OCR A Chemistry A-level

Module 6.2: Nitrogen Compounds, Polymers and Synthesis

Detailed Notes

6.2.1 Amines

Basicity and Preparation of Amines

Amines are produced when one or more of the hydrogen atoms in ammonia is **replaced with an alkyl group**. They can be classified as **primary, secondary or tertiary amines,** depending on how many alkyl groups are bonded to the nitrogen atom.

Example: Classification of amines

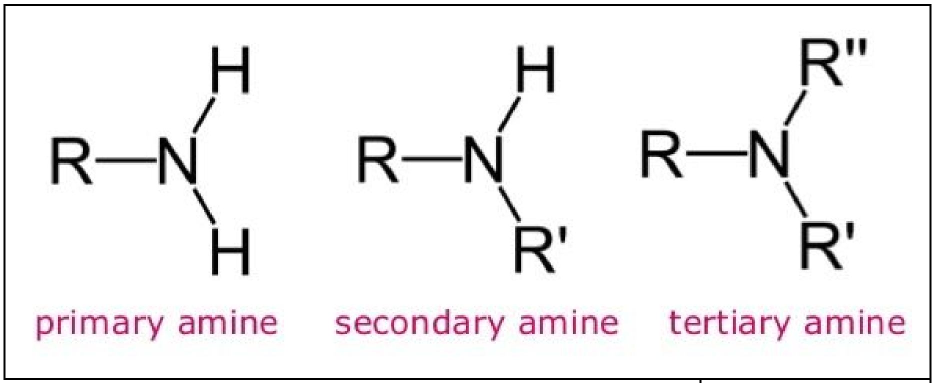


Image courtesy of SlideShare

Basicity

Amines react with water to form an **alkaline solution**. The lone pair of electrons on the amine's nitrogen atom can **accept a hydrogen** from a water molecule, therefore acting as a base. This releases **OH^- ions** into the solution.

Example:

$$CH_3CH_2NH_2 + H_2O \rightarrow CH_3CH_2{}^+NH_3 + OH^-$$

To Produce Salts

Amines react with acids to form an ammonium salt. Again, the amine acts as a base and accepts a proton to form a **quaternary ammonium salt**.

Example:

$$CH_3CH_2CH_2CH_2NH_2 + HCl \rightarrow CH_3CH_2CH_2CH_2{}^+NH_3\,Cl^-$$

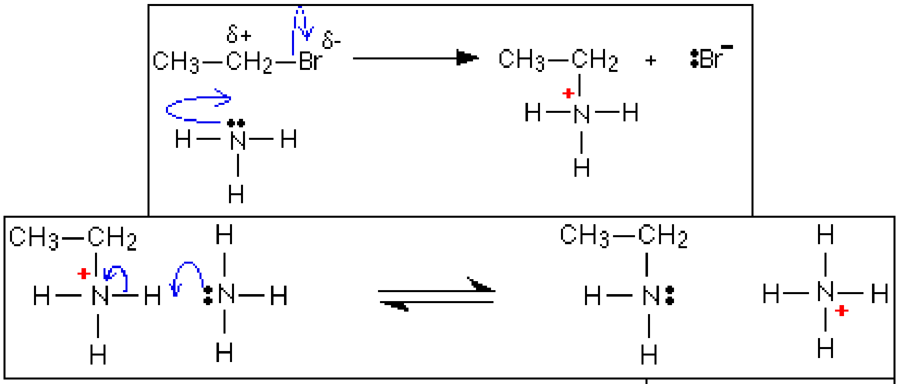
Butylamine + hydrochloric acid → butylammonium chloride

Preparation of Aliphatic Amines

Nucleophilic Substitution

Aliphatic amines can be produced from the nucleophilic substitution reaction between a **halogenoalkane and 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 bonded to a halide ion)**.

Example: Nucleophilic substitution of bromoethane with ammonia



Images courtesy of chemguide.co.uk

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

Example: Formation of a quaternary ammonium salt

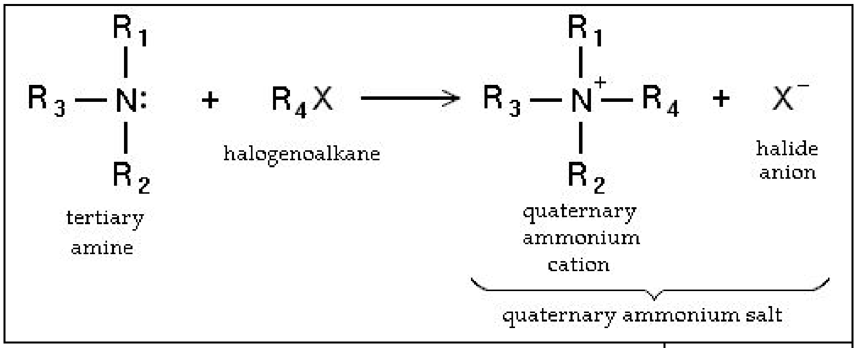


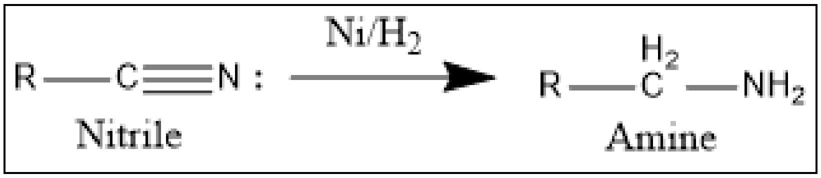
Image courtesy of Wikibooks

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

Reduction of Nitriles

Aliphatic amines can also be produced by the reduction of nitriles by **hydrogenation.** This reduction requires a combination of **hydrogen with a nickel catalyst** (catalytic hydrogenation).

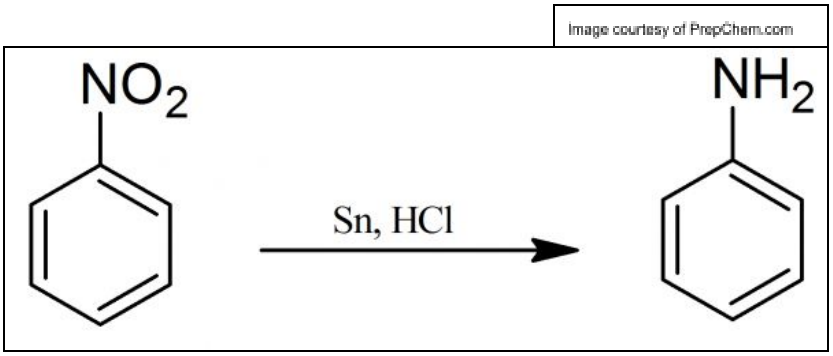
Example: Reduction of a nitrile to an amine



Preparation of Aromatic Amines

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

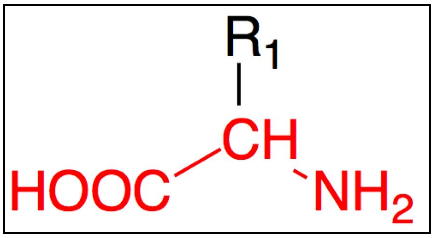
Example:



6.2.2 Amino Acids, Amides and Chirality

Reactions of Amino Acids

α-amino acids are organic molecules containing a **carboxylic acid group** and an **amine group** bonded to the same carbon atom. Their general structure is shown below, where different amino acids have different chemical groups as the 'R' side chain. The general formula for an α-amino acid is $RCH(NH_2)COOH$.



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

The **carboxylic acid** group will react with alkalis and donate a proton. The **amine group** is basic and will react with acids to accept a proton.

Zwitterions are **dipolar** ions with a positive charge in one part of the molecule and a negative charge in another part of the molecule. The zwitterionic form of an amino acid is the state in which the **amine group** has a **positive** charge (+NH3) and the **carboxyl group** has a **negative** charge (COO-).

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

Example:

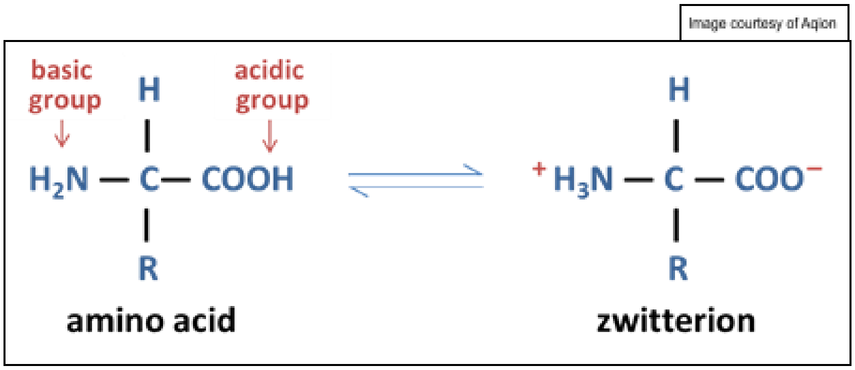


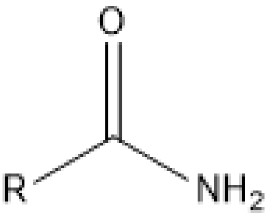
Image courtesy of Aqion

Amides

Amines can also undergo **nucleophilic addition-elimination** reactions with **acyl chlorides** to produce **amides** and **N-substituted amides**. This mechanism is described in section 6.1.3.

Amides have a C=O group and an NHR group, where R is an alkyl group or a hydrogen atom. Primary amides have the structure $RCONH_2$.

Example: Functional group of primary amides



N-substituted Amides

Secondary amides are also known as N-substituted amides. They have an additional carbon chain bonded to the nitrogen atom.

When **naming** N-substituted amides, they are treated in a similar way to **esters**. The **prefix** indicates the length of the carbon chain bonded to the **nitrogen** atom only and the **suffix** indicates the carbon chain which contains the **carbonyl** bond.

Example:

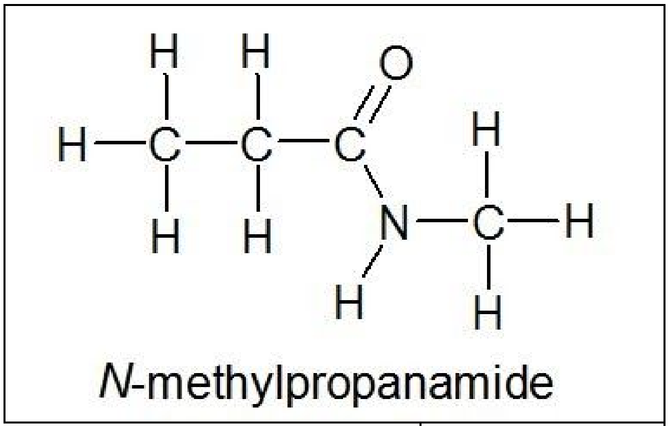


Image courtesy of callmedrrob.com

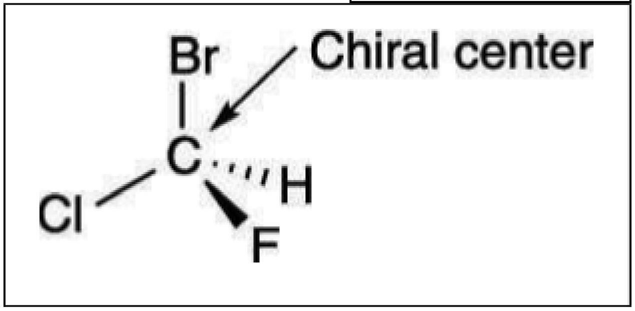
Chirality

Chiral Centres

A chiral centre is a carbon atom with **four different groups** bonded around it, so that the molecule has **no line of symmetry**.

Example:

Image courtesy of Dummies.com



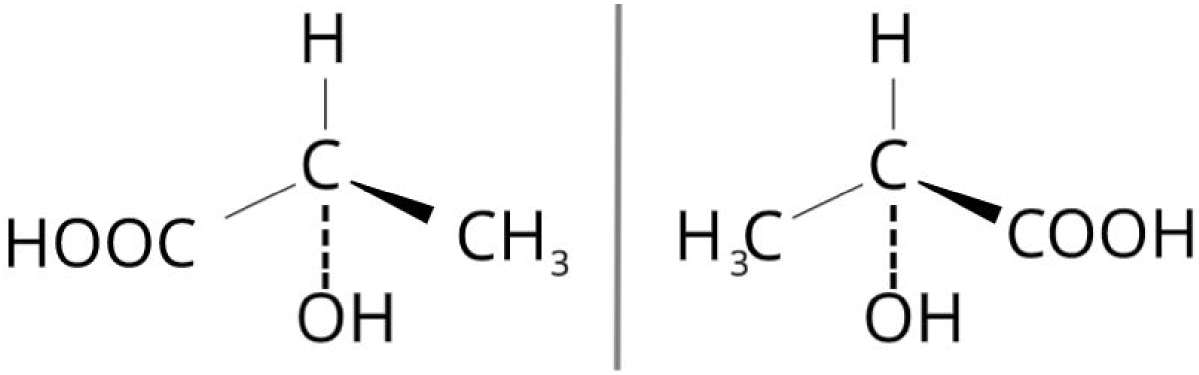
The chiral centre is commonly **indicated** using * next to the asymmetric carbon.

Optical Isomers

Optical isomerism is a type of **stereoisomerism** where molecules have the **same molecular formula** but a different **spatial arrangement** of atoms.

The presence of a chiral centre leads to **two possible isomers** that are **non-superimposable mirror images** of each other. These are called **optical isomers**.

Example: Optical isomers of 2-hydroxypropanoic acid



The two different isomers are called **enantiomers** and are unique due to their effect on **plane polarised light**. Each enantiomer rotates plane polarised light **in opposite directions.**

All amino acids, except **glycine**, contain a **chiral carbon** atom bonded to four separate groups. The R group on aminoethanoic acid (**glycine**) is just a hydrogen atom so the carbon is not bonded to four separate groups.

Since all other amino acids are chiral, they are **optically active**, so a solution of amino acids will **rotate plane-polarised monochromatic light**.

6.2.3 Polyesters and Polyamides

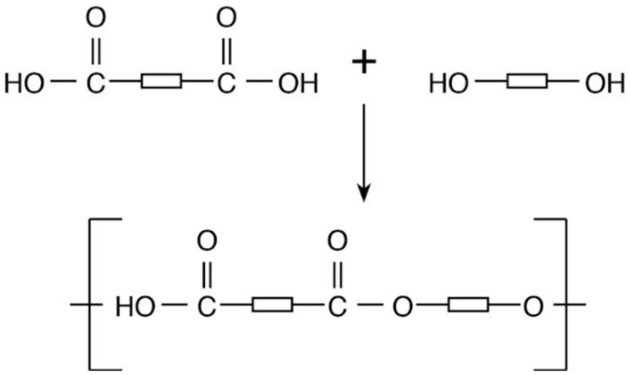
Condensation Polymers

Condensation polymers form when **a water molecule is removed** from the species of a reaction. Polyesters and polyamides can be formed in this way.

Polyesters

Polyesters are formed when a **dicarboxylic acid and a diol** react together, producing an **ester linkage**, -COO-.

Example: Formation of a polyester



Terylene (PET) is a common polyester made from ethane-1,2-diol and 1,4-benzenedicarboxylic acid.

Example:

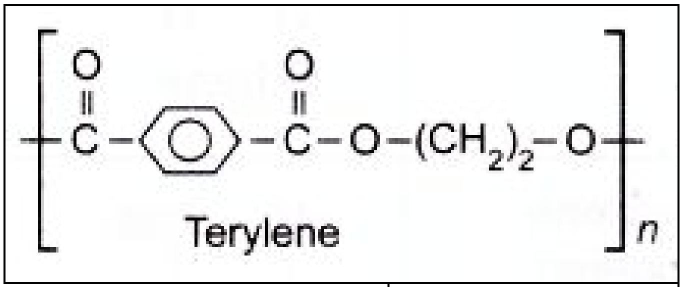


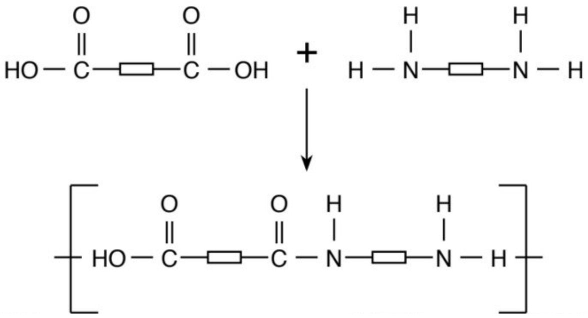
Image courtesy of aplustopper.com

Polyesters are useful as they can be broken down through **hydrolysis** due to the **polarity** within the polymer molecules. Therefore, they are **biodegradable** and can be broken down easily in nature by naturally occurring water or moisture. This means polyesters will gradually break down when they are put into **landfill**.

Polyamides

Polyamides are condensation polymers generally formed in a reaction between a **dicarboxylic acid and a diamine**. A molecule of water is removed, producing an **amide linkage**.

Example: Formation of a polyamide



-CONH- is the amide linkage

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

Example: Repeat unit of nylon-6,6

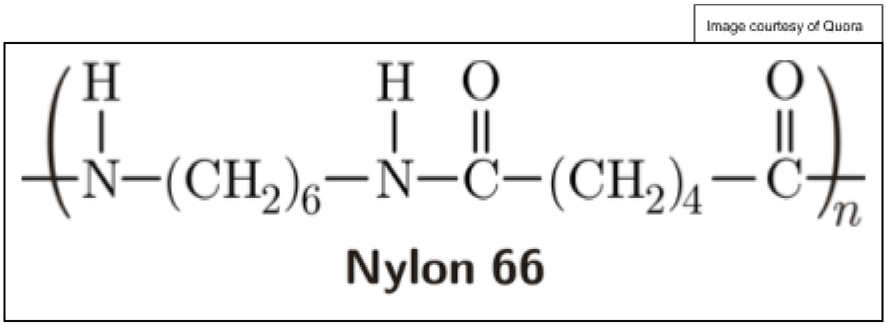


Image courtesy of Quora

Nylon 66

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

Example: Repeat unit of kevlar

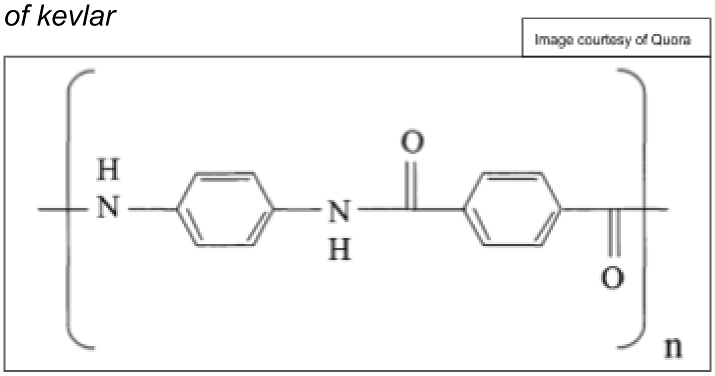


Image courtesy of Quora

Hydrolysis

The ester groups in polyesters and the amide groups in polyamides can be broken down by **acid or base hydrolysis**. The ester and amide linkages are polar, so they can be broken in the presence of water.

Ester hydrolysis is the **reverse reaction** to esterification, converting esters back into alcohols and carboxylic acids. This process is done by **adding water,** but can be carried out under **different conditions** to produce different products. For polymers, the ester linkage is broken and the polyester is converted back into the diol and dicarboxylic acid.

Acidic Conditions

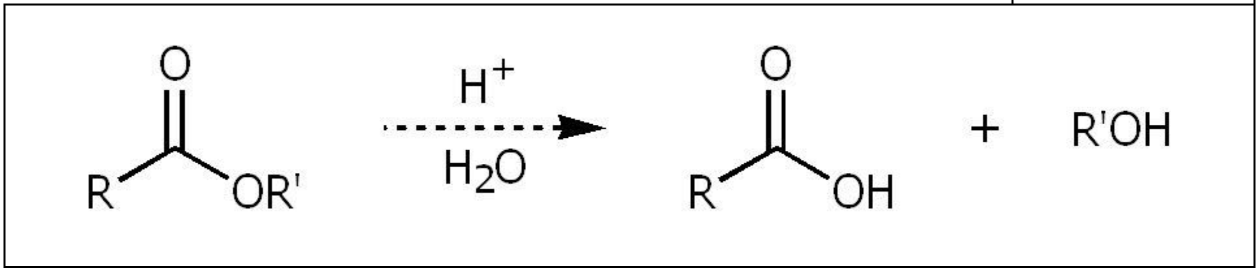
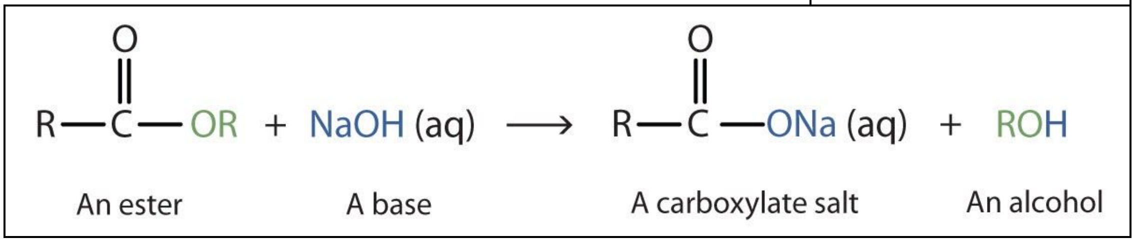


Image courtesy of SlidePlayer

This produces a simple reverse reaction back to the alcohol and carboxylic acid or diol and dicarboxylic acid.

Basic Conditions



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The carboxylic acid produced reacts further with the base to form a salt.

The same acid and base hydrolysis can be used to break the amide bond in **polyamides**. The hydrolysis reaction converts the polyamide back into the diamine and dicarboxylic acid.

6.2.4 Carbon-Carbon Bond Formation

Extending Carbon Chain Length

The **carbon chain** in organic molecules can be extended by **C-C bond formation**. This is useful in **synthesis** to form new molecules. **Nitriles** can be used to add in the extra carbon, and then other reactions can be carried out to change the nitrile group into another functional group.

Formation of C-C≡N

Nucleophilic substitution reactions can be used to form Nitriles. The nucleophile is the CN^- ion. Typically this reaction involves haloalkanes with CN^- and ethanol.

Mechanism

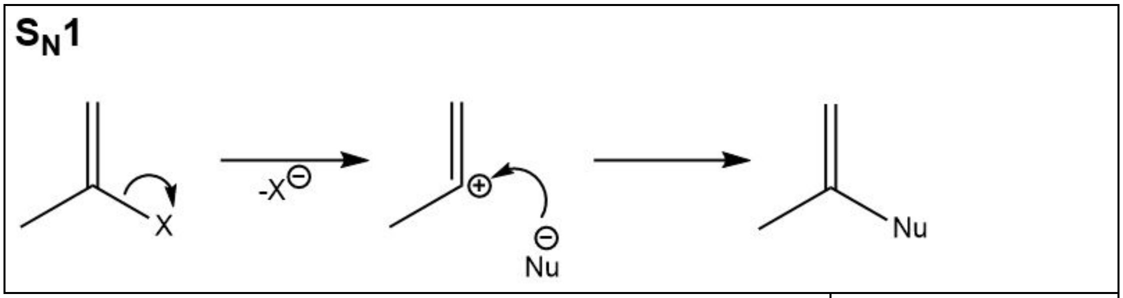


Image courtesy of Stack Exchange

In **nucleophilic addition** reactions, nucleophiles are able to attack a molecule with a **carbonyl group**. HCN is used with a carbonyl compound and the CN^- ion is the nucleophile. First, the CN^- nucleophile attacks the electrophilic carbonyl carbon, then the oxygen anion intermediate is protonated to form the **hydroxynitrile** product.

Mechanism

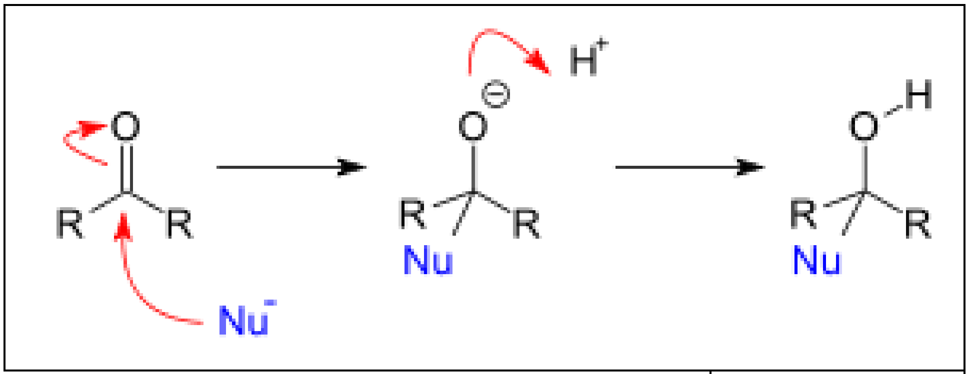
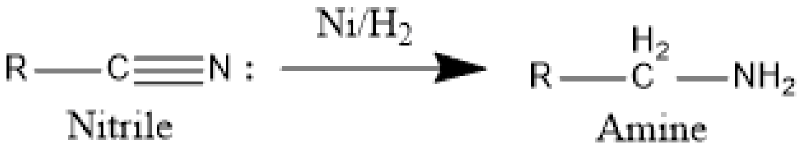


Image courtesy of Wikipedia

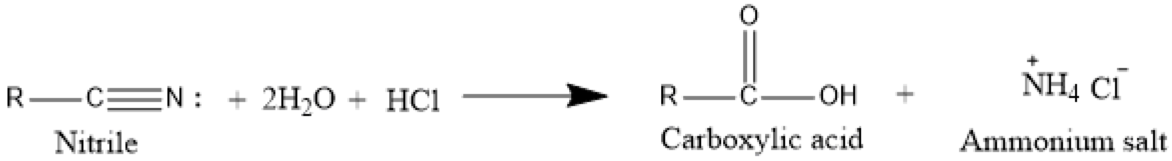
Reactions of Nitriles

The nitriles formed above can be used as a precursor to other products. Amines can be produced by the reduction of nitriles. This reduction reaction is called **hydrogenation.** The reaction requires a combination of **hydrogen with a nickel catalyst** (catalytic hydrogenation).

Example:



Acid hydrolysis of nitriles can also be used to form carboxylic acids. The nitrile is heated under reflux with dilute aqueous acid to form the carboxylic acid and ammonium salt.



Friedel-Crafts Reactions

A C-C bond can be introduced into an aromatic compound using **Friedel-Crafts Alkylation** or **Friedel-Crafts Acylation**. Both reactions occur in the presence of a halogen carrier to make the strong electrophile and allow electrophilic substitution to occur.

Friedel-Crafts Acylation

Friedel-Crafts acylation substitutes an acyl group for a hydrogen atom on the benzene ring. The electrophilic **reactive intermediate** is produced from a reaction between the acyl chloride and an **aluminium chloride catalyst**.

Example: Formation of the reactive intermediate

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

This **electrophile** is then **attacked** by the **benzene** ring. The **mechanism** can be seen on the following page.

Mechanism

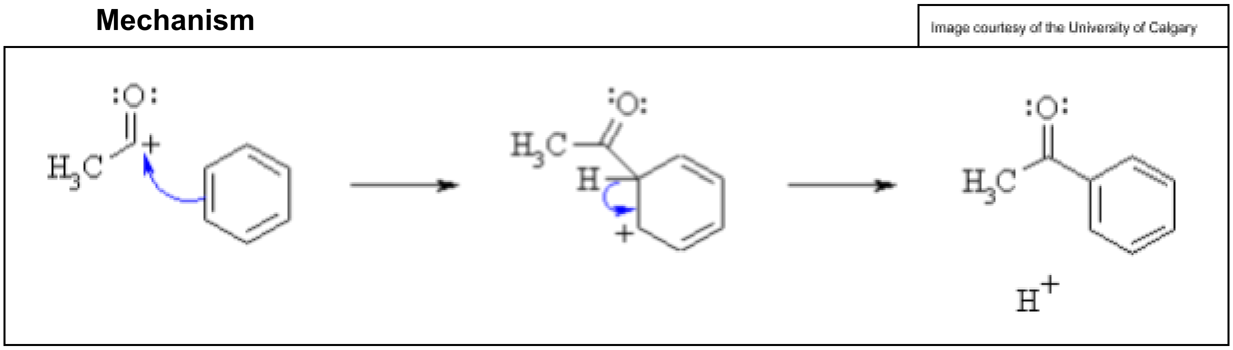


Image courtesy of the University of Calgary

At the end of the reaction, the **H⁺ ion** removed from the ring reacts with the **$AlCl_4^-$ ion** to reform the aluminium chloride, indicating it to be a **catalyst**. Steamy fumes of HCl gas are also released.

Friedel-Crafts Alkylation

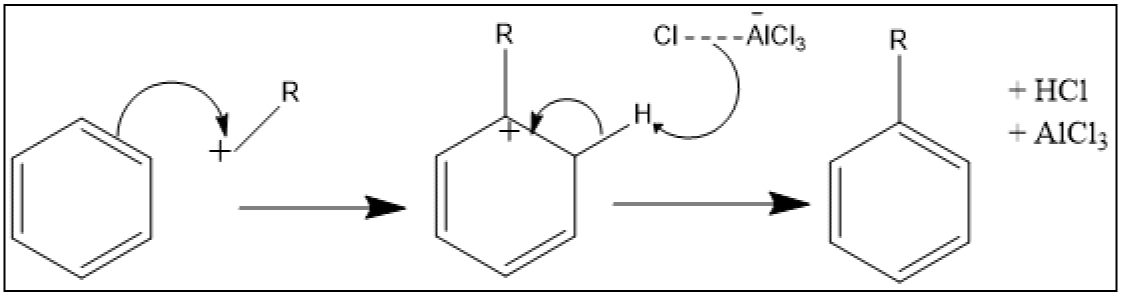
Friedel-Crafts alkylation substitutes an alkyl group for a hydrogen atom on the benzene ring. The electrophilic **reactive intermediate** is produced from a reaction between a haloalkane and an **aluminium chloride catalyst**.

Example: Formation of the reactive intermediate

$$R\text{-}CH_2Cl + AlCl_3 \longrightarrow R-\overset{+}{C}H_2 + \overset{-}{A}lCl_4$$

This electrophile is then attacked by the benzene ring, as shown in the mechanism below.

Mechanism



6.2.5 Organic Synthesis

Practical Skills

Experimental Techniques

Synthesis pathways are used to make organic compounds. They involve a variety of **preparatory** and **purification** techniques that have been introduced throughout this course. These include:

- Reflux
- Distillation
- Melting point determination
- Boiling point determination
- Washing and drying
- Recrystallisation
- Solvent extraction

Organic Preparation

The first step of synthesis is to prepare your organic compound. Common techniques for preparation are **reflux** and **distillation**.

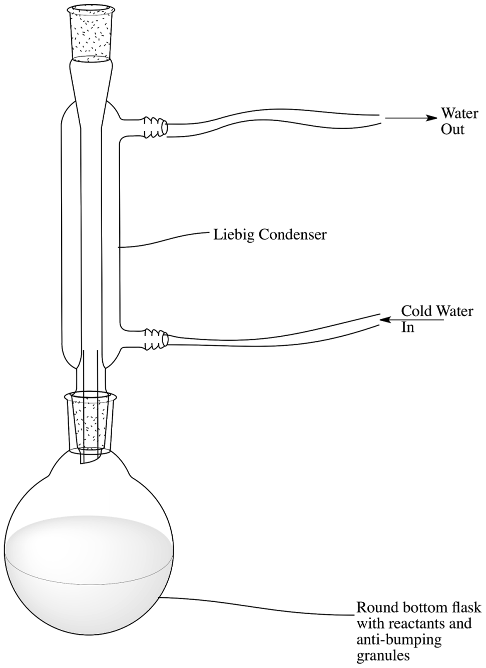
Heating under Reflux

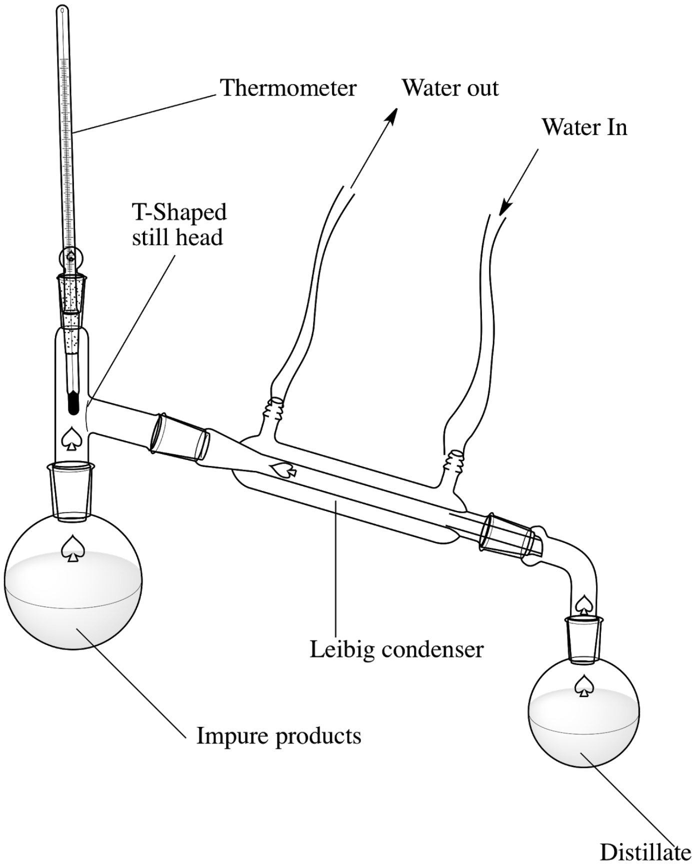
Reflux apparatus is used to **continually heat** the contents of the flask to allow reactions like the **oxidation** of primary alcohols to proceed all the way to the formation of carboxylic acids. The **condenser** helps ensure the vapours condense and **return** to the flask for further heating. This ensures the product vapours can not escape.

Distillation

Distillation apparatus is used to separate liquids with **different boiling points**. The round-bottomed flask is heated and the liquid with the lower boiling point will **evaporate** first. It rises out of the flask and into the attached tubing which is surrounded by a condenser. The condenser causes the vapour to **cool and condense** back into a liquid, which is then collected in a separate flask.

Diagrams - reflux setup (left), distillation setup (right)



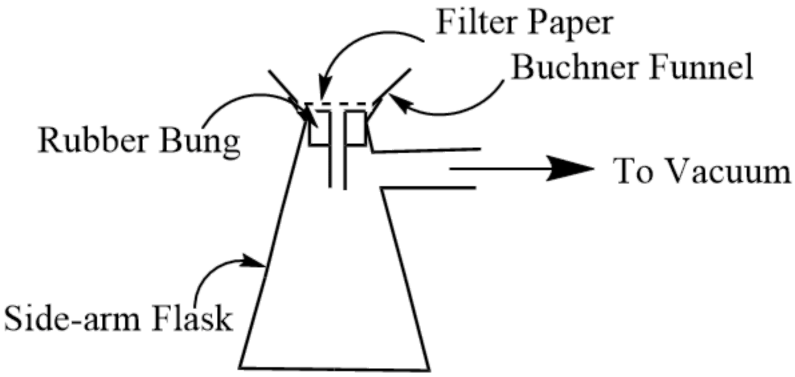


Purification of an Organic Solid

Filtration under Reduced Pressure

This technique uses a **vacuum** to assist filtration of a solid product by reducing the pressure inside the flask. This forces the solvent and air through the filter paper, making it much faster than gravity filtration. A **Buchner funnel** and **side-arm flask** are connected to the vacuum. It is important that a piece of filter paper is placed in the Buchner funnel to collect your solid product. It is also good practice to slightly wet your paper with the same solvent that you will be filtrating.

Example: Vacuum filtration set up



Recrystallisation

Recrystallisation is a **purification** technique that uses the differing solubilities of solid and impurities in different solvents.

- The solid is dissolved in a **minimum volume** of **hot solvent**. The solubility of the solute increases with temperature so it is important that the solvent is near its boiling point.
- The solution is immediately filtered through **hot apparatus** by **gravity filtration**. This removes insoluble impurities. The resulting solution is allowed to **cool and crystallise**.
- The purified crystals can then be obtained by **vacuum filtration** of this solution. This removes any impurities that were soluble in the solvent. It also helps to **dry the crystals**.

When **choosing** the **solvent**, it is important to choose a solvent in which the solute is insoluble at room temperature, but a lot more soluble at higher temperatures.

Melting Point Analysis

Determining the melting point of a compound and comparing it to a databook value is a way of testing its **purity**. The purer a substance, the **closer** to the databook melting point value it will be. If a sample has a low purity, the melting point will take place over a **range** of temperatures.

To **determine** the **melting point**, the substance is packed into a **capillary tube** which is placed inside a melting point apparatus. The substance is heated slowly until a change of phase occurs. The solid changes into a liquid. The temperature at which this change occurs is taken to be the melting point.

Synthetic Routes

Synthesis pathways are needed to convert starting materials into a **target product**. This can sometimes be achieved through single-step reactions, but other times **multistep pathways** are required. The **functional groups** in a desired product can be identified and then different transformations between functional groups can be used to get to the desired product. See section 6.3.1 for more on tests and reactions of organic functional groups.

When designing a synthetic pathway a chemist must consider several factors:

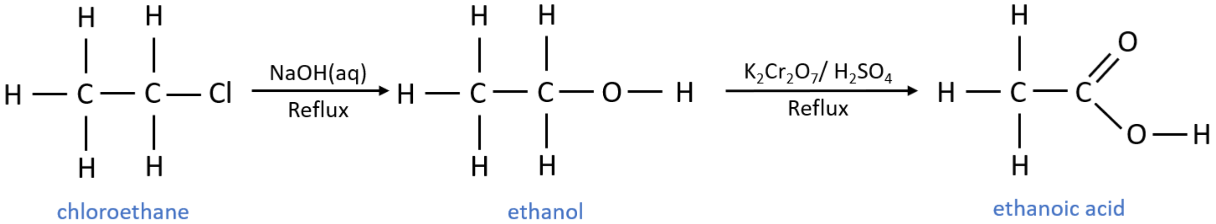
- Product **yield** (related to Le Chatelier's principle)
- Reaction **setup**, including: catalysts, reagents, and conditions
- The type of process involved - **batch** or **continuous**
- **Hazards**
- **Cost**
- Formation of **isomers** - for example, many drug targets are enzymes that are stereospecific and react with one enantiomer only. The synthetic pathway designed for these drugs should, ideally, only produce this enantiomer and not a racemic mixture.

Multi-Stage Synthesis

Some organic molecules can be prepared using a **multi-stage synthesis**. Typically, this involves two stages: reactant → intermediate → product. It can cover more stages.

Example 1

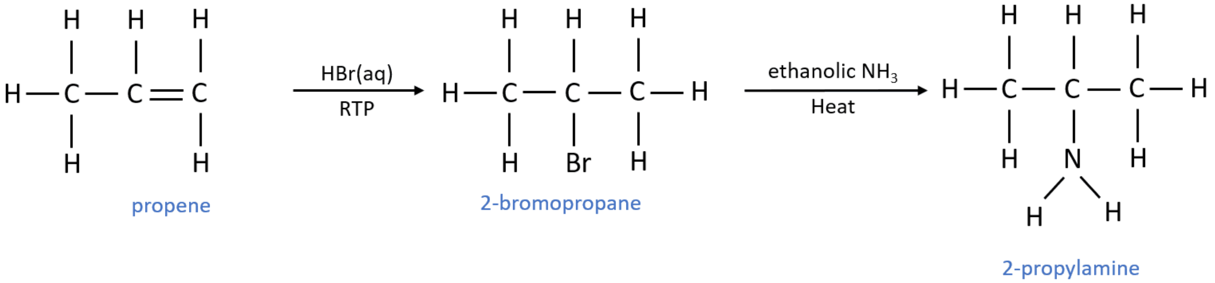
Below is a diagram showing how ethanoic acid can be synthesised from chloroethane:



chloroethane ethanol ethanoic acid

Example 2

Below is a diagram showing how 2-propylamine can be formed from propene:



propene 2-bromopropane 2-propylamine

Synthesis Maps

Synthesis maps provide a good **summary** of reactions in organic chemistry and show how multistep reactions can be used to get from one compound to another. Below is a good, detailed example of a synthesis map. Click on the link to view it in **full size**.

(http://www.compoundchem.com/2014/02/17/organic-chemistry-reaction-map/)

Image courtesy of Compound Interest