

# Edexcel Chemistry A-level

## Topic 6: Organic Chemistry I Detailed Notes



## Topic 6A: Introduction to Organic Chemistry

### Hydrocarbons

Organic chemistry mainly concerns the properties and reactions of **hydrocarbons**, compounds that contain **only carbon and hydrogen** atoms. Hydrocarbons are a series of compounds with similar structures and formulas that can be represented in many different ways.

### Nomenclature

Nomenclature is the set of rules that outline how different organic compounds should be **named** and how their **formulas are represented**.

### Formulas

There are many different ways of writing and representing organic compounds:

#### 1. Empirical Formula

- The simplest whole number ratio of atoms of each element in a compound.

#### 2. Molecular Formula

- The true number of atoms of each element in a compound.

#### 3. General Formula

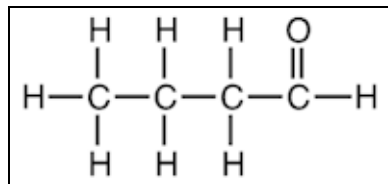
- All members of a homologous organic series follow the general formula. For example, alkanes have the general formula  $C_nH_{2n+2}$ .

#### 4. Structural Formula

- Shows the structural arrangement of atoms within a molecule. For example,  $CH_3CH_2COCH_3$ .

#### 5. Displayed Formula

- Shows every atom and every bond in an organic compound.



#### 6. Skeletal Formula

- Shows only the bonds in a compound and any non-carbon atoms. The vertices are carbon atoms and hydrogen is assumed to be bonded to them unless stated otherwise.





## Homologous Series

Organic compounds are often part of a **homologous series**, in which all members follow a **general formula** and react in a very similar way. Each consecutive member **differs by  $\text{CH}_2$**  and there is an **increase in boiling points** as chain length increases.

Example:

Image courtesy of DP Chemistry

Molecular Formula	Condensed Structural Formula	Name	Boiling Point (°C)
$\text{CH}_4$	$\text{CH}_4$	Methane	-161
$\text{C}_2\text{H}_6$	$\text{CH}_3\text{CH}_3$	Ethane	-89
$\text{C}_3\text{H}_8$	$\text{CH}_3\text{CH}_2\text{CH}_3$	Propane	-44
$\text{C}_4\text{H}_{10}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$	Butane	-0.5
$\text{C}_5\text{H}_{12}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	Pentane	36
$\text{C}_6\text{H}_{14}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	Hexane	68
$\text{C}_7\text{H}_{16}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	Heptane	98
$\text{C}_8\text{H}_{18}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	Octane	125
$\text{C}_9\text{H}_{20}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	Nonane	151
$\text{C}_{10}\text{H}_{22}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	Decane	174

Each series has a **functional group** that allows that molecule to be recognised as being able to react chemically in a certain way as a result of that group.

Example: Table of functional groups (ignore ethers)

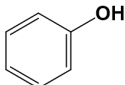



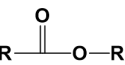
Name	Functional Group	IUPAC Ending
Alcohols	$\text{R}-\text{OH}$	-ol
Phenols		phenol
Ethers	$\text{R}-\text{O}-\text{R}'$	ether
Aldehydes		-al
Ketones		-one
Carboxylic Acids		-oic acid
Esters		-ate

Image courtesy of improvefamily.com





## Naming Compounds

Compounds are named according to rules laid out by the **International Union of Pure and Applied Chemistry (IUPAC)**. This ensures each compound is universally named the same - which helps to avoid potentially dangerous confusion.

As well as being able to name compounds from their structures, you should be able to draw structures from IUPAC names.

### Stem

The prefix of the chemical tells you **the length of the longest unbroken chain of carbon atoms** in the compound. The first 10 are given below, using alkanes as an example:

Number of C atoms	Prefix	Alkane example
1	Meth-	Methane
2	Eth-	Ethane
3	Prop-	Propane
4	But-	Butane
5	Pent-	Pentane
6	Hex-	Hexane
7	Hept-	Heptane
8	Oct-	Octane
9	Non-	Nonane
10	Dec-	Decane

### Functional Groups

The **ending** of the compound's name tells you the **functional group** present. If there is more than one functional group present, they are added as a **suffix**.

Functional group	Suffix
Alkane	-ane
Alkene	-ene
Alcohol	-ol
Carboxylic acid	-oic acid
Ketone	-one
Aldehyde	-al
Ester	-ate
Amine	-amine





If a **halogen** is present, it is represented by a **prefix**:

Functional group	Prefix
Fluorine	Fluoro-
Chlorine	Chloro-
Bromine	Bromo-
Iodine	Iodo-

### Side Chains

Carbon side chains that are **branches** from the longest carbon chain are represented by a **prefix** at the start of the word. These **alkyl groups** are made using the **stems** given above (meth-, eth-, prop-, etc) and the **suffix -yl**.

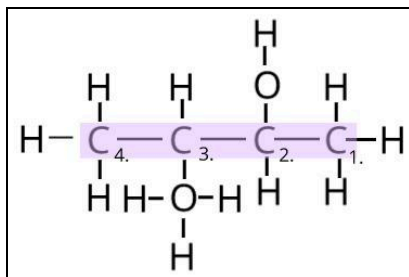
### General Rules

1. Functional groups and side chains are given, if necessary, with the number corresponding to the carbon they are attached to.
2. Numbers are separated by commas.
3. Numbers and words are separated by hyphens.
4. If more than one particular side chain or functional group is present then one of the following prefixes is added: di- (2), tri- (3), tetra- (4), etc.
5. The carbon chain is numbered in ascending order from the end of the chain nearest a functional group.
6. If multiple prefixes are present, they are included in alphabetical order.

### Examples

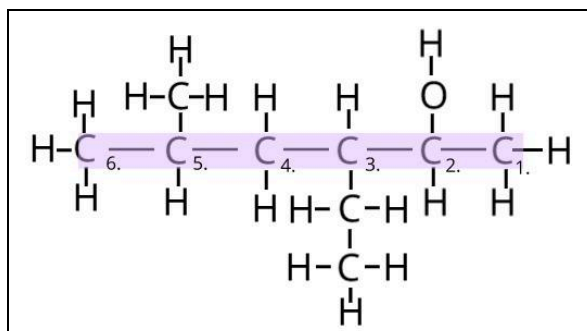
*Example 1: The displayed structure of butan-2,3-diol.*

*This compound only has single carbon-carbon bonds, so is an alkane. Its longest chain of carbon atoms is 4, giving the stem butan-, and it has two alcohol functional groups on carbons 2 and 3.*



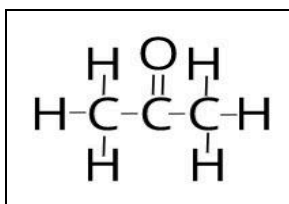


Example 2: The displayed structure of 3-ethyl,5-methylhexan-2-ol.

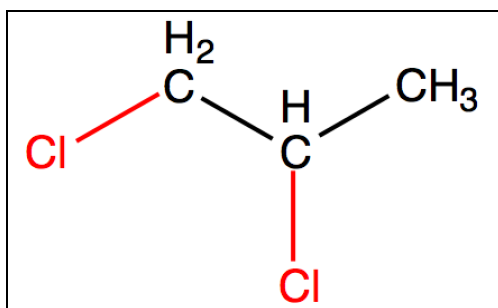


Example 3: The displayed structure of propanone.

Propan-2-one is also correct, but since the C=O can only be in the 2 position for the compound to be a ketone, the number is not necessary.



Example 4: The skeletal structure of 1,2-dichloropropane





## Reaction Mechanisms

### Types of Reactions

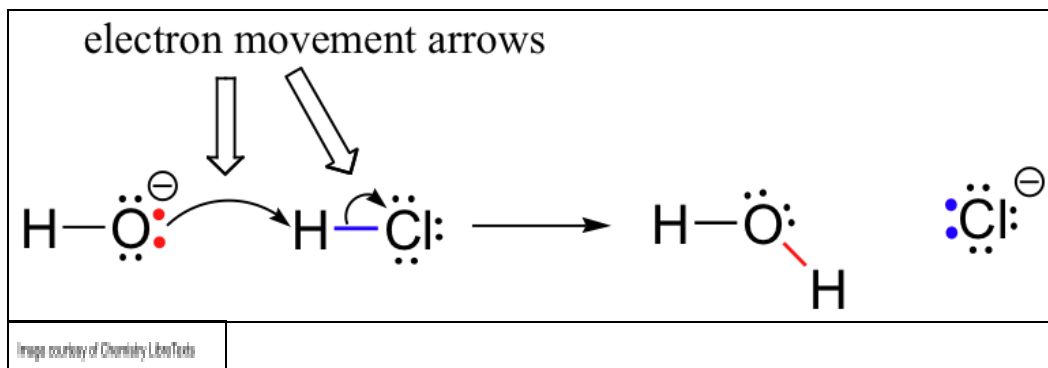
Reactions can be classified according to what happens to the reactants during the reaction and what the end products are. The main types of reaction are:

- **Addition** - In an addition reaction the reactants combine to form a **single product**.
- **Substitution** - In a substitution reaction one functional group is **replaced** by a **different functional group**.
- **Oxidation** - A species **loses** at least one electron, and is oxidised.
- **Reduction** - A species **gains** at least one electron, and is reduced.
- **Polymerisation** - A reaction in which many small molecules, known as **monomers**, join together to form a long, repeating molecule called a **polymer**.

### Mechanisms

Mechanisms show the **movement of electrons** within a reaction, shown with **curly arrows**.

*Example:*



Mechanisms are used to show the reactions of organic compounds.





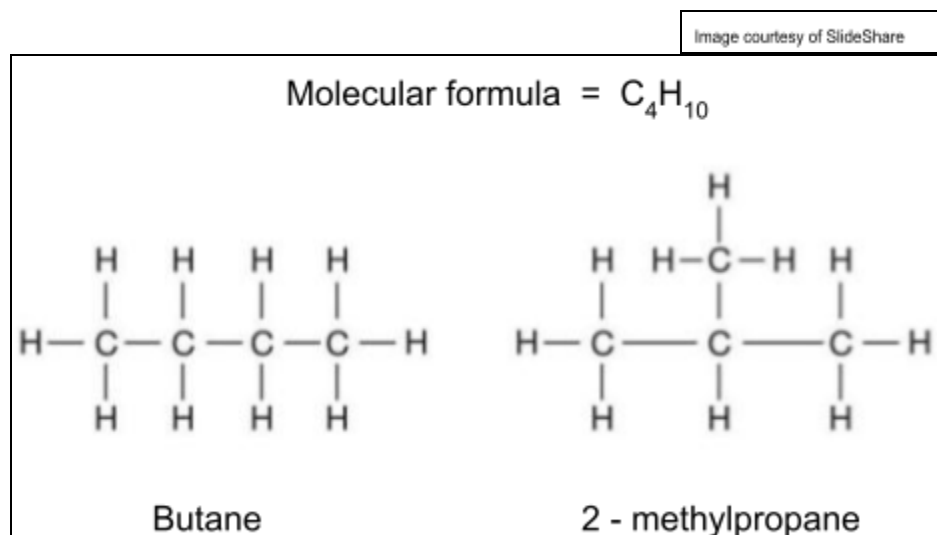
## Isomerism

Isomers are molecules with the **same molecular formula** but a **different arrangement** of atoms within the molecule.

### Structural Isomers

Structural isomers have the same molecular formula but a **different structural arrangement** of atoms. They can be **straight** chains or **branched** chains but will have the same molecular formula.

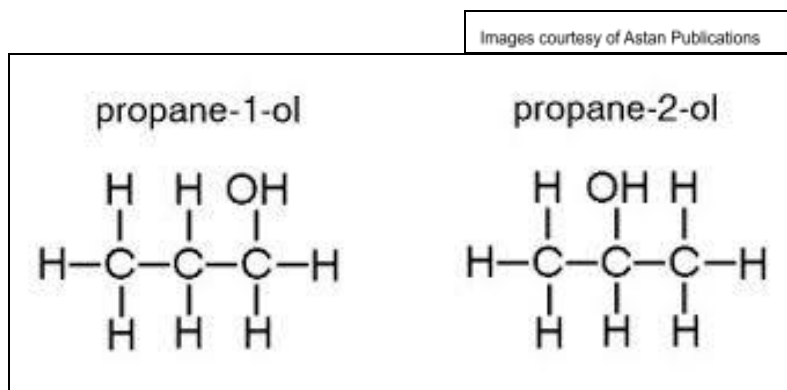
*Example:*



### Position Isomers

Position isomers have the **functional group** of the molecule in a **different position** of the carbon chain.

*Example:*



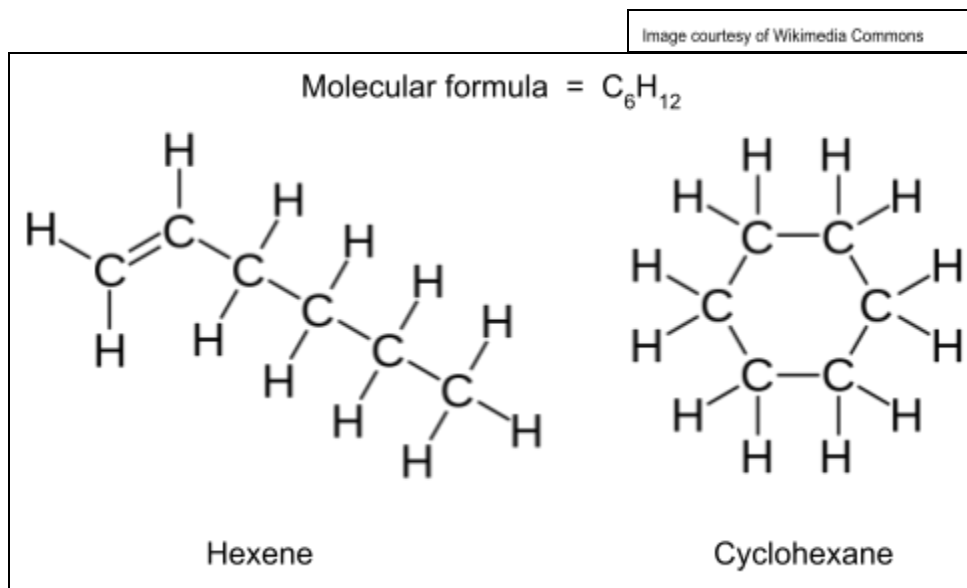




## Functional Group Isomers

These have the same molecular formula so but the molecules have a **different functional group**.

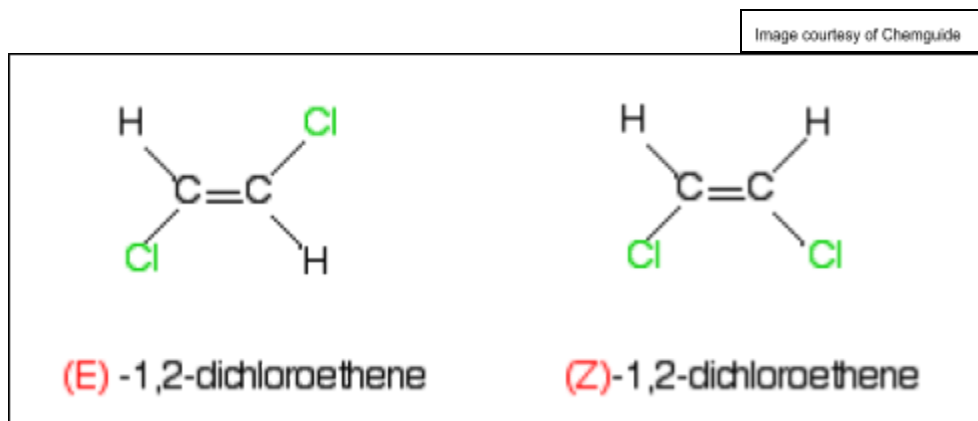
Example:



## Stereoisomers

These have a **different spatial arrangement**. A type of stereoisomerism is **E-Z isomerism**, where **limited rotation** around a double carbon bond means that functional groups can either be 'together' or 'apart'. The **E** isomer (german for entgegen meaning apart) has functional groups **on opposite sides**. The **Z** isomer (german for zusammen meaning together) has functional groups **together** on the same side of the double bond.

Example:

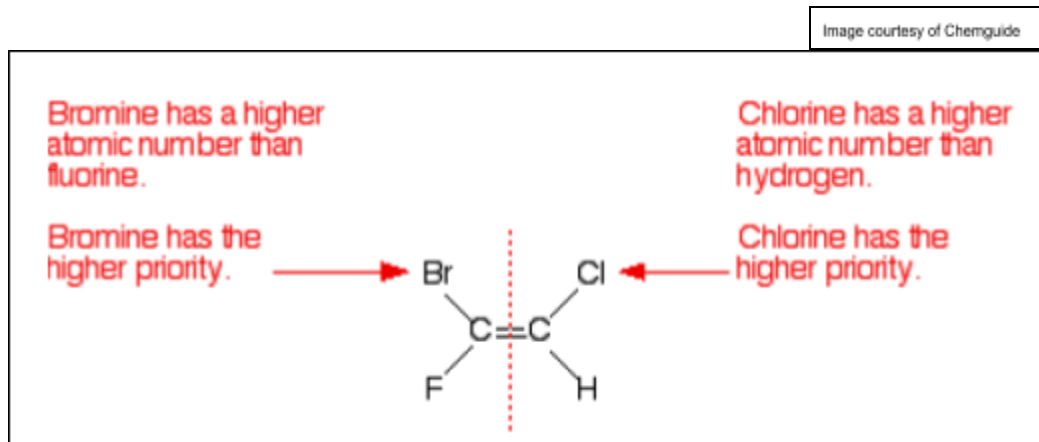




## Cahn-Ingold-Prelog (CIP) Priority Rules

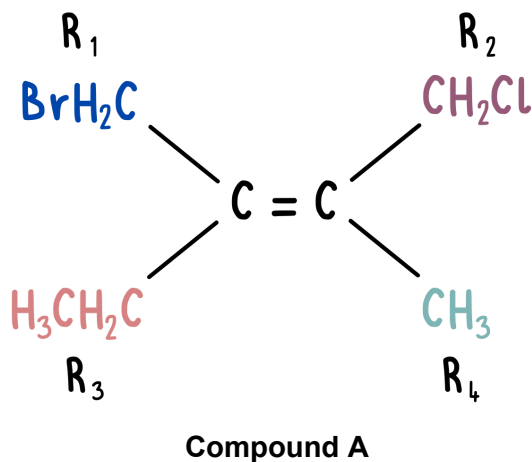
There is a **priority of different groups** in molecules that can display E-Z isomerism. The first atom which is directly bonded to the carbon with the double bond with the **higher Ar** is given the **higher priority**. These groups are used to determine if it is the E or Z isomer.

Example:



**Therefore this molecule is the Z isomer as the highest priority atoms are on the same side.**

How to determine a more complicated E/Z isomers





- **Step 1: Apply the CIP priority rules**
  - Look at R1 and R3:
    - Carbon is the **first atom** attached to the C=C bond, on the left hand side
  - Look at R2 and R4:
    - Carbon is the first atom attached to the C=C bond, on the right hand side
  - This means that we cannot deduce if compound A is an *E* or *Z* isomer by applying the CIP priority rules to the first atom attached to the C=C bond
    - Therefore, we now have to look at the **second atoms** attached
- **Step 2: Apply the CIP priority rules (using the second atoms)**
  - Look again at R1 and R3:
    - The second atoms attached to R1 are **hydrogens** and **bromine**
    - The second atoms attached to R3 are **hydrogens** and another **carbon**
    - We can ignore the hydrogens as both R groups have hydrogens
    - Bromine has a **higher atomic number** than carbon, so bromine is the **higher priority**
      - Therefore, the CH<sub>2</sub>Br group has priority over the CH<sub>3</sub>CH<sub>2</sub> group
  - Look again at R2 and R4:
    - The second atoms attached to R2 are **hydrogens** and **chlorine**
    - The second atoms attached to R4 are **hydrogens**
    - Chlorine has a **higher atomic number** than hydrogen, so chlorine is the **higher priority**
      - Therefore, the CH<sub>2</sub>Cl group has priority over the CH<sub>3</sub> group
- **Step 3: Deduce *E* or *Z***
  - In compound A, the two highest priority groups are on the **same side** (both above) the C=C bond
    - Therefore, compound A is the ***Z* isomer**

### Cis- and Trans- Isomers

Stereoisomers can be named in the same process as above, but instead using **Cis-** for when the groups are on the **same side** and **trans-** for when they are **different sides**. Cis- and trans- differs from E/Z isomerism in that cis- and trans- can only be used when there are **hydrogen atoms** to compare the two other groups to. When there are more groups present, you have to assign E/Z isomerism by using the **Cahn-Ingold-Prelog (CIP) priority rules** described above.





## Topic 6B: Alkanes

### Introduction to Alkanes

Alkanes are **saturated hydrocarbons** where all carbon-carbon bonds are **single bonds**. They are part of a homologous series with the general formula  $C_nH_{2n+2}$ . Cycloalkanes are an exception to this general formula but are still saturated hydrocarbons.

### Fractional Distillation

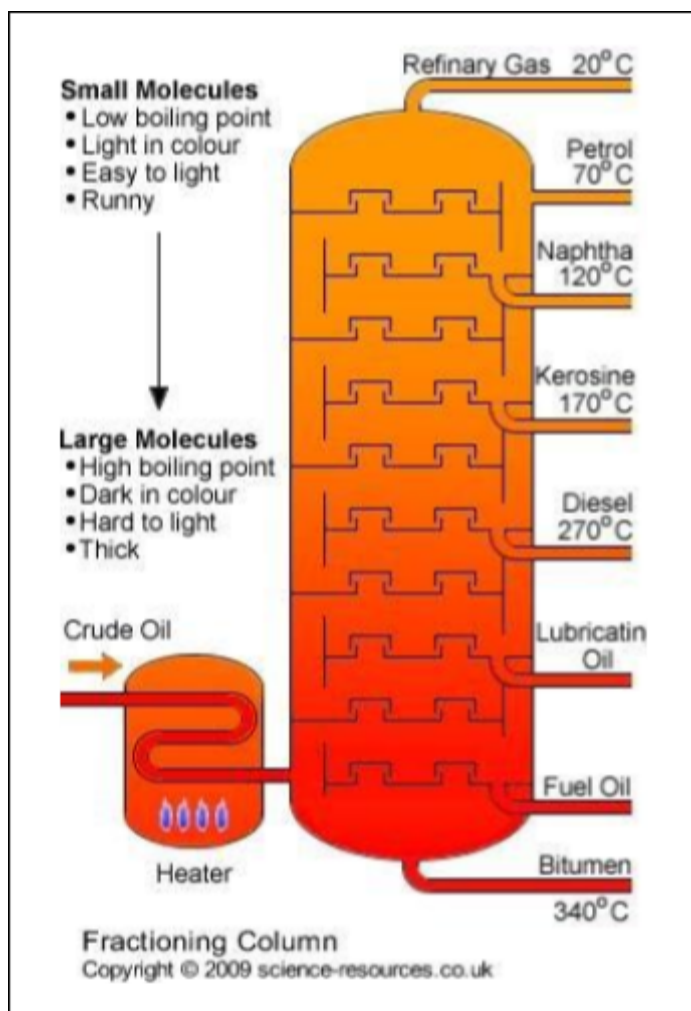
**Crude oil is a mixture** of different hydrocarbons. It can be separated into the separate molecules by **fractional distillation** as the different chain lengths of molecules result in them having **different boiling points**.

Crude oil is separated in the following way:

1. The mixture is **vapourised** and fed into the fractionating column.
2. Vapours **rise, cool** and **condense**.
3. Products are **siphoned off** for different uses.

Products with **short** carbon chains have **lower** boiling points, meaning they **rise higher** up the column before reaching their boiling point. Therefore they are **collected at the top** of the column.

Products with **long** carbon chains have **higher** boiling points, meaning they don't rise very far up the column before reaching their boiling point. They condense and are **collected at the bottom** of the fractionating column.





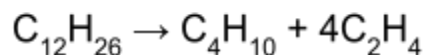
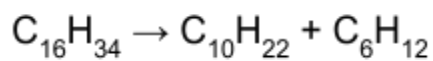
The compounds collected from the fractionating column are then **broken down further** via the method of **cracking**.

Some long-chain alkanes are also converted into **branched alkanes** and **cyclic hydrocarbons** in a process known as **reforming**. These products undergo **combustion** more **efficiently** than straight-chain alkanes.

## Cracking

Longer carbon chains are not very useful, so they are broken down to form **smaller, more useful molecules**. The carbon-carbon bonds are broken in order to do this, which requires quite **harsh reaction conditions**. There are two main types of cracking which result in slightly different organic compounds.

*Examples:*



### Thermal Cracking

Thermal cracking produces a high proportion of **alkanes and alkenes**. High temperatures around **1200 K** and pressures around **7000 kPa** are used to crack the carbon chains. The reaction always forms an alkane, and the remaining atoms form at least one alkene, which have the general formula  $\text{C}_n\text{H}_{2n}$ .

### Catalytic Cracking

Catalytic cracking produces **aromatic compounds** with carbon rings. Lower temperatures around **720 K** are used along with normal pressure, but a **zeolite catalyst** is also used to compensate for these less harsh conditions.



## Combustion of Alkanes

Alkanes make good fuels as they **release a lot of energy** when burned. With sufficient oxygen present, they undergo **complete combustion** to produce carbon dioxide and water.

*Example:*



If the oxygen present is insufficient, combustion is **incomplete** and **carbon monoxide or carbon particulates** are produced alongside water.

*Example:*



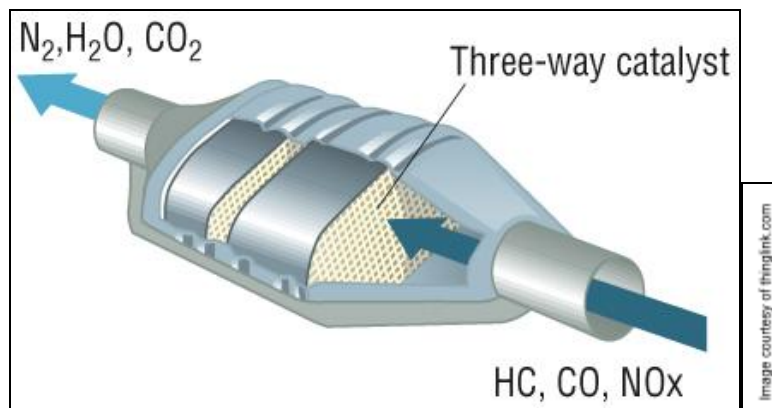
Carbon monoxide is a **toxic**, gaseous product that is especially dangerous to humans as it is odourless and colourless. Carbon monoxide is dangerous because it **replaces oxygen** in the blood, starving the brain and other organs of oxygen and causing people to **suffocate**.

**Oxides of nitrogen** and **sulfur** are also produced as a byproduct of alkane combustion along with **carbon particulates** from unburnt fuel. In clouds, these oxides can react with water and form dilute acids, which result in **acid rain**.

### Catalytic Converters

These gaseous products can be removed from systems using a **catalytic converter**. This uses a **rhodium catalyst** to convert harmful products into more stable products such as  $\text{CO}_2$  or  $\text{H}_2\text{O}$ .

*Example:*





## Alternative Fuels

Alternative fuels are now being developed such as **biofuels** that release fewer, less harmful products when burned. Carbon dioxide is released during the combustion of fuels. It is a **greenhouse gas** so causes **global warming** and contributes to **climate change**.

Ethanol is a common **biofuel**. It is said to be **carbon neutral** as the carbon given out when it is burned is equal to the carbon taken in by the crops during the growing process. It is produced by fermentation, where enzymes break down starch from crops into **sugars** which can then be **fermented to form ethanol**. It is produced in **batches**, meaning it is a relatively slow process with a **low percentage yield**. However, the environmental benefits make it viable.

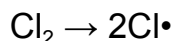
The other advantage of biofuels is that they are **sustainable**. This means their supply can be maintained at the rate they are being used, so they will not run-out - unlike **fossil fuels**.

## Chlorination of Alkanes

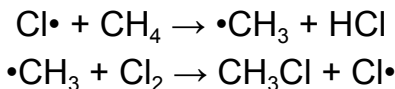
Alkanes react with halogens in the presence of **UV light** to produce halogenoalkanes. The UV light breaks down the halogen bonds (homolytic fission) producing reactive intermediates called **free radicals**. Free radicals are indicated with a dot, as shown below.

Free radicals are species containing an unpaired electron which is shown using a single dot. These attack the alkanes resulting in a series of reactions; **initiation, propagation and termination**.

1. **Initiation** - the halogen is broken down in the presence of UV light.



2. **Propagation** - a hydrogen is replaced and the  $\text{Cl}\cdot$  radical reformed as a catalyst



3. **Termination** - two radicals join to end the chain reaction and form a stable product.



The propagation step can continue many times to result in **multiple substitutions**, this is a **chain reaction**. The condition of the reaction can be altered to favour the termination step and limit the number of substitutions, however, the nature of this reaction to produce **multiple products** limits its use in organic synthesis.





## Topic 6C: Alkenes

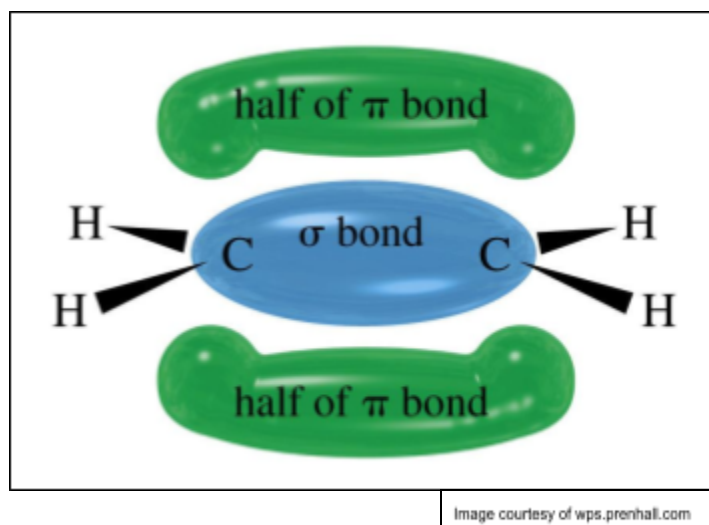
### Introduction to Alkenes

Alkenes and cycloalkenes are **unsaturated hydrocarbons** with at least one carbon-carbon **double bond**. They are part of a homologous series with the general formula  $C_nH_{2n}$ . Cycloalkanes are saturated and follow this same general formula.

### Structure and Reactivity

The carbon double bond is an area of **high electron density** making it susceptible to attack from electrophiles (species that are attracted to  $\delta$ -areas). It consists of a normal covalent  **$\sigma$  bond** and a  **$\pi$  bond**.

*Example:*



**Bromine water** is used to identify an alkene double bond and other unsaturated compounds. Alkenes cause bromine water to change colour from **orange-brown to colourless**. This is because the  $C=C$  bond can 'open up' to accept bromine atoms, and thus become saturated.





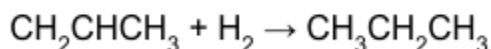
## Reactions of alkenes

The **carbon-carbon double bond** in alkenes makes them reactive. During their reactions, the double bond opens up to form single bonds to other atoms.

### Alkanes

Alkenes can undergo **electrophilic addition** with **hydrogen** to produce **alkanes**. The C=C bond opens up and forms single bonds to each of the hydrogen atoms. This reaction requires a **nickel catalyst**.

*Example:*



This reaction is also known as a **hydrogenation** reaction. **Catalytic hydrogenation** is used in the manufacture of **margarine** from **unsaturated vegetable oils**.

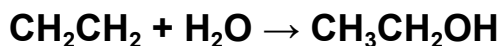
### Halogenoalkanes

**Halogenoalkanes** are organic compounds with single carbon bonds only and halogen functional groups. Alkenes undergo **addition** reactions with **halogens** to form **di-substituted halogenoalkanes**, and with **hydrogen halides** to form **mono-substituted halogenoalkanes**. The mechanism for this reaction is given on the following page of these notes.

### Alcohols

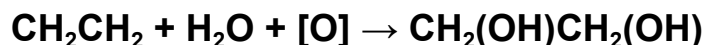
**Alcohols** are organic compounds with a **hydroxyl** functional group. Alkenes undergo **addition** reactions with **steam** to form alcohols. This reaction requires an **acid catalyst**, such as phosphoric acid.

*Example:*



**Diols**, alcohols with two hydroxyl functional groups, can also be formed from alkenes through an **oxidation** reaction. The double bond is oxidised by **acidified potassium manganate(VII)** ( $\text{KMnO}_4$ ). The manganate ions must be cold, dilute and acidified.

*Example:*



## Electrophilic Addition

Alkenes undergo electrophilic addition about the double bond.

### Electrophiles

These are **electron acceptors** and are attracted to areas of **high electron density**. Some of the most common electrophiles are:

- HBr
- Br<sub>2</sub>
- H<sub>2</sub>SO<sub>4</sub>

They can be used in the presence of steam to form **alcohols** or with hydrogen to produce **alkanes** from alkenes.

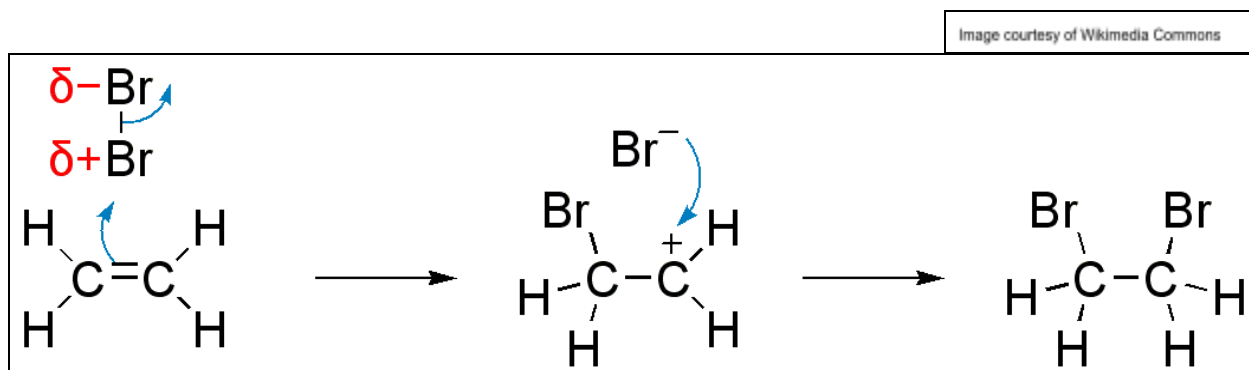
### Electrophilic Addition

Electrophilic addition is the reaction mechanism that shows how electrophiles attack the double bond in alkenes. When the double bond is broken, a **carbocation** forms. This is a carbon atom with only **three bonds**, meaning it has a **positive charge**.

Carbocations can have **varying stability**, with tertiary being the most stable and primary the least. The **more stable** the carbocation, the **more likely** it is to form. Therefore in an addition reaction, multiple products can form but the **major product** will always be the one that is formed via the **most stable carbocation intermediate** possible.

### Mechanisms

**Mechanism:** Alkene + Halogen → Dihalogenoalkane



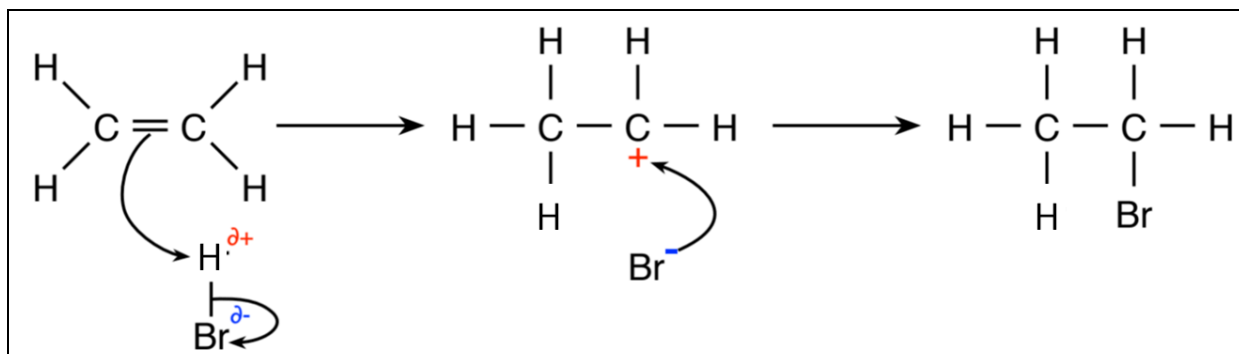
*The  $\pi$  bond causes the bromine molecule to gain a temporary dipole so that electrons are transferred.*



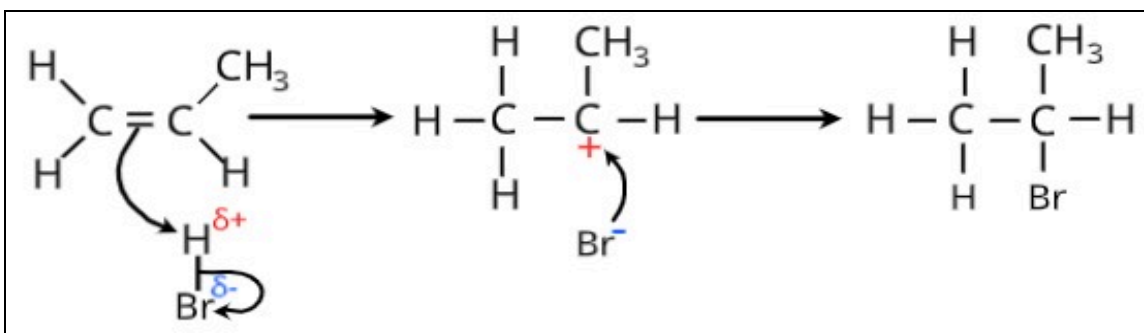


**Mechanism:** Alkene + Hydrogen Halide → Halogenoalkane

*Example: Electrophilic addition of hydrogen bromide to ethene*



*Example: Electrophilic addition of hydrogen bromide to propene*



**Hydrogen bromide** is **polar** due to the difference in the electronegativities of hydrogen and bromine. The **electron pair** in the double bond attracts  $\text{H}^{\delta+}$ , forming a covalent bond between carbon and hydrogen. This produces a positively charged **carbocation intermediate** which attracts the negatively charged bromide ion.

The hydrogen joins to the carbon atom which is bonded to the most hydrogen atoms. The bromide ion bonds to the carbon atom which is joined to the most carbon atoms. This is why **2-bromopropane** forms more often than 1-bromopropane in the mechanism of propene with hydrogen bromide.

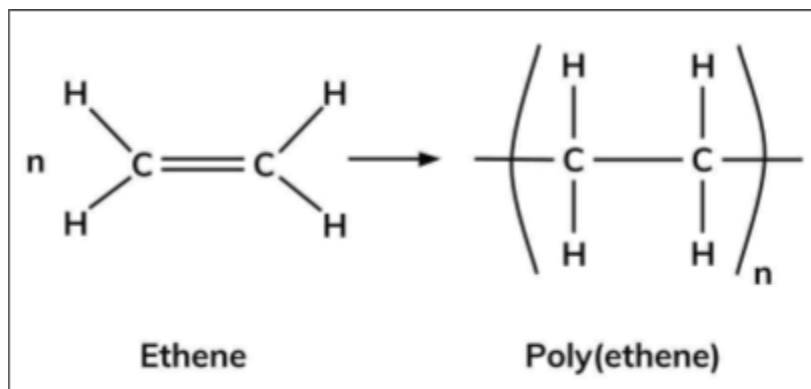




## Addition Polymers

Addition polymers are produced from **alkenes** where the double bond is broken to form a **repeating unit**. Alkenes are short chain **monomers** which join together to form **long chain** polymers.

*Example:*



The repeating unit must always be shown with **extended bonds through the brackets**, showing that it bonds to other repeating units on both sides.

The **energy** and **resources** used to make polymers are large. Polymers are made from alkenes which are obtained from **crude oil**, a non-renewable resource. The extraction and cracking of crude oil are both high energy processes and additional energy is then needed to convert these alkenes into polymers.

### Uses of Polymers

Polymers are unreactive hydrocarbon chains with **multiple strong, non-polar covalent bonds**. This makes them useful for manufacturing many everyday plastic products such as poly(ethene) **shopping bags**.

However, the unreactive nature of the bonds in addition polymers means they are **not biodegradable** and cannot be broken down by species in nature.

### Disposal of Polymers

Addition polymers are **non-biodegradable** which means disposal of them can be difficult. Waste polymers can be processed in different ways. Some can be **recycled**, some are used as **feedstock** for cracking and some are **incinerated** to produce energy for other industrial processes. Incineration can release **toxic gases** which must be removed to reduce the impact on the environment.

As well as this, scientists are developing **biodegradable polymers** to overcome these waste issues.





## Topic 6D: Halogenoalkanes

### Introduction to Halogenoalkanes

Halogenoalkanes contain **polar bonds** since the halogens are more electronegative than a carbon atom. This means electron density is drawn towards the halogen, forming  **$\delta+$  and  $\delta-$  regions**.

Example:

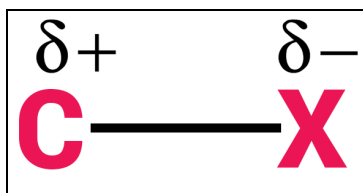
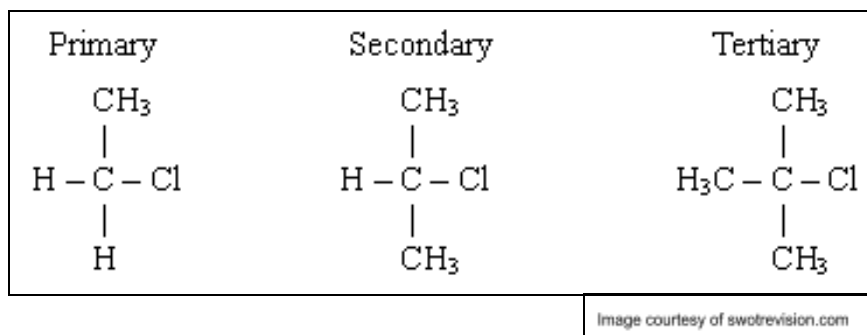


Image courtesy of byjus.com

Halogenoalkanes can be classed as **primary, secondary or tertiary** halogenoalkanes depending on the position of the halogen within the carbon chain.



### Relative Reactivity

Reactivity varies depending on the halogen present in the molecule. **Electronegativity** of the halogens **decreases down the group**, meaning that a carbon-fluorine bond is much more **polar** than a carbon-iodine bond. Along with the fact that the carbon-fluorine bond is **shorter**, this means that the carbon-fluorine bond is much stronger than the carbon-iodine bond.

The **greater the Mr** of the halogen in the polar bond, the **lower the bond enthalpy**. A lower bond enthalpy means the bond can be **broken** more easily. Therefore, the **rate of reaction increases** for halogenoalkanes as you move **down** the group.



## Reactions of Halogenoalkanes

### To Produce Alcohols

Halogenoalkanes can react with **aqueous alkali**, such as aqueous sodium or potassium hydroxide, to produce **alcohols** in a **nucleophilic substitution** reaction. The **hydroxide ion** acts as a **nucleophile**.

### To Produce Alkenes

Halogenoalkanes can react with **ethanolic potassium hydroxide** (KOH) to produce **alkenes** in an **elimination** reaction. The **hydroxide ion** acts as a **base**.

### Hydrolysis with Silver Nitrate

Halogenoalkanes can be **broken down** in their reaction with **aqueous silver nitrate and ethanol**. The **water** in the solution acts as a **nucleophile** which leads to the break down of the halogenoalkane, releasing the halide ions into the solution. The **halide ions** then react with the **silver ions** from silver nitrate to form **silver precipitates**.

The **colour** of the precipitate allows you to identify the halide ion present. The rate at which the precipitates forms allows you to identify the **relative stability** of the halogenoalkanes, because the faster the precipitate forms, the **less stable** the halogenoalkane, and therefore the more quickly it is **hydrolysed**.

<b>Cl<sup>-</sup></b>	<b>Br<sup>-</sup></b>	<b>I<sup>-</sup></b>
White precipitate (AgCl)	Cream precipitate (AgBr)	Yellow Precipitate (AgI)

**Reactivity** depends on the **strength** of the **C-X bond** (where X is a halogen atom) and not the bond polarity. Bond strength **decreases** with **increasing Mr**. Therefore, iodoalkanes would react faster than bromoalkanes and chloroalkanes, and bromoalkanes would react faster than chloroalkanes.

### To Produce Amines

Halogenoalkanes can react with **alcoholic ammonia** (for example, with ethanolic NH<sub>3</sub>) to form **amines** in a **nucleophilic substitution** reaction. **Ammonia** acts as a **nucleophile**.

### To Produce Nitriles

Halogenoalkanes can react with **alcoholic potassium cyanide** (KCN) to form **nitriles** in a **nucleophilic substitution** reaction. The **cyanide ion, CN<sup>-</sup>**, acts as a **nucleophile**. This reaction adds on a carbon atom, so it can be used in synthesis routes to increase the length of carbon chains.





## Nucleophilic Substitution

### Nucleophiles

These species are 'positive liking'. They contain a lone electron pair that is attracted to  $\delta+$  regions of molecules. Some of the most common nucleophiles are:

- $\text{CN}^-$
- $\text{:NH}_3$
- $\text{:OH}^-$

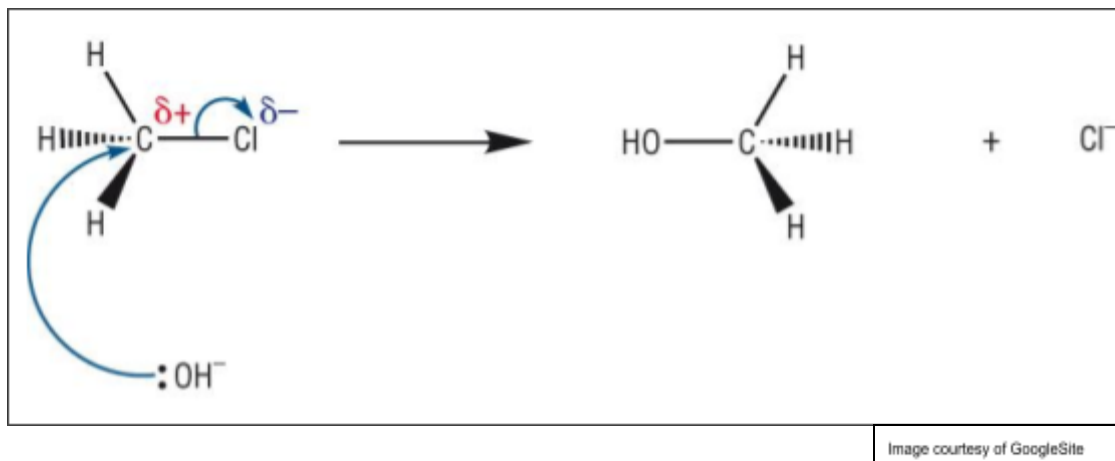
They must be shown with the lone electron pair indicating they are nucleophiles.

### Nucleophilic Substitution

This is the reaction mechanism that shows how nucleophiles attack halogenoalkanes. Starting from halogenoalkanes, aqueous potassium hydroxide is the reactant used to produce alcohols, potassium cyanide is the reactant used to produce nitriles and ammonia is the reactant used to produce amines.

The greater the Mr of the halogen in the polar bond, the lower the bond enthalpy meaning it can be broken more easily. Therefore the rate of reaction for these halogenoalkanes is faster. Nucleophilic substitution reactions can only occur for 1° (primary) and 2° (secondary) alkanes.

### Mechanism - Formation of alcohols

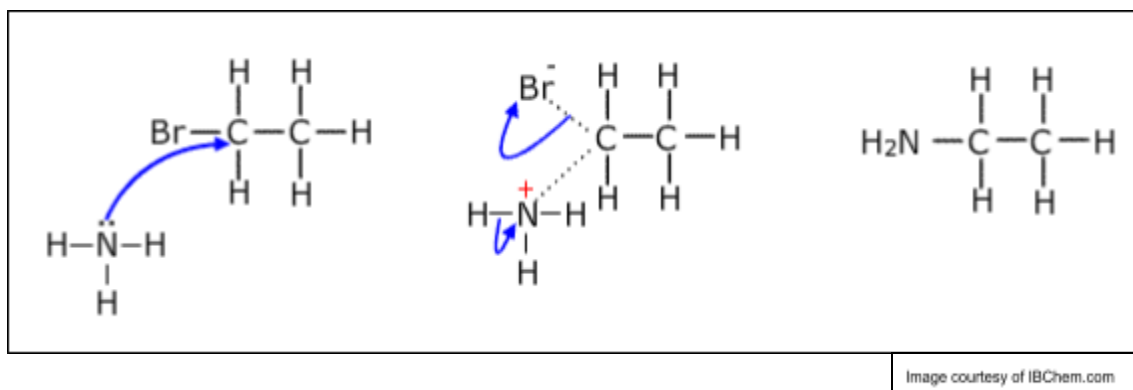


*The nucleophile attacks the  $\delta+$  carbon and the electrons are transferred to the chlorine.*





## Mechanism - Formation of amines



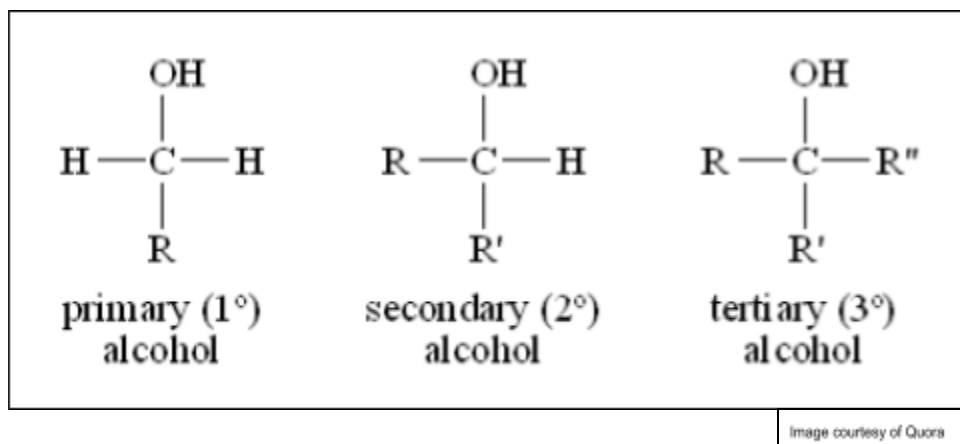
*The intermediate has a positively charged nitrogen (N<sup>+</sup>).  
Electrons are transferred to the nitrogen by the loss of a hydrogen atom.*

## Topic 6E: Alcohols

### Introduction to Alcohols

Alcohols contain an **-OH functional group** and follow the general formula **C<sub>n</sub>H<sub>2n+1</sub>OH**. They can be produced via two main methods of fermentation or hydration. Alcohols are named according to **IUPAC** rules and have the suffix -ol. Alcohols can be **primary (1°)**, **secondary (2°)** or **tertiary (3°)** depending on the position of the hydroxyl group.

Example:



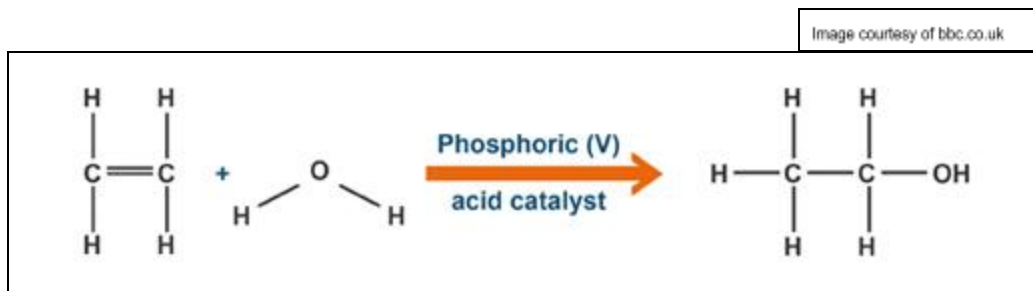




## Hydration

This method produces **alcohols from alkenes** in the presence of an **acid catalyst**, such as phosphoric acid. The reaction is also carried out in **aqueous conditions at 300°C** and under high pressures.

*Example:*



This process has a **very high percentage yield** as ethanol is the only product. Therefore the hydration method is favoured as an industrial process.

## Fermentation

In this process, enzymes break down the starch in crops into **sugars** which can then be **fermented to form alcohol**. This method is **cheaper** than hydration as it can be carried out at a lower temperature. However, the reaction is carried out in **batches**, meaning it is a much slower process with a **lower percentage yield**.

Ethanol is a common **biofuel** produced in this way. It is said to be **carbon neutral** as the amount of carbon dioxide given out when it is burned is equal to the carbon dioxide taken in by the crops during the growing process.

*Example:*

	Amyolytic enzymes		Yeast		
<b>Starch</b>	$\xrightarrow{\hspace{2cm}}$	<b>Glucose</b>	$\xrightarrow{\hspace{2cm}}$	<b>Ethanol</b>	<b>+ Carbon dioxide</b>
$\text{H}(\text{C}_6\text{H}_{10}\text{O}_5)_n\text{OH}$		$n \text{C}_6\text{H}_{12}\text{O}_6$		$2n \text{C}_2\text{H}_5\text{OH}$	$2n \text{CO}_2$
162 (n)		180 (n)		46 (2n)	44 (2n)
100%		111.11%		56.79%	54.32%

Image courtesy of www2.hawaii.edu





## Reactions of Alcohols

### Combustion

When burned in air, alcohols react with **oxygen** to form **carbon dioxide** and **water**. Alcohols make good fuels by reacting in this way as lots of **energy** is also released.

*Example:*

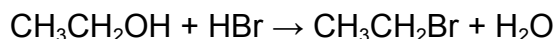


### Reactions with Halogenating Agents

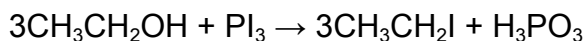
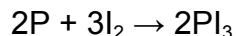
Alcohols can react with **halogenating agents** via **nucleophilic substitution**. The **-OH** group is replaced by a **halogen**, producing a **halogenoalkane**.

**PCl<sub>5</sub>** is used to produce **chloroalkanes**. This can be used as a **test for alcohols** because their reaction with PCl<sub>5</sub> produces **white steamy fumes** that turn damp blue litmus paper red.

A reaction mixture of 50% concentrated **sulfuric acid** and **potassium bromide** can be used to produce **bromoalkanes**. The potassium bromide reacts with the sulfuric acid to form HBr. This then reacts with the alcohol to produce the bromoalkane.



A reaction mixture of **red phosphorus** with iodine can be used to produce **iodoalkanes**. First, the phosphorus reacts with the iodine to produce **phosphorus(III) iodide**. This then reacts with the alcohol to form the iodoalkane.



### Elimination Reactions

Alkenes can be formed from the **dehydration of alcohols**, where a molecule of **water is removed** from the molecule. In order to do this, **concentrated phosphoric acid** is added as a reagent.



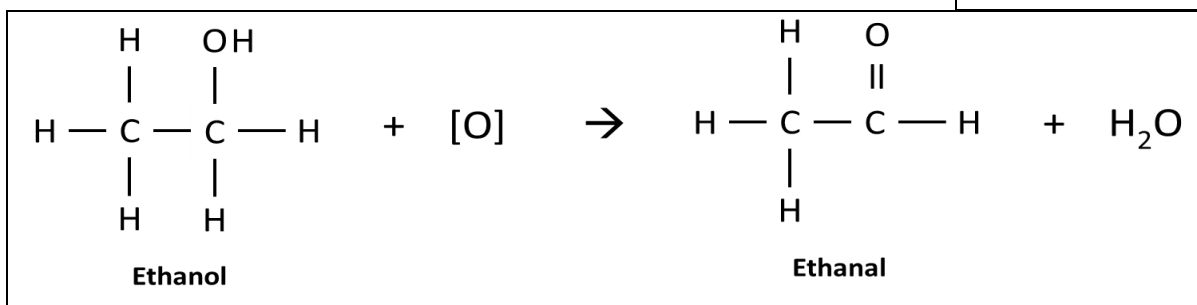


## Oxidation of Alcohols

**Primary** and **secondary** alcohols can be **oxidised** to produce various products but **tertiary** alcohols are **not easily oxidised**.

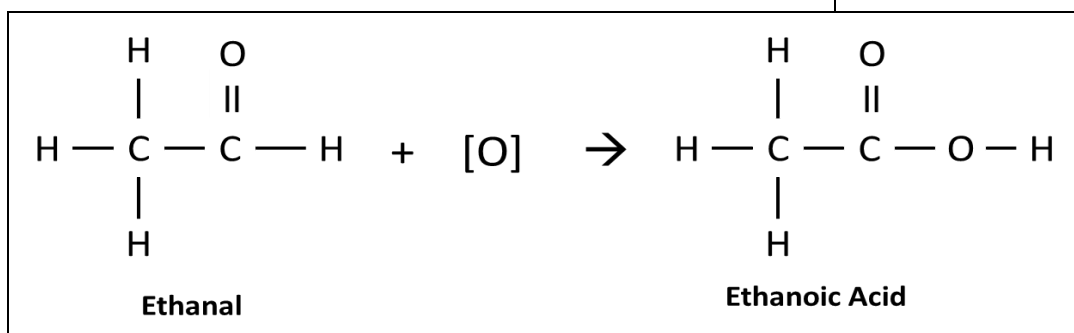
When primary alcohols are heated in the presence of **acidified potassium dichromate(VI)**, they are **oxidised** to aldehydes. **Distillation** is required to separate the **aldehyde** product

Example:



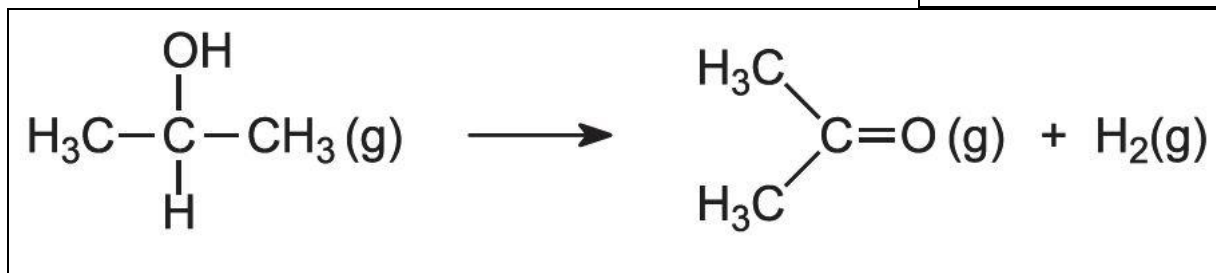
When heated under **reflux** conditions, primary alcohols are **oxidised further** to **carboxylic acids**.

Example:



Secondary alcohols can be oxidised in the presence of **acidified potassium dichromate** to produce **ketones**.

Example:

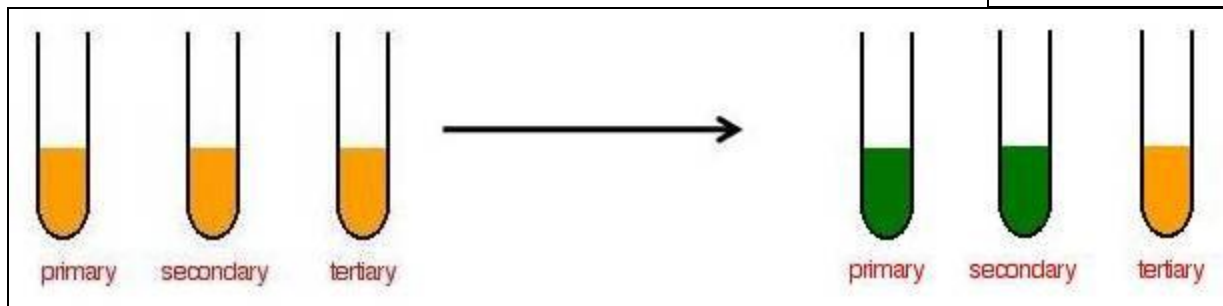




## Potassium Dichromate ( $K_2Cr_2O_7$ )

Potassium dichromate(VI) is used in the oxidation of alcohols as the **oxidising agent**. It is reduced as the alcohol is oxidised. A colour change from **orange to green** is observed when the alcohol is oxidised with potassium dichromate(VI).

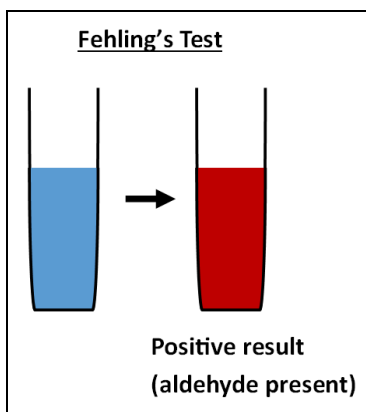
Example:



## Test for Aldehydes

Aldehydes are tested for using **Benedict's/Fehling's solution**.

A few drops of **Fehling's solution** are added and the test tube is gently warmed. If an aldehyde is present a **red precipitate** will form. If no aldehyde is present the solution will remain **blue**.



**Ketones** will not give a positive result when added to Benedict's/Fehling's solution.



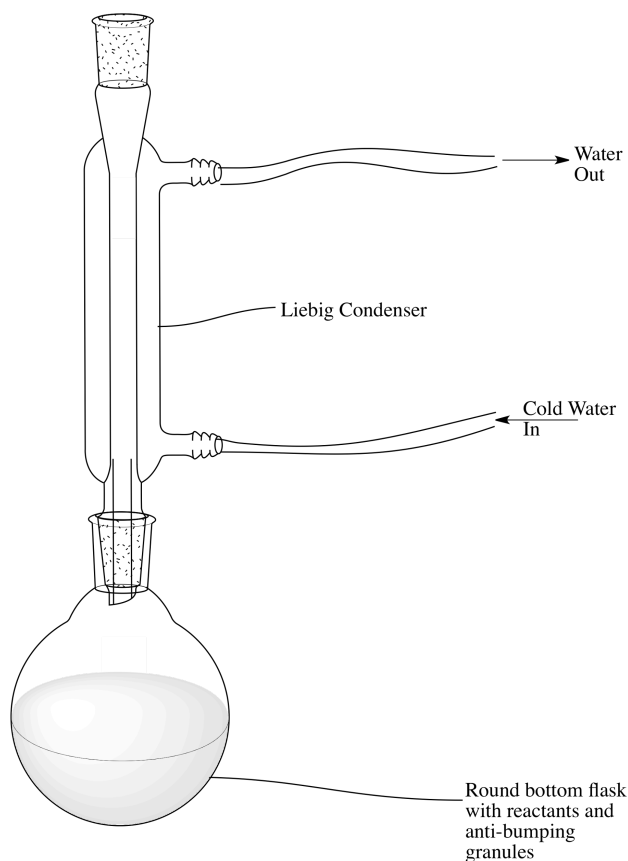


## Experimental Techniques

There are many different techniques that can be used to **prepare** and then **purify** an organic compound.

### 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.



### Separating Funnel

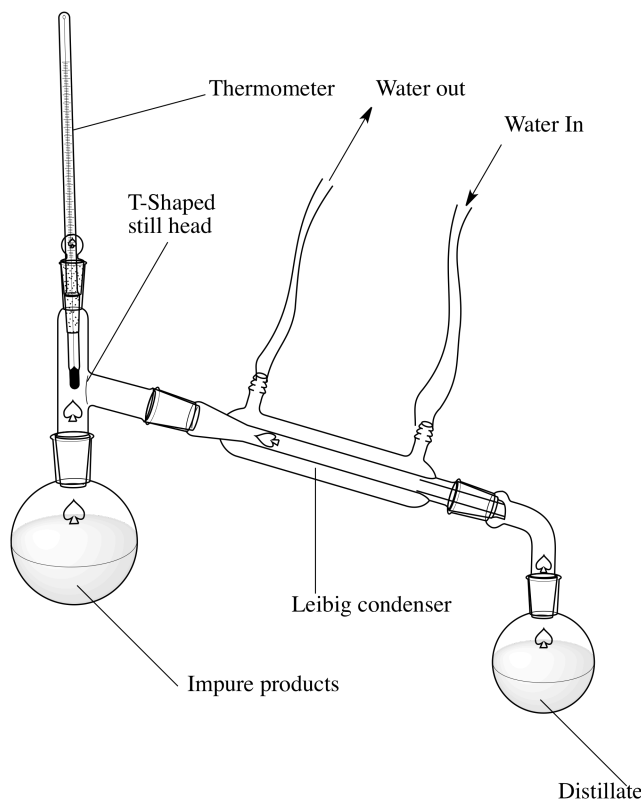
A separating funnel is used to separate two liquids with **different densities**. The mixture is added to the flask and the liquids are allowed to **separate** into **two layers**. The tap can then be opened to collect the bottom, denser liquid in one flask and the second, less dense liquid in a second flask.





## Distillation

Distillation apparatus is used to separate liquids with **different boiling points**. The pear-shaped 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.



## Drying

A compound can be dried by the addition of an **anhydrous** (contains no water) **salt**. The anhydrous salt will **absorb moisture and water** present, thus drying and purifying the compound. A common anhydrous salt used for drying is **sodium sulphate**.

## Boiling Point Determination

Finding the boiling 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 boiling point value it will be. If a sample has a low purity, the melting/boiling point will take place over a **range** of temperatures.

To determine the boiling point, the substance is packed into a **Thiele tube** which has an **inverted capillary tube** in it. The substance is heated to above its boiling point and allowed to cool. When it **condenses** into a liquid it will be drawn into the capillary tube and the temperature at which this change occurs is taken to be the boiling point.

