single negative enantiomer** so that they 'fit' into the correct cells within living organisms.

## Aromatic Amines

These can be produced from the **reduction of nitrobenzene** using concentrated hydrochloric acid (HCl) and a **tin catalyst**. They consist of an amine group and a benzene ring.

*Example:*



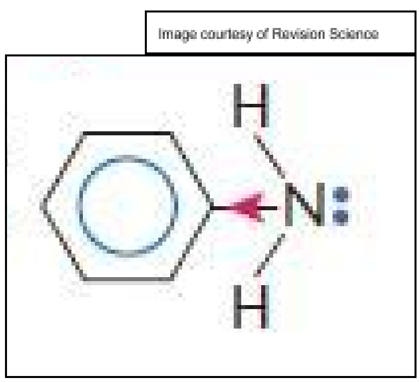

## Amine Base Properties

Amines are **weak bases** because the **lone electron pair** on the nitrogen atom can accept protons. The base strength of amines depends on **how available** the electron pair is on the molecule. The more available the electrons, the more likely it is to accept a proton, meaning it is a stronger base.

### The Inductive Effect

In an organic molecule, different functional groups can affect how available a lone electron pair is by changing **electron density** around the bond.

1. **Benzene rings** - draw electron density **away** from the nitrogen making it 'less available'
   *Example:*

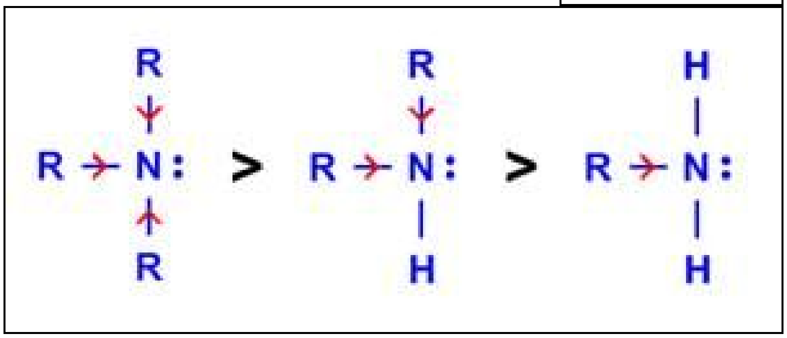



***Negative inductive effect.***

2. **Alkyl groups** - push electron density **towards** the nitrogen making it 'more available'. More alkyl groups means more 'pushing'.

*Example:*

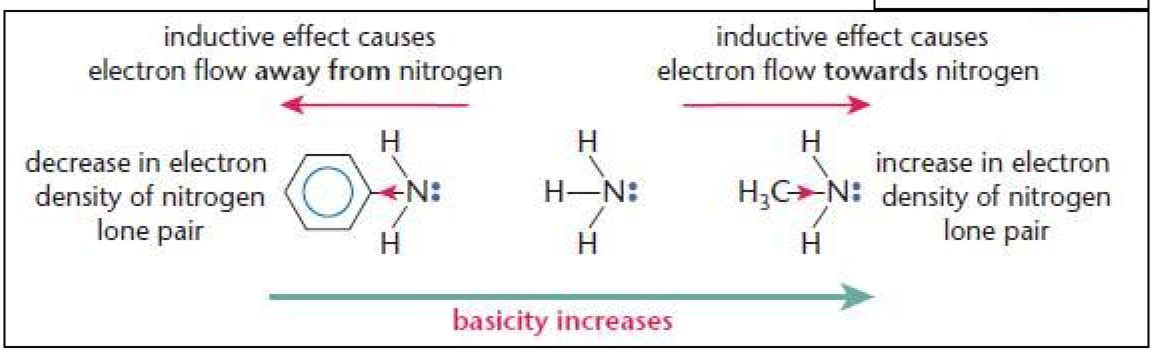
Image courtesy of Learnnext




***Positive inductive effect.***

This means **aliphatic amines are stronger** bases and **aromatic amines are weaker**.

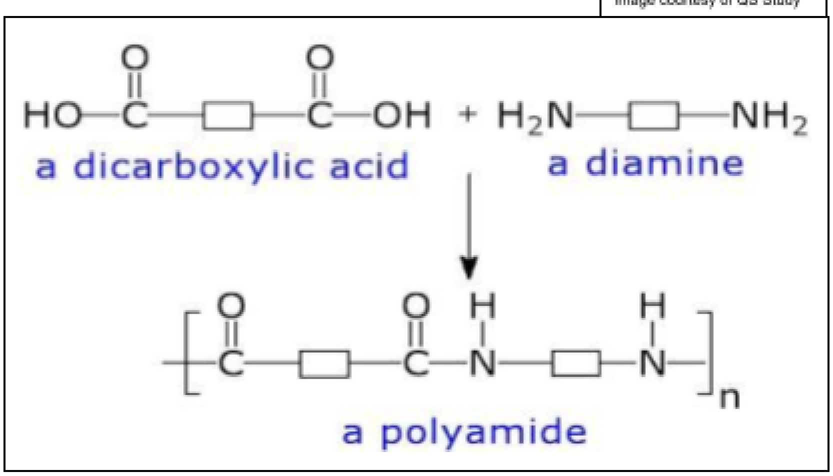
Image courtesy of Revision Science




## Polyamides

These are condensation polymers formed in a reaction between **dicarboxylic acid and a diamine**. A molecule of water is removed, leaving an **amide linkage**.
*Example:*

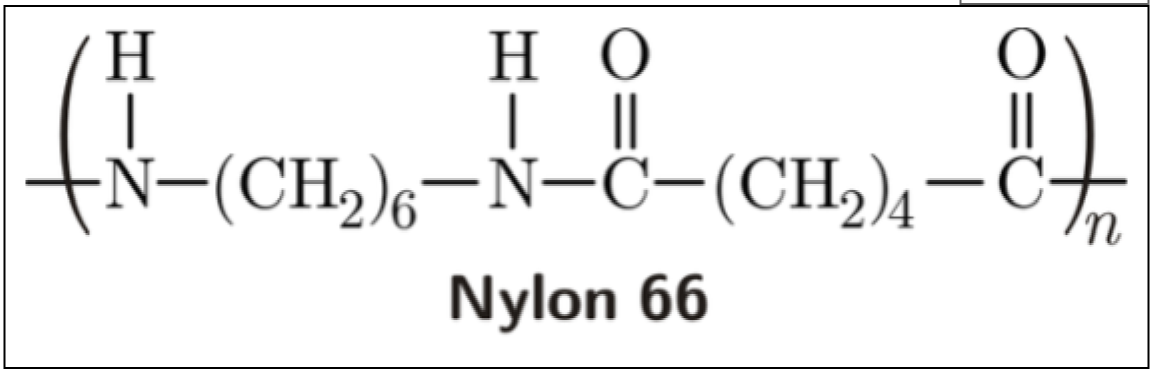
Image courtesy of QS Study




***-CONH- is the amide linkage.***

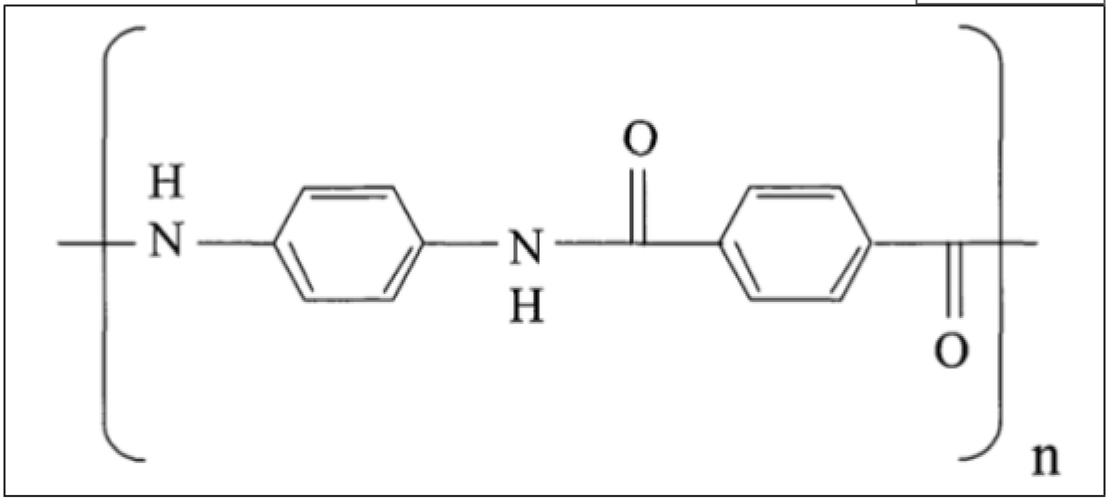
Examples of polyamides include **nylon-6,6** made from 1,6-diaminohexane and hexanedioic acid.
*Example:*

Image courtesy of Quora




**Kevlar** is another common polyamide made from benzene-1,4-dicarboxylic acid and 1,4-diaminobenzene.
*Example:*

Image courtesy of Quora

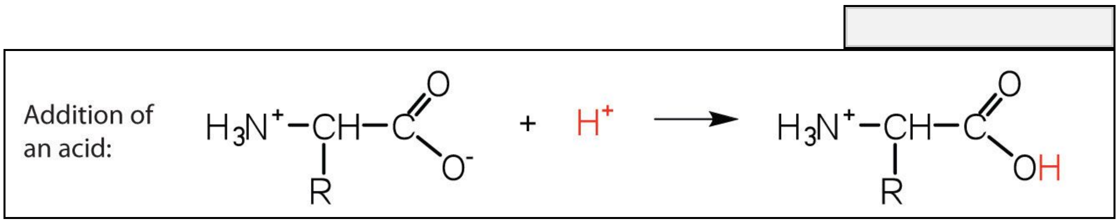


Polyamides are commonly formed from **long chain molecules** which provides them with **strength**.

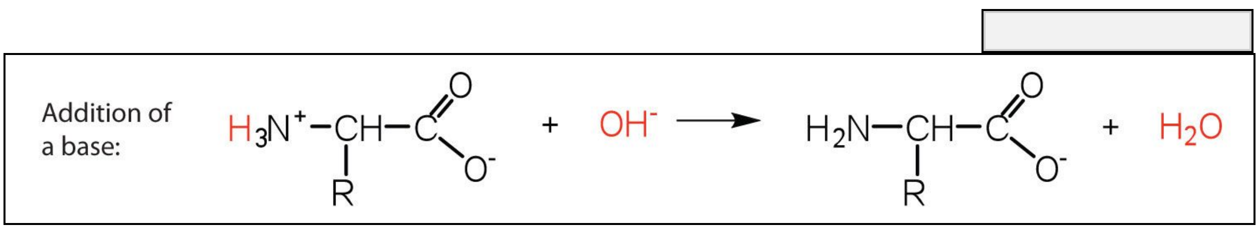
## Zwitterions

The two functional groups within a single molecule means that amino acids can **react as both acids and bases** depending on the conditions of the reaction.

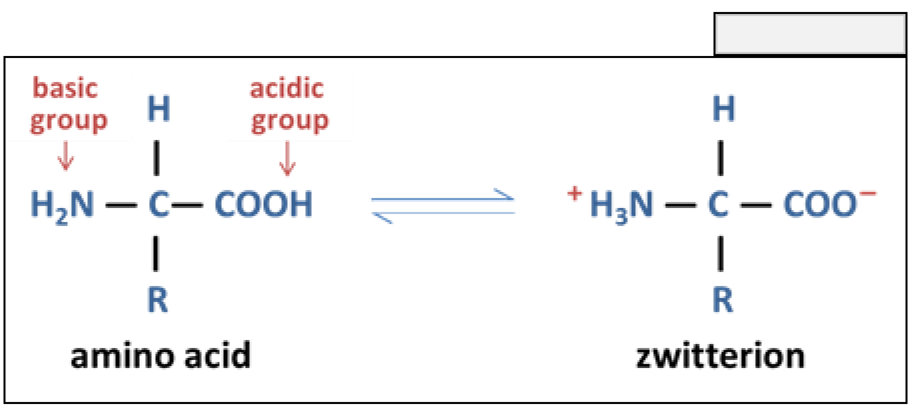
In **acidic conditions (low pH)**, the $COO^-$ group is more likely to accept a hydrogen ion, producing a **positive (acidic) end** to the molecule.
*Example:*




In **basic conditions (high pH)**, the hydrogen ion in the $NH_3^+$ group is more likely to be lost, producing a **negative (basic) end** to the molecule.
*Example:*




**Zwitterions** form at the **isoelectric** point, which is the pH at which the overall charge of the molecule is **zero**.
*Example:*



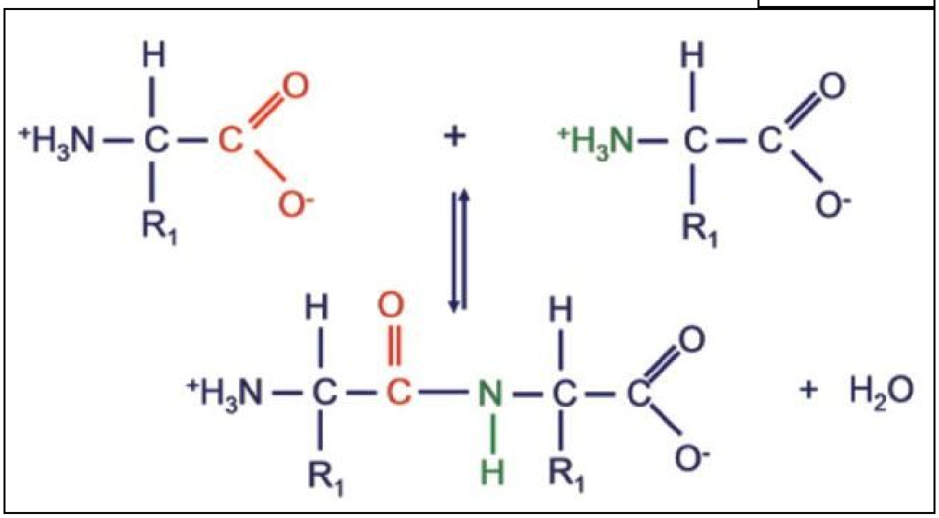
**Thin-layer chromatography** can be used to identify unknown amino acids using UV light to view the traces on the silica plate.

## Proteins

Proteins are another form of condensation polymer formed from sequences of amino acids joined together by **peptide bonds**.

*Example:*

Image courtesy of AZoM



***-CONH- is the peptide bond/amide linkage.***

# Topic 18C: Organic Synthesis

**(See organic synthesis chart)**